



- (51) **International Patent Classification:**
C25C 3/12 (2006.01) C25C 7/02 (2006.01)
- (21) **International Application Number:**
PCT/JP2015/002666
- (22) **International Filing Date:**
26 May 2015 (26.05.2015)
- (25) **Filing Language:** English
- (26) **Publication Language:** English
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- (81) **Designated States** (*unless otherwise indicated, for every kind of national protection available*): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.
- (84) **Designated States** (*unless otherwise indicated, for every kind of regional protection available*): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Published:

— with international search report (Art. 21(3))

(54) **Title:** AN ASSEMBLY BODY AND ELECTRODE FOR ELECTROLYSIS

(57) **Abstract:** An assembly body comprises a cermet member, a metal member, and an intermediate member bonding said cermet member and said metal member. The cermet member includes a cermet oxide phase and a cermet metal phase. The intermediate member includes an intermediate oxide phase and an intermediate metal phase. The intermediate oxide phase includes at least one of metal oxide.



Description

Title of Invention: AN ASSEMBLY BODY AND ELECTRODE FOR ELECTROLYSIS

Technical Field

[0001] The present invention relates to an assembly body comprising a cermet member and a metal member made as one body, and an electrode for an electrolysis using said assembly body.

Background Art

[0002] Recently, a cermet member used as an electrode material under harsh environment such as a molten salt electrolysis or so, comprising a ferrite electrode material to improve corrosion resistance and a metal component to improve conductivity is widely known (Patent document 1). The cermet member is known as it can maintain high conductivity and corrosion resistance even at high temperature range for example of 900 to 1000°C or so, thus the cermet material having good characteristics in many ways are being developed.

[0003] When using the cermet member as the electrode, the cermet member becomes a part of the electric current path. Also, the cermet member has high electric resistance compared to a metal member. Thus, the volume of the cermet member can be reduced with advantage when an assembly body of a cermet member and a metal member is used as an electrode compared to the case wherein only the cermet member is used singularly as an electrode; thereby the electric resistance of the entire electrode can be reduced. An additional benefit is the reduction of the cost of the electrode.

[0004] Therefore, a bonding technique is in demand to bond the metal member and the cermet member through which the electric current flows (Patent document 2).

[0005] However, it is difficult to obtain a sufficient bonding strength and durability when the metal member and the cermet member are bonded due to the influence of the heat strain or so. Also, when the bonded member is used as an electrode, it becomes an object to have the bonding method which secures the electric conductivity.

[0006] When bonding the cermet member and the metal member by simple heat treatment, the assembly body tends to easily crack. When the assembly body is cracked, then the mechanical strength becomes small; and when the assembly body is used as an electrode, there is a problem that the electric resistance raises compared to the case where there is no crack.

[0007] Therefore, the practical uses of the assembly body wherein the cermet member and the metal member are bonded were delayed compared to the practical use of the cermet material.

[0008] The patent document 2 discloses an assembly body used as an electrode material for aluminum production wherein the cermet member and the metal member are made as one body via an intermediate layer. Here, in said assembly body, said metal member becomes a part of the electric current path, thus the volume of the cermet member can be reduced compared to the case wherein only the cermet member is used singularly as the electrode. Further, for an electrode using said assembly body, the electric resistance can be reduced more than for an electrode using said cermet member alone, thus the electric power consumption of aluminum production or so can be reduced. Also, by substituting the carbon electrode used for the aluminum production or so by the cermet electrode or by the composite electrode, the amount of emission of CO₂ can be reduced.

[0009] Patent document 2 discloses an assembly body wherein the intermediate member is composed of foam having many voids and forming a particular network structure. It is believed that thanks to this network structure of the stress of entire assembly body is relieved, and thus no crack forms in the cermet member. However, when the intermediate member has the network structure as in patent document 2, a continuous, reproducible electrical contact cannot be ensured at working temperature which can result in heterogeneous electric current density distribution, thus when used as the electrode for the electrolysis, the electrolysis efficiency may deteriorate.

[0010] Further, when producing the assembly body by making the cermet member and the metal member as one body via the intermediate member, voids were easily formed at the inside of the intermediate member. Said voids become the focus of the point of the stress of the intermediate member, which causes the crack of the assembly body, and it significantly reduces the bonding strength of the assembly body.

PATENT DOCUMENTS

Citation List

Patent Literature

- [0011] PTL 1: US Patent No. 4,620,905
PTL 2: US Patent No. 7,316,577

Summary of Invention

[0012] The present invention was attained in view of such situation, and its object is to provide the assembly body having only little voids and cracks in the intermediate member and nearby thereof forming the assembly body, and further the assembly body made of the metal member and the cermet member having sufficient bonding strength; and the electrode for the electrolysis using said assembly body.

[0013] In order to solve the above mentioned problem and to attain the objects, the assembly body comprises a cermet member, a metal member, and an intermediate

member bonding said cermet member and said metal member, wherein
said cermet member includes a cermet oxide phase and a cermet metal phase,
said intermediate member includes an intermediate oxide phase and an intermediate metal phase, and
said intermediate oxide phase includes at least one or more metal oxide.

[0014] The assembly body according to the present invention comprises the above mentioned constitution; thereby the voids at said intermediate member are reduced, thus improves the bonding strength. Further, the crack does not appear. The reason for the improvement of the bonding strength and the suppression of the crack due to the above constitution is because 1) the oxide phase included in said intermediate member limits the metal phase in the intermediate member and as a consequence, limits the volume of voids due to metal solidification shrinkage 2) by making the values of the thermal expansion of the intermediate layer and that of the cermet member closer, the residual stress caused by the thermal strain is reduced, thus the cracking can be prevented and also the bonding strength of the assembly body can be improved.

[0015] Preferably, at least one of metal oxide among said metal oxides is selected from metal oxides included in the cermet oxide phase.

[0016] Preferably, in the assembly body according to the present invention an area ratio occupied by said intermediate oxide phase is 10% to 50% at a cut face of the assembly body being cut perpendicular with respect to a boundary between said cermet member and said intermediate member, when a total area including an area occupied by said intermediate oxide phase and an area occupied by said intermediate metal phase in a region where said intermediate oxide phase is present is defined as 100%.

[0017] Preferably, in the assembly body according to the present invention, an area ratio of voids occupying in entire said intermediate member is 30% or less.

[0018] Preferably, in the assembly body according to the present invention, a metal only layer constituted substantially only of metal is present at a region included in said intermediate member contacting a boundary between said cermet member and said intermediate member.

[0019] Preferably, in the assembly body according to the present invention, said oxide phase included in said cermet member includes at least oxide of Ni.

[0020] Preferably, in the assembly body according to the present invention, at least part of said oxide phase included in said cermet member comprises nickel ferrite.

[0021] Preferably, in the assembly body according to the present invention, said metal phase included in said cermet member includes at least one of Ni and Cu.

[0022] Preferably, in the assembly body according to the present invention, S_o/S_m satisfies below equation (1) when S_o is an area of said oxide phase and S_m is an area of said metal phase at a cross section of said cermet member, and S_o/S_m is an area ratio

between said cermet oxide phase and said cermet metal phase.

[0023] $60/40 \leq S_o/S_m \leq 90/10$...Equation (1)

[0024] Preferably, in the assembly body of the present invention, said oxide phase comprises a spinel ferrite phase expressed by a composition formula of $Ni_xFe_yM_zO_4$ ($x + y + z = 3$, $x \neq 0$, $y \neq 0$, in which M is at least one selected from the group consisting of Al, Co, Cr, Mn, Ti, Zr, Sn, V, Nb, Ta, Hf), and

a nickel oxide phase expressed by the composition formula of $Ni_{x'}Fe_{1-x'}O$ ($x' \neq 0$),

when entire said cermet member including said cermet oxide phase and said cermet metal phase is 100 wt%, then

a content ratio of said spinel ferrite phase is 40 to 80 wt%,

a content ratio of said nickel oxide phase is 0 to 10 wt% (including 0 wt%), and

a content ratio of said cermet metal phase is 15 to 45 wt%.

[0025] Preferably, an average composition of said spinel ferrite included in said cermet member is expressed by the composition formula of $Ni_{x1}Fe_{y1}M_{z1}O_4$ ($x1 + y1 + z1 = 3$, $0.60 \leq x1 \leq 0.90$, $1.90 \leq y1 \leq 2.40$, $0.00 \leq z1 \leq 0.20$).

[0026] Preferably, said nickel oxide phase is included in said cermet member, and the average composition of said nickel oxide phase is expressed by $Ni_{x'1}Fe_{1-x'1}O$ ($0.70 \leq x'1 \leq 1.00$).

[0027] Preferably, the content ratio of Ni is 20 to 90 wt%, and the content ratio of Cu is 10 to 80 wt% at said metal phase when entire said metal phase included in said cermet member is 100 wt%.

[0028] Preferably, in the assembly body according to the present invention, said metal member includes at least one of Ni, Cu, Fe.

[0029] Preferably, in the assembly body according to the present invention, said metal member includes at least Ni and Fe.

[0030] Further, preferably, a content of Ni included in said metal member is 40 to 85 wt%, and the content of Fe is 15 to 60 wt% when entire said metal member is 100 wt%.

[0031] Preferably, in the assembly body according to the present invention, said intermediate metal phase comprises at least one of Cu, Ni and Fe.

[0032] Preferably, in the assembly body according to the present invention, said metal only layer includes at least Ni.

[0033] Preferably, in the assembly body according to the present invention, at least one oxide of said intermediate member is the same oxide as that included in said cermet member.

[0034] Preferably, in the assembly body according to the present invention, a difference in absolute value between an average linear expansion coefficient of said cermet

member and the average linear expansion coefficient of said metal member being 2.0 ppm/°C or less is present within a predetermined range of 1000°C or higher.

[0035] Although there is no limitation of the use of the assembly body of the present invention, it may be used for the electrodes for electrolysis.

[0036] The electrode for electrolysis comprising the assembly body according to the present invention is an electrode for electrolysis with excellent corrosion resistance and strength compared to conventional ones comprising the cermet member and the metal member. Further, in case the cermet member and/or the metal member includes Ni, and particularly when used for the molten salt electrolysis such as electrolytic refining of the aluminum, then the electrode for the electrolysis will have low solubility to the molten salt (particularly of fluoride), and will have excellent durability.

[0037] A process for producing an assembly body of the present invention is a process for producing an assembly body having a cermet member, a metal member and an intermediate member comprising the steps of

producing a mixture comprising an oxide to become an intermediate oxide phase included in the intermediate member after heating and a metal to become an intermediate metal phase included in the intermediate member after heating,

arranging the mixture between the cermet member and the metal member, and

heating the cermet member and the metal member in order to bond the cermet member and the metal member.

Brief Description of Drawings

[0038] [fig.1] Fig.1 is a schematic diagram of the cross section of the assembly body according to one embodiment of the present invention.

[fig.2] Fig.2 is a schematic diagram of enlarged cross section of the cermet member of the assembly body according to one embodiment of the present invention.

[fig.3] Fig.3 is a temperature profile during the bonding step.

[fig.4] Fig.4 is a schematic diagram showing the definition of the average linear expansion coefficient.

[fig.5] Fig.5 is a schematic diagram showing the example of the relationship between the temperature and the size of the thermal expansion of the cermet member and the metal member.

[fig.6] Fig.6 is a schematic diagram showing the condition of carrying out the strength measurement by four points bending.

[fig.7] Fig.7 is a schematic diagram showing the shape of the assembly body used for the strength measurement by four points bending.

[fig.8] Fig.8 is a BEI image of the comparative example 1.

[fig.9] Fig.9 is a BEI image of the example 8.

[fig.10]Fig.10 is a BEI image of the example 13.

[fig.11]Fig.11 is a schematic diagram showing the breakage at the inside of the intermediate member during the four points bending test.

[fig.12]Fig.12 is a schematic diagram showing the breakage at the inside of the cermet member during the four points bending test.

Description of Embodiments

[0039] Hereinbelow, the embodiment of the present invention will be explained by referring to the figures. The present invention is not to be limited to the context described in below.

[0040] As shown in Fig.1, the assembly body according to the present invention comprises the cermet member 30, the metal member 50, and the intermediate member 40. The size of each member included in the assembly body is not particularly limited, and it may be an appropriate size depending on the usage.

[0041] Fig.2 is the schematic diagram showing the internal structure of the cermet member 30. The cermet member 30 according to the present invention comprises the cermet oxide phase 10 and the cermet metal phase 20.

[0042] The cermet oxide phase 10 preferably comprises at least the oxide of Ni. In case the assembly body according to the present embodiment is used for the electrode for the molten salt electrolysis such as electrolysis of aluminum or so, since the cermet member comprises Ni, the solubility against the molten salt (particularly of fluorides) can be lowered compared to the case of not comprising Ni. In other words, since the cermet member comprises Ni, the corrosion resistance of the cermet member at high temperature is enhanced.

[0043] Also, at least a part of the cermet oxide phase 10 is preferably made of nickel ferrite from the point of improving the conductivity and the corrosion resistance; and further preferably the cermet oxide phase 10 is made mainly of nickel ferrite. Nickel ferrite has high conductivity; hence it can make the conductivity of the cermet member 30 higher.

[0044] "The cermet oxide phase 10 is made mainly of nickel ferrite" means that the content ratio of the nickel ferrite is 70 wt% or more in case the entire oxide of Ni in the cermet oxide phase 10 is 100 wt%.

[0045] Also, in the cermet oxide phase 10, the oxide other than the nickel ferrite (for example, NiO, Fe₂O₃ or so) may be mixed. By changing the content of the oxide other than said nickel ferrite, the conductivity of the cermet member 30, and the value of the thermal expansion of the cermet member 30 during the firing can be regulated.

[0046] When S_o is an area of said cermet oxide phase 10, S_m is the area of said cermet metal phase 20, and S_o/S_m is an area ratio between said cermet oxide phase 10 and said

cermet metal phase 20, preferably S_o/S_m satisfies $60/40 \leq S_o/S_m \leq 90/10$. S_o/S_m is preferably within the above mentioned range, by covering the metal phase in the cermet member with the oxide phase, the metal phase can be prevented from dissolving into the fluorides.

[0047] The cermet metal phase 20 preferably includes at least one metal selected from Ni, and Cu; and further preferably in case the entire cermet metal phase 20 is 100 wt%, the content ratio of Ni is 20 to 90 wt%, and the content ratio of Cu is 10 to 80 wt%. The cermet metal phase 20 preferably has the above mentioned constitution because the corrosion resistance of the cermet member can be improved. Also, the cermet metal phase 20 functions to enhance the conductivity of the cermet member 30.

[0048] Note that, the area ratio between the cermet oxide phase 10 and the cermet metal phase 20 is calculated by observing the cut face of the cermet member 30 using the backscattered electron image (BEI) by the electron microscope at the magnification of 300 to 1000x.

[0049] Here, the cermet oxide phase 10 can comprise the spinel ferrite phase 12 and the nickel oxide phase 14. The spinel oxide phase 12 comprises the spinel type crystal structure and comprises the spinel ferrite expressed by the composition formula of $Ni_x Fe_y M_z O_4$ ($x + y + z = 3$, $x \neq 0$, $y \neq 0$, and M is at least one selected from the group consisting of Al, Co, Cr, Mn, Ti, Zr, Sn, V, Nb, Ta, Hf). The nickel oxide phase 14 comprises the nickel oxide expressed by the composition formula of $Ni_{x'} Fe_{1-x'} O$ ($x' \neq 0$). Also, the cermet oxide phase 10 preferably comprises at least the spinel ferrite phase 12.

[0050] The cermet metal phase 20 is dispersed in the cermet oxide phase 10, and preferably it is dispersed mainly in the spinel ferrite phase 12. In other words, preferably it forms the constitution that a lot of the cermet metal phase 20 is trapped in the spinel ferrite phase 12. Also, since the cermet member is a sintered body, the inside of the spinel ferrite phase 12, the inside of the nickel oxide phase 14, and/or the boundary part of each phase comprises small amount of voids (not shown in the figure).

[0051] When the entire cermet member 30 is 100 wt%, preferably the content ratio of the spinel ferrite phase 12 is 40 to 80 wt%, and the content ratio of the oxide nickel phase 14 is 0 to 10 wt% (including 0 wt%), and the content ratio of the cermet metal phase 20 is 15 to 45 wt%. The content ratio of each phase is preferably within the above mentioned range, since the dissolving of the cermet member to the molten salt during the molten salt electrolysis can be prevented, and also since it has the conductivity, the electrolytic efficiency can be improved.

[0052] The average composition of the entire spinel ferrite phase 12 included in the cermet member 30 is preferably within the range of $Ni_{x1} Fe_{y1} M_{z1} O_4$ ($x1 + y1 + z1 = 3$,

$0.60 \leq x_1 \leq 0.90$, $1.90 \leq y_1 \leq 2.40$, $0.00 \leq z_1 \leq 0.20$). The average composition of the entire spinel ferrite phase 12 is preferably within the above mentioned range, because it is the best compromise between good electrical conductivity and good corrosion resistance.

[0053] The cermet member 30 preferably includes the nickel oxide phase 14, and more preferably the average composition of the entire nickel oxide phase 14 included in the cermet member 30 is within the range expressed by $\text{Ni}_{x_1}\text{Fe}_{1-x_1}\text{O}$ ($0.70 \leq x_1 \leq 1.00$). The average composition of the nickel oxide phase 14 is within the above mentioned preferable range because it results from a chemical balance with the other phases (spinel ferrite phase 12 and metal phase 20).

[0054] The type of the metal included in the metal member 50 is not particularly limited.

[0055] In the assembly body of the present invention, the metal member 50 preferably includes at least one of Ni, Cu, Fe.

[0056] The metal member 50 preferably includes at least Ni and Fe. When the entire metal member 50 is 100 wt%, the content of Ni included in the metal member 50 is preferably 40 to 85 wt%, and more preferably it is 55 to 80 wt%. Also, the content of Fe included in the metal member 50 is preferably 15 to 60 wt%, and more preferably the content of Fe is 20 to 45 wt%.

[0057] Also, the metal member 50 preferably includes at least one of Ni or Cu, since the heat resistance and the anti-oxidant property of the assembly body obtained at the end can be enhanced. As for the example including at least one of Ni or Cu, pure Ni or the alloy between Ni, Cr and Fe may be mentioned.

[0058] Hereinafter, the intermediate layer included in the intermediate member 40 will be described.

[0059] As shown in Fig.1, said intermediate member 40 bonds with said cermet member 30 and said metal member 50, and comprise an intermediate metal phase 42 and an intermediate oxide phase 44.

[0060] As the intermediate member 40 of the assembly body 1 according to the present invention comprises at least one metal oxide, the voids generated in the intermediate member 40 can be limited by said oxides. In other words, at the intermediate member 40 of the assembly body 1, said intermediate oxide phase 44 comprising said metal oxide limits the volume of the voids due to metal solidification shrinkage. That is, as the intermediate oxide phase 44 is present at the intermediate member 40, the ratio of the voids present in the intermediate member 40 can be reduced significantly.

[0061] The voids can become the point of the focus of the stress at the intermediate member 40, by reducing the amount of the voids, it is thought that the bonding strength of the assembly body can be increased. In the present invention, by reducing the ratio

of the voids present in the intermediate member 40, the cracking of the assembly body 1 can be prevented, thus the bonding strength of the assembly body 1 can be improved significantly.

[0062] Preferably, at least one oxide included in the internal oxide phase 44 is the oxide included in the cermet oxide phase 10. By the above constitution, the value of the thermal expansion of the intermediate member 40 can become closer to that of the cermet member 30. By making the values of the thermal expansion of the intermediate layer 40 and that of the cermet member 30 closer, the residual stress caused by the thermal strain is reduced, thus the cracking can be prevented and also the bonding strength of the assembly body 1 can be improved.

[0063] The type of the metal constituting the intermediate member 42 is not particularly limited. The intermediate metal phase 42 may be constituted from single metal element, or it may be constituted from plurality of metal elements. Note that, it is preferable that the intermediate metal phase 42 contain at least one of Cu, Ni and Fe.

[0064] At the cut face of which the assembly body 1 is cut perpendicular to the boundary between the cermet member 30 and the intermediate member 40, the distance from the boundary between the cermet member 30 and the intermediate member 40 to the intermediate oxide phase 44 which is at the furthest position in the vertical direction is defined as "d". The range from said boundary to the distance "d" is set as the measurement range. When the total area of the area occupied by the intermediate oxide phase 44 and the area occupied by the intermediate metal phase 42 in said measurement range is 100%, then the area ratio occupied by the intermediate oxide phase 44 is preferably 10% to 50%.

[0065] As the area ratio occupied by the intermediate oxide phase 44 is 10% or more, the voids in the intermediate member 40 is sufficiently filled with the metal oxide, and the cracking can be prevented and also the bonding strength can be improved.

[0066] Note that, when the area ratio of the intermediate oxide phase 44 exceeds 50%, the wettability of the intermediate member 40 against the cermet member 30 is reduced and the bonding of the cermet member 30 and the intermediate member 40 may become difficult.

[0067] Further, preferably, the area ratio of the voids occupied by the said entire intermediate member is 30% or less.

[0068] The boundary between the cermet member 30 and the intermediate member 40, and the boundary between the intermediate member 40 and the metal member 50 can be determined by visual observation using the optical microscope against said cross section. Also, it may be determined by observing using BEI (backscattered electron) image obtained by scanning electron microscope. Also, the intermediate oxide phase 44 is the gray color part in the intermediate member 40 of BEI (backscattered electron)

image obtained by scanning electron microscope.

[0069] The assembly body 1 according to the present invention preferably comprises a layer of pure metal which is in contact with the boundary between the cermet member 30 and the intermediate member 40, and said metal only layer 46 constituted substantially only by the metal is present at the region included in the intermediate metal member 40. Note that, "constituted substantially only by the metal" means that no gray part was observed in the BEI (backscattered electron) image obtained by scanning electron microscope under the magnification of 100 to 500x. Also, the thickness of said metal only layer is 30 μm or more.

[0070] In case said metal only layer 46 is present, the wettability of the intermediate member 40 against the cermet member 30 improves, and further the bonding strength of the assembly body 1 is further improved. Also, said metal only layer 46 preferably includes at least Ni.

[0071] Note that, the intermediate member 40 is not limited to the constitution made of single layer as shown in Fig.1, and it may be a constitution wherein the intermediate member 40 itself is made of two or more layers, or the layer made of solder may be present at the part contacting with the metal member 50. Also, the lower limit of the thickness of the intermediate member 40 is 20 μm . Further the thickness of the intermediate member 40 is preferably 20 to 1000 μm .

[0072] Also, preferably the metal included in the intermediate member 40 is substantially constituted of Cu and Ni only. "Substantially constituted of Cu and Ni only" means that the content ratio of Cu and Ni in the intermediate member is 80 wt% or more when the entire metal included in the intermediate member is 100 wt%. Also, the reason as why the above constitution is preferable is because it can improve the bonding strength of the cermet member and the metal member.

[0073] Next, the suitable production method of the assembly body according to the present embodiment will be described, however the production method of the assembly body according to the present invention is not limited to the below described method.

[0074] The production method of the cermet member constituting the assembly body of the present embodiment comprises, a mixing step of obtaining the mixed powder by mixing the ferrite oxide powder and the metal powder, a molding step of obtaining the molded body by molding the mixed powder, and a firing step of obtaining the fired body by firing the molded body under predetermined atmosphere and temperature.

[0075] For the mixing step, the ferrite source material powder comprising iron oxide (for example Fe_2O_3) and metal oxide (for example NiO) in a desired mol ratio is prepared. Then, said ferrite source material powder is calcined and pulverized to obtain the ferrite oxide powder.

[0076] In case of using the assembly body according to the present embodiment to the

molten salt electrolysis such as the electrolytic refining of aluminum or so, since the cermet member which is obtained at the end comprises Ni, the solubility against the molten salt (particularly of fluorides) can be lowered compared to the case of not comprising Ni.

[0077] Also, the metal powder is prepared separately from said ferrite oxide powder. The type of said metal powder is not particularly limited, and it may be a powder of single metal such as powder of Ni metal alone or the powder of Cu metal alone, it may be metal powder of two or more types for example metal powder mixing the metal powder of Ni and metal powder of Cu in a specific weight ratio. Further, two or more metal powders may be melted to form alloy powder, and this may be used as the metal powder as well.

[0078] The metal powder preferably comprises Ni. In case of using the assembly body according to the present embodiment to the electrode for molten salt electrolysis such as the production of aluminum or so, by having Ni in the cermet member which is obtained at the end, the solubility against the molten salt (particularly of fluorides) can be lowered compared to the case of not comprising Ni.

[0079] Then, said ferrite oxide powder and said metal powder are mixed to obtain the mixed powder. The method of mixing said ferrite oxide powder and said metal powder is not particularly limited, and the usual mixing method such as by ball mill or so can be used. Also, the mixing method may be dry mixing method or wet mixing method, and it only needs to be a method which can uniformly mix said ferrite oxide powder and said metal powder.

[0080] The average primary particle diameter of the mixed powder obtained by the mixing step is not particularly limited as well, however usually the average primary particle diameter of the mixed powder having 1 to 30 μm is obtained.

[0081] In the molding step, said mixed powder is molded to produce the molded body. The molding method is not particularly limited, and for example the molded body can be produced by the usual dry molding method which is used in general. In case of carrying out the usual dry molding, said mixed powder added with a binder is filled into the usual mold, and press molded to produce the molded body. The type of the binder is not particularly limited, and the binder used for the usual molding can be used. From the point that a good molding property can be obtained, polyvinylalcohol (PVA) is preferably used as the binder.

[0082] Note that, the molding method is not limited to the dry molding method, and it may be a wet molding wherein the slurry including the mixed powder and the solvent is pressure molded while removing the solvent, further it may be other molding method.

[0083] The firing step can be carried out under the atmosphere of active gas; however it

is preferable to carry out under the atmosphere of the inactive gas such as nitrogen gas or argon gas or so. By firing the molded body under the inactive gas atmosphere, the oxidation of the metal powder can be prevented, and also nickel oxide is reduced and releases Ni which facilitates to form the metal alloy between the metal powder and the released Ni. Thus, due to the alloy between the metal powder and the Ni, the conductivity of the cermet member is prevented from lowering.

[0084] The firing temperature and the firing time during the firing step are not particularly limited, and it can be appropriately regulated by said ferrite oxide powder and said metal powder which is used as the source material. For example, the sintered body can be obtained by raising the temperature under the atmosphere of nitrogen gas or argon gas, and firing at the firing temperature of 1200 to 1400°C, more preferably of 1300 to 1400°C for preferably 1 to 10 hours and more preferably 2 to 6 hours. By setting the firing temperature within the above mentioned range, the amount of the nickel oxide phase in the oxide phase of the cermet member can be made small, thus the conductivity of the cermet member tends to improve.

[0085] Also, in case of considering the heat resistance of the firing facilities and the production costs, the firing temperature is preferably 1400°C or less.

[0086] Further, the temperature increasing speed during the firing step is preferably 30 to 500°C/hour, and more preferably 50 to 350°C/hour. By making the temperature increasing speed to 500°C/hour or lower, the density of the cermet member can be lowered. Also, by making the temperature increasing speed to 30°C/hour or more, the production cost of the cermet member can be reduced.

[0087] Also, for the temperature decreasing speed during the firing step, it is preferably 10 to 500°C/hour, and more preferably 30 to 350°C/hour. By making the temperature decreasing speed to 500°C/hour or lower, the density of the cermet member can be lowered. Also, by making the temperature decreasing speed to 30°C/hour or more, the production cost of the cermet member can be reduced.

[0088] The sintered body obtained by the firing step may be used as the cermet member without any processing, or it may be used as cermet member having desired shape by carrying some degree of processing.

[0089] For the metal member, the metal being used is not particularly limited. For example, those used for the structure such as stainless steel or so may be selected. In case the assembly body according to the present embodiment is used for the molten salt electrolysis such for aluminum production or so, it is preferable to select the Ni based alloy such as Ni-Fe alloy or so as the material of the metal member, since the heat resistance and the oxidation resistance are high and the solubility to the molten salt (particularly of fluoride) is low. Also, a metal member containing iron is preferred as the cermet member loses iron during electrolysis and can be refilled by the iron

contained in the metal member. The presence of Ni in the intermediate layer can advantageously allow a regulation of the iron migration from the metal member toward the cermet member. Also, commercially available pure Ni, the alloy including Ni and Cu, and the alloy including Ni, Cr and Fe or so can be selected as well.

[0090] Next, regarding the intermediate member included in the assembly body, the method of preparing thereof will be explained. Hereinafter, the step of making the cermet member and the metal member as one body will be referred as a bonding step.

[0091] As for the metal constituting the intermediate member of the present embodiment, it is preferable to select the metal which melts during the heating treatment of the bonding. For example, it is preferable to select the metal which melts at relatively low temperature such as alloy of Cu and Ni.

[0092] As for the oxide constituting the intermediate member of the present embodiment, it is preferable to use the oxide entirely or partially same as the oxide constituting said cermet member. For example, if the oxide included in the cermet member is constituted by the mixture of Ni based ferrite and NiO, then as the oxide constituting the intermediate member, it is preferable to include Ni based ferrite and/or NiO.

[0093] Said metal and said oxide constituting said intermediate member is thoroughly mixed while in a powder form before the heat treatment. As the mixing ratio, it is preferably metal : oxide = 95 : 5 to 65 : 35 in weight base, and more preferably 90 : 10 to 65 : 35. By having the above blending ratio, said area ratio occupied by said intermediate oxide phase becomes 10% to 50% when the total area of the area occupied by said intermediate oxide phase and the area occupied by said intermediate metal phase in said intermediate member is 100%.

[0094] By having the area ratio occupied by said intermediate oxide phase of 10% to 50%, it becomes easy to make the ratio of the occurrence of the voids in said intermediate phase to 30% or less, and further the bonding strength of the assembly body is enhanced. On the other hand, when the mixed ratio is metal : oxide = 100 : 0 to 96 : 4, it becomes difficult to make the ratio of occurrence of the voids to 30% or less. Also, when the mixed ratio is metal : oxide = 65 : 35 to 0 : 100, it may become difficult to maintain the wettability between said intermediate member and said metal member in good condition, thus it may become difficult to obtain sufficient bonding strength of the obtained assembly body.

[0095] Here, the powder of after the mixing may be made into molded body by applying a pressure, or an organic solvent may be used to the powder of after the mixing to make into a paste.

[0096] First, the method of forming the molded body by applying a pressure to the powder of after the mixing will be explained.

[0097] The powder of after the mixing is press molded so that the thickness is

preferably 0.01 to 0.1 cm, more preferably 0.015 to 0.025 cm. By making the thickness of after the molding within said range, it allows to provide a sufficient amount of intermediate member during the bonding step, and the bonding strength of the assembly body obtained at the end is enhanced, further the deformation of the intermediate member during the bonding step becomes easy to suppress to a level which can be ignored. Regarding the molding pressure, preferably it is 140 MPa or more, and more preferably 200 MPa or more. By having the molding pressure within said range, the molded body becomes easy to have suitable thickness.

[0098] By placing the obtained molded body between the cermet member 30 and the metal member 50, the preparation of the bonding step is complete.

[0099] Next, the method of making into a paste by using the organic solvent to the powder of after the mixing will be explained.

[0100] The mixed powder of metal and oxide which are the constitution element of the above mentioned intermediate member is further mixed with the organic solvent to form a paste. The type of the organic solvent is not particularly limited, and for example the organic solvent such as α -terpineol, ethylcellulose, glycerin or so can be used.

[0101] In case of using α -terpineol and ethylcellulose as the organic solvent, α -terpineol and ethylcellulose are mixed in advance to obtain an uniform mixed organic solvent. It is preferable to mix in the weight ratio of α -terpineol : ethylcellulose = 95 : 5 to 70 : 30, more preferably it is mixed in the weight ratio of α -terpineol : ethylcellulose = 90 : 10 to 85 : 15. By satisfying this condition, the viscosity of the organic solvent can be appropriately regulated, and also α -terpineol and ethylcellulose does not separate, further the cellulose will not remain in a solid form, thus it tends to easily become uniform organic solvent.

[0102] The powder of after the mixing and the above mentioned organic solvent are mixed to obtain the mixed paste.

[0103] Next, the mixed paste is coated on the bonding face of said cermet member and/or the bonding face of said metal member. When coating, it is preferable that the thickness of the mixed paste is 0.03 cm to 0.3 cm, and more preferably it is 0.03 cm to 0.1 cm. By having the thickness of the mixed paste within the above range, during the bonding step of said cermet member 30 and said metal member 50, the sufficient amount of the intermediate member for obtaining the bonding strength can be provided. By having the thickness of the mixed paste within the above mentioned range, the deformation of the intermediate member during the bonding step can be suppressed to the level which can be ignored. The mixed paste coated is placed between aid cermet member 30 and said metal member 50, thereby the preparation of the bonding step is complete.

- [0104] Fig.3 is the schematic diagram showing the time difference of the temperature in time during the bonding step according to the present embodiment. As shown in Fig.3, the bonding step includes the temperature increasing step (step S1), the high temperature maintaining step (step S2), and the temperature decreasing step (step S3). The bonding step is preferably carried out in vacuumed condition, or inactive gas atmosphere, for example Ar and N₂ or so. However, it is not limited thereto.
- [0105] The temperature increasing step (step S1) is a step of gradually heating while applying a pressure to each member in the heating furnace. The temperature increasing speed is preferably 30°C/hour to 500°C/hour, and more preferably 50°C/hour to 300°C/hour. By making the temperature increasing speed to 500°C/hour or less, the cermet member and the intermediate member, and the intermediate member and the metal member are sufficiently bonded easily. Also, by making the temperature increasing speed to 30°C/hour or more, the production cost of the assembly body can be reduced.
- [0106] The high temperature maintaining step (step S2) is the step which maintains at the predetermined temperature, and it starts from time t₁ of Fig.3. Preferably, it is carried out at the temperature where the average linear expansion coefficient difference in the absolute value between the metal member and the cermet member is 2.0 ppm/°C or less, and further preferably at the temperature where the average linear expansion coefficient of the metal member and the cermet member matches.
- [0107] Here, the average linear expansion coefficient will be explained by referring to Fig.4. Note that, in Fig.4, T₀ is the room temperature and L₀ is the length of the sample at the room temperature T₀.
- [0108] By changing the temperature (T) of the sample from T₀ to T₁ (T₀ < T₁), when the length (L) of the sample are changed from L₀ to L₁, the value wherein the amount of change in the length (L₁-L₀) divided by L₀ is the thermal expansion between the temperature T₁ and the temperature T₀. Further, the value which is obtained by dividing this thermal expansion by the temperature difference (T₁-T₀) is the average linear expansion coefficient.
- [0109] That is, in the present application, the average linear expansion coefficient $\alpha(T_1)$ between the temperature T₀ and the temperature T₁ is as shown in the below equation (A). Note that, the average linear expansion coefficient $\alpha(T_1)$ between the temperature T₀ and the temperature T₁ taking T₀ as the standard temperature may be referred simply as the average linear expansion coefficient at the temperature T₁.
- [0110]
$$\alpha(T_1) = (L_1 - L_0) / \{L_0 \times (T_1 - T_0)\} \dots (A)$$
- [0111] Fig.5 shows the change of the length of the cermet member and the change of the length of the metal member when the length of the member at the standard temperature T₀ is the same. At the temperature T₁, the average linear expansion coefficient of the cermet member and the average linear expansion coefficient of the metal

member are matched, and the length of the cermet member and the length of the metal member are matched. That is, in the temperature T_1 , the difference between the average linear expansion coefficient of the cermet member and the average linear expansion coefficient of the metal member is 0.

[0112] When the difference between the average linear expansion coefficient at the temperature T_1 is small (the difference in the absolute value is 2.0 ppm/°C or less), and when the high temperature maintaining is carried out at the temperature T_1 , the thermal strain is small when it is returned to room temperature after the high temperature maintaining, thus a bonded body without the crack can be easily obtained.

[0113] Note that, the maintaining temperature maintained during the high temperature maintaining step is preferably 1100 to 1400°C, and more preferably 1100 to 1250°C. Also, the maintaining time is preferably 1 to 10 hours, and more preferably 2 to 6 hours. By setting the maintaining temperature to the above mentioned range, the cermet member, the intermediate member and the metal member forms a sufficient bonding, and the bonding strength of the assembly body improves. Further, in said cermet member, the generation of NiO is controlled to be low, thus the conductivity can be maintained high as well.

[0114] Note that, from the point of the heat resistance of the firing facilities, and the reduction of the production cost, the upper limit of the maintaining temperature is preferably 1400°C.

[0115] The temperature decreasing step (step S3) is a step of gradually cooling the assembly body in the heating furnace. The temperature decreasing speed is 10°C/hour to 600°C/hour, and more preferably 10°C/hour to 300°C/hour. By setting the temperature decreasing speed to the above mentioned range, the stress caused by the heat expansion difference at the high temperature can be relieved, thus the cracks can be reduced.

[0116] The bonding step is carried out under an inactive gas atmosphere (for example, nitrogen gas or argon gas or so). By firing under the inactive gas, the oxidation of said metal member can be prevented.

[0117] Note that, in case of using said mixed paste, the above mentioned metal only layer tends to easily exist in the intermediate member compared to the case of using the above molded body. Also, by having the metal only layer in the intermediate member, the wettability against said cermet member of said intermediate member improves, and the bonding strength can be improved.

[0118] Also, the metal only layer is easily formed when using said mixed paste, because the part near the boundary between the cermet member and the intermediate member is reduced and metallized by having the above mentioned organic solvent in said mixed paste.

[0119] The method of forming the metal only layer is not particularly limited, and other methods for forming the intermediate member using the above mentioned mixed paste, for example the method of forming said metal only layer using CVD (chemical vapor deposition) or PVD (physical vapor deposition) or so can be used.

[0120] The obtained assembly body may be used as it is, or it may be processed depending on the usage. Also, the usage of the obtained assembly body is not particularly limited; however it is preferable to be used as the electrode for the electrolysis.

[0121] As discussed in the above, in the present embodiment, by comprising the oxide in the intermediate member, the void of the intermediate member can be filled, thus the decline of the strength can be suppressed, and further the dispersed condition of the cermet member and the intermediate member becomes good, thus the bonding strength improves.

[0122] Hereinabove, the preferable embodiment of the present invention has been discussed; however the present invention is not to be limited thereto. For example, the wettability can be regulated by comprising Al, which easily forms alloy with Ni, in the intermediate member.

[0123] Note that, the metal member of the present invention may comprise 50 wt% or less of substance other than metal. The type of the substance other than the metal is not particularly limited, and for example carbon, metal nitride or so can be mentioned.

[0124] Hereinabove, the production method in regards with the preferable embodiment of the present invention has been described. The cermet member 30 may include other phases which are different from the spinel ferrite phase 12, the nickel oxide phase 14 and the metal phase 20. Also, the material of the metal member 50 is not particularly limited. In the present embodiment, pure Ni and Ni based alloy has been listed as the metal member 50, however other alloys may be selected. In case of using other alloy, it is preferable to use the alloy having equivalent expansion value as the pure Ni or Ni based alloy. Also, from the point of increasing the bonding strength, the diffusion bonding method utilizing the mechanical pressure may be used.

Examples

[0125] The context of the present invention will be explained into further detail by referring to the examples and the comparative examples, however the present invention is not to be limited thereto.

[0126] (Experiment 1)

The commercially available nickel oxide (NiO) powder and iron oxide (Fe₂O₃) powder were blended so that the mol ratio of NiO against Fe₂O₃ is 50/50, then it was mixed using the ball mill thereby the mixed powder was obtained. This calcination was

carried out to the mixed powder by maintaining at the temperature of 1000°C for 3 hours. The obtained calcined powder was pulverized in the ball mill, thereby the ferrite oxide powder was prepared.

[0127] The obtained ferrite oxide powder and the copper (Cu) powder were blended so that the weight ratio of the ferrite oxide powder against the copper powder is 83/17. The blended powder was mixed in the ball mill, and 0.8 wt% of PVA (polyvinylalcohol) as the binder was added with respect to the total weight of the above mentioned ferrite oxide powder and the copper powder; then by mixing by the ball mill, the mixed powder was prepared.

[0128] The obtained mixed powder is press molded, thereby plurality of molded body having a rectangular parallelepiped shape were obtained. These molded bodies were fired by maintaining under N₂ atmosphere at the temperature of 1300°C for 3 hours. Then it was gradually cooled in N₂ atmosphere, thereby plurality of the sintered body (the cermet member) having the rectangular parallelepiped shape of 1.5 cm x 1.5 cm x 2.0 cm were prepared.

[0129] One of the obtained cermet member was cut, and the cut face was observed by the backscattered electron image (BEI) using electron microscope (S-2100 made by Hitachi High-Technologies) for 30 random visual fields at 500x magnification, thereby the area ratio between the oxide phase and the metal phase was calculated.

[0130] As the metal member bonding with said cermet member, Ni rod processed into 1.5 cm x 1.5 cm x 2.0 cm was prepared.

[0131] The mirror face polishing was carried out to one of the face of 1.5 cm x 1.5 cm of the cermet member and the one of the face of 1.5 cm x 1.5 cm of the metal member.

[0132] Next, the mixed molded body which will become the intermediate member by the bonding step was produced. As for the metal powder which becomes the source material of the mixed molded article, Ni powder and Cu powder were selected. Also, as the powder of oxide which was the source material of the mixed molded article, NiO-NiFe₂O₄ powder was selected. In regards with this, it was mixed so that the mixed ratio is (Ni + Cu) : NiO-NiFe₂O₄ = 100 : 0 to 50 : 50 (wt%). By changing the weight ratio of (Ni + Cu) and NiO-NiFe₂O₄, the area ratio of the metal and the oxide phase in the intermediate member can be controlled to any value. The mixed ratio between Ni powder and Cu powder was Ni : Cu = 50 : 50 (wt%). The obtained mixed powder was applied with the pressure of 195 MPa so that the thickness is 0.02 cm, thereby the mixed molded body was produced.

[0133] Then, the produced mixed molded article having the thickness of 0.02 cm was placed on the mirror polished side of the cermet member, then the firing was carried out by placing Ni rod thereon. Here, Ni rod was placed so that the mirror polished side is in contact against said mixed molded body.

- [0134] Then, the heat treatment was carried out while applying the load of 0.5 kPa towards the cermet member side from the metal member side. The temperature increasing speed and the temperature decreasing speed were both 300°C/hour, and the high temperature maintaining time in a vacuumed atmosphere was 3 hours, and the maintaining temperature was 1200°C, thereby the bonding step was carried out.
- [0135] Next, to the assembly body obtained, the evaluation was carried out following the below steps. First, a cut was made at the perpendicular plane with respect to the face of mirror polished cermet member.
- [0136] Then, from the observation result of BEI image using the scanning electron microscope (S-2100 made by Hitachi High-Technologies) against said cut face, the boundary between the cermet member and the intermediate member, and the boundary between the intermediate member and the metal member were determined.
- [0137] Further, the area ratio of said intermediate oxide phase was calculated. The steps of the calculation comprises the step of determining the measuring range in BEI image of each sample, and the step of calculating the area ratio where the intermediate oxide phase occupies in said measurement range. For each steps, it is discussed in below.
- [0138] For each sample, the BEI image of the region where said intermediate member is placed between said cermet member and said metal member was observed at the magnification of 100x. Next, the distance "d" was measured which is to the intermediate oxide phase (the gray part of BEI image) which is present at the side of said intermediate member from the boundary between said cermet member and said intermediate member, and present at the position furthest from said boundary in perpendicular direction. Specifically speaking, the distance "d" was measured which is between the boundary and the point furthest from said boundary among the intersections within the region where said intermediate oxide phase occupies in said BEI image and perpendicular line from the boundary between said cermet member and said intermediate member. The region in said intermediate member wherein the distance from the boundary is "d" or less was defined as the measuring range.
- [0139] In said measuring range, the contrast of BEI image was analyzed, and the area ratio of the gray part which reflects said intermediate oxide phase against said entire BEI image was calculated. The same calculation was carried out to 10 visual fields, and the average area ratio of said gray part was calculated. The obtained value was defined as the area ratio of said intermediate oxide phase in said intermediate member.
- [0140] Next, the void ratio in the intermediate member was calculated. The calculation of the void ratio was carried out by the analysis of the transmission X ray image taken by X ray CT machine (XVA-160 made by UNI-HITE SYSTEM Corporation). Also, the measuring area was set to 0.5 cm x 0.5 cm. The X ray enters from the metal member and passes through the intermediate member and comes out from the cermet

member, thereby the transmission image was obtained. In said obtained transmission image, the void part appears in white color. The contrast of said transmission image was analyzed, and the ratio of the white color part reflecting the void with respect to the entire transmission image was calculated. The same calculation was carried out to 10 visual fields, and the average area ratio of said white color part was calculated. The obtained value was defined as the ratio of the void in the intermediate member.

[0141] Further, by using the optical microscope against said cut face, the observation of the cross section including the intermediate member was carried out, and the presence of the cracks was verified.

[0142] Further, each of the obtained assembly body was processed respectively, to have the size of 0.4 cm x 0.3 cm x 1.2 cm.

[0143] TMA measurement was carried out using the above sample. The TMA measurement was carried out using the thermomechanical analysis apparatus (TMA 8310 made by Rigaku Corporation). From the obtained TMA curve, the average linear thermal expansion coefficient at the 1300°C of the intermediate member was calculated. Note that the standard temperature was 25°C. The results are shown in Table 1. Also, the places of the breakage were observed as well.

[0144] For the bonding strength, after 10 obtained assembly bodies were processed into rectangular parallelepiped shape, each of them was carried out with the four points bending strength test and the average value of the bonding strength was calculated.

[0145] The four points bending strength test was carried out by the method shown in the schematic diagram of Fig.6. Note that, as the four points bending strength test machine (Model 11311-D made by AIKOH ENGINEERING CO., LTD) was used. In the present examples, the bonding strength of 20 MPa or more was defined as good bonding strength. Note that, the bonding strength is more preferably 50 MPa or more, and further preferably 100 MPa or more.

[0146] The shape of the assembly body used for the four points bending machine is rectangular parallelepiped shape as shown in Fig.7, and $D1 = D4 = 1.2$ cm, $D2 = D6 = 0.4$ cm, $D3 = D5 = 0.3$ cm. Note that, in Fig.7, the intermediate member 40 is not shown.

[0147] The test results of the examples 1 to 12 and the comparative example 1 of the experiment 1 are shown in Table 1.

[0148]

[Table 1]

Table 1

Sample No.	Mixed ratio (wt%) of Metal (Cu + Ni)	Mixed ratio (wt%) of Oxides (NiO- NiFe ₂ O ₄)	Area ratio (%) of Intermediate metal phase	Area ratio (%) of Intermediate oxide phase	Average liner		Four points bending strength (MPa)
					expansion coefficient (ppm/°C) of Intermediate member	Area ratio (%) of Voids	
Comparative example 1	100.0	0.0	100.0	0.0	16.3	57.5	15.2
Example 1	98.5	1.5	97.2	2.8	16.1	50.2	20.6
Example 2	98.0	2.0	95.4	4.6	16.0	48.3	37.8
Example 3	96.5	3.5	94.8	5.2	16.0	39.5	42.3
Example 4	96.0	4.0	90.7	9.3	15.7	38.7	47.6
Example 5	95.0	5.0	89.7	10.3	15.6	34.7	52.1
Example 6	92.0	8.0	85.8	14.2	15.4	31.3	73.7
Example 7	90.0	10.0	82.5	17.5	15.2	28.7	104.7
Example 8	85.0	15.0	76.6	23.4	14.8	23.7	115.3
Example 9	80.0	20.0	68.8	31.2	14.3	19.4	124.8
Example 10	75.0	25.0	62.5	37.5	13.9	14.3	125.7
Example 11	70.0	30.0	57.5	42.5	13.6	10.2	125.4
Example 12	65.0	35.0	51.3	48.7	13.2	7.5	126.5

- [0149] As obvious from Table 1, in the intermediate member, as the mixed ratio of the oxide $\text{NiO-NiFe}_2\text{O}_4$ increases, the average linear expansion coefficient of the intermediate member continuously declines. That is, the average linear expansion coefficient of the intermediate member can be regulated by changing the ratio of the oxide in the intermediate member.
- [0150] Also, in regards with the ratio of the void in the intermediate member, according to Table 1, as the amount of the oxide included in said intermediate member increases and the area ratio of said intermediate oxide phase in the intermediate member increases, the ratio of the void in said intermediate member monotonously declined.
- [0151] This is due to the fact, the voids (the black colored part surrounded by the broken line in Fig.8 (the comparative example 1)) generated in the intermediate member contacting the cermet member were filled with the oxide $\text{NiO-NiFe}_2\text{O}_4$ as shown in Fig.9 (Example 8). Note that, the filled part (the gray part surrounded by the broken line in Fig.9) is the intermediate oxide phase.
- [0152] The void in said intermediate member decreases the residual stress inside the assembly body caused by the difference between the thermal expansion of the cermet member and the thermal expansion of the metal member, and it is thought to suppress the generation of the crack in the assembly body. However, even in the examples 1 to 12 which has reduced the ratio of the void in said intermediate member than in the comparative example 1 by changing the amount of the oxide included in the intermediate member, the cracks did not occur as same as or more than the comparative example 1.
- [0153] Also, when the relation between the void ratio and the four points bending strength is focused, the examples 1 to 12 of which the intermediate oxide phase exist in said intermediate member, the bonding strength was improved compared to the comparative example 1 without the intermediate oxide phase. Further, in the examples 5 to 12 wherein the area ratio of the oxide phase in said intermediate member was 10% or more, the bonding strength was 50 MPa or more. The reason that the bonding strength of the examples 5 to 12 was higher than the bonding strength of examples 1 to 4 is because the voids of the intermediate member which becomes the point of focus of the stress has been reduced.
- [0154] Also, in the examples 7 to 12 in which the void ratio is below 30%, the four points bending strength was 100 MPa or more. Note that, the point of the breakage was all at the intermediate member.
- [0155] (Experiment 2)
- As mentioned in above, in the present invention, the starting embodiment of the intermediate member may be said molded body or said mixed paste. In the above mentioned experiment 1, the starting embodiment of the intermediate member was said

molded body. In the experiment 2 shown in below, the starting body of the intermediate member was mixed paste.

[0156] Note that, besides the intermediate member such as said cermet member and said metal member or so, the same material as the examples 1 to 12 and the comparative example 1 were used, and the firing condition or so is same as well. Also, the embodiment of carrying out the four points bending is the same and follows the schematic diagram of Fig.6 as well.

[0157] First, as the metal of the intermediate member, Ni and Cu were selected. Also, as the oxide phase in the intermediate member, NiO-NiFe₂O₄ was selected. In regard with these, the mixed powder of (Ni + Cu) : NiO-NiFe₂O₄ = 80 : 20 (wt%) was prepared. Here, in regards with Ni powder and Cu powder, Ni : Cu = 50 : 50 (wt%). The obtained mixed powder and the organic solvent were mixed to form a paste. Here, the organic solvent was produced by mixing α -terpineol : ethylcellulose in a weight ratio of 90 : 10 (wt%). Also, the weight ratio between said mixed powder and said organic solvent was mixed powder : organic solvent = 75 : 25 (wt%).

[0158] Next, the prepared mixed paste was coated on the mirror polished side of said cermet member so that the thickness is 0.1 cm. Then, Ni rod was placed thereon and the firing was carried out. Here, the Ni rod made the mirror polished side to contact with the paste.

[0159] Note that, the condition of the bonding step is the same as the experiment 1. The result of the experiment 2 is shown in Table 2.

[0160]

[Table 2]

Table 2

No.	Mixed ratio (wt%) of Metal (Cu + Ni)	Mixed ratio (wt%) of Oxides (NiO-NiFe ₂ O ₄)	Area ratio (%) of Intermediate metal phase	Area ratio (%) of Intermediate oxide phase	Area ratio (%) of Voids	Metal only layer	Breakage part member	Four points bending strength (MPa)
Example 9	80.0	20.0	68.8	31.2	19.4	None	Intermediamet member	124.8
Example 13	80.0	20.0	69.6	30.4	6.5	Present	Cermet member	187.5

[0161] As shown in Table 2, as similar to the example 9 using the mixed molded body, the example 13 using the mixed paste did not have a crack. Also, the ratio of the void in the intermediate member was 6.5% which is below 30%.

[0162] Next, the structure near the boundary between the cermet member and the intermediate member in the example 13 will be explained using Fig.10. As shown in Fig.10, in case of using the mixed paste, at the part included in the intermediate member 40 and near the boundary between the intermediate member including oxides NiO-NiFe₂O₄ and the cermet member 30, the oxide of NiO-NiFe₂O₄ does not mixed in, thus the metal only layer 46 constituted only from the metal was formed.

[0163] When the four points bending strength tests were carried out for the examples 1 to 12 and the comparative example 1 using said mixed molded body, as shown in Fig.11, the breakage part 48 was found in the intermediate member 40. On the other hand, the example 13 using the mixed paste, when the four points bending strength test was carried out, as shown in Fig.12, the breakage part 48 changed to inside of the cermet member 30.

[0164] The breakage part has changed as mentioned in above, possibly because the strength of the intermediate member has improved, and it became difficult to break at the intermediate member. Since the strength of the intermediate member improved so much that the breakage part has changed, thus the even higher bonding strength was able to obtain in the example 13. Note that, in the example 13, the bonding strength became stronger as it got higher than 185 MPa.

[0165] Note that, to the cermet member and the metal member using the above mentioned examples, the measurement of the thermal expansion rate was carried out using TMA, thereby the average linear expansion coefficient was measured at each temperature up to 1400°C taking 25°C as the standard temperature.

[0166] For the combination of all of the cermet member and the metal member described in the above examples, a difference in absolute value between an average linear expansion coefficient of said cermet member and the average linear expansion coefficient of said metal member being 2.0 ppm/°C or less was found within a predetermined range of 1000°C to 1400°C or higher.

Industrial Applicability

[0167] As discussed in above, the assembly body having the intermediate oxide phase in the intermediate member as in the present invention shows high bonding strength of 20 MPa or more; and when the assembly body is regulated so that the presence ratio of said intermediate oxide phase is 10 to 50%, it shows high bonding strength of 50 MPa or more. By using the assembly body of the present embodiment, the electrode for the electrolysis having both advantages of the cermet material and the metal material can be made.

Reference Signs List

[0168] 1...The assembly body
 10...Cermet oxide phase
 12...Spinel ferrite phase
 14...Nickel oxide phase
 20...Cermet metal phase
 30...Cermet member
 40...Intermediate member

- 42...Intermediate metal phase
- 44...Intermediate oxide phase
- 46...Metal only layer
- 48...Breakage part
- 50...Metal member

Claims

- [Claim 1] An assembly body comprising a cermet member, a metal member, and an intermediate member bonding said cermet member and said metal member, wherein
- said cermet member includes a cermet oxide phase and a cermet metal phase,
- said intermediate member includes an intermediate oxide phase and an intermediate metal phase, and
- said intermediate oxide phase includes at least one or more metal oxide.
- [Claim 2] The assembly body as set forth in claim 1, wherein at least one of metal oxide among said metal oxides is selected from metal oxides included in the cermet oxide phase.
- [Claim 3] The assembly body as set forth in claims 1 or 2, wherein an area ratio occupied by said intermediate oxide phase is 10% to 50% at a cut face of the assembly body being cut perpendicular with respect to a boundary between said cermet member and said intermediate member, when a total area including an area occupied by said intermediate oxide phase and an area occupied by said intermediate metal phase in a region where said intermediate oxide phase is present is defined as 100%.
- [Claim 4] The assembly body as set forth in any one claims 1 to 3, wherein an area ratio of voids occupying in entire said intermediate member is 30% or less.
- [Claim 5] The assembly body as set forth in any one of claims 1 to 4, wherein a metal only layer constituted substantially only of metal is present at a region included in said intermediate member contacting a boundary between said cermet member and said intermediate member.
- [Claim 6] The assembly body as set forth in any one of claims 1 to 5, wherein said cermet oxide phase included in said cermet member includes at least oxide of Ni.
- [Claim 7] The assembly body as set forth in any one of claims 1 to 6, wherein at least part of said cermet oxide phase included in said cermet member comprises nickel ferrite.
- [Claim 8] The assembly body as set forth in any one of claims 1 to 7, wherein said cermet metal phase included in said cermet member includes at least one of Ni and Cu.

- [Claim 9] The assembly body as set forth in any one of claims 1 to 8, wherein S_o/S_m satisfies below equation (1) when S_o is an area of said cermet oxide phase and S_m is an area of said cermet metal phase at a cross section of said cermet member, and S_o/S_m is an area ratio between said cermet oxide phase and said cermet metal phase.
- $$60/40 \leq S_o/S_m \leq 90/10 \dots \text{Equation (1)}$$
- [Claim 10] The assembly body as set forth in any one claims 1 to 9, wherein said cermet oxide phase comprises a spinel ferrite phase expressed by a composition formula of $Ni_xFe_yM_zO_4$ ($x + y + z = 3$, $x \neq 0$, $y \neq 0$, in which M is at least one selected from the group consisting of Al, Co, Cr, Mn, Ti, Zr, Sn, V, Nb, Ta, Hf), and
- a nickel oxide phase expressed by the composition formula of $Ni_{x'}Fe_{1-x'}O$ ($x' \neq 0$),
- when entire said cermet member including said cermet oxide phase and said cermet metal phase is 100 wt%, then
- a content ratio of said spinel ferrite phase is 40 to 80 wt%,
- a content ratio of said nickel oxide phase is 0 to 10 wt% (including 0 wt%), and
- a content ratio of said cermet metal phase is 15 to 45 wt%.
- [Claim 11] The assembly body as set forth in claim 10, wherein an average composition of said spinel ferrite included in said cermet member is expressed by the composition formula of $Ni_{x1}Fe_{y1}M_{z1}O_4$ ($x1 + y1 + z1 = 3$, $0.60 \leq x1 \leq 0.90$, $1.90 \leq y1 \leq 2.40$, $0.00 \leq z1 \leq 0.20$).
- [Claim 12] The assembly body as set forth in claims 10 or 11, wherein said nickel oxide phase is included in said cermet member, and the average composition of said nickel oxide phase is expressed by $Ni_{x'1}Fe_{1-x'1}O$ ($0.70 \leq x'1 \leq 1.00$).
- [Claim 13] The assembly body as set forth in any one of claims 1 to 12, wherein the content ratio of Ni is 20 to 90 wt%, and the content ratio of Cu is 10 to 80 wt% at said cermet metal phase when entire said cermet metal phase included in said cermet member is 100 wt%.
- [Claim 14] The assembly body as set forth in any one of claims 1 to 13, wherein said metal member includes at least one of Ni, Cu, and Fe.
- [Claim 15] The assembly body as set forth in any one of claims 1 to 14, wherein said metal member includes at least Ni and Fe.
- [Claim 16] The assembly body as set forth in any one of claims 1 to 15, wherein a content of Ni included in said metal member is 40 to 85 wt.%, and the content of Fe is 15 to 60 wt% when entire said metal

member is 100 wt%.

[Claim 17] The assembly body as set forth in any one of claims 1 to 16, wherein said intermediate metal phase comprises at least one of Cu, Ni and Fe.

[Claim 18] The assembly body as set forth in any one of claims 5 to 17, wherein said metal only layer includes at least Ni.

[Claim 19] The assembly body as set forth in any one of claims 1 to 18, wherein at least one oxide of said intermediate member is the same oxide as that included in said cermet member.

[Claim 20] The assembly body as set forth in any one of claims 1 to 19, wherein a difference in absolute value between an average linear expansion coefficient of said cermet member and the average linear expansion coefficient of said metal member being 2.0 ppm/°C or less is present within a predetermined range of 1000°C or higher.

[Claim 21] The assembly body as set forth in any one of claims 1 to 20 used for electrodes for electrolysis.

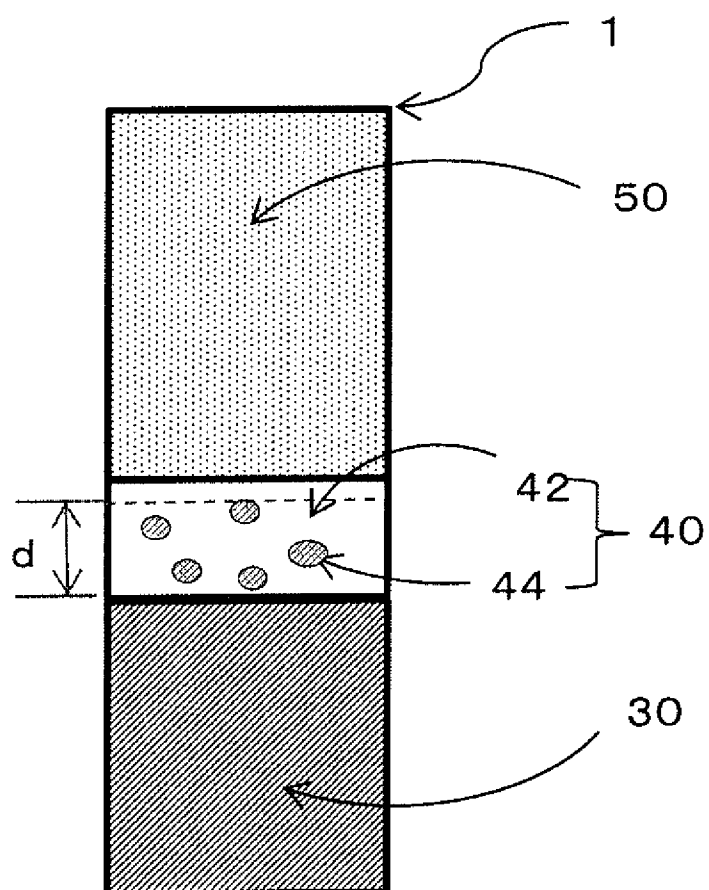
[Claim 22] An electrode for an electrolysis comprising the assembly body as set forth in any one of claims 1 to 21.

[Claim 23] A process for producing an assembly body having a cermet member, a metal member and an intermediate member comprising the steps of

producing a mixture comprising an oxide to become an intermediate oxide phase included in the intermediate member after heating and a metal to become an intermediate metal phase included in the intermediate member after heating,
arranging the mixture between the cermet member and the metal member, and
heating the cermet member and the metal member in order to bond the cermet member and the metal member.

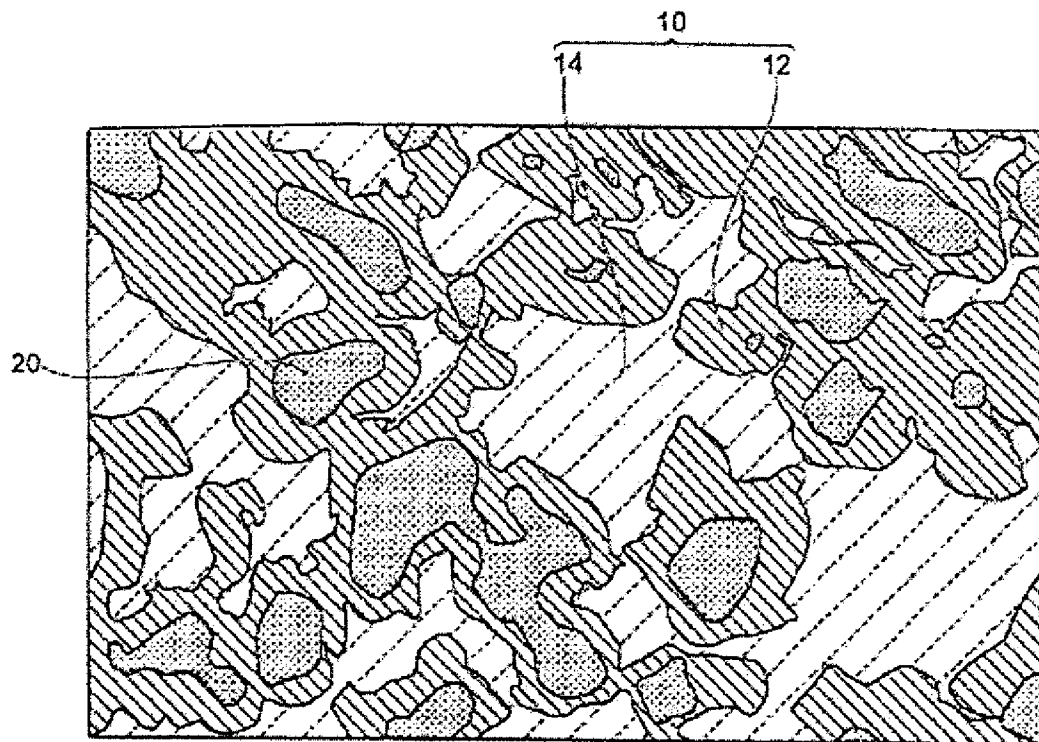
[Fig. 1]

Fig.1



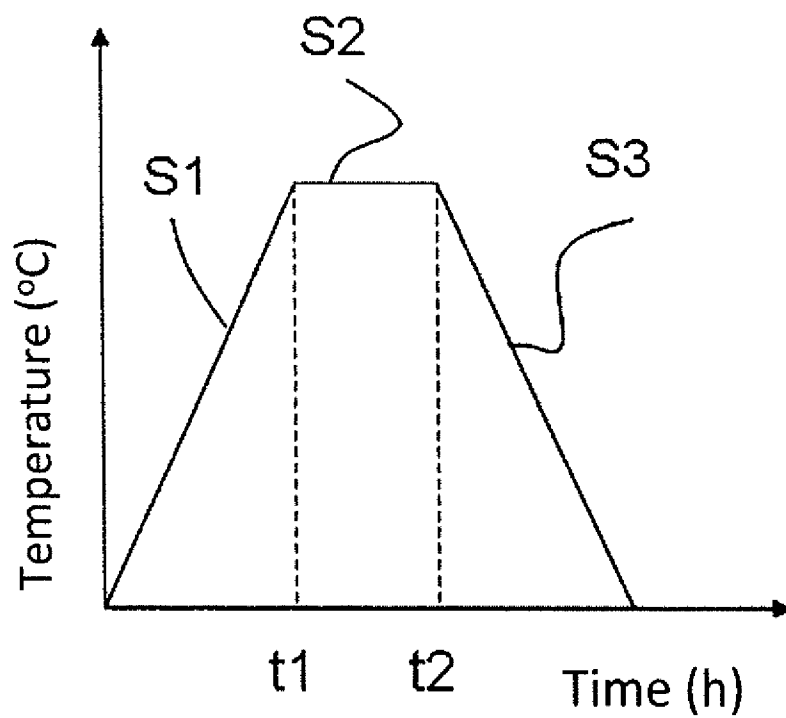
[Fig. 2]

Fig.2



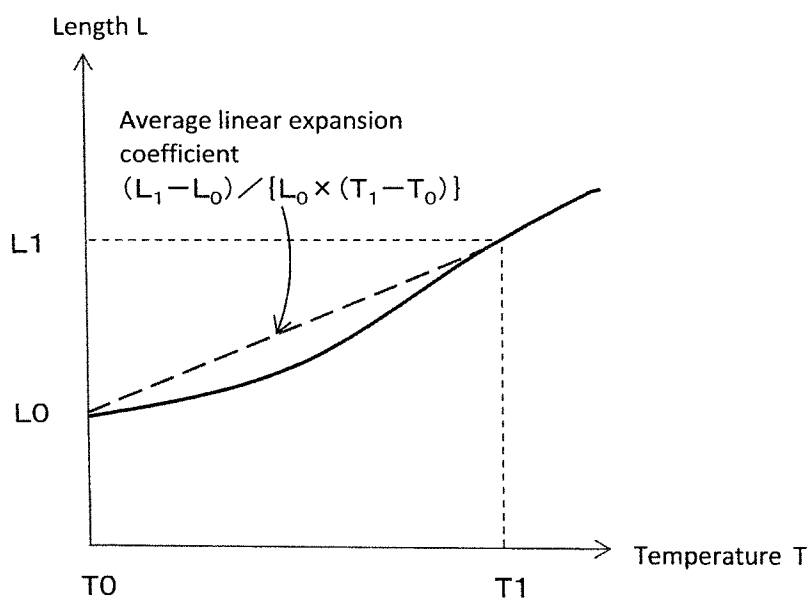
[Fig. 3]

Fig.3



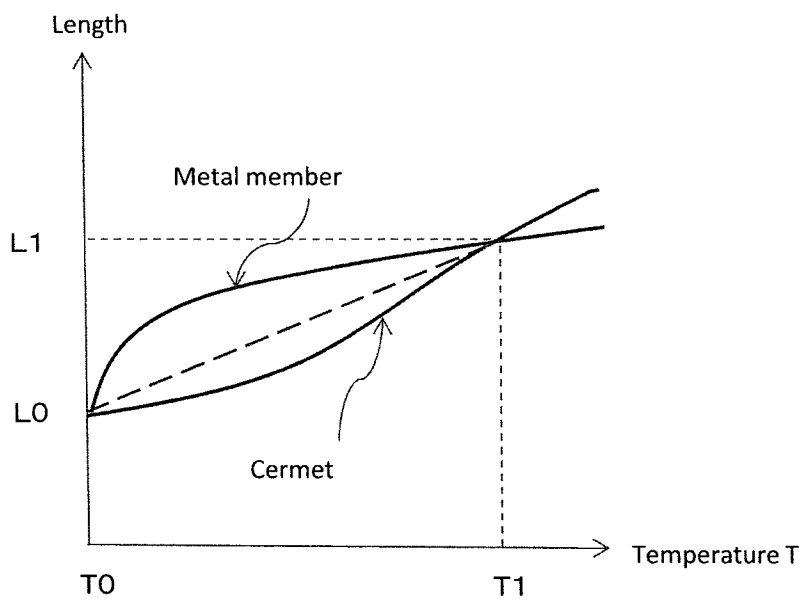
[Fig. 4]

Fig.4



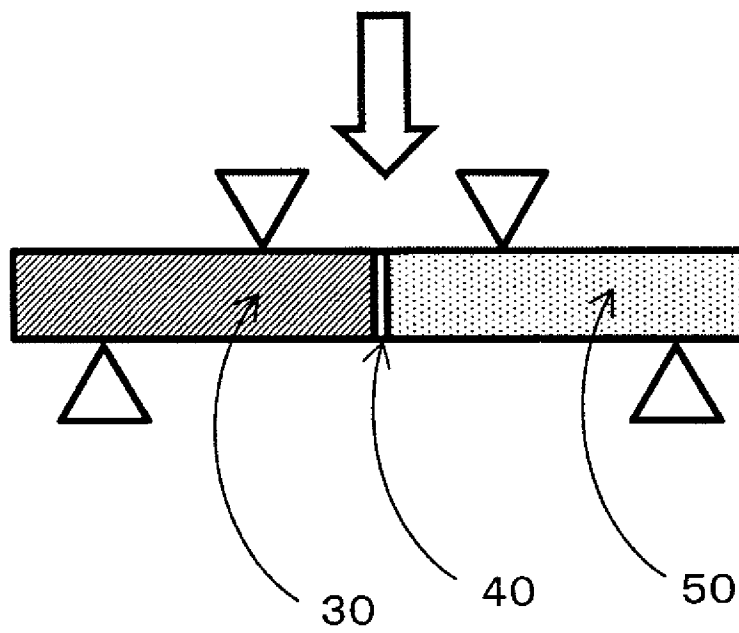
[Fig. 5]

Fig.5



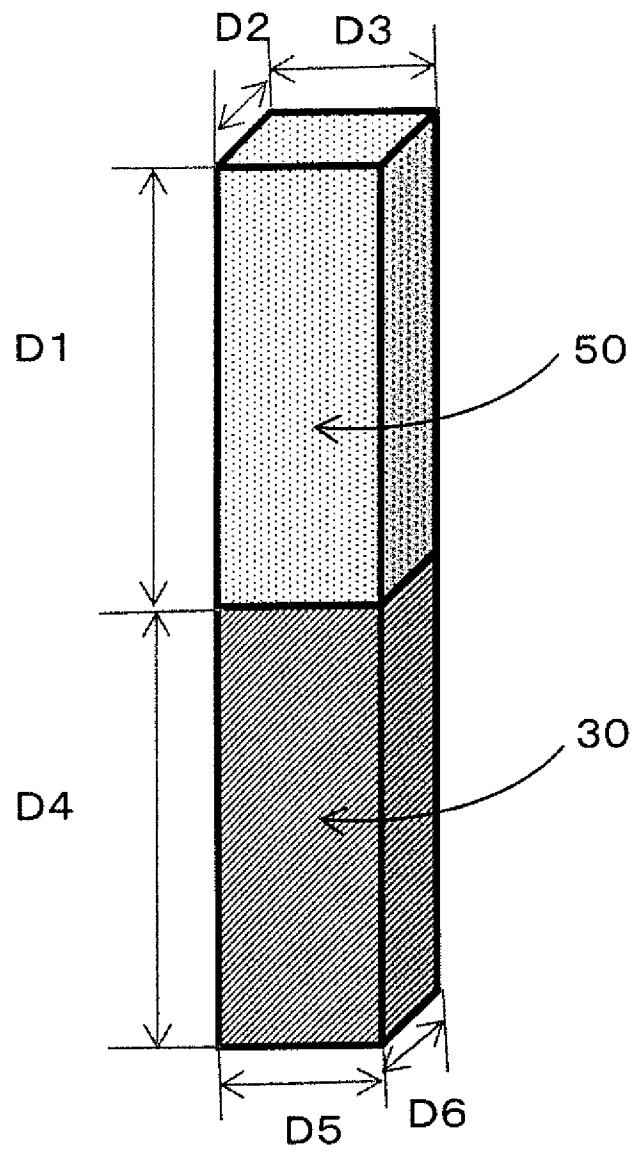
[Fig. 6]

Fig.6



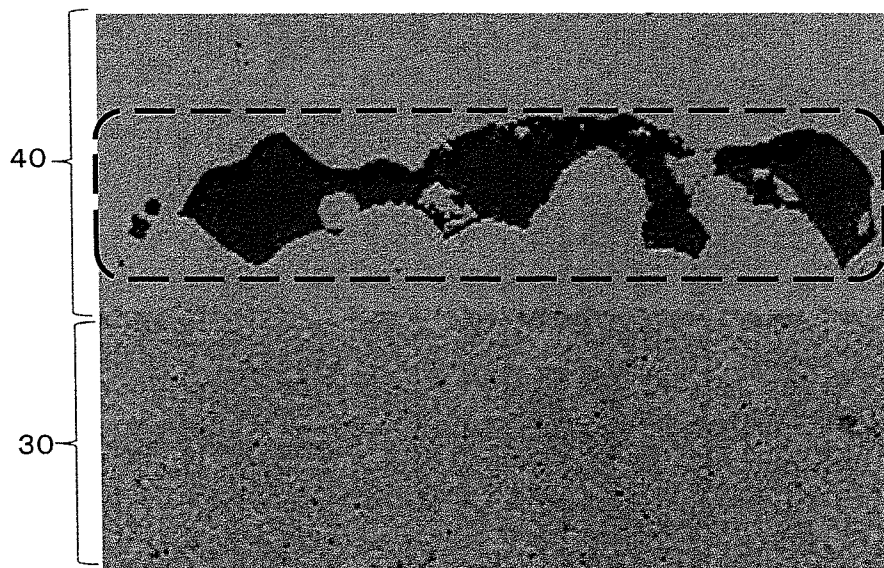
[Fig. 7]

Fig.7



[Fig. 8]

Fig.8



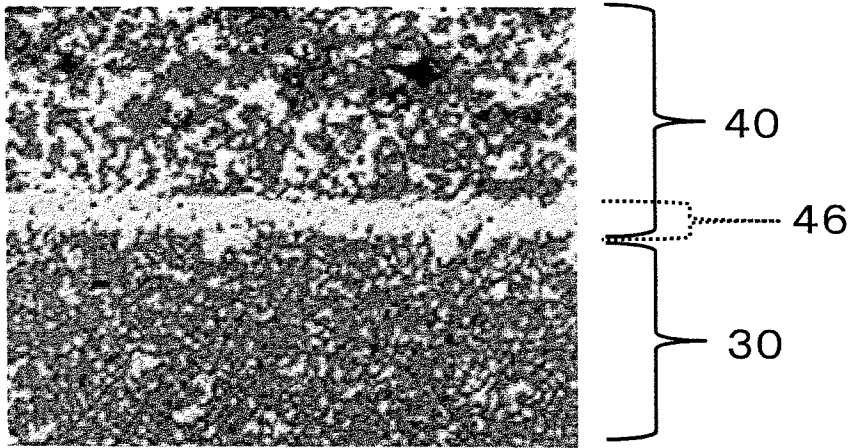
[Fig. 9]

Fig.9



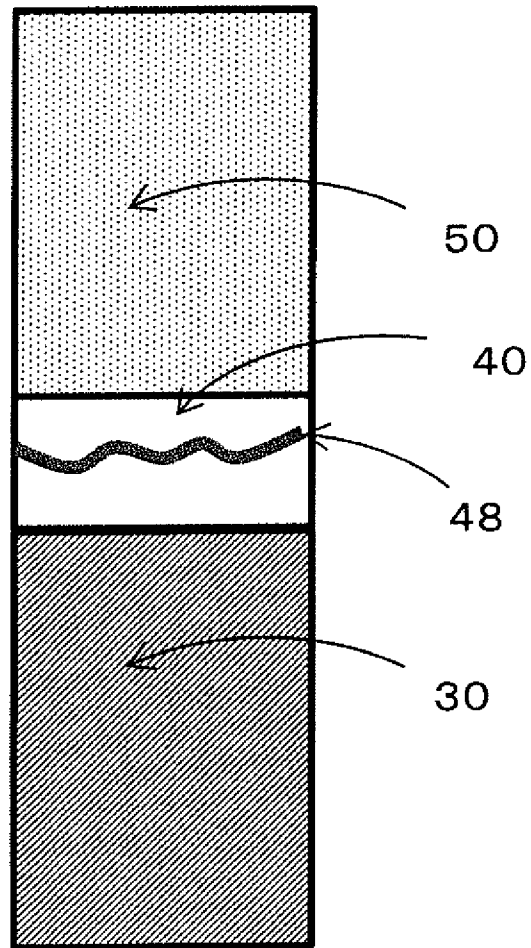
[Fig. 10]

Fig.10



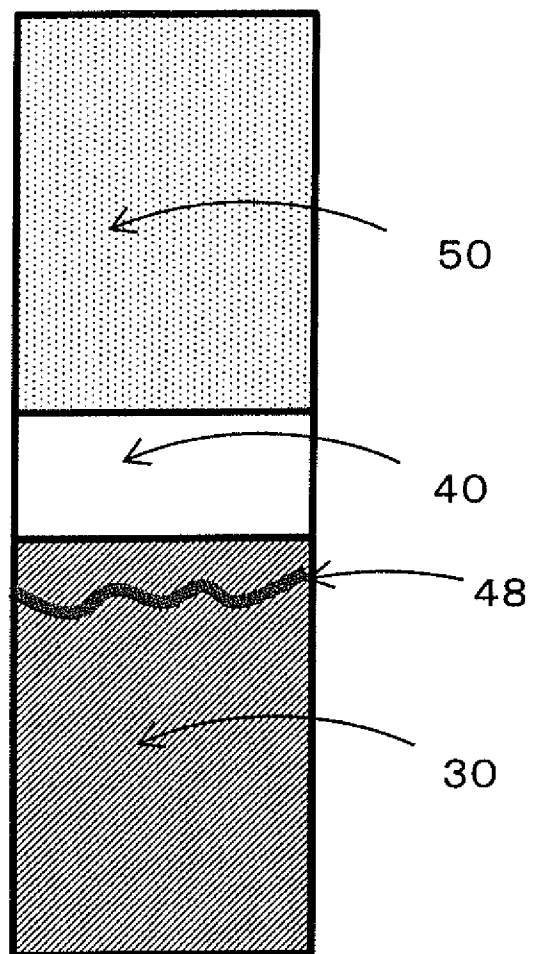
[Fig. 11]

Fig.11



[Fig. 12]

Fig.12



INTERNATIONAL SEARCH REPORT

International application No

PCT/JP2015/002666

A. CLASSIFICATION OF SUBJECT MATTER

INV. C25C3/12 C25C7/02
ADD.

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)

C25C

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

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

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 495 049 A (SECRIST DUANE R [US] ET AL) 22 January 1985 (1985-01-22)	1-4,6-9, 14-17, 19-23
Y	column 1, lines 48-51; claims 1,2; figures 3,4; examples 10-13 column 2, line 53 - column 3, line 9 column 5, lines 1-20	5,10-13, 18
Y	----- US 4 626 333 A (SECRIST DUANE R [US] ET AL) 2 December 1986 (1986-12-02) column 3, lines 29-44; claims 1-5 ----- -/-	5,18



Further documents are listed in the continuation of Box C.



See patent family annex.

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Date of the actual completion of the international search

29 January 2016

Date of mailing of the international search report

08/02/2016

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Authorized officer

Hammerstein, G

INTERNATIONAL SEARCH REPORT

International application No

PCT/JP2015/002666

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	R. P. Pawlek: "Inert Anodes: An Update" In: "Essential Readings in Light Metals", 1 March 2013 (2013-03-01), John Wiley & Sons, Inc., Hoboken, NJ, USA, XP055185837, ISBN: 978-1-11-863663-3 vol. 4, pages 1126-1133, DOI: 10.1002/9781118647745.ch150, chapter "Cermets" -----	10-13
X	US 4 529 494 A (JOO' LOUIS A [US] ET AL) 16 July 1985 (1985-07-16) claims 1,4,15; example 2 -----	1,2,6-8, 14,15, 21-23
A	US 4 443 314 A (SECRIST DUANE R [US] ET AL) 17 April 1984 (1984-04-17) the whole document -----	1-23

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/JP2015/002666

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		EP 0139699 A1 08-05-1985	
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		WO 8403721 A1 27-09-1984	