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

(11) **EP 1 930 457 A1**

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

(43) Date of publication:
11.06.2008 Bulletin 2008/24

(21) Application number: **06810940.4**

(22) Date of filing: **29.09.2006**

(51) Int Cl.:
C22C 29/04 *(2006.01)*
B21C 25/02 *(2006.01)*
C22C 1/05 *(2006.01)*
B21C 25/00 *(2006.01)*
B22F 1/00 *(2006.01)*

(86) International application number:
PCT/JP2006/319577

(87) International publication number:
WO 2007/037431 (05.04.2007 Gazette 2007/14)

(84) Designated Contracting States:
CZ

(30) Priority: **29.09.2005 JP 2005283384**
22.12.2005 JP 2005371016

(71) Applicant: **Kyocera Corporation**
Kyoto-shi
Kyoto 612-8501 (JP)

(72) Inventor: **HAMASHIMA, Hiroshi**
Satsumasendai-shi
Kagoshima; 8950211 (JP)

(74) Representative: **HOFFMANN EITLE**
Patent- und Rechtsanwälte
Arabellastrasse 4
81925 München (DE)

(54) SINTERED BODY AND METHOD FOR PRODUCING SAME; SLIDING MEMBER, FILM-FORMING MATERIAL AND DIE FOR HOT EXTRUSION MOLDING EACH USING SUCH SINTERED BODY; AND HOT EXTRUSION MOLDING APPARATUS AND HOT EXTRUSION MOLDING METHOD EACH USING SUCH DIE FOR HOT EXTRUSION MOLDING

(57) There can be provided a sliding member, a film-forming material and a die for hot extrusion molding, that have high strength, high hardness, high toughness and high sliding properties under an atmosphere at about 400 to 600˚C, as well as a hot extrusion molding device using the die for hot extrusion molding, by using a sintered body comprising 58% by mass or more and 92.5% by mass or less of TiCN, 0.01% by mass or more and 1% by mass or less of Ti, 0.01% by mass or more and 2% by mass or less of TiC, and 0.01% by mass or more and 2% by mass or less of TiN, the balance being TaC, Ni and Cr.

Printed by Jouve, 75001 PARIS (FR)

Description

TECHNICAL FIELD

[0001] The present invention relates to a sintered body, a method for producing the same and a sliding member using the sintered body, as well as a film-forming material, a die for hot extrusion molding and a hot extrusion molding device and a hot extrusion molding method that use the die for hot extrusion molding.

BACKGROUND ART

[0002] In the case of molding an extrusion material such as an aluminum alloy through hot extrusion, as shown in Fig. 5 and Fig. 9, an extrusion material 6 has hitherto been molded into a desired shape by extruding an aluminum alloy billet 5 heated to about 400 to 500˚C through a through hole 101a serving as a guiding portion of a die 101 for hot extrusion molding serving as a bearing portion mounted in a die case 102 of a hot extrusion molding device 111.

[0003] As the material of the die 101 for hot extrusion molding, a cemented carbide and SKD61 are usually used. The cemented carbide is widely used since it has high hardness and also exhibit high strength equivalent to a metallic material, while SKD61 is widely used since it is less likely to cause a decrease in hardness and strength at high temperature.

[0004] However, when cemented carbide and SKD61 are used as the material of the die 101 for hot extrusion molding of an aluminum alloy at high temperature, hardness and strength drastically decrease as a result of heat deterioration at high temperature of about 400 to 500˚C in the case of the cemented carbide. In the case of SKD61, it is impossible to obtain high hardness that is sufficiently fit for use. Furthermore, aluminum adheres to the inner face 101b of the through hole 101a serving as the guiding portion when an extrusion material 6 such as an aluminum alloy is molded. Consequently, the cemented carbide and SKD61 do not endure molding for a long time and thus there arose problems such as flaws or dimensional errors in the molded extrusion material 6 as a result of breaking or wear of the die 101 for hot extrusion molding.

[0005] It has recently been made a trial of coating the inner face 101b of the through hole 101a serving as the guiding portion of the die 101 for hot extrusion molding made of a conventional cemented carbide or SKD61 with ceramic or cermet or increasing the thickness of the inner face, or making the die 101 for hot extrusion molding using ceramic so as to solve such problems. However, such a trial is not widespread since a lot of problems are not solved.

[0006] For example, Patent Document No. 1, Patent Document No. 2 and Patent Document No. 3 disclose coating of the inner face 101b of the through hole 101a of the die 101 for hot extrusion molding serving as the bearing portion used in hot extrusion molding of an aluminum alloy with ceramics.

[0007] Patent Document No. 1 and Patent Document No. 2 disclose that sliding resistance of the inner face 101b of the through hole 101a serving as the guiding portion of the extrusion material 6 and the die 101 for hot extrusion molding can be decreased and the extrusion rate can be improved by 20% as compared with the prior art by using a high speed steel as a matrix of the die 101 for hot extrusion molding and coating at least the portion serving as the sliding surface of the extrusion material with TiC in the thickness of 1 μm.

[0008] Also, Patent Document No. 3 discloses that a ceramics layer made of TiC, VC, TaC or WC is formed at a thickness within a range from 2 to 10 μm on the inner face 101b of the through hole 101a serving as the guiding portion of the die 101 for hot extrusion molding by spark hardening treatment, and that wear resistance of the coated ceramics layer is improved, although the matrix of the die 101 for hot extrusion molding is not mentioned.

[0009] Also, Patent Document No. 4 proposed that the surface of the inner face 101b of the through hole 101a serving as the guiding portion of the die 101 for hot extrusion molding made of the SKD material is coated with a cermet in a thickness within a range from 4 to 15 mm. The publication discloses that one or two or more kinds are selected from carbide-based ceramics such as Cr_3C_2, NbC, WC, TiC and SiC as the composition of the cermet, and the cermet is made of a Ni-based or NiCr-based alloy matrix and contains 10 to 30% by weight of the ceramics. The publication also discloses that, even if it is assumed that the temperature reaches 700˚C at a depth of 4 mm from the surface of the inner face 101b of the through hole 101a upon hot extrusion molding, hardness can be ensured and wear can be prevented, and also cracking caused by thermal shock at the time of hot extrusion molding can be suppressed and flaking of the reinforced portion can be prevented.

[0010] Furthermore, Patent Document No. 5 discloses that the body of the die 101 for hot extrusion molding is made of zirconia-based ceramics such as ZrO_2-Y_2O_3 and ZrO_2-MgO or ceramics such as Si_3N_4 silicon nitride. The publication discloses that an attempt of increasing the extrusion rate is made while suppressing generation of surface defects on the extrusion material 6 upon hot extrusion molding of aluminum.

[0011] Patent Document No. 6 proposes a titanium carbonitride (TiCN) sintered body as the material suited for an injection molding material and a die casting sleeve that require pressurized strength at high temperature in casting of a molten aluminum metal, and also discloses that a titanium carbonitride-based cermet sintered body is made by using

64 parts by weight of a titanium carbonitride (TiCN) powder, 30 parts by weight of a titanium carbide (TiC) powder and 6 parts by weight of AMF ferroalloy powder as a sintering aid. Patent Document No. 1: Japanese Unexamined Patent Publication No. 2000-63972
Patent Document No. 2: Japanese Unexamined Patent Publication No. 2000-63973
Patent Document No. 3: Japanese Unexamined Patent Publication No. 2000-102816
Patent Document No. 4: Japanese Unexamined Patent Publication No. 2000-63975
Patent Document No. 5: Japanese Patent No. 2535025
Patent Document No. 6: Japanese Unexamined Patent Publication No. 2003-321718

DISCLOSURE OF THE INVENTION

PROBLEMS TO BE SOLVED BY THE INVENTION

[0012] However, when the inner face 101b of the through hole 101a made of a high speed steel proposed in Patent Document No. 1 and Patent Document No. 2 is coated with TiC in a thickness of 1 μm, flaking of the coating is likely to occur since the difference in the thermal expansion coefficient between the high speed steel as the matrix and coated TiC is large. TiC is likely to cause an oxidation phenomenon in an atmosphere at 450˚C or higher and a problem of heat deterioration in which TiC of a high hardness material is replaced by TiO_2 to cause a drastic decrease in hardness.

[0013] In the case the ceramics layer is coated on the inner face 101b of the through hole 101a in a thickness within a range from 2 to 10 μm by electric discharge machining as proposed in Patent Document No. 3, flaking of the coating cannot be avoided since a difference in a thermal expansion coefficient between the matrix and coated ceramic layer is large

[0014] In the case the inner face 101b of the through hole 101a of the SKD material is coated with the carbide-based cermet in a large thickness within a range from 4 to 15 mm as proposed in Patent Document No. 4, one or two or more kinds are selected from carbide-based ceramics such as Cr_3C_2, NbC, WC, TiC and SiC as the composition of the carbide-based cermet. Even if the content of any of the carbide-based ceramics is from 10 to 30% by weight, high sliding characteristics with an aluminum alloy cannot be obtained. Therefore, it was impossible to avoid a problem that aluminum is likely to adhere on the inner face 101b of the through hole 101a serving as the guiding portion upon molding of the extrusion material 6 such as an aluminum alloy, resulting in fracture, and problems such as generation of flaws on the molded extrusion material 6 as a result of wear, and dimensional error.

[0015] In the case the body of the die 101 for hot extrusion molding is made of zirconia-based ceramics or silicon nitride ceramics as proposed in Patent Document No. 5, it was impossible to avoid problems such as fracture of the inner face 101b of the through hole 101a, generation of flaws on the molded extrusion material 6 as a result of wear, and dimensional error since high strength enough to endure hot extrusion molding of the aluminum alloy cannot be obtained.

[0016] Patent Document No. 6 discloses a method for producing a TiCN-TiC-based cermet sintered body as a material suited for a molten aluminum metal casting material. However, it was not suited for use as a die material for hot extrusion molding of an aluminum alloy since TiC is likely to cause an oxidation phenomenon in an atmosphere at 450˚C or higher and a problem of heat deterioration in which TiC of a high hardness material is replaced by TiO_2 to cause a drastic decrease in hardness.

[0017] In light of the above problems, an object of the present invention is to provide a sintered body having high strength, high hardness, high toughness and high sliding properties in an atmosphere at about 400 to 600˚C; a sliding member, a film-forming material, a die for hot extrusion molding each using the same; and a hot extrusion molding device that use the die for hot extrusion molding.

MEANS FOR SOLVING THE PROBLEMS

[0018] The sintered body of the present invention comprises 58 to 92.5% by mass of TiCN, 0.01 to 1% by mass of Ti, 0.01 to 2% by mass of TiC and 0.01 to 2% by mass of TiN, the remnant being TaC, Ni and Cr. The sintered body preferably contains 1 to 11% by mass of TaC, 3 to 13% by mass of Ni and 3 to 13% by mass of Cr.

[0019] Grain size distribution of the sintered body preferably has two peaks, and one peak in the grain size distribution preferably exists at a grain size within a range from 1.0 to 1.3 μm and the other peak preferably exists at a grain size within a range from 1.4 to 1.7 μm, and also a weight ratio of the crystal grain at a grain size within a range from 1.0 to 1.3 μm in the grain size distribution to the crystal grain at a grain size within a range from 1.4 to 1.7 μm is preferably from 3:2 to 1:1. Furthermore, the sintered body preferably has a spherical crystal grain.

[0020] The sliding member and the film-forming material of the present invention are formed using the sintered body and include, for example, a slider and a target material.

[0021] The die for hot extrusion molding of the present invention is formed using the sintered body. The die for hot extrusion molding has a through hole proximate a center of a plate shape, an amorphous film being formed on at least an inner face of the through hole. Furthermore, the amorphous film is preferably made of alumina or silicon carbide and the amorphous film preferably has a thickness of 0.2 to 1.2 μm.

[0022] The hot extrusion molding device of the present invention comprises the die for hot extrusion molding mounted at one end of a cylindrical die case, to the other end of the die case mounted at one end of a cylindrical container and an extrusion mechanism for extruding an extrusion material through the container disposed on the container.

[0023] The method for producing die for hot extrusion molding of the present invention comprises the steps of mixing a TiCN powder having a mean grain size of 0.3 to 0.7 μm and a TiCN powder having a mean grain size of 1.2 to 2 μm in a ratio 7:3 to 9:1; adding a TaC powder having a mean grain size of 1.5 μm or less, and a Ni powder and a Cr powder, each having a mean grain size of 2 μm or less; and grinding and mixing the powder mixture together with a solvent to form a slurry.

EFFECT OF THE INVENTION

[0024] The sintered body of the present invention comprises 58 to 92.5% by mass of TiCN, 0.01 to 1% by mass of Ti, 0.01 to 2% by mass of TiC and 0.01 to 2% by mass of TiN, and thus the die for hot extrusion molding of the present invention formed using the sintered body has the effect capable of maintaining high strength and high toughness even in a high temperature environment at about 400 to 600˚C and suppressing sliding resistance of the extrusion material.

[0025] The die 1 for hot extrusion molding has a through hole proximate a center of a plate shape, an amorphous film being formed on at least an inner face of the through hole, and thus oxidation of the inner face of the through hole is prevented by the amorphous film upon preheating at about 400 to 600˚C in the hot extrusion molding and therefore a decrease in strength (decrease in strength of cohesion between grains) of the die for hot extrusion molding before hot extrusion molding can be prevented.

[0026] Furthermore, it is possible to further improve the effect of preventing oxidation of the inner face of the through hole of the die for hot extrusion molding upon preheating before hot extrusion molding since an antioxidation action up to about 600˚C is exerted by forming the amorphous film using alumina or silicon carbide.

[0027] The thickness of the amorphous film is preferably from 0.2 to 1.2 μm and, when the thickness is at least 0.2 μm or more, the surface of the die for hot extrusion molding can be uniformly protected and a problem such as oxidation from the surface layer at high temperature can be prevented. It is sufficient that the thickness is 1.2 μm since the amorphous film is formed for the purpose of preventing oxidation upon preheating. When the film has a large thickness that by far exceeds 1.2 μm, particularly 2 μm, adhesion of the film decreases by internal stress and there is a fear that the amorphous film peels upon a setting operation. Oxidation of the inner face of the through hole can be prevented by forming an amorphous film made of silicon carbide when the preheating temperature is about 500˚C or lower, or by forming an amorphous film made of alumina when the preheating temperature is about 650˚C or lower.

[0028] When the hot extrusion molding device comprising the die for hot extrusion molding mounted at one end of a cylindrical die case, the other end of the die case mounted at one end of a cylindrical container and an extrusion mechanism for extruding an extrusion material through the container disposed on the container is used as a hot extrusion molding device, wear and fracture of the die for hot extrusion molding can be prevented and also flaws on the extrusion material and a dimensional problem can be suppressed, and thus an attempt of remarkably increasing continuous molding time of hot extrusion molding is made since the die for hot extrusion molding is excellent in strength, hardness and toughness at high temperature.

[0029] The method for producing a die for hot extrusion molding of the present invention comprises the steps of mixing a TiCN powder having a mean grain size of 0.3 to 0.7 μm and a TiCN powder having a mean grain size of 1.2 to 2 μm in a ratio 7:3 to 9:1; adding a TaC powder having a mean grain size of 1.5 μm or less, and a Ni powder and a Cr powder, each having a mean grain size of 2 μm or less; and grinding and mixing the powder mixture together with a solvent to form a slurry. Therefore, covalent bond sintering or solid phase bonding is promoted by surrounding the coarse TiCN crystal grains with the fine TiCN crystal grains, and thus sintering can be performed by suppressing decomposition of the TiCN crystal grains into Ti, TiC and TiN. When the die for hot extrusion molding of the present invention is produced using the sintered body thus obtained, inclusion of Ti, TiC and TiN are suppressed, and thus the effect of suppressing oxidation resistance at high temperature is exerted and, as a result, high sliding properties can be ensured.

BRIEF DESCRIPTION OF THE DRAWINGS

[0030]

Fig. 1 is a sectional view showing one example of a hot extrusion molding device comprising a die for hot extrusion molding of the present invention mounted therein.
Fig. 2 is a perspective view of a test piece of the present invention.

Fig. 3 is a sectional view showing a method for measuring a three-point bending strength.

Fig. 4(a) is a plan view of a die for hot extrusion molding of the present invention, and Fig. 4(b) is a sectional view thereof.

Fig. 5 is a sectional view of a conventional die for hot extrusion molding.

Fig. 6 is a TG-DTA differential thermal analysis chart of a TiCN-based cermet material which is molded into a die for hot extrusion molding of the present invention.

Fig. 7 is a TG-DTA differential thermal analysis chart of an amorphous alumina film.

Fig. 8 is a TG-DTA differential thermal analysis chart of an amorphous silicon carbide film.

Fig. 9 is a sectional view of a conventional hot extrusion molding device.

Fig. 10 is a diagram showing compositions of Ti, TiC and TiN of a die for hot extrusion molding of the present invention.

PREFERRED EMBODIMENT FOR CARRYING OUT THE INVENTION

[0031] Embodiments of the present invention will now be described with reference to the accompanying drawings. It is important that the sintered body of the present invention comprises 58 to 92.5% by mass of TiCN, 0.01 to 1% by mass of Ti, 0.01 to 2% by mass of TiC and 0.01 to 2% by mass of TiN, the balance being TaC, Ni and Cr. Furthermore, the sintered body preferably contains 1 to 11% by mass of TaC. Furthermore, the sintered body preferably contains 3 to 13% by mass of Ni and 3 to 13% by mass of Cr. The balance includes inevitable impurities such as Fe.

[0032] Grain size distribution of the sintered body preferably has two peaks, and each peak in the grain size distribution preferably exists at a grain size within a range from 1.0 to 1.3 μm or exists at a grain size within a range from 1.4 to 1.7 μm. When the one peak exists at a grain size of less than 1.0 μm, adhesion of only fine grains is likely to occur and adhesion of fine grains serves as nucleus of abnormal grain growth. Therefore, there arise problems such as detachment of grains and decrease in toughness and strength. When the one peak exists at a grain size of more than 1.3 μm, there arises a problem that the TiCN crystal grains are decomposed into Ti, TiC and TiN since covalent bond sintering or solid phase bonding is insufficient.

When the other peak exists at a grain size of less than 1.4 μm, there arises a problem that sliding properties cannot be ensured since the grain size increases excessively. When the other peak exists at a grain size of more than 1.7 μm, there arises a problem that the TiCN crystal grains are decomposed into Ti, TiC and TiN since covalent bond sintering or solid phase bonding is insufficient.

[0033] The weight ratio of the peak at a grain size within a range from 1.0 to 1.3 μm in the grain size distribution to the peak at a grain size within a range from 1.4 to 1.7 μm is from 3:2 to 1:1. When the peak at a grain size within a range from 1.0 to 1.3 μm accounts for 60% or more, there arises a problem that sliding properties cannot be ensured since adhesion between fine grains is likely to occur and a nucleus of abnormal grain growth is formed and thus detachment of grains and a decrease in strength occur. When the peak at a grain size within a range from 1.0 to 1.3 μm accounts for less than 50%, there arises a problem that the TiCN crystal grains are decomposed into Ti, TiC and TiN since covalent bond sintering or solid phase bonding is insufficient.

It is possible to obtain two peaks in the grain size distribution of the sintered body having a desired grain size by using a TiCN raw powder obtained by mixing a fine powder having a predetermined grain size with a coarse powder in a predetermined mixing ratio.

[0034] The sintered body preferably has a spherical crystal grain. When the crystal grain is spherical, sliding on the surface of the die made of the sintered body becomes stable upon extrusion of the material.

[0035] The sintered body of the present invention can be used as a sliding member or a film-forming material. When the sliding member formed by using the sintered body is used for a die for hot extrusion molding or a hot drawing die, high sliding properties can be obtained. Also, when the film-forming material formed by using the sintered body is formed into the sliding portion of the die for hot extrusion molding or the hot drawing die, high sliding properties can be obtained.

[0036] In Fig. 1, a schematic longitudinal sectional view of a hot extrusion molding device 11 wherein a die for hot extrusion molding of the present invention is mounted in a cylindrical die case 2 is shown. For example, a desired extrusion material 6 is molded through a die 1 for hot extrusion molding as a mouthpiece mold by charging a billet 5 of a heated cylindrical ingot of an aluminum alloy in a cylindrical container 3 and extruding by an extrusion mechanism 4. The die 1 for hot extrusion molding of the present invention is formed using the sintered body. The sintered body constituting the die 1 for hot extrusion molding comprises 58 to 92.5% by mass of TiCN, 1 to 11% by mass of TaC, 3 to 13% by mass of Ni and 3 to 13% by mass of Cr for the following reasons. When the content of TiCN is less than 58% by mass, high sliding properties could not be obtained. In contrast, when the content of TiCN exceeds 92.5% by mass, sinterability drastically deteriorates and thus high hardness and high strength cannot be obtained.

[0037] When the content of TaC is less than 1% by mass, oxidation resistance and sinterability at high temperature deteriorate. In contrast, when the content of TaC exceeds 11% by mass, sliding characteristics deteriorate. When each content of Ni and Cr is less than 3% by mass, sinterability deteriorates and it becomes impossible to ensure densification. When each content of Ni and Cr exceeds 13% by mass, high hardness cannot be ensured and wear resistance decreases.

[0038] The content of Ti is adjusted from 0.01 to 1% by mass of Ti and the content of TiC is adjusted from 0.01 to 2% by mass of TiC, and the content of TiN is adjusted from 0.01 to 2% by mass of TiN for the following reasons. When the content of Ti exceeds 1% by mass, the content of TiC exceeds 2% by mass, and the content of TiN exceeds 2% by mass, TiC, TiN and Ti metal exist in a desired amount or more and oxidation resistance decreases. As a result, high sliding properties drastically deteriorate and, when the sintered body is used as the die 1 for hot extrusion molding, there arise problems such as heat deterioration and deterioration of sliding properties in a high temperature environment at about 400 to 600˚C.

[0039] When each content of Ti, TiC and TiN is less than 0.01% by mass, there is a fear that local crystal growth proceeds and thus the state of the crystal grains becomes non-uniform and the strength decreases. Therefore, it is important that the content of any of Ti, TiC and TiN is 0.01% by mass or more.

[0040] It is possible to obtain those in which each proportion of TiCN, and Ti, TiC and TiN formed by decomposition of TiCN becomes a desired proportion by sintering a predetermined amount of a TiCN raw powder obtained by mixing a predetermined fine powder and a coarse powder in a predetermined mixing ratio.

[0041] In the case molding of the extrusion material 6 is once stopped, when the die is used again after removing a deposit such as an aluminum alloy by alkali cleaning of an inner face 1b of a through hole 1a serving as the guiding portion of the die 1 for hot extrusion molding using NaOH, the surface layer of cemented carbide or SKD61 used as a die material is corroded with a cleaning fluid and the surface hardness sometimes decreases drastically. However, the sintered body containing TiCN-TaC-Ni-Cr as main components of the die 1 for hot extrusion molding of the present invention is not corroded by alkali cleaning using NaOH, and can be repeatedly used until it becomes unusable as a result of wear.

[0042] Surface roughness Ra of the inner face 1b of the through hole 1a is preferably 0.05 μm or less. When the Ra exceeds 0.05 μm, it becomes impossible to obtain smoothness of the surface of the extrusion material 6.

[0043] It is preferred that the through hole 1a is formed proximate a center of the die 1 for hot extrusion molding of the plate shape, and an amorphous film 1c is formed on at least the inner face 1b of the through hole 1a. In hot extrusion molding of an aluminum alloy, the inner face of the hot extrusion molding device 11 is preheated to a temperature of about 400 to 600˚C for about 1 hour, for the purpose of uniform heating of the billet 5 and releasing air existing in the interior. Therefore, an amorphous film 1c is formed for the purpose of preventing oxidation of the inner face 1b of the through hole 1a upon preheating.

[0044] While the TiCN-based cermet of the present invention is a material which is not easily oxidized at high temperature as compared with a conventional cemented carbide and SKD61, furthermore a carbide-based cermet, some degree of oxidation cannot be suppressed. Therefore, an amorphous film 1c is preferably formed on the inner face 1b of the through hole 1a so as to prevent a decrease in the strength of cohesion between grains as a result of oxidation.

[0045] Furthermore, the amorphous film 1c is preferably formed of alumina or silicon carbide. Thermal oxidation reaction of alumina or silicon carbide starts at a temperature of higher than about 600˚C, and thus a decrease in strength caused by oxidation of the inner face 1b upon preheating can be prevented when the preheating temperature upon hot extrusion molding is about 600˚C or lower. More specifically, oxidation of the inner face 1b of the through hole 1a can be prevented by forming an amorphous film 1c of silicon carbide when the preheating temperature of the extrusion material 6 before molding is about 550˚C or lower, or by forming an amorphous film 1c of alumina when the preheating temperature is about 600˚C or lower. Namely, the material of the amorphous film 1c may be appropriately selected according to the preheating temperature.

[0046] The material of the amorphous film 1c is not necessarily limited to alumina or silicon carbide, and silicon nitride, titanium nitride and titania may be used as long as they are conventionally used for hot extrusion molding for an aluminum refrigerant pipe for a heat exchanger.

[0047] Furthermore, the thickness t of the amorphous film 1c is preferably from 0.2 to 1.2 μm. When the thickness t of the amorphous film 1c is at least 0.2 μm or more, the inner face 1b of the through hole 1a can be uniformly protected and a problem such as oxidation from the surface layer at high temperature can be prevented. In contrast, when the thickness t of the amorphous film 1c exceeds 1.2 μm, particularly 2 μm, adhesion of the film decreases and the amorphous film 1c sometimes peels upon a setting operation. The thickness t of the amorphous film 1c is more preferably from 0.5 to 1.0 μm.

[0048] When the amorphous film 1c is formed not only on the inner face 1b of the through hole 1a of the die 1 for hot extrusion molding, but also on a side 1d, deterioration caused by oxidation from surroundings can be suppressed.

[0049] Although the amorphous film 1c immediately peels and disappears through sliding resistance with the billet 5 when hot extrusion molding of the extrusion material 6 is initiated, a contact temperature of the guiding portion decreased by absorption of oxygen and heat by the extrusion material 6 and thus oxidation does not reach a level to cause a problem.

[0050] In the case molding of the extrusion material 6 is once stopped and molding is initiated again, the die is used again after removing a deposit such as an aluminum alloy by alkali cleaning of the inner face 1b of the through hole 1a using NaOH. In that case, the die can be repeatedly used without causing any problem if the flaked amorphous film 1c is formed again so as to prevent oxidation upon preheating again.

[0051] As shown in Fig. 1, the hot extrusion molding device 11 of the present invention comprises the die 1 for hot extrusion molding mounted of the present invention at one end of a cylindrical die case 2, the other end of the die case 2 mounted at one end of a cylindrical container 3 and an extrusion mechanism 4 for extruding an extrusion material 6 through the container 3 disposed on the container 3. When the hot extrusion molding device 11 is used for hot extrusion molding at high temperature of about 400 to 600˚C, the die 1 for hot extrusion molding, which is most severely damaged, is excellent in strength, hardness and toughness at high temperature, and there is less fear of wear and fracture. Therefore, flaws on the extrusion material 6 and a dimensional problem can be suppressed, and thus an attempt of remarkably increasing continuous molding time of hot extrusion molding is made.

[0052] The method for producing a die 1 for hot extrusion molding of the present invention will now be described.

[0053] The method for producing the die 1 for hot extrusion molding of the present invention comprises the steps of mixing a predetermined amount of a fine TiCN powder having a mean grain size of 0.3 to 0.7 μm and a predetermined amount of a coarse grain TiCN powder having a mean grain size of 1.2 to 2 μm as raw powers in a ratio 7:3 to 9:1; adding a predetermined amount of a TaC powder having a mean grain size of 1.5 μm or less, and a predetermined amount of a Ni powder and a Cr powder, each having a mean grain size of 2 μm or less; and grinding and mixing the powder mixture together with a solvent to form a slurry.

[0054] Herein, a predetermined amount of the fine TiCN powder having a mean grain size of 0.3 to 0.7 μm and a predetermined amount of the coarse grain TiCN powder having a mean grain size of 1.2 to 2 μm as TiCN raw powders are mixed in the mixing ratio of 7:3 to 9:1 for the following reason. Namely, covalent bond sintering or solid phase bonding is promoted by surrounding the coarse TiCN crystal grains with the fine TiCN crystal grains, and thus sintering can be performed by suppressing decomposition of the TiCN crystal grains into Ti, TiC and TiN.

[0055] Then, the resulting slurry is granulated by drying using a known spray dryer.

[0056] The powder obtained by the above method is molded into a tabular green compact by a known rubber press and then a desired shape is obtained by known cutting process. When a through hole is preliminarily formed proximate a center of the tabular green compact, a desired through hole can be formed by wire electric discharge machining after firing the green compact.

[0057] Next, the green compact is fired in a known vacuum furnace in an atmosphere under reduced pressure of 1.33 Pa or less at a maximum temperature maintained at 1,350 to 1,500˚C 1 hour firing. When the firing temperature is 1,350˚C or lower, the green compact is not sufficiently densified. In contrast, when the firing temperature exceeds 1500˚C, a metal component is sublimated and decomposition of TiCN composition begins. Therefore, the firing temperature is preferably from 1,350 to 1,500˚C.

[0058] The resulting sintered body is formed into a desired shape by wire electric discharge machining and grinding, and then the inner face 1b of the through hole 1a of the extrusion material 6 is polished using a fluid abrasive grain so as to adjust the surface roughness Ra to 0.05 μm or less.

[0059] The die 1 for hot extrusion molding of the present invention is produced by the above steps. When an amorphous film 1c is formed on the inner face 1b of the through hole 1a, a film having a thickness t of 0.2 to 1.2 μm is preferably formed by a sputtering method using alumina or silicon carbide. The amorphous film 1c may be formed not only on the inner face 1b of the through hole 1a, but also on the side 1d. In that case, both sides 1d may be subjected to sputtering.

[0060] As described above, the die 1 for hot extrusion molding of the present invention and the hot extrusion molding device 11 using the same of the present invention have high strength and wear resistance at high temperature and are therefore suited for hot extrusion molding of aluminum alloy extrusion materials for industrial and home use. Particularly, they can be preferably used for molding of refrigerant pipes and fins of on-vehicle radiators, intercoolers and air condensers.

[0061] The application is not limited to the aluminum alloy hot extrusion molding, and they are preferably used for hot extrusion molding of copper alloys and titanium alloys.

[0062] Examples of the present invention will now be described in detail, but the present invention is not limited to these Examples.

Example 1

[0063] A sintered body made of a TiCN-based cermet as a matrix of the die 1 for hot extrusion molding of the present invention was produced using each powder in six levels of the content. A predetermined amount of a fine TiCN powder having a mean grain size of 0.5 μm and a predetermined amount of a coarse grain TiCN powder having a mean grain size of 1.7 μm were mixed in a mixing ratio of 8:2. The resulting powder mixture, a predetermined amount of a TaC powder having a mean grain size of 1.2 μm, a Ni powder having a mean grain size of 1.6 μm and a Cr powder having a mean grain size of 1.4 μm were charged in a SUS ball mill, and then an amount corresponding to the total powder of an SUS grinding ball having a size of ϕ5, a two-fold amount of ethanol and an amount of 3% by mass, based on the total powder, of paraffinic wax were added, and then the powder mixture was ground and mixed for 48 hours to form a slurry.

[0064] The total content of TiCN, TaC, Ni and Cr is 100% by mass. A sample No. 1 contains 63% by mass of TiCN, 11% by mass of TaC, 13% by mass of Ni and 13% by mass of Cr, a sample No. 2 contains 79% by mass of TiCN, 6% by mass of TaC, 7% by mass of Ni and 8% by mass of Cr, and a sample No. 3 contains 93% by mass of TiCN, 1% by mass of TaC, 3% by mass of Ni and 3% by mass of Cr.

[0065] In the Comparative Examples, which are not within the scope of the present invention, the mean grain size of the TiCN raw powder is the same as in the Examples of the present invention, and the ratio of the fine TiCN powder and the coarse grain TiCN powder is 8:2, which is the same as in the Examples of the present invention. A sample No. 4 contains 60% by mass of TiCN, 12% by mass of TaC, 14% by mass of Ni and 14% by mass of Cr, a sample No. 5 contains 63% by mass of TiCN, 1% by mass of TaC, 18% by mass of Ni and 18% by mass of Cr, and a sample No. 6 contains 96% by mass of TiCN, 0% by mass of TaC, 2% by mass of Ni and 2% by mass of Cr.

[0066] Furthermore, a sample was also produced by changing the mixing ratio of the fine TiCN powder and the coarse grain TiCN powder.

[0067] Samples No. 8 and 9 of the Examples of the present invention were produced by using a fine TiCN powder having a mean grain size of 0.5 μm and a coarse grain TiCN powder having a mean grain size of 1.7 μm as a TiCN powder, a predetermined amount of a TaC powder having a mean grain size of 1.2 μm, a Ni powder having a mean grain size of 1.6 μm and a Cr powder having a mean grain size of 1.4 μm, and adjusting the content of each component as follows: TiCN = 79% by mass, TaC = 6% by mass, Ni = 7% by mass and Cr = 8% by mass, and adjusting the mixing ratio of the fine TiCN powder and the coarse grain TiCN powder to 7:3 and 9:1. Samples No. 7 and No. 10 wherein the mixing ratio was adjusted to 6:4 and 9.5:0.5 are not within the scope of the present invention. Other additives and mixing method are as the same as described above.

[0068] Next, the resulting slurry was granulated by highspeed drying at a temperature of 120°C for an exposure time of 1 second using a spray-dryer.

[0069] Next, a rectangular green compact used as a test piece of a three-point bending strength after sintering was produced using a hydraulic hand press machine.

[0070] Next, the green compact was fired in an atmosphere at vacuum degree of 1.33 Pa and a maximum temperature of 1,450°C for 1 hour using a vacuum furnace to produce a sintered body made of a TiCN-based cermet.

[0071] The sintered body was ground using a surface grinding machine (using #400 resin diamond) to form a rectangular test piece 12 measuring 3 mm in a short side 12a, 4 mm in a long side 12b and 40 mm in a length 12c for a three-point bending test method in conformity to JIS-R1601 as shown in Fig. 2.

[0072] With respect to samples Nos. 1 to 3, 8 and 9 of the Examples of the present invention of the test piece 12, and samples Nos. 4 to 7 and 10 of the Comparative Examples, which are not within the scope of the present invention, analysis of the composition of the sintered body after firing, and three-point bending strength, Vickers hardness and fracture toughness value of samples (each five) after subjected to a heat treatment in an air atmosphere at 550°C for 1 hour were measured, respectively.

[0073] Analysis of the composition was carried out under the conditions of X-ray 40 kV and 40 mA using an X-ray diffraction device, Model RINT 1100, manufactured by Rigaku Corporation. Herein, the composition ratio of each component was determined by obtaining a quantitative value based on a calibration curve made separately from a diffraction peak of each component of a sample measured by an X-ray diffraction device, and calculating the ratio of each component from the sum. The measuring threshold is 0.01% by mass and therefore a value less than 0.01% by mass was expressed by the symbol "-".

[0074] Three-point flexural strength was determined by measuring the strength at which a test piece 12 is fractured under the conditions of a span 13 of 30 mm and a crosshead 14 speed of 0.5 mm/min by a three-point bending test method in conformity to JIS-R1601 (Testing method for flexural strength of fine ceramics) using a digital load tester manufactured by Aikoh Engineering Co. Ltd. as shown in Fig. 3.

[0075] Vickers hardness was measured under a Hv Load of 10 kg by the method defined in JIS-R1610 (Test methods for hardness of fine ceramics) using a hardness tester, Model AVK-A manufactured by Akashi Seisakusho Inc.

[0076] Fracture toughness value was measured by SEPB method (Single Edge Precracked Beam) in conformity to JIS-R1607 (Testing methods for fracture toughness of fine ceramics) using a hardness tester, Model AV K-A, manufactured by Akashi Seisakusho Inc., a universal testing machine, Model 1125 type, manufactured by Instron Corporation, an autograph, Model AGS-500B, manufactured by Shimadzu Corporation, and an optical length measuring instrument manufactured by Mitsutoyo Corporation.

[0077] With respect to the criteria of three-point bending strength, Vickers hardness and fracture toughness value, the three-point bending strength is 1,150 MPa or more, the Vickers hardness is 1,400 GPa or more and the fracture toughness value is 10 MPa·m$^{1/2}$ or more. With respect to general evaluation, samples which satisfy all items were rated "Good" (o), while samples which do not satisfy one or more items were rated "Poor" (x). When the three-point bending strength is less than 1,150 MPa, cracking is likely to occur upon hot extrusion molding since the strength is insufficient. When the Vickers hardness is less than 1,400 GPa, wear and deformation are likely to occur since wear resistance becomes insufficient. When the fracture toughness value is less than 10 MPa·m$^{1/2}$, chipping and cracking are likely to occur upon hot extrusion molding.

[0078] The above results are shown in Table 1. The composition and the characteristic value are expressed by the average of the measured values of the five samples.

[Table 1]

Sample No.	Raw powder component (% by mass)							Analysis of composition of sintered body (% by mass)								Three-point bending strength (MPa)	Vickers hardness Hv (GPa)	Fracture toughness value (MPa·m$^{1/2}$)	General evaluation
	Mixing ratio$^{Note)}$	TiCN	TaC	Ni	Cr	Ti	TiC	TiN	TiCN	TaC	Ni	Cr	Ti	TiC	TiN	Others (Fe, etc.)				
1	8:2	63	11	13	13	0	0	0	58	11	13	13	1	2	2	—	1480	1460	14	○
2	8:2	79	6	7	8	0	0	0	78	6	7	8	0.01	0.01	0.01	0.97	1320	1500	12	○
3	8:2	93	1	3	3	0	0	0	92.5	1	3	3	0.02	0.01	0.02	0.45	1180	1610	10	○
* 4	8:2	60	12	14	14	0	0	0	51	12	14	14	2	3	3	1	1040	1030	11	×
* 5	8:2	63	1	18	18	0	0	0	54.9	0.9	18	18	3	2	3.1	0.1	900	1040	7	×
* 6	8:2	96	0	2	2	0	0	0	95	—	2	2	—	—	—	1	890	1180	7	×
* 7	6:4	79	6	7	8	0	0	0	69	6	7	8	3	3	4	—	980	1000	8	×
8	7:3	79	6	7	8	0	0	0	75	6	7	8	1	1	2	—	1400	1500	13	○
9	9:1	79	6	7	8	0	0	0	78	6	7	8	0.98	0.01	0.01	—	1330	1520	12	○
* 10	9.5:0.5	79	6	7	8	0	0	0	74	6	7	8	2	1	2	—	1210	1050	8	×

The samples marked "*" are out of the scope of the present invention.
Note) Mixing ratio of TiCN (Fine powder : Coarse powder)

[0079] As is apparent from the results shown in Table 1, regarding samples No. 1, 2 and 3 of sintered bodies used for the die 1 for hot extrusion molding of the present invention, the composition contains 58 to 92.5% by mass of TiCN, 1 to 11% by mass of TaC, 3 to 13% by mass of Ni and 3 to 13% by mass of Cr and TiCN is decomposed into 0.01 to 1% by mass of Ti and 0.01 to 2% by mass of TiC and TiN. Therefore, even after the sintered body is heat-treated to 550˚C, strength of cohesion between grains does not decrease as a result of oxidation of the surface of the sintered body and original characteristics such as high strength, high hardness and high toughness can be maintained. Thus, the three-point bending strength is 1,180 MPa or more, the Vickers hardness is 1,460 GPa or more and the fracture toughness value is 10 MPa·m$^{1/2}$ or more, and deterioration of the surface at high temperature is not observed and general evaluation is excellent.

[0080] In contrast, regarding sample No.4 which is not within the scope of the present invention, oxidation of the surface of the sintered body was promoted after heat-treated to 550˚C, and the strength of cohesion between grains decreased. Therefore, the three-point bending strength was low at 1,040 MPa and the Vickers hardness was low at 1,030 GPa. Regarding sample No. 5, the content of TaC is less than 1% by mass, the content of Ti by far exceeded 1% by mass and also the content of TiN exceeded 2% by mass since TiCN is decomposed into Ti, TiC and TiN. Thus, oxidation of the surface of the sintered body is promoted after heat-treated to 550˚C, and the strength of cohesion between grains decreased, and also sinterability is low. Therefore, the three-point bending strength was low at 900 MPa, the Vickers hardness was low at 1,040 GPa, and the fracture toughness value was low at 7 MPa· m$^{1/2}$. Regarding sample No. 6, TiCN was decomposed into Ti, TiC and TiN of less than 0.01% by mass, and particularly, the content of TaC was less than 1% by mass. Therefore, heat deterioration is generated after heat-treated to 550˚C. Also, since sinterability is originally poor, the three-point bending strength was low at 890 MPa, the Vickers hardness was low at 1,180 GPa and the fracture toughness value was low at 7 MPa·m$^{1/2}$. Accordingly, the general evaluation was poor in samples Nos. 4, 5 and 6 and these samples were generally evaluated to be unusable.

[0081] In samples Nos. 2 to 4 and 6, 0.45 to 0.97% by mass of Fe was detected as inevitable impurities. The content of inevitable impurities is preferably close to 0 and the temperature of deterioration caused by oxidation on surroundings is high at 800˚C. Therefore, the temperature when used as the die for hot extrusion molding is from about 400 to 600˚C, and the Fe content of about 1% by mass causes no problem since it is not the cause of a decrease in strength.

[0082] Regarding samples Nos. 8 and 9 of the Examples of the present invention in which the mixing ratio of the fine TiCN powder and the coarse grain TiCN powder is 7:3 and 9:1, it was possible to promote sinterability and to suppress abnormal grain growth upon sintering, and thus formation of Ti, TiC and TiN can be suppressed. As a result, oxidation does not proceed in a high temperature environment and all of the three-point bending strength, the Vickers hardness and the fracture toughness value did not decrease, and also general evaluation was excellent.

[0083] Regarding sample No.7 among samples Nos. 7 and 10, that are not within the scope of the present invention, in which the mixing ratio of the fine TiCN powder and the coarse grain TiCN powder is adjusted to 6:4 and 9.5:0.5, crystal grains were locally decomposed and grown, and thus a lot of Ti, TiC and TiN were formed upon sintering. As a result, oxidation proceeded in a high temperature environment. Regarding sample No. 7, the three-point bending strength was less than 1,150 MPa, the Vickers hardness was less than 1,400 GPa and the fracture toughness value was less than 10 Mpa·m$^{1/2}$. Regarding sample No. 10, the Vickers hardness was less than 1,400 GPa and the fracture toughness value was less than 10 Mpa·m$^{1/2}$, and general evaluation was inferior and these samples were evaluated to be unusable.

[0084] As is apparent from the results described above, the TiCN-based cermet material comprising 58 to 92.5% by mass of TiCN, 1 to 11% by mass of TaC, 3 to 13% by mass of Ni and 3 to 13% by mass of Cr, 0.01 to 1% by mass of Ti formed by decomposition of TiCN and 0.01 to 2% by mass of TiC and TiN formed by decomposition is a material suited for use as a matrix of the die 1 for hot extrusion molding since a strength, hardness and toughness do not decrease in a high temperature environment.

Example 2

[0085] Dies 1, 101 for hot extrusion molding shown in Fig. 4(a) and Fig. 4(b) were produced and mounted to a hot extrusion molding device 11, 111 and, after performing hot extrusion molding, the dies 1, 101 for hot extrusion molding was evaluated. Samples Nos. 11 to 13 of the Example which are within the scope of the present invention were the die 1 for hot extrusion moldings produced by using sintered bodies of samples Nos. 1 to 3 of Example 1, and samples Nos. 14 and 15 which are not within the scope of the present invention were the die 1 for hot extrusion moldings produced by using sintered bodies of samples Nos. 4 and 6 of Example 1.

[0086] As a Comparative Example, sample No. 16 was produced using zirconia-based ceramics as the material comprising 94% by mass of ZrO_2 and 6% by mass of Y_2O_3 of the die 101 for hot extrusion molding.
As a Comparative Example, sample No. 17 was produced by making the body of the die 101 for hot extrusion molding using SKD61 and forming a reinforced portion 7 having a thickness t of 5 mm using a cermet material of NiCr/Cr_3C_2/NbC with the composition of 25% by mass of Cr_3C_2-NbC on the inner face 101b of the through hole 101a. The reinforced portion 7 of the cermet material was formed by a discharge fusion method.

[0087] In both the Examples of the present invention and the Comparative Examples, the dies 1, 101 for hot extrusion molding are in the form of a disk which has a thickness T of 20 mm and an outer diameter φ1 of 30 mm, through holes 1a, 101a being formed proximate a center of the disk, and the through holes 1a, 101a are a rectangular slit measuring 1.5 mm in width d and 15 mm in length 1 and four corners are made of C-surface c of about 0.5 mm.

[0088] The dies 1, 101 for hot extrusion molding were mounted to a hot extrusion molding device 11, 111 and subjected to a preheating treatment at 500˚C for 1 hour, and then hot extrusion molding of an aluminum alloy was carried out at a temperature of 460˚C. Molding was carried out while controlling the pressure of an extrusion mechanism 4 so as to adjust the extrusion rate to 30 m/min. Then, continuous molding was carried out until abnormal flaws generated on the surface of the extrusion material 6.

[0089] Herein, the criteria of abnormality of flaws generated on the surface of the extrusion material 6 were as follows: the depth of flaws is 10 μm and the width is 20 μm or more. Although this standard is not based on an industry standard, it is anticipated to be a more severe flaw standard since an aluminum refrigerant pipe for a car air-conditioner tends to use a high-pressure gas as compared with the prior art in the case of being free from a chlorofluorocarbon. The measurement of flaws was carried out using a surface roughness meter manufactured by Kosaka Laboratory Ltd.

[0090] In hot extrusion molding, first, generation of abnormality appears in a surface state of the extrusion material 6. Simultaneously, the dies 1, 101 for hot extrusion molding may be fractured or flaking may occur on the inner faces 1b, 101b. Abnormalities including fracture and flaking was confirmed. The number of each sample is 1.

[0091] The case where the continuous molding time until generation of any abnormality is less than 24 hours was generally evaluated to be unusable (x), the continuous molding time of 24 hours or more and less than 36 hours was generally evaluated to be usable (Δ), and the continuous molding time of 36 hours or more and less than 48 hours was generally evaluated to be "Good" (○). Lifetime of the die 101 for hot extrusion molding made of cemented carbide or SKD61 as a current product is only half a day to one day, and thus the case the continuous molding time is less than 24 hours as the level of the prior art was evaluated to be unusable, while 1.5 to 2 days as an expected value was evaluated to be "Good" and the intermediate value was evaluated to be usable. The above results are shown in Table 2.

[Table 2]

	Sample No.	Composition of die for hot extrusion molding (% by mass)								Continuous molding time until generation of any abnormality (hr)	Presence or absence of fracture of die for hot extrusion molding	Presence or absence of flaking of inner face of through hole of die for hot extrusion molding	General evaluation
		TiCN	TaC	Ni	Cr	Ti	TiC	TiN	Fe				
	11	58	11	13	13	1	2	2	-	$42^{1)}$	Absence	Absence	○
	12	78	6	7	8	0.01	0.01	0.01	0.97	$47^{1)}$	Absence	Absence	○
	13	92.5	1	3	3	0.02	0.01	0.02	0.45	$45^{1)}$	Absence	Absence	○
*	14	51	12	14	14	2	3	3	1	$27^{1)}$	Absence	Absence	Δ
*	15	95	-	2	2	-	-	-	1	$29^{1)}$	Absence	Absence	Δ
*	16	$ZrO_2$94 % by mass, $Y_2O_3$6 % by mass								$5^{2)}$	Presence	Absence	×
*	17	The body is using SKD 61, and inner peripheral face of through hole is reinforced with NiCr/Cr_3C_2/NbC.Cr_3C_2-NbC25% by mass.								$18^{1)}$	Absence	Presence	×

The samples marked "*" are out of the scope of the present invention.
1) "Abnormality " means generation of flaws on extrusion material.
2) "Abnormality means generation of cracking of die for hot extrusion molding.

[0092] As is apparent from the results shown in Table 2, regarding samples Nos. 11 to 13 of the Examples of the present invention, the continuous molding of the extrusion material 6 of the aluminum alloy can be carried out for at least 42 hours and abnormalities are generated only by flaws on the extrusion material 6. At the point of time, cracking and fracture of the die 1 for hot extrusion molding and flaking of the inner face 1b were not generated, and general evaluation was excellent.

[0093] Regarding samples Nos. 14 and 15, which are not within the scope of the present invention, the continuous molding time is 27 hours or 29 hours and is about 40% less than that in the case of the Examples of the present invention. Abnormalities are generated only by flaws on the extrusion material 6. At this point of time, cracking, fracture and flaking of the die 1 for hot extrusion molding are not observed, however, the inner face 1b of the through hole 1a as the guiding portion is deteriorated by an influence of a decrease in strength, hardness and toughness at high temperature. These samples were generally evaluated to be usable since continuous molding could be carried out for at least one day.

[0094] Regarding sample No. 16 of the Comparative Examples in which the body of the die 101 for hot extrusion molding was formed of zirconia-based ceramics, the continuous molding time is only 5 hours since the die 101 for hot extrusion molding was fractured. Although there is a merit that zirconia-based ceramics have a smooth surface and has excellent sliding properties, high temperature strength is low because of an increase in a monoclinic phase. Therefore, zirconia-based ceramics are not suited for use as the material of the die for hot extrusion molding and general evaluation was x.

[0095] Regarding sample No. 17 of the Comparative Examples in which the body of the die 101 for hot extrusion molding is formed of a SKD material and a thick film of cermet comprising NiCr/Cr_3C_2/NbC is formed on the inner face 101b of the through hole 101a of the extrusion material 6, abnormal flaws on the extrusion material 6 generated at the continuous molding time of 18 hours because of flaking of the reinforced portion 7 of the inner face 101b. It is considered that flaking of the reinforced portion 7 occurred since a difference in the thermal expansion coefficient between the SKD61 material and the NiCr/Cr_3C_2/NbC-based cermet material is large at about 6×10^{-6}. Even if flaking does not occur, NiCr/Cr_3C_2/NbC-based cermet is made of carbide-based cermet, and thus deterioration due to oxidation in a high temperature environment is likely to occur as compared with the TiCN-based cermet of the present invention.

[0096] As is apparent from the above results, when the die 1 for hot extrusion molding made of the TiCN-based cermet material of the present invention is used for hot extrusion molding of an aluminum alloy, a long lifetime of 1 to 2 days or more can be expected as compared with the die formed of a conventional cemented carbide, SKD61, zirconia-based ceramics, cermet material and carbide-based cermet.

Example 3

[0097] When the amorphous film 1c is formed or not formed on the inner face 1b of the through hole 1a of the die 1 for hot extrusion molding of the present invention, and the amorphous film 1c is formed of alumina or silicon carbide, and when the thickness t of the film is within a range from 0.1 to 1.5 μm, the effect on the continuous molding time in a high temperature environment was confirmed.

[0098] The sintered body constituting the die 1 for hot extrusion molding to be used has the same composition and shape as those of sample No. 12 of Example 2. An amorphous film 1c made of alumina and silicon carbide shown in Fig. 1 was formed on the inner face 1b of the through hole 1a and the thickness t was selected from the following six levels 0.1, 0.2, 0.5, 1.0, 1.2, and 1.5 μm. Each of the resulting dies was mounted to a hot extrusion molding device 11 and, after preheating for 1 hour, continuous molding of the extrusion material 6 such as an aluminum alloy was carried out at a rate of 30 m/min. In sample No. 12 of Example 2, the amorphous film 1c is not formed and this sample was used as a standard for comparison.

[0099] Herein, preheating of sample No. 12 in which the amorphous film 1c is not formed on the inner face 1b of the through hole 1a was performed at 500°C for 1 hour, and molding of an aluminum alloy was performed at a temperature of 460°C. Preheating of the sample in which the amorphous film 1c is formed of alumina was performed at a temperature of 550°C and molding was performed at temperature of 480°C. Preheating of sample in which the amorphous film 1c is formed of silicon carbide was performed at a temperature of 500°C and molding was performed at a temperature of 460°C. The preheating temperature is usually lower than the molding temperature so as to prevent deterioration of the inner face of the through hole caused by oxidation upon preheating. However, preheating is originally performed so as to maintain dimensional accuracy and quality of the surface state of the extrusion material 6 immediately after the initiation of molding, and thus the preheating temperature is preferably set to the molding temperature or higher. Therefore, the molding temperature was set to a temperature higher than the preheating temperature in this example.

[0100] The method for forming the amorphous film 1c made of alumina and silicon carbide is a sputtering method and the heating condition was set to 250°C.

[0101] Samples Nos. 21 to 26 of the Examples of the present invention are samples in which the material of the amorphous film 1c is alumina and the thickness t is 0.1, 0.2, 0.5, 1.0, 1.2 or 1.5 μm.

[0102] Samples Nos. 27 to 32 of the Examples of the present invention are samples in which the material of the amorphous film 1c is silicon carbide and the thickness t is 0.1, 0.2, 0.5, 1.0, 1.2 or 1.5 μm.

[0103] As described above, after predetermined preheating, continuous molding of the aluminum alloy was carried out. When flaws measuring 10 μm in depth and 20 μm or more in width appear on the surface of the extrusion material 6, the continuous molding time was measured. Similar to Example 2, samples of the continuous molding time of less than 24 hours were generally evaluated to be unusable (x), samples of 24 hours or more and less than 36 hours were generally evaluated to be usable (Δ), samples of 36 hours or more and less than 48 hours were generally evaluated as "Good" (○), and samples of 48 hours or more were generally evaluated to be excellent (◎)

[0104] The above results are shown in Table 3.

[0105] The results of TG-DTA differential thermal analysis of the die 1 for hot extrusion molding of the TiCN-based cermet material according to the present invention are shown in Figs. 6, 7 and 8. Fig. 6 is an analytical chart of TiCN-based cermet in which the amorphous film 1c is not formed on the inner face 1b of the through hole 1a, Fig. 7 is an analytical chart of the amorphous film 1c made of alumina formed on the inner face 1b of the through hole 1a, and Fig. 8 is an analytical chart of the amorphous film 1c made of silicon carbide formed on the inner face 1b of the through hole 1a.

[0106] In TG-DTA differential thermal analysis, a differential thermal analysis device, Model SSC5000, manufactured by SII Nano Technology Inc. was used.

[Table 3]

Sample No.	Composition of die for hot extrusion molding (% by mass)								Presence or absence of amorphous film	Material of amorphous film	Thickness of amorphous film (mm)	Continuous molding time until generation of flaws on extrusion material (hr)	General evaluation
	TiCN	TaC	Ni	Cr	Ti	TiC	TiN	Fe					
12	78	6	7	8	0.01	0.01	0.01	0.97	Absence	-	0	47	○
21	78	6	7	8	0.01	0.01	0.01	0.97	Presence	Alumina	0.1	61	◎
22	78	6	7	8	0.01	0.01	0.01	0.97	Presence	Alumina	0.2	73	◎
23	78	6	7	8	0.01	0.01	0.01	0.97	Presence	Alumina	0.5	80	◎
24	78	6	7	8	0.01	0.01	0.01	0.97	Presence	Alumina	1	85	◎
25	78	6	7	8	0.01	0.01	0.01	0.97	Presence	Alumina	1.2	84	◎
26	78	6	7	8	0.01	0.01	0.01	0.97	Presence	Alumina	1.5	80	◎
27	78	6	7	8	0.01	0.01	0.01	0.97	Presence	Silicon carbide	0.1	59	◎
28	78	6	7	8	0.01	0.01	0.01	0.97	Presence	Silicon carbide	0.2	68	◎
29	78	6	7	8	0.01	0.01	0.01	0.97	Presence	Silicon carbide	0.5	76	◎
30	78	6	7	8	0.01	0.01	0.01	0.97	Presence	Silicon carbide	1	77	◎
31	78	6	7	8	0.01	0.01	0.01	0.97	Presence	Silicon carbide	1.2	72	◎
32	78	6	7	8	0.01	0.01	0.01	0.97	Presence	Silicon carbide	1.5	63	◎

The samples marked "*" are out of the scope of the present invention.

[0107] As is apparent from the results shown in Table 3, as compared with sample No. 12 in which the amorphous film 1c is not formed on the inner face 1b of the through hole 1a of the extrusion material 6 of the die 1 for hot extrusion molding, the continuous molding time increased by about 25 to 80% in the sample in which the amorphous film 1c was formed.

[0108] Regarding samples Nos. 21 to 26 in which the amorphous film 1c is formed of alumina, the continuous molding time increased by about 10% although the preheating temperature is 50˚C higher than that of samples Nos. 27 to 32 in which the amorphous film 1c is formed of silicon carbide. Therefore, in hot extrusion molding of an aluminum alloy in which preheating and molding are performed at a temperature of about 400 to 600˚C, the die 1 for hot extrusion molding in which the amorphous film 1c made of alumina is preferably used in a comparatively high temperature range, while the die 1 for hot extrusion molding in which the amorphous film 1c made of silicon carbide is formed is preferably used in a low temperature range.

[0109] With respect to a relation between the thickness t of the amorphous film 1c and the continuous molding time, as shown in samples Nos. 21, 22 and 23 in which the amorphous film 1c made of alumina is formed, and samples Nos. 27, 28 and 29 in which the amorphous film 1c made of silicon carbide is formed, the continuous molding time is improved as the thickness t increases in order of 0.1, 0.2 and 0.5 μm. In samples Nos. 22 to 26 in which the thickness t of the amorphous film 1c made of alumina is 0.2 μm or more, the continuous molding time increased by about 55% or more as compared with sample No. 12 in which the amorphous film 1c is not formed. Samples Nos. 22 to 26 of the Examples of the present inventionenable continuous molding for about 3 to 3.5 days and exert remarkable effect as compared with lifetime of about half day of the die 101 for hot extrusion molding made of a conventional cemented carbide or a SKD61 material.

[0110] However, regarding samples Nos. 21 and 27 in which the thickness t of the amorphous film 1c is 0.1 μm, the continuous molding time increased more as compared with the case where the amorphous film 1c is not formed. However, the effect is not so remarkable since the thickness is too small and oxidation begins from the surface upon preheating.

[0111] Regarding samples Nos. 26 and 32 in which the thickness t of the amorphous film 1c is 1.5 μm, the continuous molding time decreased as compared with the case where the thickness t is 1.0 and 1.2 μm. The reason is considered to be oxidation due to slight flaking of the amorphous film 1c. When the thickness t is about 2 μm or more, the amorphous film 1c easily peels when collision arises sometimes upon setting of the die 1 for hot extrusion molding (not described in the Examples). Taking account of only an increase in the time of formation of the amorphous film 1c by sputtering, the thickness t of the amorphous film 1c is preferably from 0.2 to 1.2 μm, and more preferably from 0.5 to 1.2 μm.

[0112] As is apparent from the TG-DTA differential thermal analysis charts shown in Figs. 6, 7 and 8, the oxidation reaction temperature of the TiCN-based cermet material used for the die 1 for hot extrusion molding of the present invention was about 550˚C, the oxidation reaction temperature of the amorphous film 1c made of alumina was 600˚C at most, and the oxidation reaction temperature of the amorphous film 1c made of silicon carbide was about 600˚C or higher.

[0113] From the TG-DTA differential thermal analysis chart shown in Fig. 6, it can be confirmed that the oxidation reaction is initiated at about 550˚C. Therefore, even if the amorphous film 1c is not formed on the inner face 1b of the through hole 1a of the extrusion material 6 of the die 1 for hot extrusion molding of the present invention, there is not any fear of deterioration when the preheating temperature is set to about 500˚C. Regarding the sample in which the amorphous film 1c made of alumina or silicon carbide is formed, there is not a fear of deterioration of the inner face 1b of the through hole 1 caused by thermal oxidation, even if the preheating temperature is raised to about 600˚C.

[0114] As described above, when the die 1 for hot extrusion molding of the present invention is used for hot extrusion molding, it is not necessary to limit the preheating temperature to a temperature lower than the molding temperature as in the prior art. Therefore, it is possible to obtain those having stable dimensions and surface quality immediately after initiation of molding of the extrusion material 6 and to remarkably increase the continuous molding time.

[0115] Critical significance of the respective compositions will now be described.

[0116] First, critical significance of the compositions of TiCN, Ti, TiC and TiN is shown in Table 4.

[Table 4]

	Sample No.	TiCN (58 to 92.5%)	Ti (0.01 to 1%)	TiC (0.01 to 2%)	TiN (0.01 to 2%)	TaC (1.0 to 11%)	Ni (3 to 13%)	Cr (3 to 13%)	Extrusion rate (Sliding properties) As compared with the prior art (%)
	33	75.0	0.50	1.00	1.00	5.00	8.00	8.00	1.20
	34	58.0	0.50	1.00	1.00	5.00	8.00	8.00	1.10
	35	92.5	0.50	1.00	1.00	5.00	8.00	8.00	1.30
	36	75.0	0.01	1.00	1.00	5.00	8.00	8.00	1.20
	37	75.0	1.00	1.00	1.00	5.00	8.00	8.00	1.10
	38	75.0	0.50	0.01	1.00	5.00	8.00	8.00	1.20
	39	75.0	0.50	2.00	1.00	5.00	8.00	8.00	1.10
	40	75.0	0.50	1.00	0.01	5.00	8.00	8.00	1.20
	41	75.0	0.50	1.00	2.00	5.00	8.00	8.00	1.10
*	42	57.0	0.50	1.00	1.00	5.00	8.00	8.00	1.00
*	43	93.0	0.50	1.00	1.00	5.00	8.00	8.00	-Note)
*	44	75.0	0.00	1.00	1.00	5.00	8.00	8.00	1.00
*	45	75.0	1.10	1.00	1.00	5.00	8.00	8.00	1.00
*	46	75.0	0.50	0.00	1.00	5.00	8.00	8.00	1.00
*	47	75.0	0.50	2.10	1.00	5.00	8.00	8.00	1.00
*	48	75.0	0.50	1.00	0.00	5.00	8.00	8.00	1.00
*	49	75.0	0.50	1.00	2.10	5.00	8.00	8.00	1.00

The samples marked "*" are out of the scope of the present invention.
Note) It can't be produced due to deteriorating sinterability.

[0117] Herein, a test for comparing the extrusion rate with a conventional die was carried out as evaluation of sliding properties.

[0118] Sample No. 43 could not be produced since it does not satisfy sinterability.

[0119] As the content of TiCN increases, sliding properties are improved and each content of Ti, TiN and TiC as a decomposition product of TiCN should not exceed the upper limit. However, high sliding properties were exhibited when Ti, TiN and TiC are contained in a proper amount. When impurities such as Ti, TiN and TiC are not contained in a proper amount, the portion where TiCN is locally crystallized is generated and thus the state of the die surface becomes unstable.

[0120] Next, critical significance of the composition of TaC is shown in Table 5.

[Table 5]

Sample No.	TiCN (58 to 92.5%)	Ti (0.01 to 1%)	TiC (0.01 to 2%)	TiN (0.01 to 2%)	TaC (1.0 to 11%)	Ni (3 to 13%)	Cr (3 to 13%)	Oxidation resistance Oxidation area ratio (%)
33	75.0	0.50	1.00	1.00	5.00	8.00	8.00	5
50	75.0	0.50	1.00	1.00	1.00	8.00	8.00	10
51	75.0	0.50	1.00	1.00	11.00	8.00	8.00	0

(continued)

Sample No.	TiCN (58 to 92.5%)	Ti (0.01 to 1%)	TiC (0.01 to 2%)	TiN (0.01 to 2%)	TaC (1.0 to 11%)	Ni (3 to 13%)	Cr (3 to 13%)	Oxidation resistance Oxidation area ratio (%)
52	75.0	0.50	1.00	1.00	0.90	8.00	8.00	20
53	75.0	0.50	1.00	1.00	12.00	8.00	8.00	0Note)
Note) Sliding properties deteriorate.								

[0121] Herein, the oxidation area ratio of the surface was compared as evaluation of oxidation resistance by XPS (X-ray Photoelectron Spectroscopy) analysis.

[0122] As the content of TaC increases, oxidation resistance is improved. However, when the content exceeds the upper limit, sliding properties tend to deteriorate and thus it becomes impossible to use as the die.

[0123] Critical significance of the compositions of Ni and Cr is shown in Table 6.

[Table 6]

Sample No.	TiCN (58 to 92.5%)	Ti (0.01 to 1%)	TiC (0.01 to 2%)	TiN (0.01 to 2%)	TaC (1.0 to 11%)	Ni (3 to 13%)	Cr (3 to 13%)	Denseness Ratio to ideal density(%)
33	75.0	0.50	1.00	1.00	5.00	8.00	8.00	98
54	75.0	0.50	1.00	1.00	5.00	3.00	8.00	97
55	75.0	0.50	1.00	1.00	5.00	13.00	8.00	97
56	75.0	0.50	1.00	1.00	5.00	8.00	3.00	97
57	75.0	0.50	1.00	1.00	5.00	8.00	13.00	97
58	75.0	0.50	1.00	1.00	5.00	2.90	8.00	95Note1)
59	75.0	0.50	1.00	1.00	5.00	14.00	8.00	95Note2)
60	75.0	0.50	1.00	1.00	5.00	8.00	2.80	95Note1)
61	75.0	0.50	1.00	1.00	5.00	8.00	14.00	95Note2)
Note1) However, sinterability deteriorate. Note2) However, wear resistance decrease.								

[0124] Herein, relative density (by Archimedes' method), namely, a ratio to ideal density, was evaluated as denseness.

[0125] When Ni and Cr are contained in a proper amount, the density becomes close to ideal density. However, when the content exceeds the upper limit, wear resistance tends to decrease and when the content is lower than the lower limit, sinterability tends to deteriorate.

[0126] Next, the grain size range with respect to two peaks in the grain size distribution of the sintered body of the present invention, and critical significance of the weight ratio are shown in Table 7.

[Table 7]

Sample No.	One peak A in grain size distribution (μm)	The other peak B in grain size distribution (μm)	Crystal grains of A : Crystal grains of B	Toughness (MPa·m$^{1/2}$)		Strength (MPa)		Sliding properties (Presence or absence of flaws)	
62	0.9	1.55	5.5:4.5	Δ	8.5	○	1300	Δ	Slightly presence
63	1	1.55	5.5:4.5	○	10.5	○	1350	○	Absence
64	1.1	1.55	5.5:4.5	○	12	○	1330	○	Absence
65	1.2	1.55	5.5:4.5	○	12	○	1300	○	Absence
66	1.3	1.55	5.5:4.5	○	13	○	1300	○	Absence
67	1.4	1.55	5.5:4.5	Δ	9	○	1270	○	Absence
68	1.15	1.3	5.5:4.5	○	11	○	1370	Δ	Slightly presence
69	1.15	1.4	5.5:4.5	○	12	○	1370	○	Absence
70	1.15	1.5	5.5:4.5	○	12	○	1350	○	Absence
71	1.15	1.6	5.5:4.5	○	14	○	1270	○	Absence
72	1.15	1.7	5.5:4.5	○	13.5	○	1200	○	Absence
73	1.15	1.8	5.5:4.5	○	13	Δ	1100	○	Absence
74	1.15	1.55	6.5:3.5	○	10	○	1380	Δ	Slightly presence
75	1.15	1.55	6.0:4.0	○	12	○	1340	○	Absence
76	1.15	1.55	5.5:4.5	○	13	○	1300	○	Absence
77	1.15	1.55	5.0:5.0	○	13	○	1210	○	Absence
78	1.15	1.55	4.5:5.5	○	12	Δ	1130	Δ	Slightly presence

[0127] Herein, a test for evaluation of sliding properties and decomposition properties of TiCN was carried out. The sintered body to be evaluated has the same composition as that of sample No. 1 of Example 1. Samples Nos. 62 to 73 in which two peaks in the grain size distribution are different were obtained by using the same method. Regarding samples Nos. 74 to 78, the ratio of the crystal grains of the two peaks varies.

Toughness, strength and sliding properties of the sintered body were evaluated. The standard value of the toughness is 10 MPa·m$^{1/2}$ or more, and samples having 10 MPa· m$^{1/2}$ or more were rated "Good" (o) and samples having 7 MPa· m$^{1/2}$ or more and less than 10 MPa·m$^{1/2}$ were judged to be usable (Δ). The standard value of the strength is 1,150 MPa or more, and samples having 1,150 MPa or more were rated "Good" (o) and samples having 1,000 MPa or more and less than 1,150 MPa were judged to be usable (Δ). Regarding sliding properties, it was examined whether or not flaws of the aluminum material occur 24 hours after actually extruding an aluminum material. Samples with no flaws were rated "Good" (○), while samples with slight flaws were evaluated to be usable (Δ).

[0128] As is apparent from the results shown in Table 7, when the grain size range and the ratio of the two peaks in the grain size distribution of the sintered body of the present invention are within the scope of the present invention, TiCN is not decomposed and sliding properties are excellent.

When one peak in the grain size distribution is smaller than the lower limit within the scope of the present invention, the grain size distribution excessively lowers and thus a decrease in strength is caused by detachment of grains and sliding properties deteriorate by a decrease in toughness. When one peak in the grain size distribution is larger than the upper limit, strength and toughness tend to decrease.

When the other peak in the grain size distribution is smaller than the lower limit within the scope of the present invention, the grain size distribution excessively lowers and thus TiCN is likely to be decomposed and sliding properties deteriorate. When the other peak in the grain size distribution is larger than the upper limit, an influence of coarse grains is exerted and strength decreases.

When the ratio of crystal grains of two peaks is smaller than the lower limit within the scope of the present invention, strength decreases. When the ratio is larger than the upper limit, sliding properties deteriorate. When the ratio is small, an influence of detachment of grains is likely to be exerted. In contrast, when the ratio is large, TiCN is likely to be decomposed.

[0129] Fig. 10 is a diagram showing the compositions with respect to Ti, TiC and TiN of the die for hot extrusion molding of the present invention, in which each apex of Ti, TiC and TiN is 3% for convenience.

[0130] The hexagonal hatched portion indicated by the symbol "CL1" corresponds to the range with respect to Ti, TiC and TiN according to claim 1 of the present application.

Claims

1. A sintered body comprising 58 to 92.5% by mass of TiCN, 0.01 to 1% by mass of Ti, 0.01 to 2% by mass of TiC and 0.01 to 2% by mass of TiN, and the balance being TaC, Ni and Cr.

2. The sintered body according to claim 1, which contains 1 to 11% by mass of TaC.

3. The sintered body according to claim 1 or 2, which contains 3 to 13% by mass of Ni and 3 to 13% by mass of Cr.

4. The sintered body according to any one of claims 1 to 3, wherein grain size distribution of the sintered body has two peaks.

5. The sintered body according to claim 4, wherein one peak in the grain size distribution exists at a grain size within a range from 1.0 to 1.3 μm and the other peak exists at a grain size within a range from 1.4 to 1.7 μm.

6. The sintered body according to claim 5, wherein a ratio of the peak at a grain size within a range from 1.0 to 1.3 μm in the grain size distribution to the peak at a grain size within a range from 1.4 to 1.7 μm is from 3:2 to 1:1.

7. The sintered body according to any one of claims 1 to 6, wherein the sintered body has a spherical crystal grain.

8. A sliding member comprising the sintered body according to any one of claims 1 to 7.

9. A film-forming material comprising the sintered body according to any one of claims 1 to 7.

10. A die for hot extrusion molding comprising the sintered body according to any one of claims 1 to 7.

11. The die for hot extrusion molding according to claim 10, which has a through hole proximate a center of a plate shape, and an amorphous film being formed on at least an inner face of the through hole.

12. The die for hot extrusion molding according to claim 11, wherein the amorphous film is composed of alumina or silicon carbide.

13. The die for hot extrusion molding according to claim 11, wherein the amorphous film has a thickness of 0.2 to 1.2 μm.

14. A hot extrusion molding device comprising the die for hot extrusion molding according to any one of 10 to 13, a cylindrical die case wherein the die is mounted to one end thereof, a cylindrical container wherein the other end of the die case is mounted to one end thereof, and an extrusion mechanism disposed to the container to extrude an extrusion material through the container.

15. A hot extrusion molding method, which comprises using the die for hot extrusion molding according to any one of claims 10 to 13.

16. A hot extrusion molding method, which comprises molding an aluminum alloy using the die for hot extrusion molding according to any one of claims 10 to 13.

17. A method for producing the sintered body according to any one of claims 1 to 7, which comprises the steps of mixing a TiCN powder having a mean grain size of 0.3 to 0.7 μm and a TiCN powder having a mean grain size of 1.2 to 2 μm in a weight ratio 7:3 to 9:1; adding a TaC powder having a mean grain size of 1.5 μm or less, and a Ni powder and a Cr powder, each having a mean grain size of 2 μm or less; and grinding and mixing the powder mixture together with a solvent to form a slurry.

Fig. 1

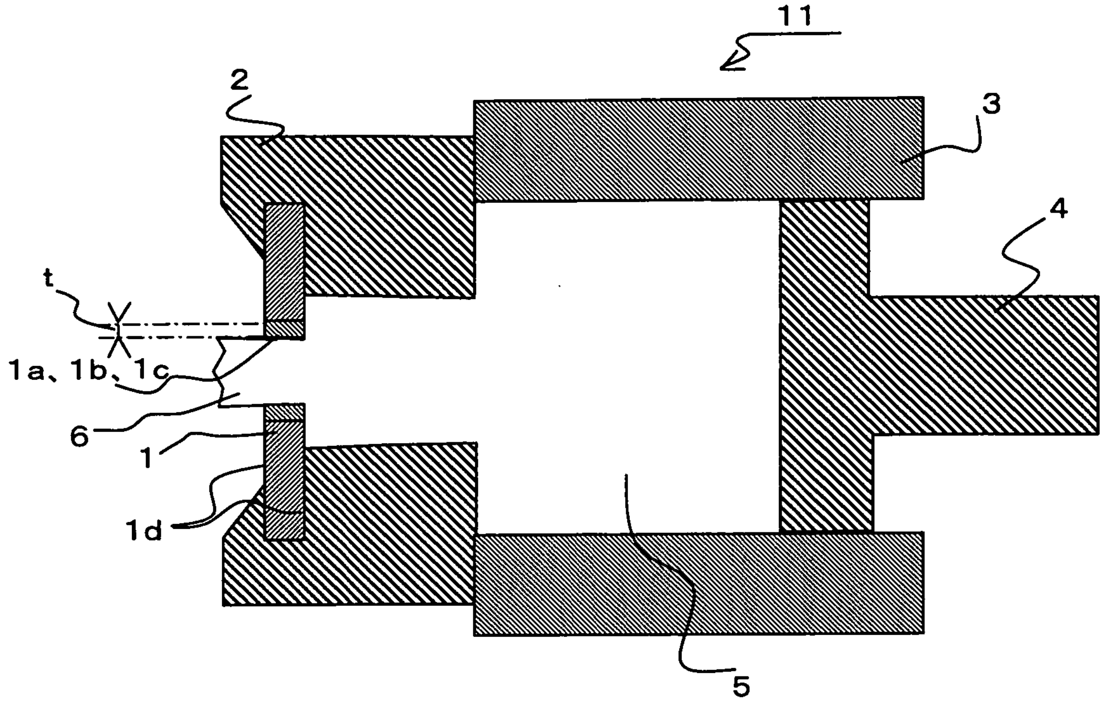


Fig. 2

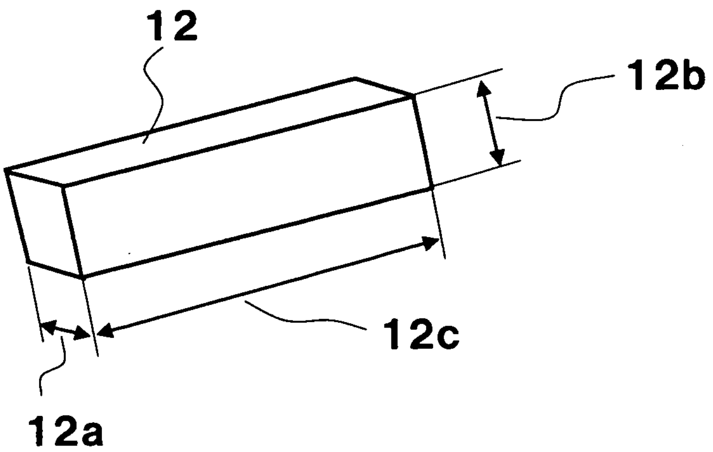


Fig. 3

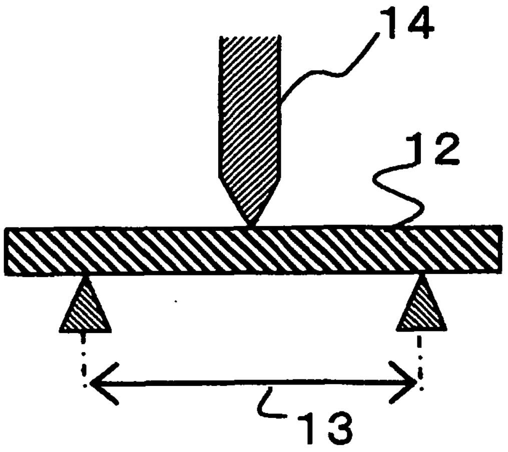


Fig. 4

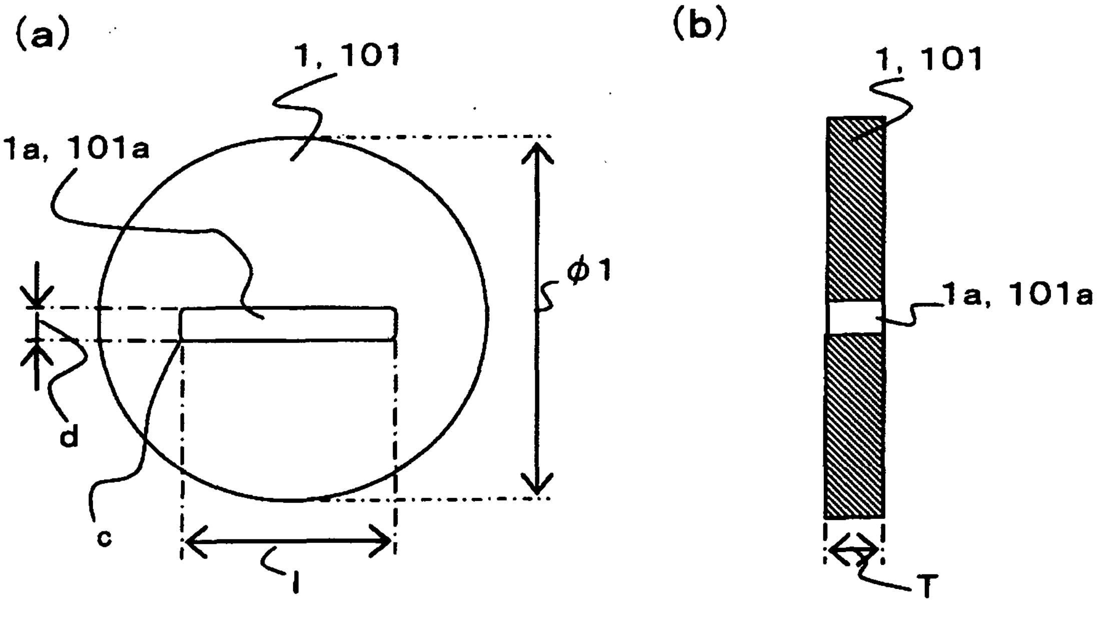


Fig. 5

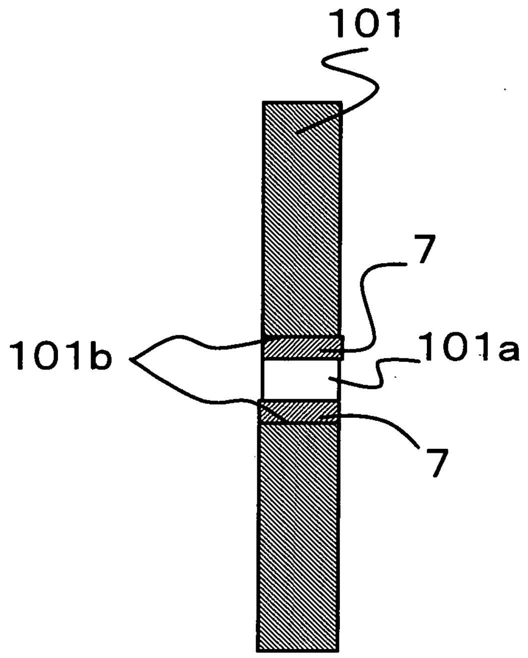

101
7
101b
101a
7

Fig. 6

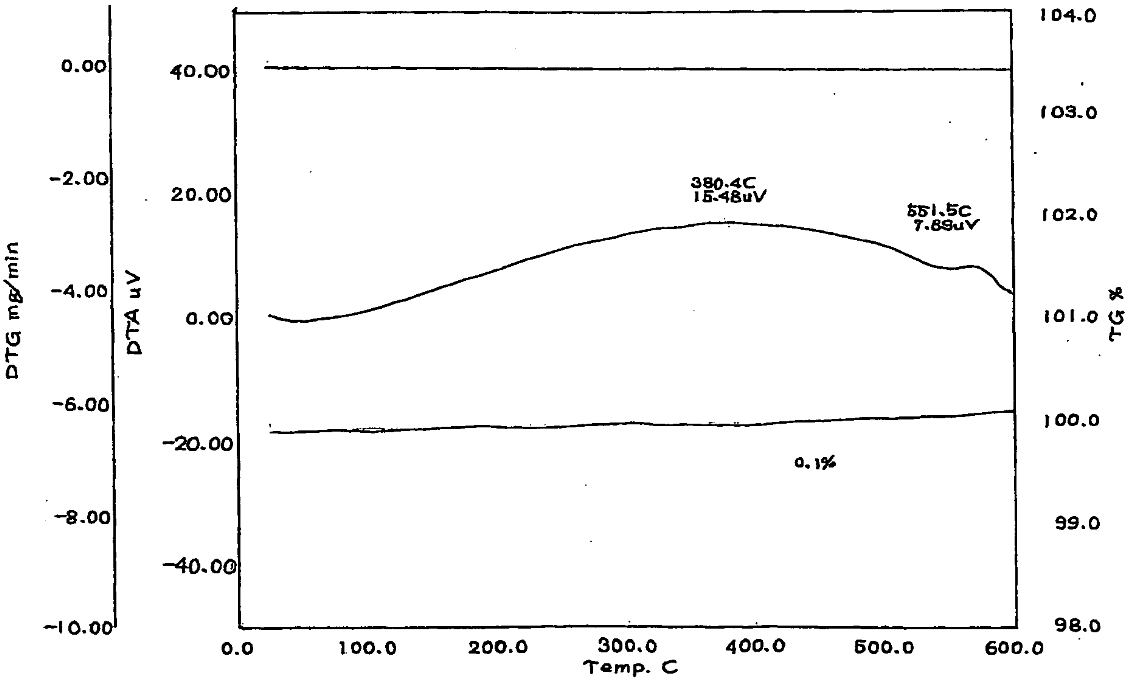

DTG mg/min
0.00
-2.00
-4.00
-6.00
-8.00
-10.00
DTA uV
40.00
20.00
0.00
-20.00
-40.00
TG %
104.0
103.0
102.0
101.0
100.0
99.0
98.0
0.0
100.0
200.0
300.0
400.0
500.0
600.0
Temp. C
380.4C
15.48uV
551.5C
7.89uV
0.1%

Fig. 7

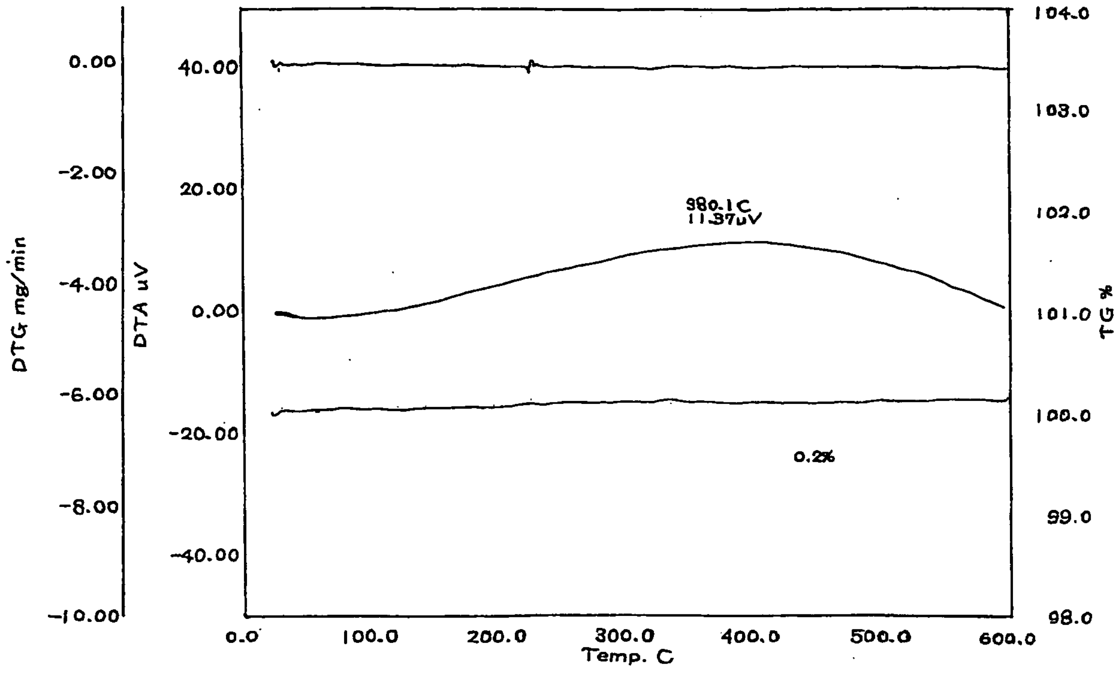

DTG mg/min
0.00
-2.00
-4.00
-6.00
-8.00
-10.00
DTA uV
40.00
20.00
0.00
-20.00
-40.00
TG %
104.0
103.0
102.0
101.0
100.0
99.0
98.0
380.1C
11.37uV
0.2%
0.0
100.0
200.0
300.0
400.0
500.0
600.0
Temp. C

Fig. 8

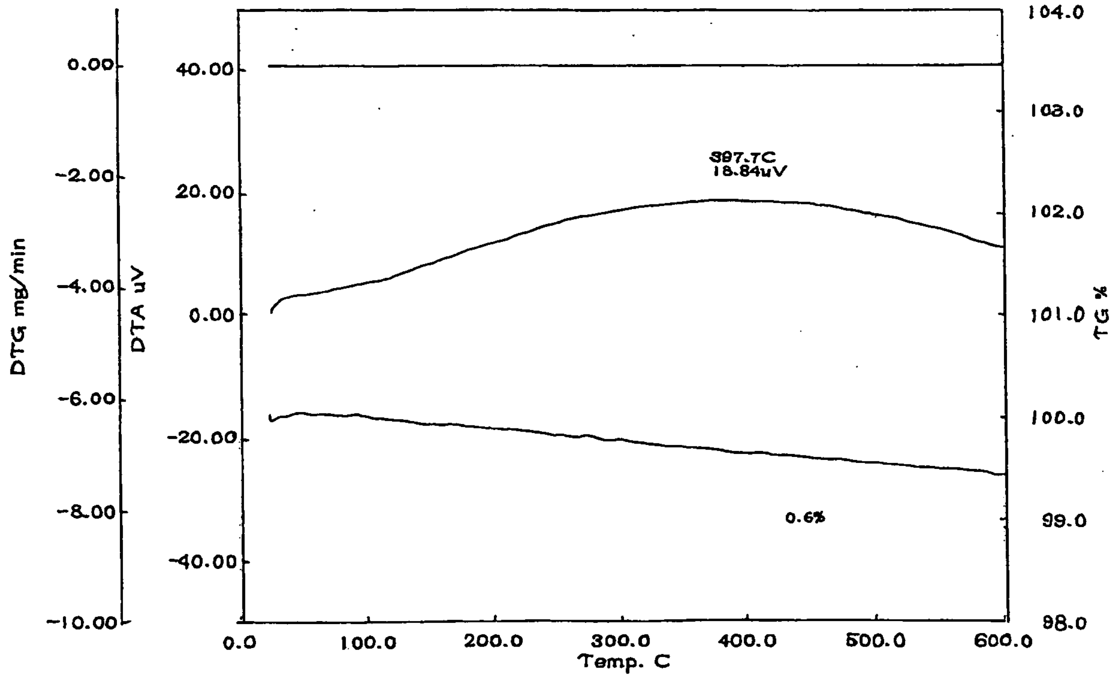

DTG mg/min
0.00
-2.00
-4.00
-6.00
-8.00
-10.00
DTA uV
40.00
20.00
0.00
-20.00
-40.00
TG %
104.0
103.0
102.0
101.0
100.0
99.0
98.0
397.7C
18.84uV
0.6%
0.0
100.0
200.0
300.0
400.0
500.0
600.0
Temp. C

Fig. 9

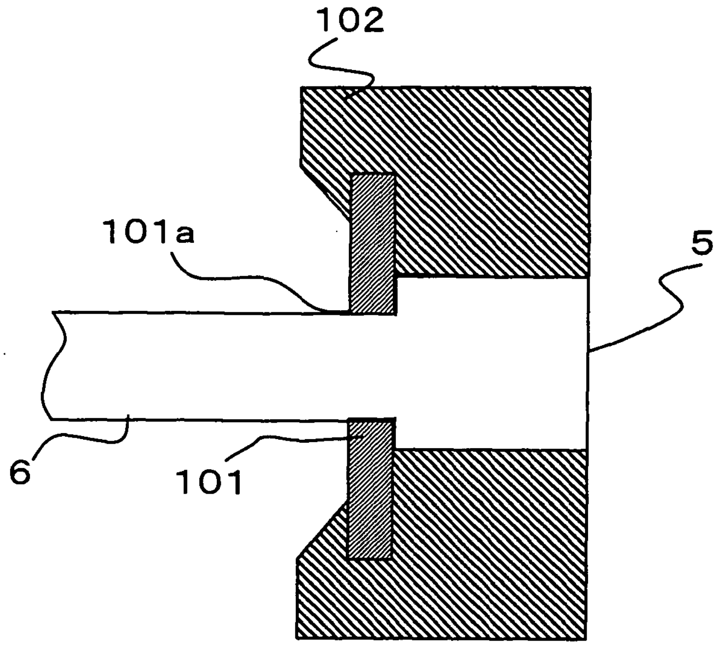
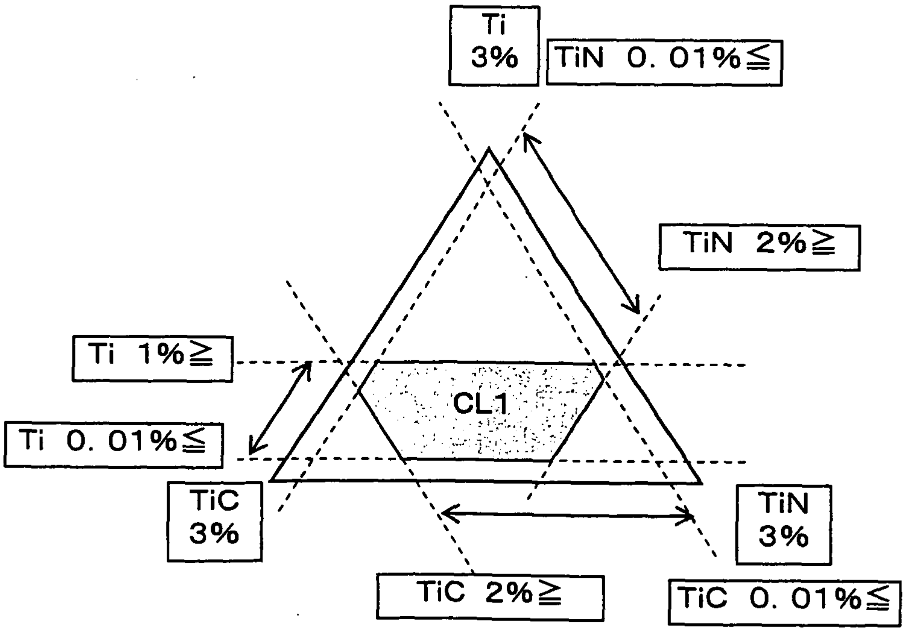

102
101a
5
6
101

Fig. 10


Ti 3%
TiN 0. 01%≦
TiN 2%≧
Ti 1%≧
CL1
Ti 0. 01%≦
TiC 3%
TiN 3%
TiC 2%≧
TiC 0. 01%≦

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2006/319577

A. CLASSIFICATION OF SUBJECT MATTER
C22C29/04(2006.01)i, *B21C25/00*(2006.01)i, *B21C25/02*(2006.01)i, *B22F1/00*(2006.01)i, *C22C1/05*(2006.01)i

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C22C29/04, B21C25/00, B21C25/02, B22F1/00, C22C1/05

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	1996-2006
Kokai Jitsuyo Shinan Koho	1971-2006	Toroku Jitsuyo Shinan Koho	1994-2006

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 51-103914 A (Mitsubishi Metal Corp.), 14 September, 1976 (14.09.76), Claims (Family: none)	1-17

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

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

Date of the actual completion of the international search 26 December, 2006 (26.12.06)	Date of mailing of the international search report 09 January, 2007 (09.01.07)
Name and mailing address of the ISA/ Japanese Patent Office Facsimile No.	Authorized officer Telephone No.

Form PCT/ISA/210 (second sheet) (April 2005)

REFERENCES CITED IN THE DESCRIPTION

Patent documents cited in the description

- JP 2000063972 A **[0011]**
- JP 2000063973 A **[0011]**
- JP 2000102816 A **[0011]**
- JP 2000063975 A **[0011]**
- JP 2535025 B **[0011]**
- JP 2003321718 A **[0011]**