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(54) **THERMAL BARRIER COATING
FORMATION METHOD, THERMAL
BARRIER COATING, AND
HIGH-TEMPERATURE MEMBER**

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(57) **ABSTRACT**

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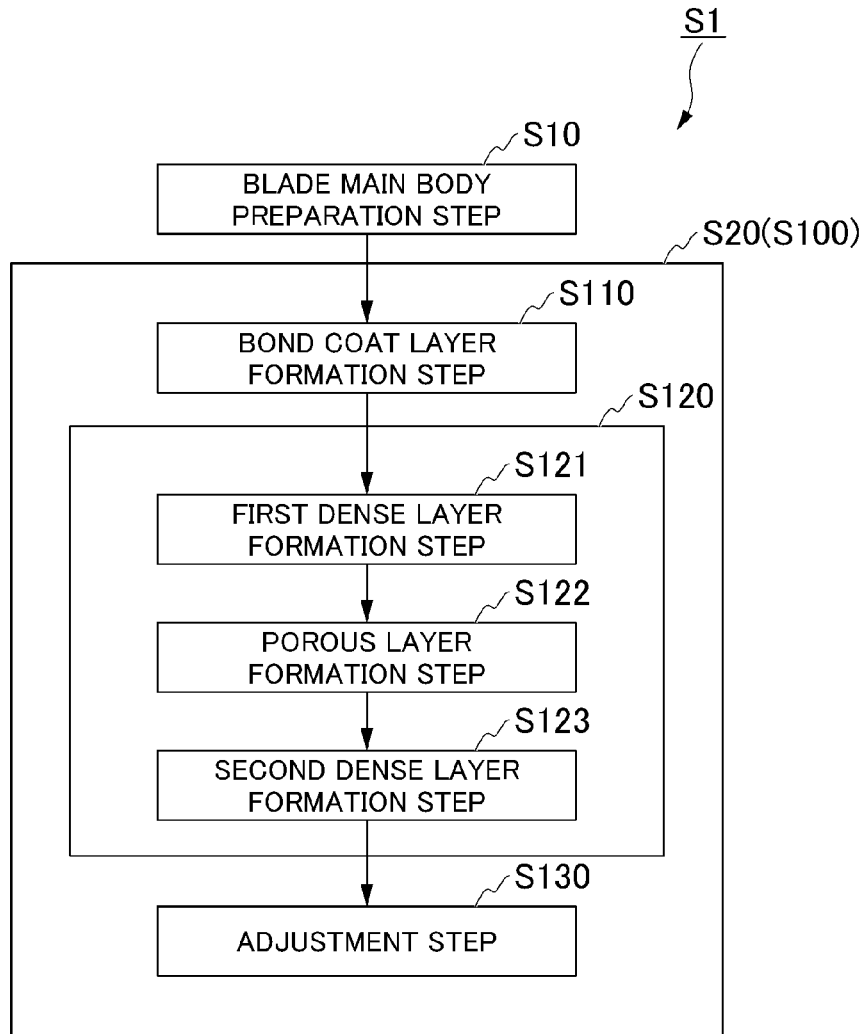
A thermal barrier coating is provided that includes a ceramic layer (120) formed on a heat-resistant alloy substrate and containing a ceramic. The ceramic layer (120) has: a first dense layer (121); an intermediate porous layer (122) which is laminated on the first dense layer (121), which has a higher density than the first dense layer (121), and in which numerous pores are formed; and a second dense layer (123) that is laminated on the intermediate porous layer (122) and has a lower density than the intermediate porous layer (122).

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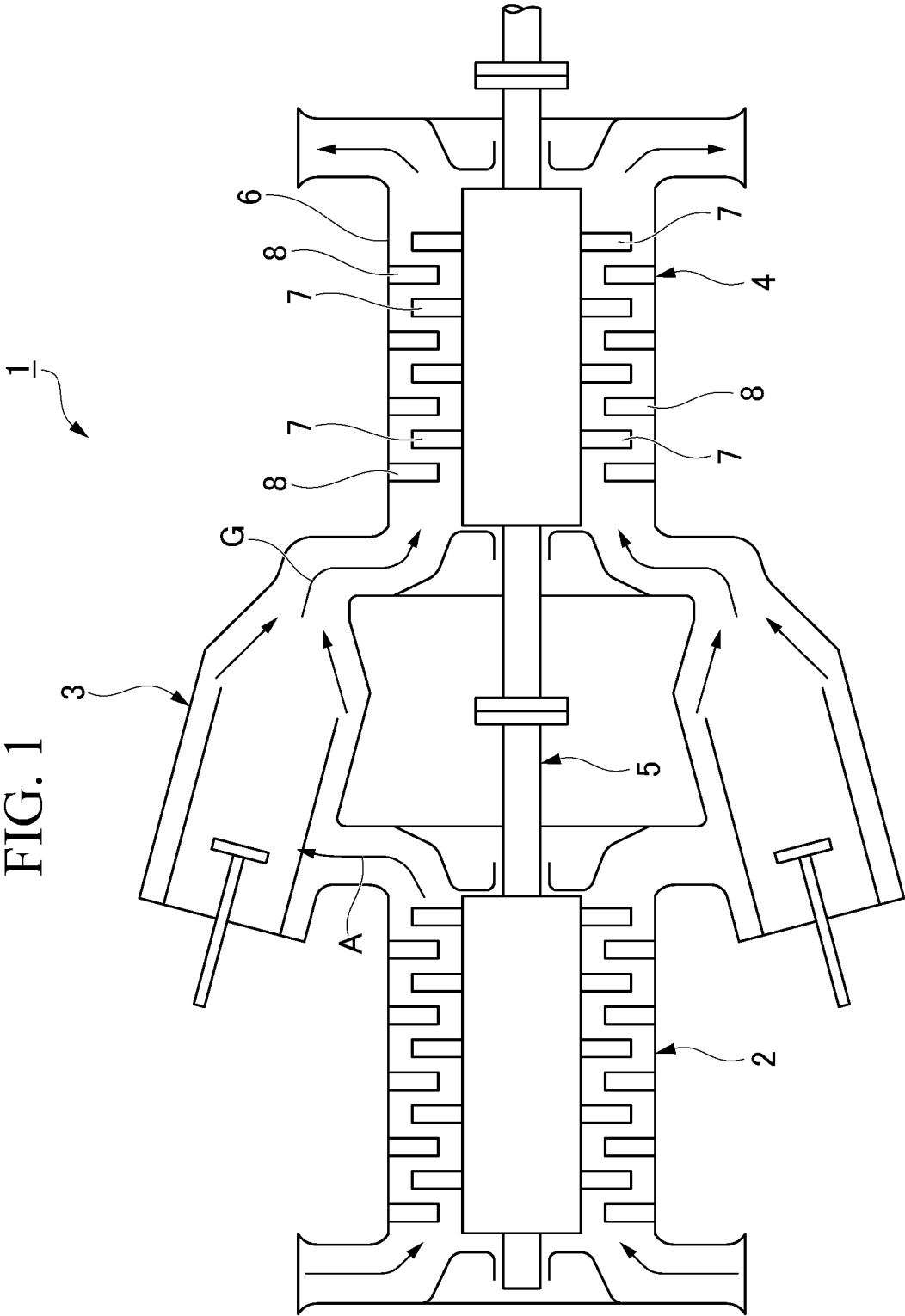


FIG. 1

FIG. 2

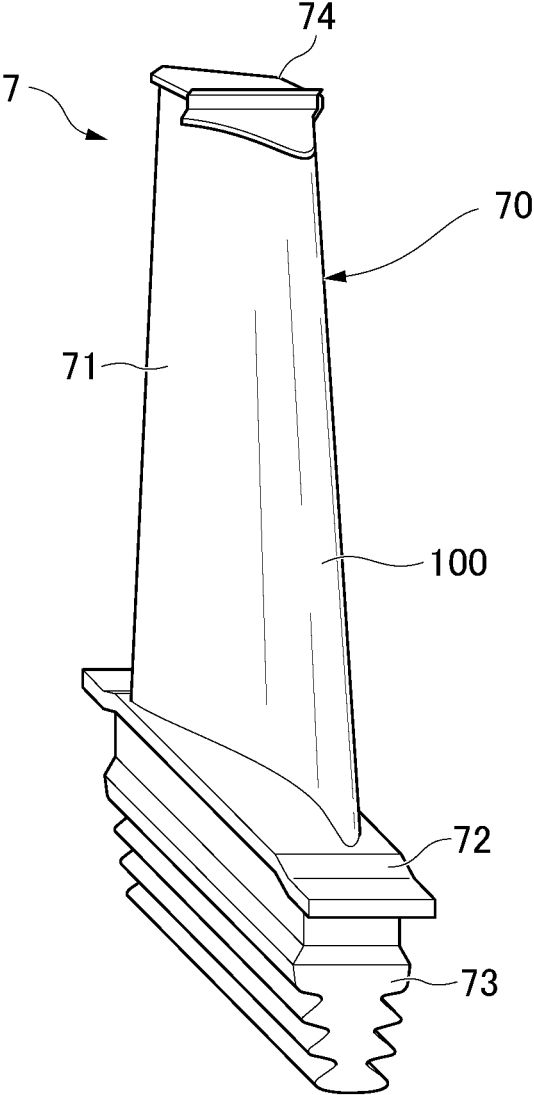


FIG. 3

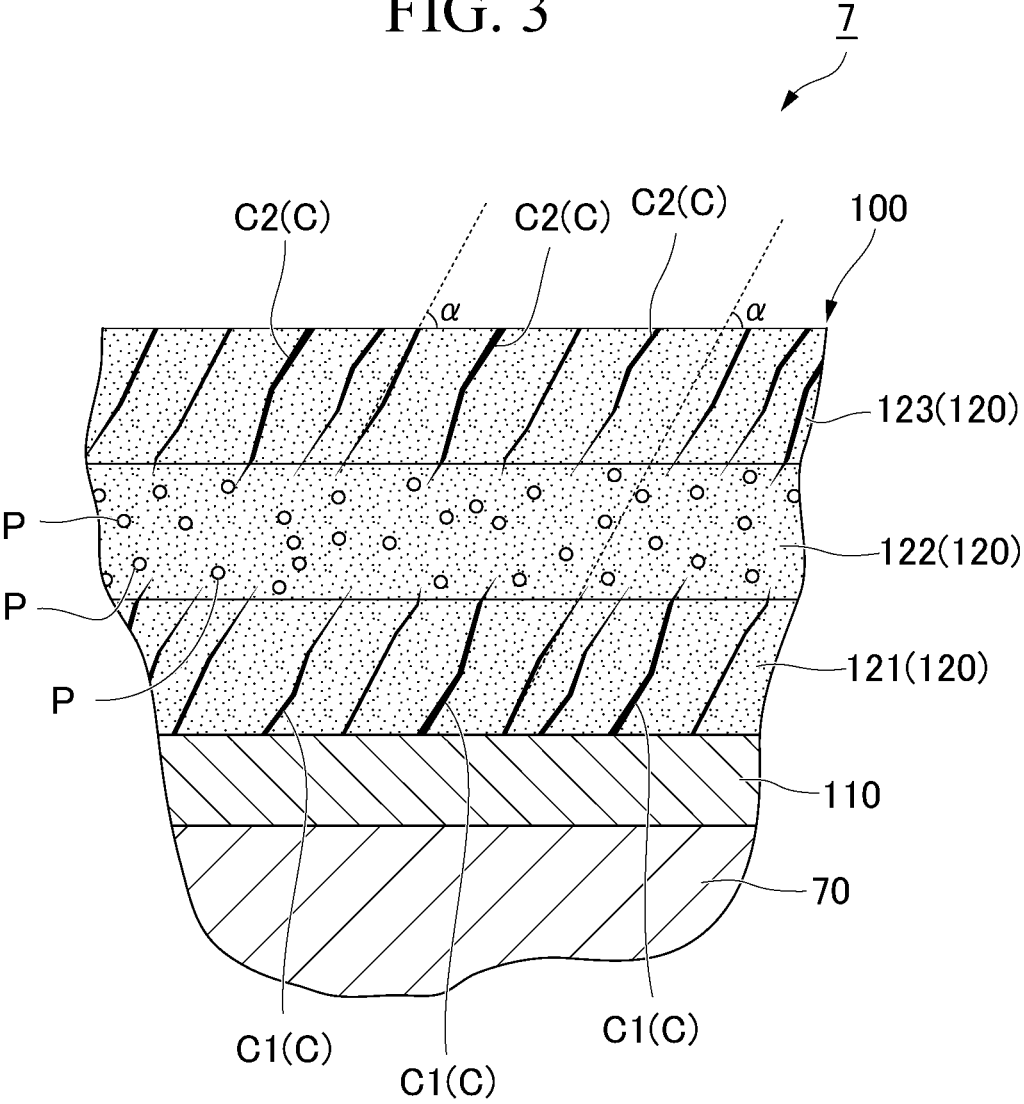


FIG. 4

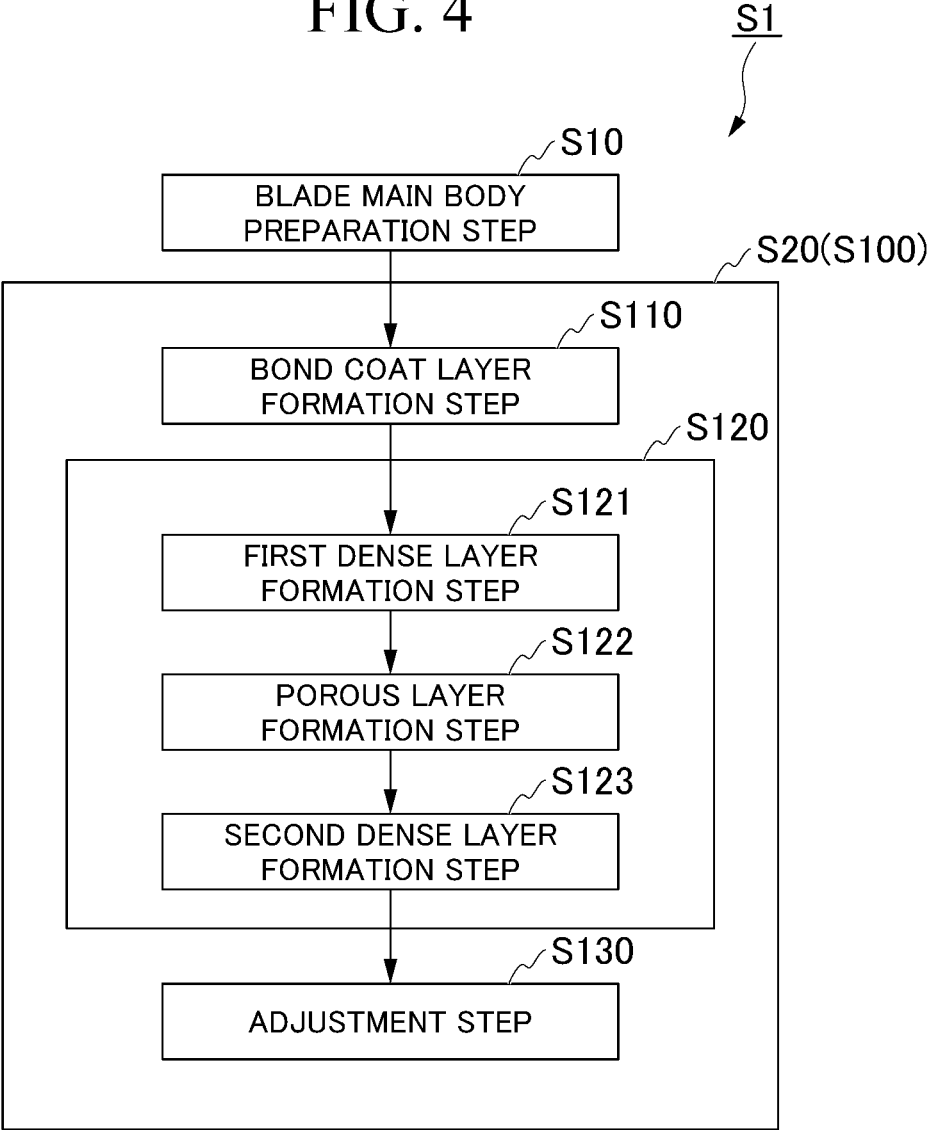


FIG. 5

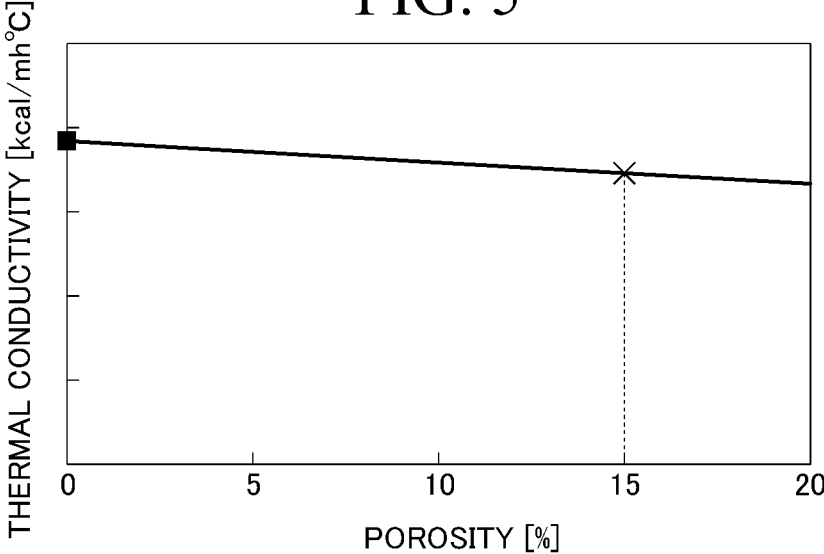


FIG. 6

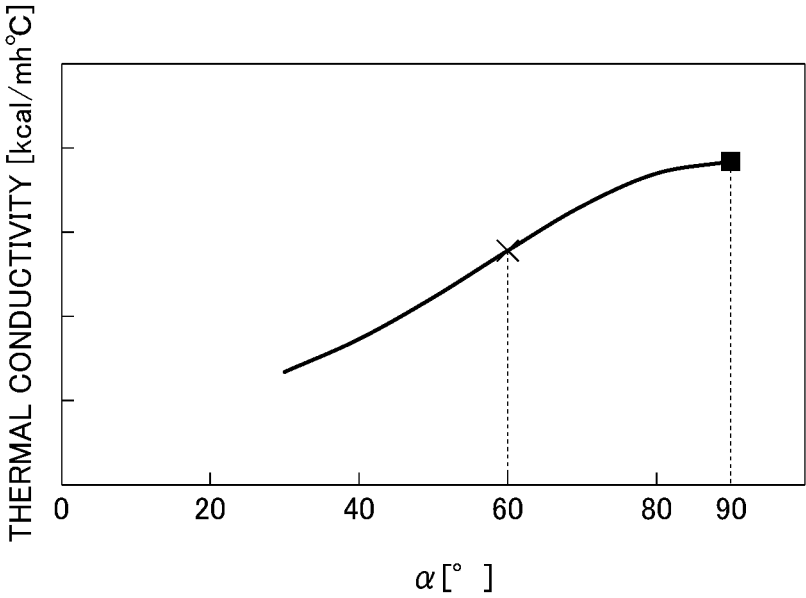


FIG. 7

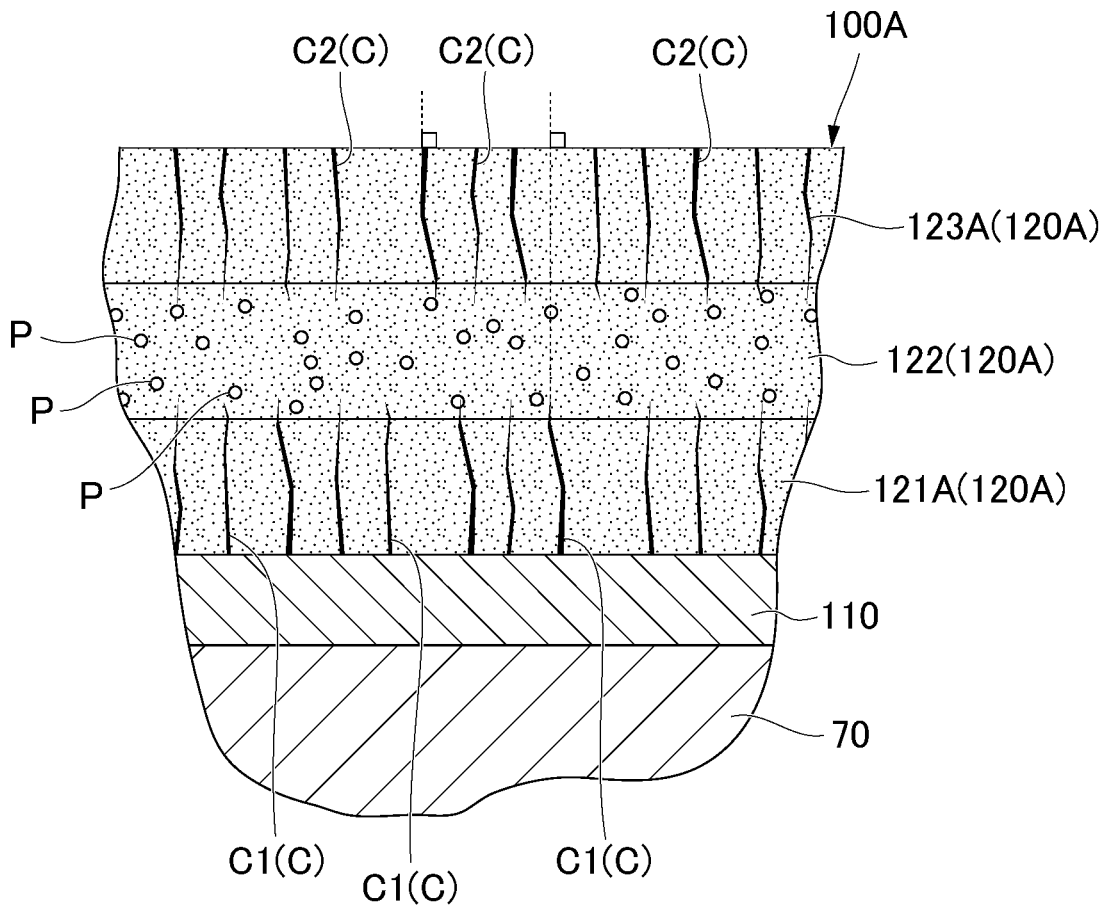
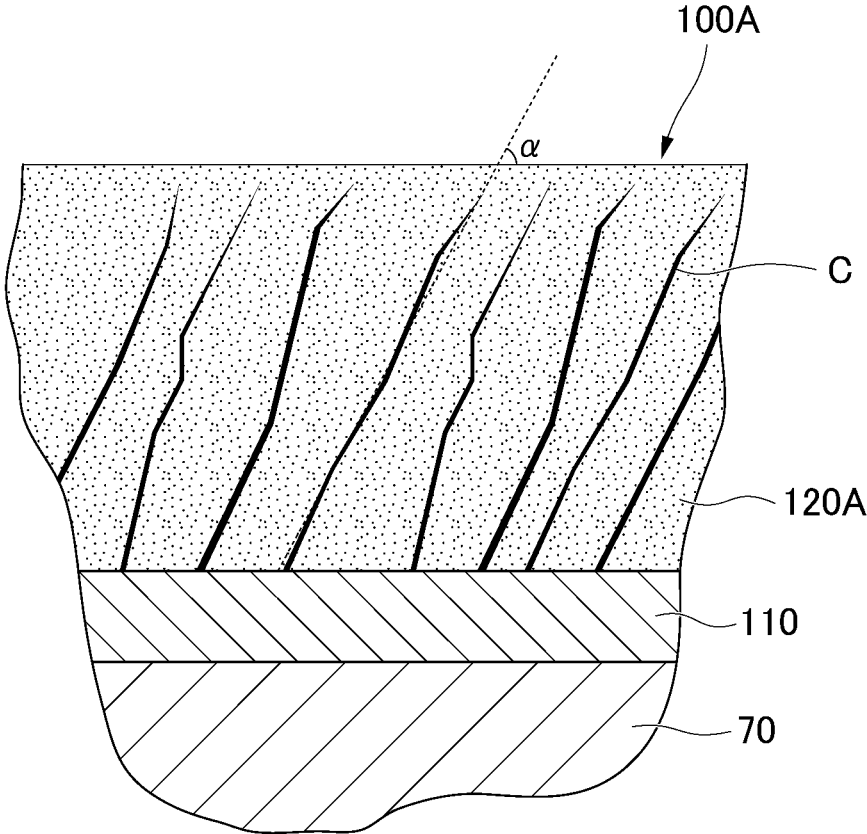


FIG. 8



**THERMAL BARRIER COATING
FORMATION METHOD, THERMAL
BARRIER COATING, AND
HIGH-TEMPERATURE MEMBER**

TECHNICAL FIELD

[0001] The present invention relates to a thermal barrier coating formation method, a thermal barrier coating, and a high-temperature member.

[0002] Priority is claimed on Japanese Patent Application Nos. 2017-087472 and 2017-087471, filed Apr. 26, 2017, the contents of which are incorporated herein by reference.

BACKGROUND ART

[0003] To improve efficiency of a gas turbine, a temperature of a gas to be used is set to be high. A thermal barrier coating (TBC) is applied to surfaces of turbine members such as blades or vanes exposed to such a high-temperature gas. The thermal barrier coating is for coating the surface of the turbine member that is an object to be thermally sprayed with a thermal spraying material having a low thermal conductivity (e.g., a ceramic-based material having a low thermal conductivity) by means of thermal spraying. The thermal barrier coating is formed on the surface, and thereby a temperature of the high-temperature member exposed under a high-temperature high-pressure environment falls, and durability of the high-temperature member is improved.

[0004] A method that uses suspension plasma spraying as a method of forming a thermal barrier coating on a metal component of a gas turbine engine is disclosed in Patent Literature 1. The suspension plasma spraying includes performing plasma thermal spraying using a suspension in which microparticles are dispersed in water or an alcohol-based carrier. The suspension plasma spraying includes depositing microparticles, which are subjected to evaporation or combustion by a plasma jet and thereby melted, on a contact surface. As a result, a homogeneous ceramic layer is formed on a surface of a substrate by the melted microparticles.

CITATION LIST

Patent Literature

[Patent Literature 1]

[0005] Japanese Unexamined Patent Application, First Publication No. 2015-166479

SUMMARY OF INVENTION

Technical Problem

[0006] Meanwhile, a dense vertical crack (DVC) coating having vertical cracks may be formed as the dense ceramic layer in the thermal barrier coating. The DVC coating becomes a dense structure having a vertical crack structure, and thereby erosion resistance is improved. However, the DVC coating is known to reduce porosity and degrade a thermal barrier property because the structure is dense. That is, when the porosity is reduced to improve the erosion resistance in the thermal barrier coating, thermal conductivity is raised, and thermal barrier performance is reduced.

[0007] Therefore, an object of the present invention is to provide a thermal barrier coating formation method, a ther-

mal barrier coating, and a high-temperature member capable of raising a thermal barrier effect while curbing a drop in erosion resistance.

Solution to Problem

[0008] A thermal barrier coating according to a first aspect of the present invention includes a ceramic layer formed on a heat-resistant alloy substrate and configured to contain a ceramic. The ceramic layer has: a first dense layer; an intermediate porous layer which is laminated on the first dense layer, which has a higher density than the first dense layer, and in which numerous pores are formed; and a second dense layer which is laminated on the intermediate porous layer and has a lower density than the intermediate porous layer.

[0009] According to this constitution, the intermediate porous layer is formed between the first dense layer and the second dense layer, and thereby heat input to the ceramic layer in a thickness direction is inhibited by the intermediate porous layer. As a result, thermal conductivity of the ceramic layer can be further reduced. The first dense layer of the ceramic layer is formed close to the heat-resistant alloy substrate, and thereby adhesiveness to the heat-resistant alloy substrate can be secured. Further, the second dense layer of the ceramic layer is formed close to the surface, and thereby erosion resistance can be secured.

[0010] Further, in a thermal barrier coating according to a second aspect of the present invention, in the first aspect, a porosity may continuously vary at a first boundary part that is a boundary part between the intermediate porous layer and the first dense layer and a second boundary part that is a boundary part between the intermediate porous layer and the second dense layer.

[0011] Further, in a thermal barrier coating according to a third aspect of the present invention, in the first or second aspect, a porosity of the intermediate porous layer may be 10% or more and 20% or less.

[0012] With this constitution, an effect of inhibiting the heat input to the ceramic layer in the thickness direction over a wide region in the surface direction is raised. As a result, the thermal conductivity in the top coat layer can be greatly reduced without greatly reducing erosion resistance in the intermediate porous layer.

[0013] Further, in a thermal barrier coating according to a fourth aspect of the present invention, in any one of the first to third aspects, a porosity of the first dense layer and a porosity of the second dense layer may be 10% or less and 5% or more.

[0014] Further, in a thermal barrier coating according to a fifth aspect of the present invention, in any one of the first to fourth aspects, the first dense layer may have first vertical cracks that extend in a thickness direction and are distributed in a surface direction, and the second dense layer may have second vertical cracks that extend in a thickness direction and are distributed in a surface direction.

[0015] Further, in a thermal barrier coating according to a sixth aspect of the present invention, in the fifth aspect, the first vertical cracks and the second vertical cracks may extend to be inclined with respect to a surface of the ceramic layer.

[0016] With this constitution, the heat input in the thickness direction in the ceramic layer is inhibited by the first and second vertical cracks that extend obliquely. Thus, the thermal conductivity in the ceramic layer can be reduced by

the first vertical cracks and the second vertical cracks. On the other hand, the ceramic layer is densely formed as the first and second vertical cracks are formed, and thereby a drop in erosion resistance can be curbed.

[0017] Further, in a thermal barrier coating according to a seventh aspect of the present invention, in the fifth or sixth aspect, angles of inclination of the first vertical cracks with respect to the surface of the ceramic layer may be different from those of the second vertical cracks with respect to the surface of the ceramic layer.

[0018] Further, a thermal barrier coating formation method according to an eighth aspect of the present invention includes a ceramic layer formation step of forming a ceramic layer containing a ceramic on a surface of a heat-resistant alloy substrate. The ceramic layer formation step includes: a first dense layer formation step of forming a first dense layer; a porous layer formation step, performed after the first dense layer formation step, of forming an intermediate porous layer, which has a higher density than the first dense layer and in which numerous pores are formed, on the first dense layer; and a second dense layer formation step, performed after the porous layer formation step, of forming a second dense layer, which has a lower density than the intermediate porous layer, on the intermediate porous layer.

[0019] With this constitution, the intermediate porous layer is formed between the first dense layer and the second dense layer, and thereby heat input to the ceramic layer in a thickness direction is inhibited by the intermediate porous layer. As a result, thermal conductivity of the ceramic layer can be reduced. Further, the first dense layer of the ceramic layer is formed close to the heat-resistant alloy substrate, and thereby adhesiveness to the heat-resistant alloy substrate can be secured. Further, the second dense layer of the ceramic layer is formed close to the surface, and thereby erosion resistance can be secured.

[0020] Further, in a thermal barrier coating formation method according to a ninth aspect of the present invention, in the eighth aspect, a thermal spraying method may be used in the ceramic layer formation step, and a distance between a spraying hole of a thermal spraying gun and a surface of a thermal spraying target may be shorter in the first and second dense layer formation steps than in the porous layer formation step.

[0021] Further, in a thermal barrier coating formation method according to a tenth aspect of the present invention, in the eighth or ninth aspect, the first dense layer formation step may include forming the first dense layer such that first vertical cracks extending in a thickness direction are distributed in a surface direction, and the second dense layer formation step may include forming the second dense layer such that second vertical cracks extending in a thickness direction are distributed in a surface direction.

[0022] Further, in a thermal barrier coating formation method according to an eleventh aspect of the present invention, in any one of the eighth to tenth aspects, thermal spraying particles may have a particle size of 0.1 μm or more and 1.0 μm or less.

[0023] Further, in a thermal barrier coating formation method according to a twelfth aspect of the present invention, in any one of the eighth to eleventh aspects, at least a part of the ceramic layer formation step may use suspension plasma spraying.

[0024] Further, a high-temperature member according to a thirteenth aspect of the present invention includes: a heat-

resistant alloy substrate; and a ceramic layer formed on the heat-resistant alloy substrate and configured to contain a ceramic. The ceramic layer has: a first dense layer; an intermediate porous layer which is laminated on the first dense layer, which has a higher density than the first dense layer, and in which numerous pores are formed; and a second dense layer which is laminated on the intermediate porous layer and has a lower density than the intermediate porous layer.

[0025] In a thermal barrier coating according to a fourteenth aspect of the present invention, in the first aspect, the ceramic layer may have vertical cracks that extend in a thickness direction and are distributed in a surface direction, and the vertical cracks may extend to be inclined with respect to a surface of the ceramic layer.

[0026] According to this constitution, the heat input in the thickness direction in the ceramic layer is inhibited by the vertical cracks that extend obliquely. Thus, the thermal conductivity in the ceramic layer can be reduced by the vertical cracks. On the other hand, the ceramic layer is densely formed as the vertical cracks are formed, and thereby a drop in erosion resistance can be curbed.

[0027] In a thermal barrier coating according to a fifteenth aspect of the present invention, in the fourteenth aspect, angles of inclination of the vertical cracks may be different between a side close to the surface of the ceramic layer and a side close to the heat-resistant alloy substrate.

[0028] In a thermal barrier coating according to a sixteenth aspect of the present invention, in the fourteenth or fifteenth aspect, the vertical cracks may have a distribution rate per 1 mm of 6 cracks/mm or more and 12 cracks/mm or less.

[0029] In a thermal barrier coating according to a seventeenth aspect of the present invention, in any one of the fourteenth to sixteenth aspects, the vertical cracks may extend intermittently.

[0030] In a thermal barrier coating according to an eighteenth aspect of the present invention, in any one of the fourteenth to seventeenth aspects, all the plurality of vertical cracks may be inclined toward one side in the surface direction as those vertical cracks go to the surface of the ceramic layer.

[0031] With this constitution, heat input in the thickness direction is inhibited over a wide region of the ceramic layer in the surface direction. As a result, the thermal conductivity in the ceramic layer over a wide range can be reduced.

[0032] In a thermal barrier coating according to a nineteenth aspect of the present invention, in any one of the fourteenth to eighteenth aspects, angles of inclination of the vertical cracks may be angles of 45° or more and 80° or less with respect to the surface of the ceramic layer.

[0033] With this constitution, the angles of inclination become small, and thereby an effect of inhibiting the heat input in the thickness direction due to the vertical cracks is increased. As a result, the thermal conductivity in the ceramic layer can be remarkably reduced. Further, by setting the angles of inclination of the vertical cracks to 45° or more, a phenomenon in which it is difficult for the thermal spraying particles to attach to the surface when the ceramic layer is formed is curbed. For this reason, a drop in manufacturing efficiency of the ceramic layer can be curbed.

[0034] In a thermal barrier coating formation method according to a twentieth aspect of the present invention, in the eighth aspect, a thermal spraying gun may be inclined with respect to the surface of the heat-resistant alloy sub-

strate by a predetermined angle of inclination, and perform thermal spraying using a suspension in which thermal spraying particles are dispersed, and the ceramic layer which contains a ceramic and in which vertical cracks, which extend in a thickness direction and extend to be inclined by the angle of inclination, are distributed in a surface direction may be formed in the heat-resistant alloy substrate.

[0035] With this constitution, the heat input in the thickness direction in the ceramic layer is inhibited by the vertical cracks that extend obliquely. Thus, the thermal conductivity in the ceramic layer can be reduced by the vertical cracks. On the other hand, the ceramic layer is densely formed as the vertical cracks are formed, and thereby a drop in erosion resistance can be curbed. Further, the ceramic layer is formed by suspension plasma spraying, and thereby the particle sizes of the thermal spraying particles of which the ceramic layer is formed are reduced. As a result, the ceramic layer can be formed in a very dense structure. Thereby, adhesiveness of the ceramic layer after the formation can also be improved.

[0036] In a thermal barrier coating formation method according to a twenty-first aspect of the present invention, in the twentieth aspect, the thermal spraying may be suspension plasma spraying.

[0037] In a thermal barrier coating formation method according to a twenty-second aspect of the present invention, in the twentieth or twenty-first aspect, the thermal spraying particles may have a particle size of 0.1 μm or more and 1.0 μm or less.

[0038] A high-temperature member according to a twenty-third aspect of the present invention may include: in the thirteenth aspect, a heat-resistant alloy substrate; and a ceramic layer formed on the heat-resistant alloy substrate, having vertical cracks that extend in a thickness direction and are distributed in a surface direction, and configured to contain a ceramic. The vertical cracks may extend to be inclined with respect to a surface of the ceramic layer.

Advantageous Effects of Invention

[0039] According to the thermal barrier coating formation method, the thermal barrier coating, and the high-temperature member, a thermal barrier effect can be raised while curbing a drop in erosion resistance.

BRIEF DESCRIPTION OF DRAWINGS

[0040] FIG. 1 is a schematic constitutional view of a gas turbine according to an embodiment of the present invention.

[0041] FIG. 2 is a schematic constitutional perspective view of a blade according to an embodiment of the present invention.

[0042] FIG. 3 is an enlarged sectional view of key parts of the blade for illustrating a thermal barrier coating according to an embodiment of the present invention.

[0043] FIG. 4 is a process view illustrating processes of a thermal barrier coating formation method according to a first embodiment of the present invention.

[0044] FIG. 5 is a view in which a relationship between thermal conductivity and porosity in a top coat layer in an embodiment of the present invention is obtained by simulation.

[0045] FIG. 6 is a view in which a relationship between thermal conductivity and an angle of inclination of each

vertical crack in the top coat layer in which the vertical cracks are formed in the embodiment of the present invention is obtained by simulation.

[0046] FIG. 7 is an enlarged sectional view of key parts of a blade for illustrating a thermal barrier coating according to a modification of the present invention.

[0047] FIG. 8 is an enlarged sectional view of key parts of a blade for illustrating a thermal barrier coating according to another modification of the present invention.

DESCRIPTION OF EMBODIMENTS

[0048] Hereinafter, an embodiment of the present invention will be described with reference to FIGS. 1 to 7.

[0049] As illustrated in FIG. 1, a gas turbine 1 of the present embodiment includes a compressor 2, combustors 3, a turbine main body 4, and a rotor 5. A large quantity of air is introduced into the inside of the compressor 2, and is compressed. The combustors 3 mix a fuel with the compressed air A that is compressed by the compressor 2, and burn the mixture.

[0050] The turbine main body 4 converts thermal energy of a combustion gas G introduced from the combustors 3 into rotational energy. The turbine main body 4 blows the combustion gas G to blades 7 provided on the rotor 5, thereby converting the thermal energy of the combustion gas G into mechanical rotational energy and generating power. In addition to the plurality of blades 7 close to the rotor 5 of the turbine main body 4, a plurality of vanes 8 are provided in a casing 6 of the turbine main body 4. In the turbine main body 4, the blades 7 and the vanes 8 are alternately arranged in an axial direction of the rotor 5. The rotor 5 transmits some of the rotating power of the turbine main body 4 to the compressor 2, and rotates the compressor 2.

[0051] Hereinafter, in this embodiment, each blade 7 of the turbine main body 4 will be described as an example of a high-temperature member of this invention.

[0052] As illustrated in FIG. 2, the blade 7 has a blade main body 70 and a thermal barrier coating 100. The blade main body 70 is a heat-resistant alloy substrate that is formed of, for example, a well-known heat-resistant alloy material such as a Ni-based alloy. The blade main body 70 of the present embodiment includes a blade main body part 71, a platform part 72, a blade root part 73, and a shroud part 74.

[0053] The blade main body part 71 has a blade-shaped cross section. The blade main body part 71 is disposed in a channel of the combustion gas G inside the casing 6 of the turbine main body 4. The platform part 72 is provided at a base end of the blade main body part 71. The platform part 72 defines the channel of the combustion gas G in the vicinity of the base end of the blade main body part 71. The blade root part 73 is formed by protruding from the platform part 72 to the side opposite to the blade main body part 71. The shroud part 74 is provided at a tip of the blade main body part 71. The shroud part 74 defines the channel of the combustion gas G in the vicinity of the tip of the blade main body part 71.

[0054] As illustrated in FIG. 3, the thermal barrier coating 100 is formed on a surface of the blade main body 70 that is a heat-resistant alloy substrate. The thermal barrier coating 100 is formed to cover a surface of the blade main body part 71, a surface of the platform part 72 which is on a side connected to the blade main body part 71, and a surface of the shroud part 74 which is on a side connected to the blade

main body part **71** out of the surface of the blade main body **70**. The thermal barrier coating **100** of the present embodiment is formed by suspension plasma spraying to be described below. The thermal barrier coating **100** of the present embodiment includes a bond coat layer **110** and a top coat layer (a ceramic layer) **120**.

[0055] The bond coat layer **110** is directly formed on the surface of the blade main body **70**. The bond coat layer **110** inhibits the top coat layer **120** from being delaminated from the blade main body **70**. The bond coat layer **110** is a metallic bond layer that is excellent in corrosion resistance and oxidation resistance. The bond coat layer **110** is formed, for example, by thermally spraying a metal spraying powder of a MCrAlY alloy that is a thermal spraying material on the surface of the blade main body **70**. Here, "M" of the MCrAlY alloy of which the bond coat layer **110** is formed is a metal element. The metal element "M" is, for example, a single metal element such as Ni, Co, or the like, or a combination of two or more thereof.

[0056] The top coat layer **120** is formed on the blade main body **70** via the bond coat layer **110**. The top coat layer **120** has a layer that contains a ceramic in which vertical cracks **C** extending in a thickness direction are distributed in a surface direction. Here, the surface direction is a direction parallel to a surface of the top coat layer **120**. The top coat layer **120** of the present embodiment is formed at a thickness of 0.3 mm or more and 1.5 mm or less. The top coat layer **120** has a first dense layer **121**, an intermediate porous layer **122**, and a second dense layer **123**.

[0057] The first dense layer **121** is directly laminated on the bond coat layer **110**. In the first dense layer **121**, first vertical cracks **C1** are distributed as the vertical cracks **C** in the surface direction in which the surface spreads. Thus, in the first dense layer **121**, the plurality of first vertical cracks **C1** are formed apart in the surface direction. The first dense layer **121** of the present embodiment is, for example, a dense vertical crack (DVC) coating in which the first vertical cracks **C1** are distributed in the surface direction. The first dense layer **121** is formed closest to the heat-resistant alloy substrate among the layers of the top coat layer **120**. The thermal spraying material used when the first dense layer **121** is formed includes, for example, yttria-stabilized zirconia (YSZ) or ytterbia-stabilized zirconia (YbSZ) that is zirconia (ZrO_2) which is partly stabilized by ytterbium oxide (Yb_2O_3).

[0058] The first vertical cracks **C1** extend to be inclined with respect to the surface of the top coat layer **120** by a prescribed angle of inclination α . To be specific, for each of the first vertical cracks **C1**, an extending direction of a virtual straight line that connects a base end thereof close to a surface of the heat-resistant alloy substrate in a thickness direction and a tip thereof close to the surface of the top coat layer **120** is set as an extending direction. The extending directions of the first vertical cracks **C1** are inclined with respect to the surface direction in which the surface of the top coat layer **120** spreads. Thus, the first vertical cracks **C1** extend toward one side in the surface direction with respect to the base ends thereof from the base ends thereof toward the surface of the top coat layer **120**. The angle of inclination α in the present embodiment is an angle in the extending direction with respect to the surface direction. In the present embodiment, the plurality of first vertical cracks **C1** are all inclined in the same direction. That is, all the plurality of first vertical cracks **C1** are inclined toward one side in the

surface direction toward the surface of the top coat layer **120**. Further, the first vertical cracks **C1** are inclined not only at a part of the base end side or the tip side thereof, but over the entire area in the thickness direction.

[0059] The angle of inclination α in the present embodiment is preferably an angle of 45° or more and 80° or less with respect to the surface of the top coat layer **120**. The angle of inclination α is more preferably an angle of 50° or more and 70° or less with respect to the surface of the top coat layer **120**. The angle of inclination α is particularly preferably an angle of 55° or more and 65° or less with respect to the surface of the top coat layer **120**.

[0060] In the first dense layer **121**, a distribution rate of the first vertical cracks **C1** per mm is preferably 6 cracks/mm or more and 12 cracks/mm or less. In the first dense layer **121**, a distribution rate of the first vertical cracks **C1** per 1 mm is more preferably 8 cracks/mm or more and 10 cracks/mm or less.

[0061] A porosity of the first dense layer **121** preferably falls within a range of 10% or less and 5% or more. The porosity in the present embodiment is not only an occupancy rate of only pores **P** per unit volume, but also an occupancy rate adding up the vertical cracks **C** and the pores **P**.

[0062] The intermediate porous layer **122** is laminated on the first dense layer **121**. The intermediate porous layer **122** has a higher density than the first dense layer **121**, and numerous pores **P** are formed therein. Thus, the intermediate porous layer **122** is a porous film that is formed at a higher porosity than the first dense layer **121**, and has few vertical cracks **C** therein. The intermediate porous layer **122** of the present embodiment is formed at the same thickness as the first dense layer **121**. The intermediate porous layer **122** of the present embodiment is formed of the same thermal spraying material as the first dense layer **121**.

[0063] The porosity of the intermediate porous layer **122** of the present embodiment is preferably 10% or more and 20% or less. The porosity of the intermediate porous layer **122** is more preferably 12% or more and 18% or less. The porosity of the intermediate porous layer **122** is particularly preferably 14% or more and 16% or less.

[0064] The porosity continuously varies at a first boundary portion that is a boundary portion between the intermediate porous layer **122** and the first dense layer **121**. Thus, the porosity is formed to become gradually higher from the vicinity of the middle of the first dense layer **121** in the thickness direction to the vicinity of the middle of the intermediate porous layer **122** in the thickness direction.

[0065] The second dense layer **123** is directly laminated on the intermediate porous layer **122**. In the second dense layer **123**, second vertical cracks **C2** are distributed as the vertical cracks **C** in the surface direction. Thus, in the second dense layer **123**, the plurality of second vertical cracks **C2** are formed apart in the surface direction. The second dense layer **123** has a higher density than the intermediate porous layer **122**. The second dense layer **123** is formed closest to the surface among the layers of the top coat layer **120**. Thus, a surface of the second dense layer **123** is the surface of the top coat layer **120**. The second dense layer **123** of the present embodiment is, for example, a DVC coating in which the second vertical cracks **C2** are distributed in the surface direction. The second dense layer **123** of the present embodiment is a film having the same structure as the first dense layer **121**. Thus, the thermal spraying material used when the

second dense layer **123** is formed is the same thermal spraying material as the first dense layer **121**.

[0066] Like the first vertical cracks **C1**, the second vertical cracks **C2** extend to be inclined with respect to the surface of the top coat layer **120** by an angle of inclination α . To be specific, for each of the second vertical cracks **C2**, an extending direction of a virtual straight line that connects a base end thereof close to the surface of the heat-resistant alloy substrate in the thickness direction and a tip thereof close to the surface of the top coat layer **120** is set as an extending direction. The extending directions of the second vertical cracks **C2** are inclined with respect to the surface direction in which the surface of the top coat layer **120** spreads. Thus, like the first vertical cracks **C1**, the second vertical cracks **C2** extend toward one side in the surface direction with respect to the base ends thereof from the base ends thereof toward the surface of the top coat layer **120**. The second vertical cracks **C2** of the present embodiment are inclined at the same angle in the same direction as the first vertical cracks **C1**. The plurality of second vertical cracks **C2** are all inclined in the same direction. That is, all the plurality of second vertical cracks **C2** are inclined toward one side in the surface direction toward the surface of the top coat layer **120**. Further, the second vertical cracks **C2** are inclined not only at a part of the base end side or the tip side thereof, but over the entire area in the thickness direction.

[0067] In the second dense layer **123**, a distribution rate of the second vertical cracks **C2** per 1 mm is preferably 6 cracks/mm or more and 12 cracks/mm or less. In the second dense layer **123**, a distribution rate of the second vertical cracks **C2** per 1 mm is more preferably 8 cracks/mm or more and 10 cracks/mm or less. A porosity of the second dense layer **123** preferably falls within a range of 10% or less and 5% or more. In the second dense layer **123**, the distribution rate of the second vertical cracks **C2** per 1 mm is preferably the same as that of the first vertical cracks **C1** of the first dense layer **121**. The porosity of the second dense layer **123** is preferably the same as that of the first dense layer **121**.

[0068] The porosity continuously varies at a second boundary portion that is a boundary portion between the intermediate porous layer **122** and the second dense layer **123**. Thus, the porosity is formed to become gradually lower from the vicinity of the middle of the intermediate porous layer **122** in the thickness direction to the vicinity of the middle of the second dense layer **123** in the thickness direction.

[0069] Next, a manufacturing method **S1** of a high-temperature member will be described. The manufacturing method **S1** of the high-temperature member of the present embodiment is a manufacturing method of the blade **7** in which the aforementioned blade **7** is manufactured as the high-temperature member. As illustrated in FIG. 4, the manufacturing method **S1** of the high-temperature member of the present embodiment includes a blade main body preparation step **S10** and a thermal barrier coating formation step **S20**.

[0070] The blade main body preparation step **S10** includes preparing a heat-resistant alloy substrate as the blade main body **70** in advance. The blade main body preparation step **S10** of the present embodiment includes preparing a material by forming the material in the shape of the target high-temperature member (e.g., the blade main body **70** in the present embodiment).

[0071] The thermal barrier coating formation step **S20** includes forming a thermal barrier coating **100** on a surface of the blade main body **70** prepared in the blade main body preparation step **S10** in a thermal barrier coating formation method **S100**. In the thermal barrier coating formation step **S20** of the present embodiment, a bond coat layer **110** and a top coat layer **120** are formed on the surface of the blade main body **70**. The thermal barrier coating formation step **S20** of the present embodiment is performed according to the thermal barrier coating formation method **S100** below.

[0072] The thermal barrier coating formation method **S100** includes forming the thermal barrier coating **100** on the blade main body **70**. The thermal barrier coating formation method **S100** of the present embodiment includes a bond coat layer formation step **S110**, a top coat layer formation step (a ceramic layer formation step) **S120**, and an adjustment step **S130**.

[0073] The bond coat layer formation step **S110** includes forming the bond coat layer **110** on the surface of the blade main body **70**. The bond coat layer formation step **S110** is performed after the blade main body preparation step **S10**. In the bond coat layer formation step **S110**, thermal spraying particles of a MCrAlY alloy are thermally sprayed on the surface of the blade main body **70**, for example, by a thermal spraying gun. In the bond coat layer formation step **S110**, the thermal spraying gun is moved with a spraying hole of the thermal spraying particles directed perpendicular to the surface of the blade main body **70**. The bond coat layer formation step **S110** of the present embodiment includes performing high-velocity oxygen fuel spraying (HVOF) or low-pressure plasma spraying (LPPS) using the thermal spraying gun, thereby forming the bond coat layer **110**.

[0074] The top coat layer formation step **S120** includes forming the top coat layer **120** containing a ceramic on the surface of the blade main body **70**. The top coat layer formation step **S120** is performed after the bond coat layer formation step **S110**. The top coat layer formation step **S120** includes laminating the top coat layer **120** on the bond coat layer **110** formed in the bond coat layer formation step **S110**. In the top coat layer formation step **S120**, a thermal spraying method is used. Thus, the top coat layer formation step **S120** of the present embodiment includes thermally spraying thermal spraying particles on a surface of the bond coat layer **110** formed on the blade main body **70**, and forming the top coat layer **120**. The top coat layer formation step **S120** includes a first dense layer formation step **S121**, a porous layer formation step **S122**, and a second dense layer formation step **S123**.

[0075] The first dense layer formation step **S121** is performed after the bond coat layer formation step **S110**. The first dense layer formation step **S121** includes forming a first dense layer **121** on the bond coat layer **110**. The first dense layer formation step **S121** includes performing suspension plasma spraying to form the first dense layer **121**. The first dense layer formation step **S121** includes inclining the thermal spraying gun with respect to the surface of the blade main body **70** by a prescribed angle of inclination α , and performing the suspension plasma spraying. The suspension plasma spraying is a thermal spraying method of supplying a suspension in which fine thermal spraying particles are dispersed in a plasma jet and forming a coating. A distance between the spraying hole of the thermal spraying gun and the surface of the blade main body **70** that is a thermal

spraying target is shorter in the first dense layer formation step S121 than in the porous layer formation step S122.

[0076] The fine thermal spraying particles preferably have particle sizes of 0.1 μm or more and 1.0 μm or less. A carrier used in the suspension includes, for example, water or ethanol. The suspension plasma spraying may use a thermal spraying gun having an axial flow internal supply system that is a supply system of the suspension to the plasma jet or a thermal spraying gun having an axial flow external supply system.

[0077] The porous layer formation step S122 is performed after the first dense layer formation step S121. The porous layer formation step S122 includes forming an intermediate porous layer 122 on the first dense layer 121. The porous layer formation step S122 includes performing suspension plasma spraying to form the intermediate porous layer 122. The porous layer formation step S122 includes keeping a thermal spraying gun more apart from the blade main body 70 than in the first dense layer formation step S121, and thermally sprays thermal spraying particles. In the porous layer formation step S122, the thermal spraying is performed first while moving the thermal spraying gun to gradually move apart from a thermal spraying distance in the first dense layer formation step S121. Afterward, the thermal spraying distance is gradually brought close to a thermal spraying distance in the second dense layer formation step S123 at a point in time when the intermediate porous layer 122 is formed up to approximately half of a desired film thickness of the intermediate porous layer 122. Finally, the thermal spraying gun is moved such that the thermal spraying distance is identical to the thermal spraying distance in the second dense layer formation step S123 at a point in time when the intermediate porous layer 122 having a desired film thickness is formed.

[0078] The second dense layer formation step S123 is performed after the porous layer formation step S122. The second dense layer formation step S123 includes forming a second dense layer 123 on the intermediate porous layer 122. The second dense layer formation step S123 includes performing suspension plasma spraying to form the second dense layer 123. The second dense layer formation step S123 includes bringing a thermal spraying gun closer to the blade main body 70 than in the porous layer formation step S122, and thermally sprays thermal spraying particles. The second dense layer formation step S123 of the present embodiment is performed under the same conditions as the first dense layer formation step S121. Thus, the second dense layer formation step S123 includes inclining the thermal spraying gun with respect to the surface of the blade main body 70 by a predetermined angle of inclination α , and performing the suspension plasma spraying. A distance between a spraying hole of the thermal spraying gun and the surface of the blade main body 70 that is a thermal spraying target is shorter in the second dense layer formation step S123 than in the porous layer formation step S122.

[0079] The adjustment step S130 is performed after the second dense layer formation step S123. The adjustment step S130 includes adjusting a state of a surface of the thermal barrier coating 100. To be specific, in the adjustment step S130, a surface of the top coat layer 120 is slightly scraped to adjust a film thickness of the thermal barrier coating 100 or to be made smoother. For example, thermal conductivity to the blade 7 can be reduced by the adjustment step S130. In the adjustment step S130 of this embodiment,

a surface of the second dense layer 123 is scraped by several microns. Thereby, the surface of the top coat layer 120 is smoothed, and the film thickness is adjusted.

[0080] According to the thermal barrier coating 100, the thermal barrier coating formation method S100, and the blade 7 as described above, the intermediate porous layer 122 is formed between the first dense layer 121 and the second dense layer 123, and thereby heat input to the top coat layer 120 in the thickness direction is inhibited by the intermediate porous layer 122. As a result, the thermal conductivity of the top coat layer 120 can be further reduced. The first dense layer 121 of the top coat layer 120 is formed on a side on which it adheres to the bond coat layer 110 that is close to the blade main body 70, and thereby adhesiveness to the bond coat layer 110 can be secured. Further, the second dense layer 123 of the top coat layer 120 is formed close to the surface, and thereby the erosion resistance can be secured. Thereby, the thermal barrier effect can be raised while curbing a drop in erosion resistance in the thermal barrier coating 100.

[0081] To be specific, the thermal conductivity is reduced by existence of the intermediate porous layer 122, which will be described using FIG. 5. FIG. 5 is a view in which a relationship between thermal conductivity and porosity in the top coat layer 120 is obtained by simulation. As illustrated in FIG. 5, in the top coat layer 120, as the porosity becomes higher, the thermal conductivity in the top coat layer 120 becomes lower. To be more specific, the porosity rises from 0% to 15%, and thereby the thermal conductivity is reduced by about 10%. Thus, since the intermediate porous layer 122 having a high porosity is formed between the first dense layer 121 and the second dense layer 123, it is found that the thermal conductivity in the top coat layer 120 can be reduced.

[0082] Further, the porosity in the intermediate porous layer 122 is set to 10% or more and 20% or less, and thereby an effect of inhibiting the heat input in the thickness direction due to the first vertical cracks C1 and the second vertical cracks C2 is increased. As a result, the thermal conductivity in the top coat layer 120 can be greatly reduced without greatly reducing the erosion resistance in the intermediate porous layer 122.

[0083] Further, like the first vertical cracks C1 or the second vertical cracks C2, the vertical cracks C formed obliquely in the top coat layer 120 are formed. For this reason, the heat input in the thickness direction in the first dense layer 121 is inhibited by the first vertical cracks C1 that extend obliquely. Likewise, the heat input in the thickness direction in the second dense layer 123 is inhibited by the second vertical cracks C2 that extend obliquely. Thus, the thermal conductivity in the top coat layer 120 can be reduced by the first vertical cracks C1 and the second vertical cracks C2. On the other hand, the second dense layer 123 is formed close to the surface of the top coat layer 120. Since the second dense layer 123 is densely formed as the vertical cracks C are formed, a drop in erosion resistance can be curbed. Thereby, the thermal barrier effect can be raised while curbing a drop in erosion resistance in the vicinity of the surface of the thermal barrier coating 100.

[0084] To be specific, the thermal conductivity is reduced by inclining the vertical cracks C, which will be described using FIG. 6. FIG. 6 is a view in which a relationship between thermal conductivity and an angle of inclination α of each vertical crack C in the top coat layer 120 in which

the vertical cracks C are formed is obtained by simulation. As illustrated in FIG. 6, in the top coat layer 120, as the angle of inclination α of each vertical crack C becomes smaller, the thermal conductivity in the top coat layer 120 becomes smaller. To be more specific, in a case where the angle of inclination α of each vertical crack C is set to 60° compared to a state in which the vertical cracks C are not inclined (a case where the angle of inclination α is 90°), the thermal conductivity is reduced by 25% or more. Thus, since the vertical cracks C are made oblique, it is found that the thermal conductivity in the top coat layer 120 can be reduced.

[0085] Further, the top coat layer 120 is formed by suspension plasma spraying, and thereby the particle sizes of the thermal spraying particles of which the top coat layer 120 is formed are reduced compared to atmospheric plasma spraying (APS). As a result, the first dense layer 121 or the second dense layer 123 can be formed in a very dense structure. For this reason, adhesiveness of the first dense layer 121 to the bond coat layer 110 or adhesiveness between the layers of the top coat layer 120 can be improved.

[0086] Further, the first vertical cracks C1 and the second vertical cracks C2 are all inclined in the same direction, and thereby the heat input in the thickness direction is inhibited over wide regions of the first dense layer 121 and the second dense layer 123 in the surface direction. As a result, the thermal conductivity in the top coat layer 120 can be reduced over a wide range.

[0087] Further, the angles of inclination α of the first and second vertical cracks C1 and C2 are set to 45° or more and 80° or less. The angles of inclination α become small, and thereby the effect of inhibiting the heat input in the thickness direction due to the first vertical cracks C1 and the second vertical cracks C2 is increased. As a result, the thermal conductivity in the top coat layer 120 can be remarkably reduced. Further, when the angles of inclination α of the first vertical cracks C1 and the second vertical cracks C2 are set to 45° or more, it is curbed that the thermal spraying particles are difficult to be attached to the surface when the first dense layer 121 and the second dense layer 123 are formed. For this reason, a drop in manufacturing efficiency of the top coat layer 120 can be further curbed.

Other Modifications of the Embodiments

[0088] While embodiments of the present invention have been described in detail with reference to the drawings, components in each of the embodiments and combinations thereof are one example, and additions, omissions, substitutions, and other modifications of the constitution are possible without departing from the spirit of the present invention. The present invention is not limited by each of the embodiments, but is only limited by the claims.

[0089] In the above embodiments, the first vertical cracks C1 and the second vertical cracks C2 have an inclined structure, but the top coat layer 120 is not limited to this structure. For example, as illustrated in FIG. 7, a top coat layer 120A of a thermal barrier coating 100A of a structure having vertical cracks C extending perpendicular to a surface direction (vertical cracks that are not inclined) may be formed. Thus, first vertical cracks C1 of a first dense layer 121A and second vertical cracks C2 of a second dense layer 123A extend in a direction perpendicular to a surface of the top coat layer 120A.

[0090] In the above embodiments, the top coat layer 120 has a multilayered structure in which the intermediate porous layer 122 is formed between the first dense layer 121 and the second dense layer 123. However, the top coat layer 120 is not limited to this structure. For example, as illustrated in FIG. 8, the top coat layer 120A of the thermal barrier coating 100A may be formed as a single layer structure having inclined vertical cracks C.

[0091] Further, in the thermal barrier coating formation method S100 of the present embodiment, the bond coat layer formation step S110 may not be performed. For example, the bond coat layer 110 may be formed by another method, and the bond coat layer 110 itself may not be formed. In the case where the bond coat layer 110 is not formed, the ceramic layer may be directly formed on the surface of the blade main body 70.

[0092] Further, the high-temperature member is not limited to the blade 7, and may be a member exposed to a high temperature. The present invention may be applied to the high-temperature member, for example, a member such as the vane 8 of the gas turbine 1, a nozzle or a cylinder constituting the combustor 3. Further, the high-temperature member may be a member exposed to a high temperature exclusive of the gas turbine 1. For example, the high-temperature member may be a member exposed under a high-temperature environment in a gas engine.

[0093] Further, the intermediate porous layer 122 is not limited to the structure in which the vertical cracks C are not completely formed and only the pores P are formed. In the intermediate porous layer 122, if the porosity is sufficiently high, the vertical cracks C may be somewhat formed. Likewise, in the first dense layer 121 or the second dense layer 123, if the vertical cracks C are formed, the pores P may be somewhat formed.

[0094] Further, the extending directions of the vertical cracks such as the first vertical cracks C1 and the second vertical cracks C2 are not limited to being set as the extending directions of the virtual straight lines that connect the base ends and the tips thereof as described above. The extending directions of the vertical cracks may acquire approximate straight lines from complicatedly bent vertical cracks by means of an image analysis or the like, and may be set as extending direction of the approximate straight lines.

[0095] Further, the first vertical cracks C1 and the second vertical cracks C2 may be inclined, and are not limited to being inclined over the entire area in the same direction. The angles of inclination α of the vertical cracks C may be different in the vicinity of the surface of the ceramic layer and the vicinity of the blade main body 70. That is, the vertical cracks may be inclined at different angles in the middle of the extending directions, for example, as long as they are inclined in the same direction. Thus, the first vertical cracks C1 and the second vertical cracks C2 may be formed, for example, such that the angles of inclination α thereof in a region of the side close to the surface of the top coat layer 120 are smaller than those in a region of the side close to the surface of the blade main body 70.

[0096] Further, the present embodiment has a structure in which the angles of inclination α of the first vertical cracks C1 of the first dense layer 121 and the angles of inclination α of the second vertical cracks C2 of the second dense layer 123 are identical to each other, but the first dense layer 121 and the second dense layer 123 are not limited to this

structure. Thus, the angles of inclination α of the first vertical cracks C1 with respect to the surface of the top coat layer 120 may be different from those of the second vertical cracks C2 with respect to the surface of the top coat layer 120. In this case, the angles of inclination α of the first vertical cracks C1 may be preferably smaller than those of the second vertical cracks C2.

[0097] Further, in the present embodiment, the distribution rate of the vertical cracks C per 1 mm in the first dense layer 121 and the distribution rate of the vertical cracks C per 1 mm in the second dense layer 123 are set to be the same, but the first dense layer 121 and the second dense layer 123 are not limited to this structure. For example, the distribution rate of the vertical cracks C per 1 mm in the second dense layer 123 may be made greater or smaller than the distribution rate of the vertical cracks C per 1 mm in the first dense layer 121.

[0098] Further, in the present embodiment, the porosity of the first dense layer 121 and the porosity of the second dense layer 123 are set to be the same, but the first dense layer 121 and the second dense layer 123 are not limited to this structure. For example, the porosity of the first dense layer 121 and the porosity of the second dense layer 123 may be different from each other as long as they are lower than the porosity of the intermediate porous layer 122.

[0099] Further, the vertical cracks C of the present embodiment are formed to provide an interval in the intermediate porous layer 122 in the vicinity of the middle of the thickness direction in the single top coat layer 120 like the first vertical cracks C1 and the second vertical cracks C2. In this way, the vertical cracks C are not limited to the structure in which they continue from a surface facing toward the blade main body 70 of the ceramic layer to the surface. Thus, the vertical cracks C may intermittently extend in the single ceramic layer in the thickness direction. For this reason, the first vertical cracks C1 and the second vertical cracks C2 are also not limited to the continuously extending structure like the present embodiment. For example, the first vertical cracks C1 may be formed in the first dense layer 121 at an interval in the thickness direction. Likewise, the second vertical cracks C2 may be formed in the second dense layer 123 at an interval in the thickness direction.

[0100] Further, in the porous layer formation step S122 of the present embodiment, the thermal spraying gun is moved to change (gradually change) the thermal spraying distance. However, the porous layer formation step S122 is not limited to moving the thermal spraying gun in this way. For example, in the porous layer formation step S122, the thermal spraying gun may be moved to abruptly vary from the thermal spraying distance in the first dense layer formation step S121 to the target thermal spraying distance in the porous layer formation step S122.

[0101] Further, the thermal spraying conditions listed in each process are an example, and the present invention is not limited thereto. The thermal spraying conditions may be appropriately set depending on the device used or a type of the target thermal spraying particles.

INDUSTRIAL APPLICABILITY

[0102] This prevent can be applied to the thermal barrier coating formation method, the thermal barrier coating, and the high-temperature member, and can raise the thermal barrier effect while curbing a drop in erosion resistance.

REFERENCE SIGNS LIST

- | | |
|--------|--|
| [0103] | 1 Gas turbine |
| [0104] | 2 Compressor |
| [0105] | 3 Combustor |
| [0106] | 4 Turbine main body |
| [0107] | 5 Rotor |
| [0108] | 6 Casing |
| [0109] | 7 Blade |
| [0110] | 70 Blade main body |
| [0111] | 71 Blade main body part |
| [0112] | 72 Platform part |
| [0113] | 73 Blade root part |
| [0114] | 74 Shroud part |
| [0115] | 8 Vane |
| [0116] | A Compressed air |
| [0117] | G Combustion gas |
| [0118] | 100 Thermal barrier coating |
| [0119] | 110 Bond coat layer |
| [0120] | 120 Top coat layer |
| [0121] | 121 First dense layer |
| [0122] | C1 First vertical crack |
| [0123] | α Inclined angle |
| [0124] | 122 Intermediate porous layer |
| [0125] | P Pore |
| [0126] | 123 Second dense layer |
| [0127] | C2 Second vertical crack |
| [0128] | S1 Manufacturing method of high-temperature member |
| [0129] | S10 Blade main body preparation step |
| [0130] | S20 Thermal barrier coating formation step |
| [0131] | S100 Thermal barrier coating formation method |
| [0132] | S110 Bond coat layer formation step |
| [0133] | S120 Top coat layer formation step |
| [0134] | S121 First dense layer formation step |
| [0135] | S122 Porous layer formation step |
| [0136] | S123 Second dense layer formation step |
| [0137] | S130 Adjustment step |
| [0138] | C Vertical crack |
1. A thermal barrier coating, comprising
 - a ceramic layer formed on a heat-resistant alloy substrate and configured to contain a ceramic, wherein the ceramic layer has
 - a first dense layer;
 - an intermediate porous layer which is laminated on the first dense layer, which has a higher density than the first dense layer, and in which numerous pores are formed; and
 - a second dense layer which is laminated on the intermediate porous layer and has a lower density than the intermediate porous layer, wherein:
 - the first dense layer has first vertical cracks that extend in a thickness direction and are distributed in a surface direction,
 - the second dense layer has second vertical cracks that extend in a thickness direction and are distributed in a surface direction, and
 - the first vertical cracks and the second vertical cracks extend to be inclined with respect to a surface of the ceramic layer.
 2. The thermal barrier coating according to claim 1, wherein a porosity continuously varies at a first boundary part that is a boundary part between the intermediate porous layer and the first dense layer and a second boundary part

that is a boundary part between the intermediate porous layer and the second dense layer.

3. The thermal barrier coating according to claim 1, wherein a porosity of the intermediate porous layer is 10% or more and 20% or less.

4. The thermal barrier coating according to claim 1, wherein a porosity of the first dense layer and a porosity of the second dense layer are 10% or less and 5% or more.

5. (canceled)

6. (canceled)

7. The thermal barrier coating according to claim 1, wherein angles of inclination of the first vertical cracks with respect to the surface of the ceramic layer are different from those of the second vertical cracks with respect to the surface of the ceramic layer.

8. A thermal barrier coating formation method, comprising

a ceramic layer formation step of forming a ceramic layer containing a ceramic on a surface of a heat-resistant alloy substrate,

wherein the ceramic layer formation step includes:

a first dense layer formation step of forming a first dense layer;

a porous layer formation step, performed after the first dense layer formation step, of forming an intermediate porous layer, which has a higher density than the first dense layer and in which numerous pores are formed, on the first dense layer; and

a second dense layer formation step, performed after the porous layer formation step, of forming a second dense layer, which has a lower density than the intermediate porous layer, on the intermediate porous layer, wherein:

a thermal spraying gun is inclined with respect to the surface of the heat-resistant alloy substrate by a pre-determined angle of inclination, and performs thermal spraying using a suspension in which thermal spraying particles are dispersed, and the ceramic layer which contains a ceramic and in which vertical cracks, which extend in a thickness direction and extend to be inclined by the angle of inclination, are distributed in a surface direction is formed on the heat-resistant alloy substrate.

9. The thermal barrier coating formation method according to claim 8, wherein:

a thermal spraying method is used in the ceramic layer formation step; and

a distance between a spraying hole of a thermal spraying gun and a surface of a thermal spraying target is shorter in the first and second dense layer formation steps than in the porous layer formation step.

10. The thermal barrier coating formation method according to claim 8, wherein:

the first dense layer formation step includes forming the first dense layer such that first vertical cracks extending in a thickness direction are distributed in a surface direction; and

the second dense layer formation step includes forming the second dense layer such that second vertical cracks extending in a thickness direction are distributed in a surface direction.

11. The thermal barrier coating formation method according to claim 8, wherein the thermal spraying particles have a particle size of 0.1 μm or more and 1.0 μm or less.

12. The thermal barrier coating formation method according to claim 8, wherein at least a part of the ceramic layer formation step uses suspension plasma spraying.

13. (canceled)

14. A thermal barrier coating, comprising a ceramic layer formed on a heat-resistant alloy substrate and configured to contain a ceramic, wherein the ceramic layer has:

a first dense layer;

an intermediate porous layer which is laminated on the first dense layer, which has a higher density than the first dense layer, and in which numerous pores are formed; and

a second dense layer which is laminated on the intermediate porous layer and has a lower density than the intermediate porous layer, wherein:

the ceramic layer has vertical cracks that extend in a thickness direction and are distributed in a surface direction; and

the vertical cracks extend to be inclined with respect to a surface of the ceramic layer.

15. The thermal barrier coating according to claim 14, wherein angles of inclination of the vertical cracks are different between a side close to the surface of the ceramic layer and a side close to the heat-resistant alloy substrate.

16. The thermal barrier coating according to claim 14, wherein the vertical cracks have a distribution rate per 1 mm of 6 cracks/mm or more and 12 cracks/mm or less.

17. The thermal barrier coating according to claim 14, wherein the vertical cracks extend intermittently.

18. The thermal barrier coating according to claim 14, wherein all the plurality of vertical cracks are inclined toward one side in the surface direction as those vertical cracks go to the surface of the ceramic layer.

19. The thermal barrier coating according to claim 14, wherein angles of inclination of the vertical cracks are angles of 45° or more and 80° or less with respect to the surface of the ceramic layer.

20. (canceled)

21. The thermal barrier coating formation method according to claim 8, wherein the thermal spraying is suspension plasma spraying.

22. The thermal barrier coating formation method according to claim 8, wherein the thermal spraying particles have a particle size of 0.1 μm or more and 1.0 μm or less.

23. The high-temperature member, comprising: a heat-resistant alloy substrate; and the thermal barrier coating according to claim 14 formed on the heat-resistant alloy substrate.

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