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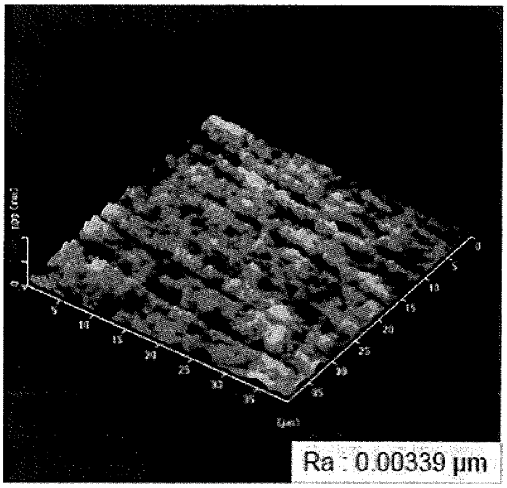
(54) **DECORATIVE MEMBER**

(57) A decoration member with excellent abrasion resistance and light weight, exhibiting black-based metallic luster derived from metal is provided. A cermet containing a hard phase containing at least two or more of TiCN, TiC, TiN, and MoC_2 in a proportion of 70 mass% or more and 97 mass% or less with the remainder constituted by a binder phase and inevitable impurities is processed into a decoration member, whereby the abrasion resistance and the lightness in weight are achieved. By making the surface roughness of the decoration member equal to the mirror surface state, the decoration member whose abrasion resistance, lightness in weight, and black-based metallic luster satisfy the users can be provided.



Figur 4

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Description

TECHNICAL FIELD

[0001] The present invention relates to a decoration member exhibiting metallic luster, which is suitable for a decoration member used for a decoration member for accessories, a decoration member for watches, a decoration member for building materials, a decoration member for kitchen members, a decoration member for home appliances, a decoration member for automobiles, etc., and particularly to a decoration member for watches, which provides beautiful metallic luster suitably applied to a watch case and a band piece.

BACKGROUND ART

[0002] In watch and jewelry stores in Europe, black-based decoration members for watches have conventionally been popular and black-based decoration members for watches have recently been in fashion. In contrast to many decoration members having the chromatic colors, the black-based decoration members have traditionally been used as the one having formal color and highly evaluated for the simple but sophisticated appearance. One kind of the black-based members has the metallic luster obtained by making a certain metal surface into a mirror surface, which is popular for its tone of color and metallic texture.

[0003] In such circumstances, various black-based decoration members have been suggested so far. For example, Patent Document 1 has disclosed the black and white single-color cemented carbide mainly containing WC, TiC, or NbC as the black and white single-color decoration member.

[0004] Patent Document 2 has disclosed the article for decoration, which mainly contains black zirconia. Of the black zirconia, 3 to 70 wt% is the matrix of at least one kind of stabilized zirconia selected from the group consisting of yttrium oxide, magnesium oxide, cerium oxide, and calcium oxide, 25 to 50 wt% is cobalt oxide, and the rest is the powder of cobalt oxide and iron oxide or the powder of spinel type $CoFe_2O_4$.

[0005] Patent Document 3 has disclosed the black zirconia ceramic containing a colorant including 40 to 70 mass% of cobalt oxide (at least one kind of CoO, Co_2O_3, and Co_3O_4), iron oxide (Fe_2O_3), and chromium oxide (Cr_2O_3). The iron oxide is contained by 15 to 30 mass% and the cobalt oxide is contained by 40 to 70 mass%, and also disclosed the decoration member using the same.

CITATION LIST

PATENT DOCUMENT

[0006]

Patent Document 1: JP-A-60-4051
Patent Document 2: Japanese Patent No. 3714563
Patent Document 3: Japanese Patent No. 4960070

SUMMARY OF THE INVENTION

PROBLEMS TO BE SOLVED BY THE INVENTION

[0007] The cemented carbide disclosed in Patent Document 1 has the monochromatic and gold-based metallic luster owing to the hard metal; however, since the cemented carbide is employed, the density is as large as 12.8 to 14.3 g/m^3, which is too heavy for the user to wear for a long time.

[0008] The article for decoration mainly containing black zirconia according to Patent Document 2 has the mechanical characteristics that zirconia originally has, such as high strength and high toughness, and has the density as low as 6.0 g/cm^3. However, the tone of color is a little bluish black and the color is black derived from zirconia ceramic, which fails to achieve the black metallic luster without the use of metal.

[0009] The black zirconia ceramic according to Patent Document 3 exhibits the black tone of color called extreme black and has a density that can be set in the range of 5.9 g/cm^3 to 6.1 g/cm^3; however, since the ceramic is made without the use of metal, the black-based metallic luster and the metallic texture cannot be reproduced. Further, since the material is zirconia, the Vickers hardness is lower than 1450 Hv, which is the Vickers hardness of cemented carbide.

[0010] The present invention has been made in view of the above, and has an object to provide a decoration member with abrasion resistance as high as cemented carbide and light weight, and enabling a user to wear the member for a long time, and moreover enabling a user to feel a high-grade sense and aesthetic satisfaction with the black-based tone

of color derived from metal and the smooth texture unique to metal.

SOLUTIONS TO THE PROBLEMS

[0011] A decoration member according to the present invention includes a hard phase containing at least two or more of TiCN, TiC, TiN, and MoC_2 in a proportion of 70 mass% or more and 97 mass% or less with the remainder constituted by a binder phase and inevitable impurities. The decoration member has light weight, excellent abrasion resistance, and a surface roughness Ra of 0.008 μm or less.

[0012] The above decoration member according to the present invention has a surface roughness of 0.004 μm or less and Rz of 0.02 μm or less.

EFFECTS OF THE INVENTION

[0013] The decoration member according to the present invention includes a hard phase containing at least two or more of TiCN, TiC, TiN, and MoC_2 in a proportion of 70 mass% or more and 97 mass% or less with the remainder constituted by a binder phase and inevitable impurities. The decoration member has light weight, excellent abrasion resistance, and a surface roughness Ra of 0.008 μm or less. Because of having at least two or more of TiCN, TiC, TiN, and MoC_2, the apparent density can be made as low as 6.1 g/cm^3 or less, so that the weight can be as light as or lighter than that of zirconia. For this reason, the user can wear the member for a long time without feeling tired. Moreover, since the Vickers hardness is 1450 or more and the abrasion resistance is equal to that of the cemented carbide, the decoration member can have scratch resistance. Moreover, by setting the surface roughness to Ra = 0.008 μm or less, the decoration member with the excellent texture causing less scattering and exhibiting the black-based metallic luster can be provided. As a result, with the black-based metallic luster and the metallic texture, the decoration member becomes popular in the use for the decoration member for accessories such as a watch case, a band piece, a broach, a neckless, earrings, a ring, a tiepin, a tie tack, a medal, a glass frame, or a button, a decoration article for building materials, such as tiles for a floor, a wall, and a ceiling, or a door knob, a decoration member for kitchen members, such as a spoon or a fork, a decoration member for home appliances, or a decoration member for automobiles, especially for the watch case and the band piece.

[0014] More preferably, when the surface roughness of the cermet decoration member according to the present invention is set to Ra = 0.004 μm or less and Rz = 0.02 μm or less, the mirror surface reflection from the surface of the decoration member is larger than the scattering, so that the white color due to the scattering of the visible light disappears and the black-based metallic luster appears. Thus, the deep metallic luster and the smooth texture comfortable to skin, which the decoration member originally has, can be obtained and the high-grade sense, aesthetic satisfaction, and spiritual comfort can be obtained further and it is expected that such a decoration member will become popular in the market.

BRIEF DESCRIPTION OF THE DRAWINGS

[0015]

Fig. 1 illustrates a decoration member that does not have a mirror surface.

Fig. 2 illustrates a decoration member that has a mirror surface.

Fig. 3 illustrates the decoration member that does not have a mirror surface, which is magnified by 500 times with the atomic force microscope (Seiko Instruments Inc., Nanopics 1000).

Fig. 4 illustrates the decoration member that has a mirror surface, which is magnified by 500 times with the atomic force microscope (Seiko Instruments Inc., Nanopics 1000).

Fig. 5 is a perspective view illustrating an example of a structure of a watch case corresponding to a decoration member for a watch according to the present invention.

Fig. 6 is a schematic view illustrating an example of a structure of a watch band corresponding to a decoration member for a watch according to the present invention.

DESCRIPTION OF EMBODIMENTS

[0016] An example of an embodiment of the present invention is hereinafter described.

[0017] A decoration member according to the present invention includes a hard phase containing at least two or more of TiC, TiCN, TiN, and MoC_2 in a proportion of 70 mass% or more and 97 mass% or less with the remainder constituted by a binder phase and inevitable impurities. The decoration member has light weight, excellent abrasion resistance, and a surface roughness Ra of 0.008 μm or less.

[0018] As a result of concerted studies on various materials for the decoration members enabling a user to wear for a long time because of the excellent abrasion resistance and the light weight while achieving the black-based metallic luster, the present inventors have discovered that when a cermet formed of a hard phase containing TiC, TiCN, TiN, and MoC_2 in a proportion of 70 mass% or more and 97 mass% or less with the remainder constituted by a binder phase and inevitable impurities is molded into a decoration member so that the cermet decoration member has a surface roughness of Ra = 0.008 μm or less, an owner pursuing the decorative value can feel the high-grade sense, the aesthetic satisfaction, spiritual comfort, and the like and the decoration member exhibits the black-based tone of color that is currently popular in the market.

[0019] In the present invention, the excellent abrasion resistance refers to the metal surface of the decoration member whose Vickers hardness is 1450 or more. Mainly containing TiC, TiCN, TiN, or MoC_2 makes it possible to achieve the intended Vickers hardness.

[0020] In the present invention, the light weight refers to the density of the decoration member that is 6.1 g/cm^3 or less. The targeted light density can be achieved by avoiding the heavy materials such as TaC, PbC, and WC whose molecular weights are 192 g, 219 g, and 195 g, respectively.

[0021] Note that in the present invention, the surface roughness Ra is measured by the laser microscope or the atomic force microscope (Seiko Instruments Inc.. Nanopics 1000). When the decoration member has a surface roughness of Ra = 0.008 μm or less, the decoration member can have a mirror surface that reflects visible light.

[0022] The difference between the mirror surface and the non-mirror surface is described with reference to Figs. 1 and 2. Fig. 1 is a photograph of a surface of a decoration member with a non-mirror surface whose Ra is more than 0.008 μm, and Fig. 2 is a photograph of a surface of a decoration member with a mirror surface whose Ra is 0.008 μm or less.

[0023] On the metal surface with the non-mirror surface in Fig. 1, the luster is dim and blurry, and the surface seems a little white due to the light scattering. On the other hand, in Fig. 2, the metal surface with the mirror surface has clear luster and it is understood that Fig. 2 shows the mirror surface exhibiting the black-based metallic luster.

[0024] In the present invention, it has been discovered that by changing the surface roughness of the cermet, the degree of metallic luster of the cermet to be obtained varies; in particular, it has been clarified that when the surface roughness is Ra = 0.004 μm or less and Rz = 0.02 μm or less, the difference is large. The surface roughness Ra is measured by the atomic force microscope (Seiko Instruments Inc., Nanopics 1000) and Rz is measured with the laser microscope.

[0025] Figs. 3 and 4 each show the magnified area of 40 μm of the member surface obtained by the atomic force microscope (Seiko Instruments Inc., Nanopics 1000). Fig. 3 shows the surface of the cermet decoration member with a surface roughness Ra of more than 0.004 μm. Fig. 4 shows the surface of the cermet decoration member with a surface roughness Ra of 0.004 μm or less.

[0026] The comparison between Figs. 3 and 4 indicates that the scattering of the visible light is less on the mirror surface with Ra = 0.004 μm or less and the mirror surface contains a black area. Therefore, it is understood that as the surface roughness is smaller, the black-based metallic luster is exhibited.

[0027] Moreover, Rz and the luster are as shown in Table 1. Table 1 contains the values of the surface roughness Ra and Rz of the cermet measured with the laser microscope and the surface state obtained by the actual visual observation.

[Table 1]

Surface state (visual observation)	Surface roughness		
	Ra	Rt	Rz
Non-mirror surface	0.031	0.356	0.194
Non-mirror surface	0.018	0.176	0.09
Non-mirror surface	0.013	0.18	0.078
Mirror surface (a little white)	0.004	0.048	0.023
Mirror surface (black-based)	0.002	0.032	0.014

[0028] As shown in Table 1, it has been determined that the mirror surface state is not obtained when the surface roughness Ra is more than or equal to 0.01 μm and the surface is a mirror surface when Ra = 0.004 μm or less. Moreover, attention is paid to not just the mean roughness Ra but also the ten-point mean roughness Rz obtained from the five high positions and five low positions on the metal surface, and by setting Rz = 0.02 μm or less in addition to Ra = 0.004 μm or less, the fascinating black-based metallic luster without the scattering observed can be exhibited.

[0029] Therefore, specular reflection on the metal surface provides clearer metallic luster as the metal surface has

smaller surface roughness. The surface roughness of the metal surface is preferably Ra = 0.008 μm or less, in which case the black-based metallic luster with less scattering is exhibited. The surface roughness of the metal surface is more preferably Ra = 0.004 μm or less and Rz = 0.02 μm or less, in which case the fascinating black-based metallic luster without the appearance of the scattering observed is exhibited.

[0030] By satisfying any of the above surface roughness Ra and Rz, the light scattering on the metal surface is suppressed and while the black-based metallic luster is exhibited, the smooth texture of metal can be reproduced; thus, the high-grade sense is enhanced and the aesthetic satisfaction becomes higher.

[0031] Next, an example of a manufacturing method for a cermet decoration member according to the present invention is described.

[0032] For obtaining a cermet decoration member according to the present invention, a cermet containing TiC/TiCN and MoC_2 by 70 mass% or more and 97 mass% or less with the remainder constituted by a binder phase and inevitable impurities is molded into a shape of a predetermined decoration member. A molding method is not limited in particular, and extrusion molding, injection molding, sintering, polishing, grinding, eiectroforming, electrochemical processing, discharging processing, laser processing, and the like are given. For example, in the example of the present invention, the cermet is molded into a shape of a watch case or a band piece as shown in Figs. 5 and 6 by the use of any of the above methods.

[0033] The molded watch case or band piece is processed additionally, so that the watch case or band piece has a mirror surface exhibiting the metallic luster. A method of forming a mirror surface with the metallic luster may be, but not limited to, etching, evaporation, plating, polishing, washing, laser processing, ion plating, or the like; in this example, the barrel polishing is employed to form the mirror surface because the mass production is easy and the chamfering and rounding can be performed at one time.

[0034] In the case of the watch case or the band piece in this example, the black-based metallic luster starts to be exhibited when the surface roughness is set to Ra = 0.008 μm to 0.004 μm or more, and the black-based metallic luster is exhibited when the surface roughness is set to Ra = 0.004 μm or less and Rz = 0.02 μm or less. Theoretically, the darkest black-based metallic luster is exhibited when the surface roughness is Ra = 0.000 μm and Rz = 0.00 μm.

[0035] The watch case and the band piece according to the example of the present invention has an apparent density of 5.8 g/cm^3 and a Vickers hardness of 1570 Hv, which is as lightweight as zirconia and as hard as or harder than the cemented carbide. Thus, a user can wear the watch case and the band piece for a long time without feeling tired, and the watch case and the band piece are scratch-resistant.

[0036] The watch case and the band piece obtained as above have the mirror surface exhibiting the metallic luster; therefore, the decoration member for a watch that provides the high-grade sense and the aesthetic satisfaction can be provided.

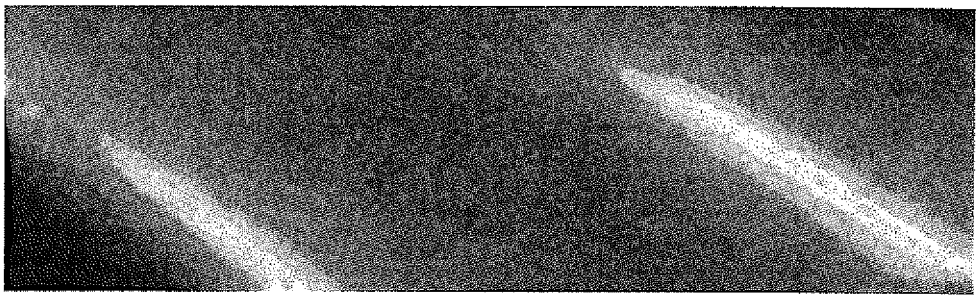
[0037] The present invention is applicable to not just the decoration member for a watch but also a decoration member for accessories such as a brooch, a neckless, earrings, a ring, a tiepin, a tie tack, a medal, a glass frame, or a button, a decoration article for building materials, such as tiles for a floor, a wall, and a ceiling, or a door knob, a decoration member for kitchen members, such as a spoon or a fork, a decoration member for home appliances, or a decoration member for automobiles.

[0038] According to the present invention, the cermet decoration member with excellent abrasion resistance, hardness high enough to resist the scratch, and light weight, thereby enabling a user to wear for a long time and exhibiting the metallic luster is provided.

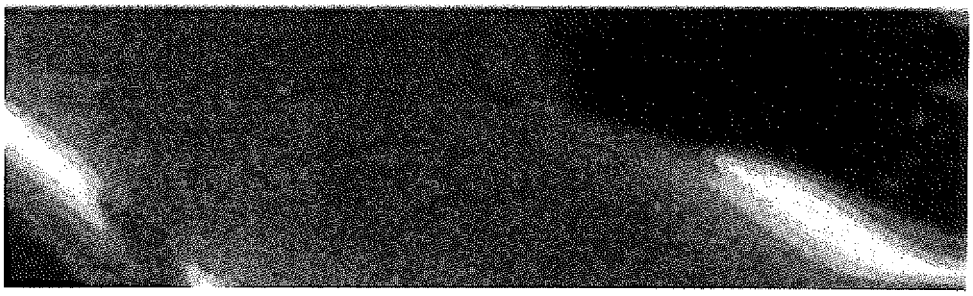
Claims

1. A decoration member comprising
   a hard phase containing at least two or more of TiCN, TiC, TiN, and MoC_2 in a proportion of 70 mass% or more and 97 mass% or less with the remainder constituted by a binder phase and inevitable impurities, wherein
   the decoration member has light weight, excellent abrasion resistance, and surface roughness Ra of 0.008 μm or less.

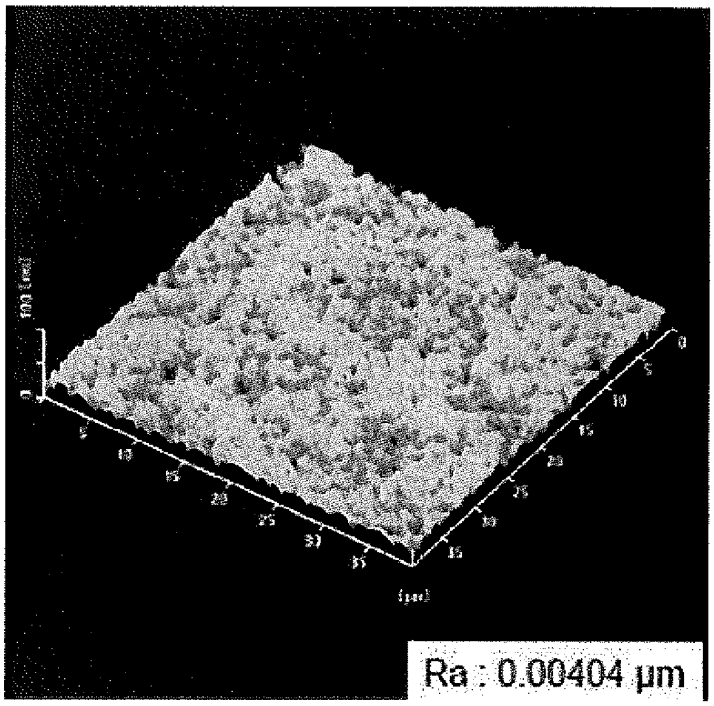
2. The decoration member according to claim 1, wherein the decoration member has surface roughness Ra of 0.004 μm or less and Rz of 0.02 μm or less.



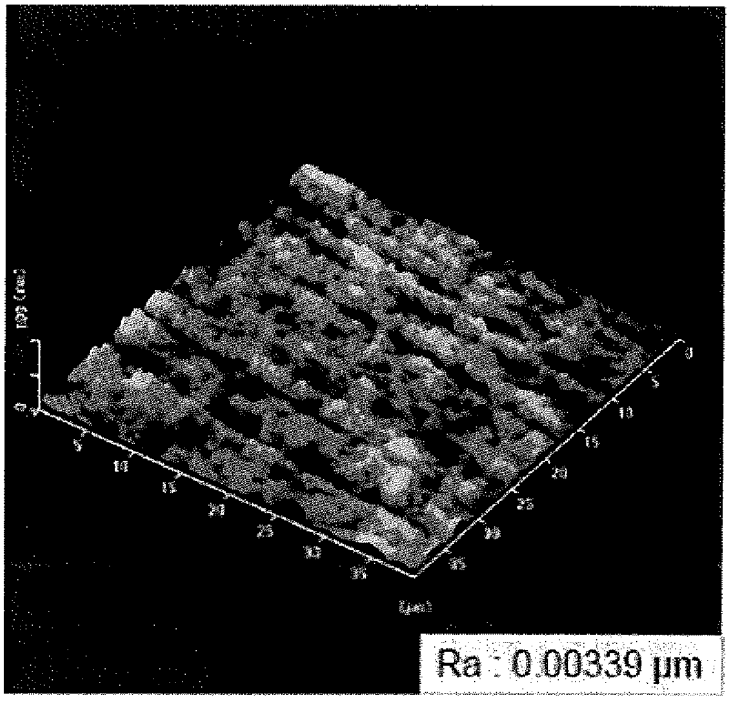
Figur 1



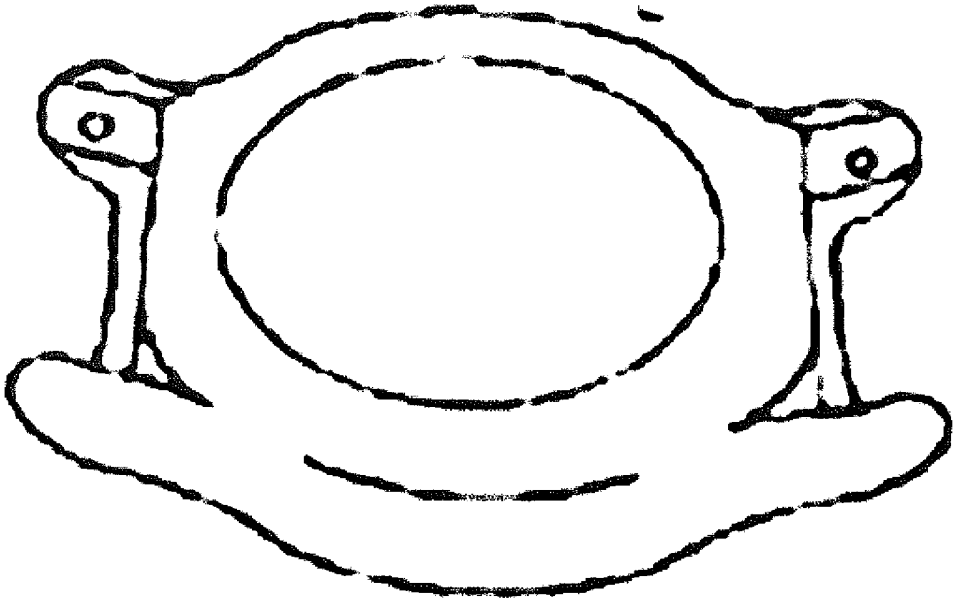
Figur 2



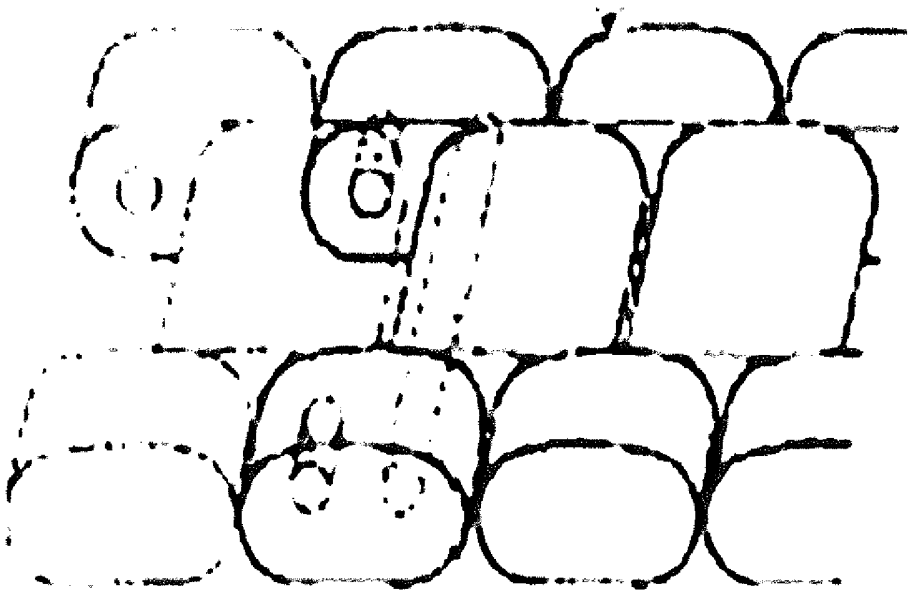
Figur 3



Figur 4



Figur 5



Figur 6

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2013/084832

A. CLASSIFICATION OF SUBJECT MATTER
C22C29/02(2006.01)i, *A44C5/00*(2006.01)i, *A44C5/02*(2006.01)i, *C22C29/04*(2006.01)n, *C22C29/16*(2006.01)n

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)
C22C29/02, A44C5/00, A44C5/02, C22C29/04, C22C29/16

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
Jitsuyo Shinan Koho 1922-1996 Jitsuyo Shinan Toroku Koho 1996-2014
Kokai Jitsuyo Shinan Koho 1971-2014 Toroku Jitsuyo Shinan Koho 1994-2014

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO 2012/121023 A1 (Sumitomo Electric Hardmetal Corp.), 13 September 2012 (13.09.2012), claims & EP 2568055 A1 & WO 2012/121023 A1 & CA 2801479 A	1-2
Y	JP 03-068739 A (Kyocera Corp.), 25 March 1991 (25.03.1991), claims (Family: none)	1-2
Y	JP 03-068738 A (Kyocera Corp.), 25 March 1991 (25.03.1991), claims (Family: none)	1-2

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

* Special categories of cited documents:
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Date of the actual completion of the international search	Date of mailing of the international search report
01 April, 2014 (01.04.14)	15 April, 2014 (15.04.14)
Name and mailing address of the ISA/ Japanese Patent Office	Authorized officer
Facsimile No.	Telephone No.

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

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2013/084832

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	JP 2012-214372 A (Kyocera Corp.), 08 November 2012 (08.11.2012), claims; paragraphs [0001], [0025] (Family: none)	1-2
Y	WO 2007/058177 A1 (Nippon Tungsten Co., Ltd.), 24 May 2007 (24.05.2007), claims; paragraph [0032] & JP 4977033 B2	1-2

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REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

- JP 60004051 A **[0006]**
- JP 3714563 B **[0006]**
- JP 4960070 B **[0006]**