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(54) CERAMIC HEATER AND GLOW PLUG

(57) [Objective] To reduce the specific resistance of a heat-generating resistor of a ceramic heater while ensuring the strength of the ceramic heater and to suppress the occurrence of cracks in the heat-generating resistor.

[Means for Solution] The ceramic heater 100 includes a substrate 10 formed from an insulating ceramic and a heat-generating resistor 20 formed inside the substrate 10 and containing tungsten carbide (WC) and silicon nitride (Si_3N_4). In any cross section of the heat-generating resistor 20, the ratio of the area of tungsten carbide portions to the total area of the cross section is 33 to 67%, and the average diameter of tungsten carbide aggregates that is measured by a line intercept method is 1.4 to 7.0 μm.

	WC (mass%)	Diameter of WC raw material particles (μm)	Firing time (min.)	Area ratio of WC (%)	Diameter of WC aggregates (μm)	Diameter of silicon nitride particles (μm)	Specific resistance	Component strength	Crack occurrence rate	Overall rating
Sample 1	67	0.7	60	28	1.4	1.1	C	A	AA	C
Sample 2	73	0.5	60	33	1.1	1.1	A	A	B	B
Sample 3		0.7	60		1.4	1.0	A	A	AA	AA
Sample 4			120			4.5	A	A	A	A
Sample 5		2.5	60		3.5	1.4	A	A	AA	AA
Sample 6			120			4.5	A	A	A	A
Sample 7		3.5	90		7.0	2.9	A	A	AA	AA
Sample 8			150			7.4	A	A	A	A
Sample 9		5.1	150		8.9	7.4	A	C	A	C
Sample 10	77	0.5	60	50	1.0	1.2	A	A	C	C
Sample 11		0.7	60		1.4	1.2	A	A	AA	AA
Sample 12			90			3.1	A	A	A	A
Sample 13		2.5	60		3.5	1.4	A	A	AA	AA
Sample 14			120			5.0	A	A	A	A
Sample 15		3.5	60		7.0	1.7	A	A	AA	AA
Sample 16			150			7.5	A	A	A	A
Sample 17		5.1	150		10	8.0	A	C	A	C
Sample 18	85	0.7	90	67	1.4	2.1	A	A	AA	AA
Sample 19			120			5.6	A	A	A	A
Sample 20		2.5	60		3.5	1.4	A	A	AA	AA
Sample 21			120			5.0	A	A	A	A
Sample 22		3.5	90		7.0	2.9	A	A	AA	AA
Sample 23			150			7.3	A	A	A	A
Sample 24		5.1	180		11	9.1	A	C	A	C
Sample 25	90	3.0	120	72	7.0	4.5	A	C	C	C

FIG. 4

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Description

[Technical Field]

[0001] The present invention relates to a ceramic heater and to a glow plug.

[Background Art]

[0002] In compression ignition internal combustion engines such as diesel engines, glow plugs are used as auxiliary heat sources for startup. Various glow plug structures have been known, and one known type of glow plug includes a ceramic heater. In one known type of ceramic heater, a heat-generating resistor is disposed inside an insulating ceramic substrate. In an exemplary known structure of such a ceramic heater (see, for example, Patent Document 1), a sintered body containing tungsten carbide (WC) serving as an electrically conductive component and silicon nitride (Si_3N_4) serving as an insulating component is used as the heat-generating resistor. In this structure, the resistance of the heat-generating resistor can be easily controlled by changing the ratio of the tungsten carbide to the silicon nitride, and the transverse strength of the ceramic heater including the heat-generating resistor can also be increased by adjusting this ratio.

[0003] Generally, a battery is installed on a vehicle or the like on which the above-described internal combustion engine is mounted, and the electric power necessary for glow plugs to generate heat is supplied from the battery. However, when the internal combustion engine is started while the glow plugs are activated, electric power is supplied from the battery also to a starter for starting the internal combustion engine, and this causes a drop in battery voltage. Therefore, there is a need to further reduce the specific resistance of the ceramic heater included in each glow plug, in order to ensure the heat generation performance of the glow plugs even under the conditions that the battery voltage decreases. In heat-generating resistors included in ceramic heaters, there is a tendency to increase the content of tungsten carbide (WC) in order to reduce the specific resistance of the ceramic heaters.

[Prior Art Document]

[Patent Document]

[0004]

[Patent Document 1] Japanese Patent Application Laid-Open (*kokai*) No. 2006-127995
[Patent Document 2] Japanese Patent Application Laid-Open (*kokai*) No. 2002-220285
[Patent Document 3] Japanese Patent Application Laid-Open (*kokai*) No. 2007-335397

[Summary of the Invention]

[Problems to be Solved by the Invention]

[0005] However, when the content of tungsten carbide (WC) in the heat-generating resistor is large, the difference in thermal expansion coefficient between the insulating ceramic substrate and the heat-generating resistor becomes large. This may increase the possibility of the occurrence of cracks in the ceramic heater particularly during sintering in the production process of the heater. When the content of tungsten carbide (WC) in the heat-generating resistor increases, the content of silicon nitride (Si_3N_4) decreases accordingly. In this case, sinterability decreases, and this may cause a reduction in the strength of the ceramic heater.

[0006] As described above, it is required to ensure the strength of the heat-generating resistor and suppress the occurrence of cracks in the heat-generating resistor while reducing the specific resistance of the ceramic heater. Such a requirement is common not only to ceramic heaters included in glow plugs but also to ceramic heaters included in heaters for igniting burners, heaters for gas sensors, etc.

[Means for Solving the Problems]

[0007] The present invention has been made to solve the foregoing problems and can be embodied in the following modes.

(1) According to one mode of the present invention, a ceramic heater comprising a substrate formed from an insulating ceramic and a heat-generating resistor formed inside the substrate and containing tungsten carbide (WC) and silicon nitride (Si_3N_4) is provided. In the ceramic heater, in any cross section of the heat-generating resistor, the ratio of the area of tungsten carbide portions to the total area of the any cross section is 33 to 67%, and the average diameter of tungsten carbide aggregates that is measured by a line intercept method is 1.4 to 7.0 μm.
In the ceramic heater of this mode, in any cross section of the heat-generating resistor, the ratio of the area of the tungsten carbide portions to the total area of the cross section is 33 to 67%. Therefore, the specific resistance of the ceramic heater can be reduced. Further, in the ceramic heater of this mode, in any cross section of the heat-generating resistor, the average diameter of the tungsten carbide aggregates that is measured by the line intercept method is 1.4 to 7.0 μm. Therefore, the occurrence of cracks in the heat-generating resistor can be suppressed, and a reduction in the strength of the ceramic heater can be suppressed.

(2) In the ceramic heater of the above-described mode, in the any cross section of the heat-generating resistor, the average diameter of silicon nitride par-

ticles that is measured by the line intercept method may be smaller than the average diameter of the tungsten carbide aggregates.

In the ceramic heater of this mode, the effect of suppressing the propagation of cracks in the heat-generating resistor can be further enhanced.

(3) According to another mode of the present invention, there is provided a glow plug comprising a ceramic heater; a tubular member that surrounds and holds the ceramic heater with a heat-generating end portion of the ceramic heater protruding forward; and an electrically conductive member for applying voltage to the ceramic heater. In the glow plug, the ceramic heater is the ceramic heater described in (1) or (2).

[0008] In the glow plug of this mode, the specific resistance of the ceramic heater is small. Therefore, even when the voltage applied to the glow plug is relatively low, the ceramic heater can be energized sufficiently, and a sufficient amount of heat can be generated. In addition, a reduction in the strength of the ceramic heater is suppressed, and the occurrence of cracks in the heat-generating resistor is suppressed, so that the overall durability of the glow plug can be improved.

[0009] The present invention can be embodied in various modes different from the above modes. For example, the present invention can be embodied as a method of producing the ceramic heater and a method of producing the glow plug.

[Brief Description of the Drawings]

[0010]

[FIG. 1] Schematic cross-sectional view schematically showing the structure of a glow plug.

[FIG. 2] Photograph showing an example of a cross section of a heat-generating resistor observed under an SEM.

[FIG. 3] Flowchart showing a method for producing a ceramic heater.

[FIG. 4] Table summarizing the production conditions of each of ceramic heater samples and the results of evaluation of the ceramic heater samples.

[Modes for Carrying out the Invention]

A. Overall structure of glow plug

[0011] FIG. 1 is a schematic cross-sectional view schematically showing the structure of a glow plug 500 according to a first embodiment of the present invention. The glow plug 500 of the present embodiment is to be attached to an internal combustion engine such as a diesel engine and functions as a heat source for assisting ignition during startup of the internal combustion engine. The glow plug 500 can also be used in a regeneration burner system of a diesel particulate filter (DPF). As shown in FIG. 1, the glow plug 500 includes, as main components, a metallic shell 510, an outer tube 540, a ceramic heater 100, a center shaft 520, and a ring 550. In the present specification, the lower side of the glow plug 500 in the direction of an axial line O in FIG. 1 is referred to as the "forward side" of the glow plug 500, and the upper side is referred to as the "rear side."

[0012] The metallic shell 510 is a generally cylindrical tubular member extending along the axial line O and, in the present embodiment, is formed from carbon steel. An axial hole 512 extending through the metallic shell 510 along the axial line O is formed in the metallic shell 510. An external threaded 511 is formed on the outer circumferential surface of a rear portion of the metallic shell 510. The external threaded 511 is threadingly engaged with an internal thread formed on the wall surface of a plug attachment hole of a cylinder head (not shown) of an internal combustion engine, and the glow plug 500 is thereby fixed to the internal combustion engine.

[0013] The outer tube 540 is a generally cylindrical tubular metallic member extending along the axial line O. An axial hole 542 extending through the outer tube 540 along the axial line O is formed in the outer tube 540. The inner diameter of the axial hole 542 is equal to the outer diameter of the ceramic heater 100 or slightly smaller than the outer diameter of the ceramic heater 100, and the ceramic heater 100 is press-fitted into the axial hole 542. A rear end portion of the outer tube 540 is fitted into a forward end portion of the axial hole 542 of the metallic shell 510, and the metallic shell 510 is welded to the outer tube 540 at the forward end of the metallic shell 510.

[0014] The ceramic heater 100 is a generally cylindrical columnar member extending along the axial line O and includes a substrate 10 and a heat-generating resistor 20. A central portion of the ceramic heater 100 is fitted into the axial hole 542 of the outer tube 540. A portion located forward of the central portion of the ceramic heater 100 protrudes from the forward end of the outer tube 540. A portion located rearward of the central portion of the ceramic heater 100 is accommodated in the axial hole 512 of the metallic shell 510. The ceramic heater 100 generates heat when electric power is suppled thereto.

[0015] The substrate 10 is formed from an insulating ceramic. No particular limitation is imposed on the insulating ceramic forming the substrate 10. For example, the insulating ceramic may contain at least one material selected from silicon nitride (Si_3N_4), SiAlON, and aluminum nitride (AlN). Particularly, it is preferable to form the substrate 10 from an insulating ceramic containing silicon nitride (Si_3N_4), i.e., a silicon nitride-based ceramic.

[0016] Examples of the silicon nitride-based ceramic include ceramics in which primary phase particles composed mainly of silicon nitride (Si_3N_4) are bonded through a grain boundary phase originating from a sintering aid component(s). Preferably, the content of the sintering aid component(s) with respect to the total mass of the substrate 10 is, for example, 2 to 8% by mass. When a rare-earth element is contained as a sintering aid component, the rare-earth element contained may be at least one element selected from scandium (Sc), yttrium (Y), lanthanum (La), cerium (Ce), praseodymium (Pr), neodymium (Nd), samarium (Sm), europium (Eu), gadolinium (Gd), terbium (Tb), dysprosium (Dy), holmium (Ho), erbium (Er), thulium (Tm), ytterbium (Yb), and lutetium (Lu).

[0017] In addition to or instead of the above rare-earth element, at least one selected from magnesium (Mg), group 4 elements, group 5 elements, group 13 elements (e.g., aluminum: Al), and group 14 elements (e.g., silicon: Si) may be contained as a sintering aid component. The content of the sintering aid component(s) other than the rare-earth element with respect to the total mass of the substrate 10 may be, for example, 1 to 10% by mass. The sintering aid component(s) other than the rare-earth element is added mainly in the form of oxide and contained in the substrate 10 mainly in the form of oxide, silicate, or complex oxide. A component (such as silicon carbide: SiC) other than the sintering aid may be further added to the silicon nitride-based ceramic.

[0018] The heat-generating resistor 20 is embedded inside the substrate 10 and formed from an electrically conductive resistance heating ceramic that generates heat when energized. In the present embodiment, the heat-generating resistor 20 contains tungsten carbide (WC) and silicon nitride (Si_3N_4). The heat-generating resistor 20 may further contain a sintering aid etc. The features of the microstructure of the materials forming the heat-generating resistor 20 will be described later in detail.

[0019] The heat-generating resistor 20 has a U-shaped structure extending in the direction of the axial line O and having a bent forward apex. The bent portion (lower semicircular portion) of the U shape is a forward end portion 25, which is a part of the heat-generating resistor 20. Portions of the heat-generating resistor 20 that are connected to the forward end portion 25 and extend along the axial line O are a pair of first and second lead portions 21 and 22. The area of a cross section of the forward end portion 25 that extends perpendicularly to the extending direction of the heat-generating resistor 20 is smaller than the cross sectional areas of the first and second lead portions 21 and 22.

[0020] The rear ends of the first and second lead portions 21 and 22 are exposed at the outer surface of a rear end portion of the ceramic heater 100. The rear end of the first lead portion 21 is a first-potential-side end (negative-side end) 27, and the rear end of the second lead portion 22 is a second-potential-side end (positive-side end) 28 that is to be at a higher potential than the first-potential-side end 27. The first lead portion 21 has a first-potential-side connection terminal (negative-side connection terminal) 23 formed so as to be exposed at the side surface of the ceramic heater 100. The second lead portion 22 has a second-potential-side connection terminal (positive-side connection terminal) 24 formed at a position rearward of the first-potential-side connection terminal 23 so as to be exposed at the side surface of the ceramic heater 100. When the ceramic heater 100 is fitted into the axial hole 542 of the outer tube 540, the first-potential-side connection terminal (negative-side connection terminal) 23 comes into contact with the inner wall of the axial hole 542 and is thereby electrically connected to the outer tube 540. In the present embodiment, the first-potential-side connection terminal 23 and the second-potential-side connection terminal 24 are formed from the same material as other portions of the heat-generating resistor 20 and are formed as part of the heat-generating resistor 20. However, the first-potential-side connection terminal 23 and the second-potential-side connection terminal 24 may be formed as members independent of the other portions of the heat-generating resistor 20.

[0021] The center shaft 520 is a rod-shaped member extending along the axial line O and formed from an electrically conductive material and is disposed within the axial hole 512 of the metallic shell 510 to be located on the rear end side of the ceramic heater 100. The center shaft 520 may be formed from a metal material such as SUS430. The outer diameter of the center shaft 520 is smaller than the inner diameter of the axial hole 512 of the metallic shell 510, and a space for electrically insulating the center shaft 520 and the inner wall of the axial hole 512 from each other is formed therebetween. In the present embodiment, the rear end surface of the ceramic heater 100 at which the first-potential-side end 27 and the second-potential-side end 28 are exposed is spaced apart from the forward end surface of the center shaft 520.

[0022] The ring 550 is a cylindrical tubular member formed from an electrically conductive material and is installed between the center shaft 520 and the ceramic heater 100 within the axial hole 512 of the metallic shell 510. Specifically, a rear end portion of the ceramic heater 100 and a forward end portion of the center shaft 520 are fitted into the ring 550. By fitting the rear end portion of the ceramic heater 100 into the ring 550, the second-potential-side connection terminal (positive-side connection terminal) 24 exposed at the side surface of the ceramic heater 100 comes into contact with the inner wall of the ring 550. As a result, the second-potential-side connection terminal (positive-side connection terminal) 24 of the heat-generating resistor 20 of the ceramic heater 100 is electrically connected to the center shaft 520 through the ring 550. The ring 550 may be formed from a metal material such as SUS410 or SUS630.

[0023] In the glow plug 500, a metallic terminal 530 is fixed to a rear end portion of the center shaft 520 by means of crimping.

[0024] A cylindrical tubular insulating member 560 is disposed at a rear end portion of the metallic shell 510 so as to be interposed between the center shaft 520 and the inner wall of the axial hole 512 of the metallic shell 510 and between the metallic terminal 530 and the rear end of the metallic shell 510. The insulating member 560 holds and positions the center shaft 520 within the metallic shell 510 such that the space for electrically insulating the center shaft 520 and the metallic shell 510 from each other is formed, and the insulating member 560 electrically insulates the metallic terminal 530 and the metallic shell 510 from each other. The insulating member 560 may be formed from a material having electrically insulating properties and heat resistance appropriate for its use environment, e.g., an electrically insulating resin such as Nylon (registered trademark) or a PPS resin (polyphenylene sulfide resin).

[0025] On the forward side of the insulating member 560, a cylindrical tubular seal member 570 is disposed between the center shaft 520 and the inner wall of the axial hole 512 of the metallic shell 510. The seal member 570 is in close contact with each of the center shaft 520, the insulating member 560, and the metallic shell 510 to thereby seal the space inside the metallic shell 510. The seal member 570 may be formed from a material having electrically insulating properties, elasticity, and heat resistance appropriate for its use environment, e.g., an elastomer such as fluorocarbon rubber or silicone rubber.

[0026] In the glow plug 500 configured as described above, electric power is supplied from the metallic terminal 530. The electric power is supplied to the heat-generating resistor 20 through the center shaft 520, the ring 550, and the second-potential-side connection terminal 24, and the ceramic heater 100 thereby generates heat. In this case, the first-potential-side connection terminal 23 of the heat-generating resistor 20 is grounded through the outer tube 540, the metallic shell 510, and the cylinder head of the internal combustion engine. In the glow plug 500, the center shaft 520, the metallic terminal 530, and the ring 550 correspond to the "electrically conductive member" in Means for Solving the Problems.

B. Features of ceramic heater

[0027] As described above, the heat-generating resistor 20 of the ceramic heater 100 is formed from an electrically conductive ceramic containing tungsten carbide (WC) and silicon nitride (Si_3N_4). In any cross section of the heat-generating resistor 20 of the present embodiment, the ratio of the area of tungsten carbide portions to the total area of the cross section is preferably 33 to 67%. In any cross section of the heat-generating resistor 20, the ratio of the area of tungsten carbide portions to the total area of the cross section may be 40% or more and may be 45% or more. In any cross section, the ratio of the area of tungsten carbide portions to the total area of the cross section may be 60% or less and may be 55% or less.

[0028] The ratio of the area of tungsten carbide portions in a cross section to the total area of the cross section can be determined as follows. First, a cross section of the ceramic heater 100 that includes the heat-generating resistor 20 is obtained. Then the cross section obtained is mirror-polished and subjected to plasma etching treatment to reveal grain boundaries in the cross section. Then an electron probe microanalyzer (EPMA) is used to identify, in a field of view in which the heat-generating resistor 20 in the cross section is magnified 3,000 times, regions in which the relative intensity of tungsten detected is high (these regions are hereinafter referred to as WC regions). The identified regions in which the relative intensity of tungsten detected is high are considered as tungsten carbide portions. Then the total area of the tungsten carbide portions identified in the field of view is computed. The "ratio of the area of tungsten carbide portions" described above is a value obtained by dividing the total area of the tungsten carbide portions obtained as described above by the overall area of the field of view.

[0029] FIG. 2 is a photograph showing an example of a cross section of the heat-generating resistor 20. The cross section was obtained in the manner described above and observed under a scanning electron microscope (SEM) at a magnification of 3,000 times. In FIG. 2, tungsten carbide portions appear whiter. In FIG. 2, portions other than the tungsten carbide portions appear darker. These portions are silicon nitride portions composed mainly of silicon nitride. As shown in FIG. 2, the tungsten carbide portions and also the silicon nitride portions are dispersed over the entire field of view.

[0030] When, in any cross section of the heat-generating resistor 20, the ratio of the area of tungsten carbide portions to the total area of the cross section is 33% or more, the content of tungsten carbide (WC) in the heat-generating resistor 20 can be easily ensured sufficiently, and the specific resistance of the heat-generating resistor 20 can be reduced. When, in any cross section of the heat-generating resistor 20, the ratio of the area of tungsten carbide portions to the total area of the cross section is 67% or less, the content of tungsten carbide (WC) in the heat-generating resistor 20 is limited so as to ensure a sufficiently large content of silicon nitride (Si_3N_4). Therefore, the difference in thermal expansion coefficient between the heat-generating resistor 20 and the substrate 10 can be easily reduced. This can suppress the occurrence of cracks in the ceramic heater 100 that are caused by the difference in thermal expansion coefficient between the heat-generating resistor 20 and the substrate 10 during sintering in the production process of the ceramic heater 100. By ensuring a sufficiently large content of silicon nitride (Si_3N_4), a reduction in the sinterability of the heat-generating resistor 20 is suppressed, and a reduction in strength of the ceramic heater 100 can be suppressed.

[0031] In the heat-generating resistor 20 of the present embodiment, the average diameter of tungsten carbide portions in any cross section is preferably from 1.4 to 7.0 μm inclusive. The average diameter of tungsten carbide portions in any cross section may be 2.0 μm or more and may be 3.0 μm or more. The average diameter of tungsten carbide portions in any cross section may be 6.0 μm or less, may be 5.0 μm or less, and may be 4.0 μm or less. In the following description, the dispersed tungsten carbide portions are referred to also as tungsten carbide aggregates, and the average diameter of the tungsten carbide portions is referred to also as the average diameter of the tungsten carbide aggregates. In the following description, the dispersed silicon nitride portions are referred to also as silicon nitride particles.

[0032] In the present embodiment, the average diameter of the tungsten carbide aggregates is measured in the above-described field of view at 3,000 times using a line intercept method. Specifically, in the line intercept method, a plurality of parallel straight lines with a prescribed length are drawn on the observed image, and the average of the lengths of intersecting portions of the straight lines that intersect particles (tungsten carbide aggregates) is used as the average particle diameter (the average diameter of the tungsten carbide aggregates). In the present embodiment, at least 50 straight lines are drawn to determine the average diameter of the tungsten carbide aggregates. With the line intercept method described above, the average particle diameter can be determined even when the tungsten carbide aggregates and the silicon nitride particles are not fully isolated particles, as shown in FIG. 2.

[0033] In the case where the average diameter of the tungsten carbide aggregates is set to 1.4 μm or more as described above, the overall toughness of the heat-generating resistor 20 can be improved because the toughness of tungsten carbide is higher than the toughness of silicon nitride. In addition, in the case where the average diameter of the tungsten carbide aggregates is set to 1.4 μm or more, even when stress that can cause cracks to occur in the heat-generating resistor 20 is generated, the propagation of cracks is suppressed by the tungsten carbide aggregates, so that the occurrence of cracks in the heat-generating resistor 20 can be suppressed. The reason for this may be as follows. Suppose that a crack occurs in the heat-generating resistor and propagates and that a tungsten carbide aggregate having a relatively large diameter is present in the propagation path of the crack. In such a case, the crack is likely to propagate into the tungsten carbide aggregate without making a detour around the tungsten carbide aggregate. Since the toughness of the tungsten carbide is relatively high as described above, the propagation of the crack is suppressed in the tungsten carbide aggregate.

[0034] In the present embodiment, since the average diameter of the tungsten carbide aggregates is 7.0 μm or less, the entire heat-generating resistor 20 has an increased strength. Specifically, the sinterability of the tungsten carbide is lower than the sinterability of the silicon nitride. Therefore, the greater the diameter of the tungsten carbide aggregates, the higher the possibility that the tungsten carbide aggregates serve as starting points of internal fracture such as cracks because lower-strength regions are present in a concentrated manner. When the average diameter of the tungsten carbide aggregates is within the above range, the strength of the entire heat-generating resistor 20 can be increased.

[0035] In the heat-generating resistor 20 of the present embodiment, it is preferable that, in any cross section, the average diameter of the silicon nitride particles that is measured by the line intercept method is smaller than the average diameter of the tungsten carbide aggregates. This structure increases the possibility that when a crack occurring in the heat-generating resistor 20 propagates, the crack does not propagate through a silicon nitride particle having lower toughness but propagates through a tungsten carbide aggregate having higher toughness is high. Therefore, when the average diameter of the tungsten carbide aggregates is within the range described above, the effect of suppressing the propagation of cracks in the heat-generating resistor 20 can be increased.

C. Method for producing ceramic heater

[0036] FIG. 3 is a flowchart showing a method for producing the ceramic heater 100. When the ceramic heater 100 is produced, first, tungsten carbide powder and silicon nitride powder are prepared (step S100). The average diameter of the tungsten carbide aggregates in the heat-generating resistor 20 can be controlled by changing the particle diameter (average particle diameter) of the tungsten carbide powder prepared in step S100, and the average diameter of the silicon nitride particles in the heat-generating resistor 20 can be controlled by changing the particle diameter (average particle diameter) of the silicon nitride powder. For example, by increasing the particle diameter of the tungsten carbide powder prepared in step S100, the average diameter of the tungsten carbide aggregates in the heat-generating resistor 20 can be increased. The average particle diameter of the tungsten carbide powder may be measured by the Fisher method, which is one of air permeability methods.

[0037] After step S100, the tungsten carbide powder and silicon nitride powder prepared in step S100, sintering aid powder, a solvent, etc., are mixed at a prescribed ratio (wet mixing) and then dried to prepare a powder mixture (step S110). By changing the mixing ratios of the tungsten carbide powder and the silicon nitride powder, the ratio of the area of tungsten carbide portions in a cross section of the heat-generating resistor 20 to the total area of the cross section can be controlled. By increasing the mixing ratio of the tungsten carbide powder, the ratio of the area of tungsten carbide portions in a cross section of the heat-generating resistor to the total area of the cross section can be increased. In order to make the ratio of the area of tungsten carbide portions to the total area fall within the above-described preferred range, the mixing ratio of the tungsten carbide powder in step S110 is preferably, for example, 73 to 85% by mass, based on the total mass of the tungsten carbide powder and the silicon nitride powder.

[0038] No particular limitation is imposed on the sintering aid powder used in step S110. The sintering aid powder used may be a powder of the oxide of a rare-earth element selected from the group consisting of yttrium (Y), lanthanum (La), neodymium (Nd), samarium (Sm), gadolinium (Gd), erbium (Er), etc., or may be a powder of a compound that contains any of the above rare-earth elements and forms oxide by heating. The sintering aid used in step S110 may be the oxide of at least one element selected from group 4 elements, group 5 elements, and group 6 elements or may be a compound of any of the above elements that forms oxide by heating. In addition to the above materials, SiO_2, Al_2O_3, etc., may be used as the sintering aid. The sintering aid may be only one material or two or more materials selected from the above-described materials. Preferably, two or more materials are used. The content of the sintering aid is preferably, for example, 10% by mass or less, based on the total mass of the heat-generating resistor 20 taken as 100% by mass. In step S110, a component other than the sintering aid may be added.

[0039] The solvent used in step S110 may be at least one solvent selected from water and organic solvents. Examples of the organic solvents include Carbitol, Cellosolve, acetates, monohydric alcohols, and ketones. No particular limitation is imposed on the amount of the solvent used. However, the amount of the solvent may be 25% by mass or more and is preferably 50% by mass or more, based on the total mass of the tungsten carbide powder and the silicon nitride powder taken as 100% by mass. The amount of the solvent may be 200% by mass or less and is preferably 100% by mass or less, based on the total mass of the tungsten carbide powder and the silicon nitride powder taken as 100% by mass.

[0040] After step S110, the powder mixture prepared in step S110 and a binder (an organic binder) are kneaded, and a U-shaped electrically conductive ceramic compact that later becomes the heat-generating resistor 20 is formed by injection molding (step S120). No particular limitation is imposed on the binder used. For example, an appropriate mixture of a plasticizer such as polypropylene, a wax, a dispersant, etc. may be used. Only one type of binder may be used, or a combination of a plurality of types may be used. No particular limitation is imposed on the content of the binder during the kneading. However, for example, the content of the binder may be 25% by mass or more and is preferably 50% by mass or more, based on the total mass of the tungsten carbide powder and the silicon nitride powder taken as 100% by mass. The content of the binder may be 200% by mass or less and is preferably 100% by mass or less, based on the total mass of the tungsten carbide powder and the silicon nitride powder taken as 100% by mass.

[0041] After step S120, the obtained electrically conductive ceramic compact is embedded in insulating ceramic powder for forming the substrate 10, and the insulating ceramic powder is formed into a shape corresponding to the ceramic heater 100 by press forming (step S130). Specifically, for example, the insulating ceramic powder, which is the material forming the substrate 10, is pressed to produce a pair of half compacts each having a recess corresponding to the shape of the electrically conductive ceramic compact. The electrically conductive ceramic compact is disposed at a prescribed position between the pair of half compacts, and then press forming is performed. A green ceramic heater is thereby obtained, in which the electrically conductive ceramic compact that later becomes the heat-generating resistor 20 is embedded in a compact made of the insulating ceramic powder and having the shape of the substrate 10. Either of the step of producing the electrically conductive ceramic compact in step S120 and the step of producing the pair of half compacts that is included in step S130 may be performed before the other.

[0042] After step S130, the green ceramic heater obtained in step S130 is subjected to preliminary firing to remove the binder (debindering) (step S140). The temperature of the preliminary firing may be, for example, 600 to 800°C.

[0043] After the preliminary firing in step S140, the green ceramic heater is fired (step S150) to complete the ceramic heater 100. Specifically, for example, the green ceramic heater is held between hot press dies and placed in a firing furnace to perform hot press firing. The hot press firing may be performed in, for example, an inert atmosphere (in a nitrogen atmosphere). The firing temperature may be, for example, 1,750°C to 1,850°C. The firing time may be, for example, 30 to 180 minutes. By changing the firing time in step S150, the diameter of the above-described silicon nitride particles in the heat-generating resistor 20 can be controlled. Specifically, by increasing the firing time in step S150, the average diameter of the silicon nitride particles can be increased. The pressing pressure during the sintering may be, for example, 15 to 40 MPa.

[0044] After the firing in step S150, the ceramic heater 100 obtained may be polished as needed.

[0045] In any cross section of the heat-generating resistor 20 in the above-configured ceramic heater 100 of the present embodiment, the ratio of the area of tungsten carbide portions to the total area of the cross section is 33 to 67%, and this allows the specific resistance of the ceramic heater 100 to be reduced. Therefore, even when the voltage applied to the glow plug including the ceramic heater 100 is relatively low, the ceramic heater 100 can be energized sufficiently, and a sufficient amount of heat can be generated.

[0046] In the present embodiment, in any cross section of the heat-generating resistor 20, the average diameter of the tungsten carbide aggregates that is measured by the line intercept method is 1.4 to 7.0 μm. As described above, the ratio of tungsten carbide in the heat-generating resistor 20 is increased, and therefore the difference in thermal expansion coefficient between the heat-generating resistor 20 and the substrate 10 tends to be large. Even in this case, the occurrence of cracks in the heat-generating resistor 20 of the ceramic heater 100 during sintering in its production process can be suppressed.

Since the average diameter of the tungsten carbide aggregates falls within the above-described range, a reduction in strength of the ceramic heater 100 can be suppressed even when the ratio of tungsten carbide in the heat-generating resistor 20 is increased as described above.

D. Modifications

Modification 1

[0047] In the embodiment described above, the electrically conductive ceramic forming the heat-generating resistor 20 is uniform, but a different structure may be used. For example, in the heat-generating resistor 20, the content of tungsten carbide (WC) may vary among different portions thereof. In this case, the specific resistance varies among the different portions. Specifically, for example, the specific resistance of a forward end portion of the heat-generating resistor 20 may be rendered larger than that on the rear end side thereof by rendering the ratio of tungsten carbide (WC) in the forward end portion lower than that on the rear end side. Even in this case, when, in any cross section of any portion of the heat-generating resistor, the ratio of the area of tungsten carbide portions to the total area of the cross section and the average diameter of the tungsten carbide aggregates fall within the ranges described above, the same effects as those of the embodiment are obtained. When a heat-generating resistor 20 in which the content of tungsten carbide (WC) varies among different portions thereof is used, the portions with different tungsten carbide contents may be produced separately by injection molding, for example, when the electrically conductive ceramic compact is produced in step S120.

Modification 2

[0048] In the embodiment, in any cross section of the heat-generating resistor 20, the average diameter of silicon nitride particles that is measured by the line intercept method is smaller than the average diameter of the tungsten carbide aggregates, but a different structure may be used. The average diameter of the silicon nitride particles may be equal to or larger than the average diameter of the tungsten carbide aggregates. In this case, when, in any cross section of the heat-generating resistor 20, the ratio of the area of tungsten carbide portions to the total area of the cross section and the average diameter of the tungsten carbide aggregates fall within the ranges described above, the same effects as those of the embodiment are obtained.

Modification 3

[0049] In the embodiment, the ceramic heater 100 is used as a heater for a glow plug, but a different configuration may be used. The present invention can be applied to ceramic heaters included in heaters for igniting burners, heaters for gas sensors, and various heaters for indoor heating etc.

Modification 4

[0050] In the embodiment, the heat-generating resistor 20 has a U shape but may have a different shape. A shape different from the U shape may be appropriately used according to the application of the ceramic heater.

[Examples]

[0051] Various ceramic heaters were produced as ceramic heater samples 1 to 25. These ceramic heaters differ from one another in terms of the ratio of the area of tungsten carbide portions in a cross section of the heat-generating resistor to the total area of the cross section and the average diameter of tungsten carbide aggregates. For each ceramic heater sample, the specific resistance and strength of the ceramic heater and the rate of occurrence of cracks during firing in the production process were examined.

<Production of samples>

[0052] With the method described with reference to FIG. 3, the ceramic heater samples 1 to 25 were produced. These samples were produced using the same materials except that tungsten carbide powders used as the raw materials of the heat-generating resistors had different average particle diameters. The average particle diameter of a tungsten carbide powder is a value measured by the Fisher method, which is one of air permeability methods. The conditions when a powder mixture is prepared in step S110 are as follows.

[0053] FIG. 4 is a table summarizing the production conditions of each of the ceramic heater samples 1 to 25 and the results of evaluation described later.

[0054] In sample 1, the ratio of the tungsten carbide powder mixed in step S110 to the total mass of the tungsten carbide powder and the silicon nitride powder was 67% by mass. The average particle diameter of the tungsten carbide powder used as a raw material was 0.7 μm, and the firing time in step S150 was 60 minutes.

[0055] In samples 2 to 9, the ratio of the tungsten carbide powder mixed in step S110 to the total mass of the tungsten carbide powder and the silicon nitride powder was 73% by mass. In sample 2, the average particle diameter of the tungsten carbide powder used as a raw material was 0.5 μm, and the firing time in step S150 was 60 minutes. In samples 3 and 4, the average particle diameter of the tungsten carbide powder used as a raw material was 0.7 μm. The firing time in step S150 was 60 minutes for sample 3 and 120 minutes for sample 4. In samples 5 and 6, the average particle diameter of the tungsten carbide powder used as a raw material was 2.5 μm. The firing time in step S150 was 60 minutes for sample 5 and 120 minutes for sample 6. In samples 7 and 8, the average particle diameter of the tungsten carbide powder used as a raw material was 3.5 μm. The firing time in step S150 was 90 minutes for sample 7 and 150 minutes for sample 8. In sample 9, the average particle diameter of the tungsten carbide powder used as a raw material was 5.1 μm, and the firing time in step S150 was 150 minutes.

[0056] In samples 10 to 17, the ratio of the tungsten carbide powder mixed in step S110 to the total mass of the tungsten carbide powder and the silicon nitride powder was 77% by mass. In sample 10, the average particle diameter of the tungsten carbide powder used as a raw material was 0.5 μm, and the firing time in step S150 was 60 minutes. In samples 11 and 12, the average particle diameter of the tungsten carbide powder used as a raw material was 0.7 μm. The firing time in step S150 was 60 minutes for sample 11 and 90 minutes for sample 12. In samples 13 and 14, the average particle diameter of the tungsten carbide powder used as a raw material was 2.5 μm. The firing time in step S150 was 60 minutes for sample 13 and 120 minutes for sample 14. In samples 15 and 16, the average particle diameter of the tungsten carbide powder used as a raw material was 3.5 μm. The firing time in step S150 was 60 minutes for sample 15 and 150 minutes for sample 16. In sample 17, the average particle diameter of the tungsten carbide powder used as a raw material was 5.1 μm, and the firing time in step S150 was 150 minutes.

[0057] In samples 18 to 24, the ratio of the tungsten carbide powder mixed in step S110 to the total mass of the tungsten carbide powder and the silicon nitride powder was 85% by mass. In samples 18 and 19, the average particle diameter of the tungsten carbide powder used as a raw material was 0.7 μm. The firing time in step S150 was 90 minutes for sample 18 and 120 minutes for sample 19. In samples 20 and 21, the average particle diameter of the tungsten carbide powder used as a raw material was 2.5 μm. The firing time in step S150 was 60 minutes for sample 20 and 120 minutes for sample 21. In samples 22 and 23, the average particle diameter of the tungsten carbide powder used as a raw material was 3.5 μm. The firing time in step S150 was 90 minutes for sample 22 and 150 minutes for sample 23. In sample 24, the average particle diameter of the tungsten carbide powder used as a raw material was 5.1 μm, and the firing time in step S150 was 180 minutes.

[0058] In sample 25, the ratio of the tungsten carbide powder mixed in step S110 to the total mass of the tungsten carbide powder and the silicon nitride powder was 90% by mass. The average particle diameter of the tungsten carbide powder used as a raw material was 3.0 μm, and the firing time in step S150 was 120 minutes.

[0059] The firing temperature in step S150 was 1,800°C for all the samples. When the temperature inside a firing furnace was increased in step S150, press-pressurization was started before the temperature reached 1,450°C, which is equal to or lower than the shrinkage start temperature (liquid phase formation start temperature) of the constituent materials, and then the pressurized state was maintained. When the temperature inside the firing furnace reached 1,650°C, the pressure of the nitrogen atmosphere in the furnace was set to 0.1 to 1.0 MPa to start pressurization by the pressurized atmosphere, and then this pressurized state was maintained.

[0060] In each of the samples obtained, a ceramic with a thermal expansion coefficient of 3.2 to 4.0 ppm/K was used as the insulating ceramic forming the substrate 10.

<Area ratio of WC>

[0061] For each of the samples, the ratio of the area of tungsten carbide portions in a cross section of the heat-generating resistor to the total area of the cross section (the area ratio of WC) was measured using an electron probe microanalyzer (EPMA, JXA-8800 manufactured by JEOL Ltd.) as described above. Specifically, for each sample, a cross section including the heat-generating resistor was obtained, then mirror-polished, and subjected to plasma etching treatment. Then the EPMA was used to identify WC regions in a field of view in which the cross section was magnified 3,000 times, and the total area of the identified WC regions was divided by the overall area of the field of view to determine the area ratio of WC. FIG. 2 described above shows an SEM image of sample 2.

<Diameter of WC aggregates and diameter of silicon nitride particles>

[0062] For each sample, the average diameter of the tungsten carbide aggregates (the diameter of the WC aggregates) and the average diameter of the silicon nitride particles in a cross section of the heat-generating resistor were measured by the line intercept method, as described above. Specifically, on an image of a field of view in which the cross section of the heat-generating resistor was observed at 3,000 times , a plurality of parallel straight lines with a prescribed length were drawn, and the average of the lengths of intersecting portions of the straight lines that intersected particles (tungsten carbide aggregates or silicon nitride particles) was used as the average particle diameter. When particle diameters were measured, the number of particles intersected by the above straight lines was at least 50.

<Specific resistance>

[0063] The specific resistance of the heat-generating resistor of each sample was measured as follows. First, a test piece for resistance measurement was cut from each ceramic heater. Specifically, the test piece was cut from a portion of the heat-generating resistor with a constant cross sectional area (a portion other than the U-shaped bent portion of the heat-generating resistor). Then the length L (cm) of the test piece and the cross sectional area S (cm^2) of the heat-generating resistor were measured. The length of each test piece was set to 1 cm. The resistance value of the heat-generating resistor in the cut test piece was measured at room temperature (23 to 25°C) using a milliohm meter. Then the specific resistance value was computed from the measured resistance value using the following computational formula.

Specific resistance value ($\mu\Omega\cdot$cm) = (resistance value [$\mu\Omega$] $\times$ cross-sectional area of test piece) [S (cm^2)] / length of test piece [L (cm)]

[0064] When the specific resistance was measured, 10 test pieces were prepared for each sample (n = 10), and the average value was determined. The specific resistance was evaluated as follows. When the specific resistance value was 200 $\mu\Omega\cdot$cm or less, an "A" rating was assigned. When the specific resistance value exceeded 200 $\mu\Omega\cdot$cm, a "C" rating was assigned.

<Component strength>

[0065] As for the strength of each ceramic heater sample, its transverse strength was measured as follows. To measure the transverse strength, the three-point bending strength of the sample was measured according to JIS R 1601. In this case, a span of 12 mm and a cross head speed of 0.5 mm/min were used. The diameter of each sample used for the measurement was 3.3 mm, and its overall length was 45 mm.

[0066] When the transverse strength was measured, 30 ceramic heaters were prepared for each sample (n = 30). The transverse strength was evaluated as follows. When the lowest value among the strength values of the 30 ceramic heaters of the sample was 800 MPa or more, an "A" rating was assigned. When the lowest value was less than 800 MPa, a "C" rating was assigned.

<Rate of occurrence of cracks>

[0067] As for the rate of the occurrence of cracks for each sample, the presence or absence of cracks was visually checked, and then the rate of the occurrence was computed. Specifically, a ceramic heater of the sample was mirror-polished to the boundary between the substrate and the heat-generating resistor. The obtained mirror-polished surface was observed under an optical microscope, and the heat-generating resistor at the boundary was visually checked to determine the occurrence of cracks. To evaluate the rate of the occurrence of cracks, 100 ceramic heaters were prepared for each sample (n = 100). The rate of the occurrence of cracks was evaluated as follows. When the rate of the occurrence of cracks was 0% or more and less than 2%, an "AA" rating was assigned. When the rate of the occurrence was 2% or more and less than 4%, an "A" raging was assigned. When the rate of the occurrence was 4% or more and less than 6%, a "B" rating was assigned. When the rate of the occurrence was 6% or more, a "C" rating was assigned.

[0068] In FIG. 4, when any of the rating of the specific resistance and the rating of the component strength was "C," a "C" overall rating was assigned. When both the rating of the specific resistance and the rating of the component strength were "A," the rating of the rate of the occurrence of cracks was used as the overall rating.

[0069] As shown in FIG. 4, it was found that a ceramic heater in which its specific resistance is reduced and its strength is ensured while the rate of the occurrence of cracks is suppressed is obtained when, in any cross section of the heat-generating resistor, the ratio of the area of tungsten carbide portions to the total area of the cross section is 33 to 67% and the average diameter of the tungsten carbide aggregates that is measured by the line intercept method is 1.4 to 7.0 μm. It was also found that when, in any cross section of the heat-generating resistor, the average diameter of the silicon nitride particles that is measured by the line intercept method is smaller than the average diameter of the tungsten carbide aggregates, the rate of the occurrence of cracks can be further reduced.

[0070] In sample 1 in which the ratio of the area of tungsten carbide portions in a cross section of the heat-generating resistor to the total area of the cross section was not 33% or more, the specific resistance value of the ceramic heater was insufficient because the content of tungsten carbide was small. In samples 2 and 10 in which the average diameter of the tungsten carbide aggregates was not 1.4 μm or more, the rate of the occurrence of cracks was high. In samples 9, 17, and 24 in which the average diameter of the tungsten carbide aggregates was not 7.0 μm or less, the strength of the ceramic heater was insufficient. In sample 25 in which the ratio of the area of tungsten carbide portions in a cross section of the heat-generating resistor to the total area of the cross section was not 67% or less, the difference in thermal expansion coefficient between the substrate and the heat-generating resistor was excessively large, so that the rate of the occurrence of cracks was high.

[0071] The present invention is not limited to the above described embodiment, examples, and modifications and may be embodied in various other forms without departing from the spirit of the invention. For example, the technical features in the embodiment, examples, and modifications corresponding to the technical features in the modes described in Summary of the Invention can be appropriately replaced or combined to solve some of or all the foregoing problems or to achieve some of or all the foregoing effects. A technical feature which is not described as an essential feature in the present specification may be appropriately deleted.

[Description of Reference Numerals]

[0072]

10: substrate
20: heat-generating resistor
21: first lead portion
22: second lead portion
23: first-potential-side connection terminal
24: second-potential-side connection terminal
25: forward end portion
27: first-potential-side end
28: second-potential-side end
100: ceramic heater
500: glow plug
510: metallic shell
511: male threaded portion
512: axial hole
520: center shaft
530: metallic terminal
540: outer tube
542: axial hole
550: ring
560: insulating member
570: seal member

Claims

1. A ceramic heater (100) comprising a substrate (10) formed from an insulating ceramic and a heat-generating resistor (20) formed inside the substrate (10) and containing tungsten carbide (WC) and silicon nitride (Si_3N_4),
wherein, in any cross section of the heat-generating resistor (20),
the ratio of the area of tungsten carbide portions to the total area of the any cross section is 33 to 67%, and
the average diameter of tungsten carbide aggregates that is measured by a line intercept method is 1.4 to 7.0 μm.

2. The ceramic heater (100) according to claim 1, wherein, in the any cross section of the heat-generating resistor (20), the average diameter of silicon nitride particles that is measured by the line intercept method is smaller than the average diameter of the tungsten carbide aggregates.

3. A glow plug (500) comprising:

a ceramic heater (100);
a tubular member (540) that surrounds and holds the ceramic heater (100) with a heat-generating end portion of the ceramic heater (100) protruding forward; and
an electrically conductive member (520, 530, 550) for applying voltage to the ceramic heater (100),
wherein the ceramic heater (100) is the ceramic heater (100) according to claim 1 or 2.

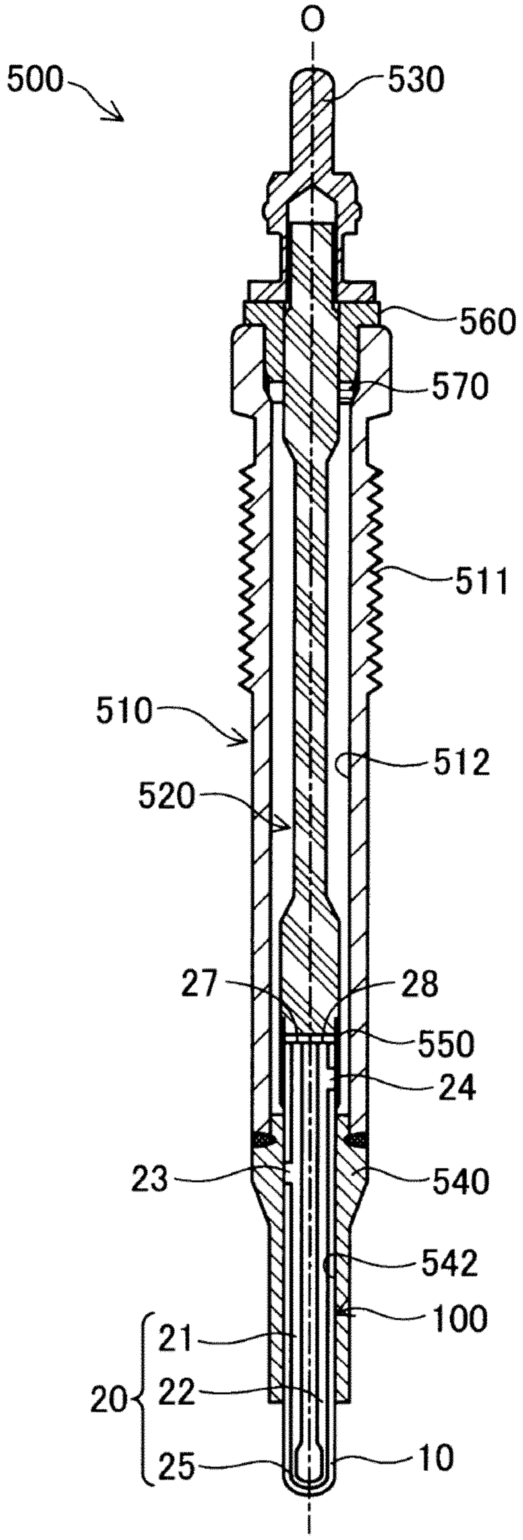
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FIG. 1

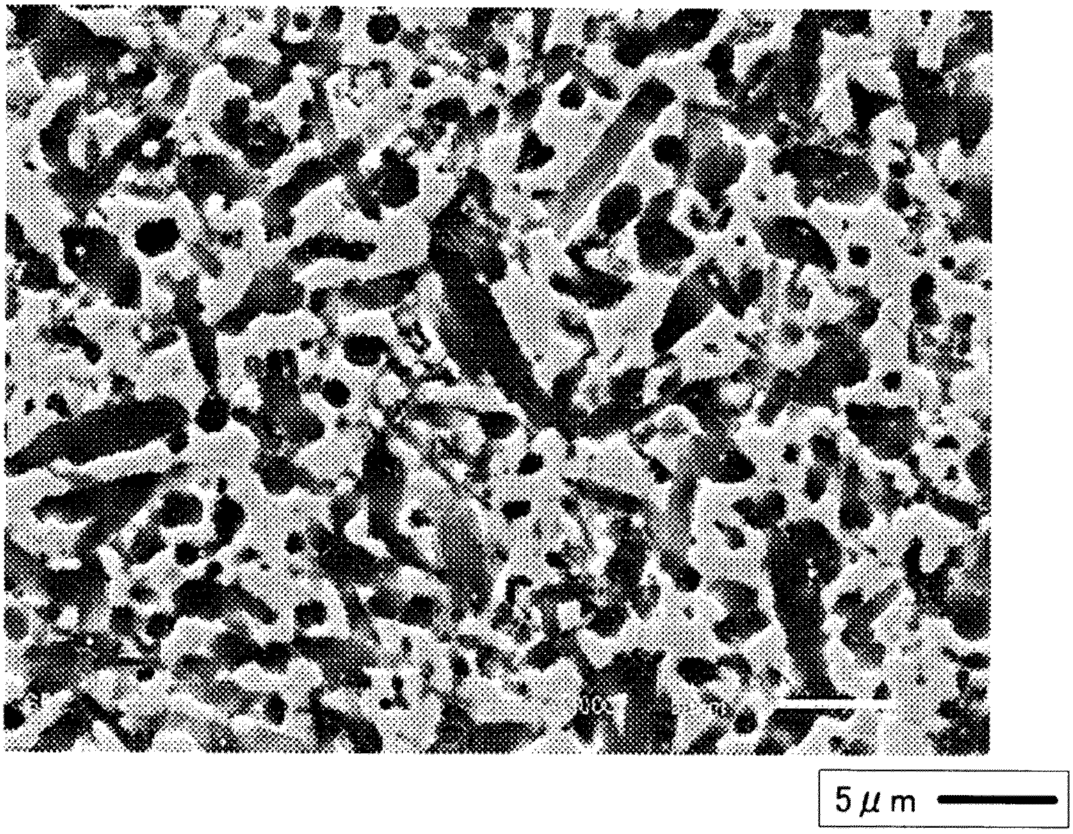

FIG. 2

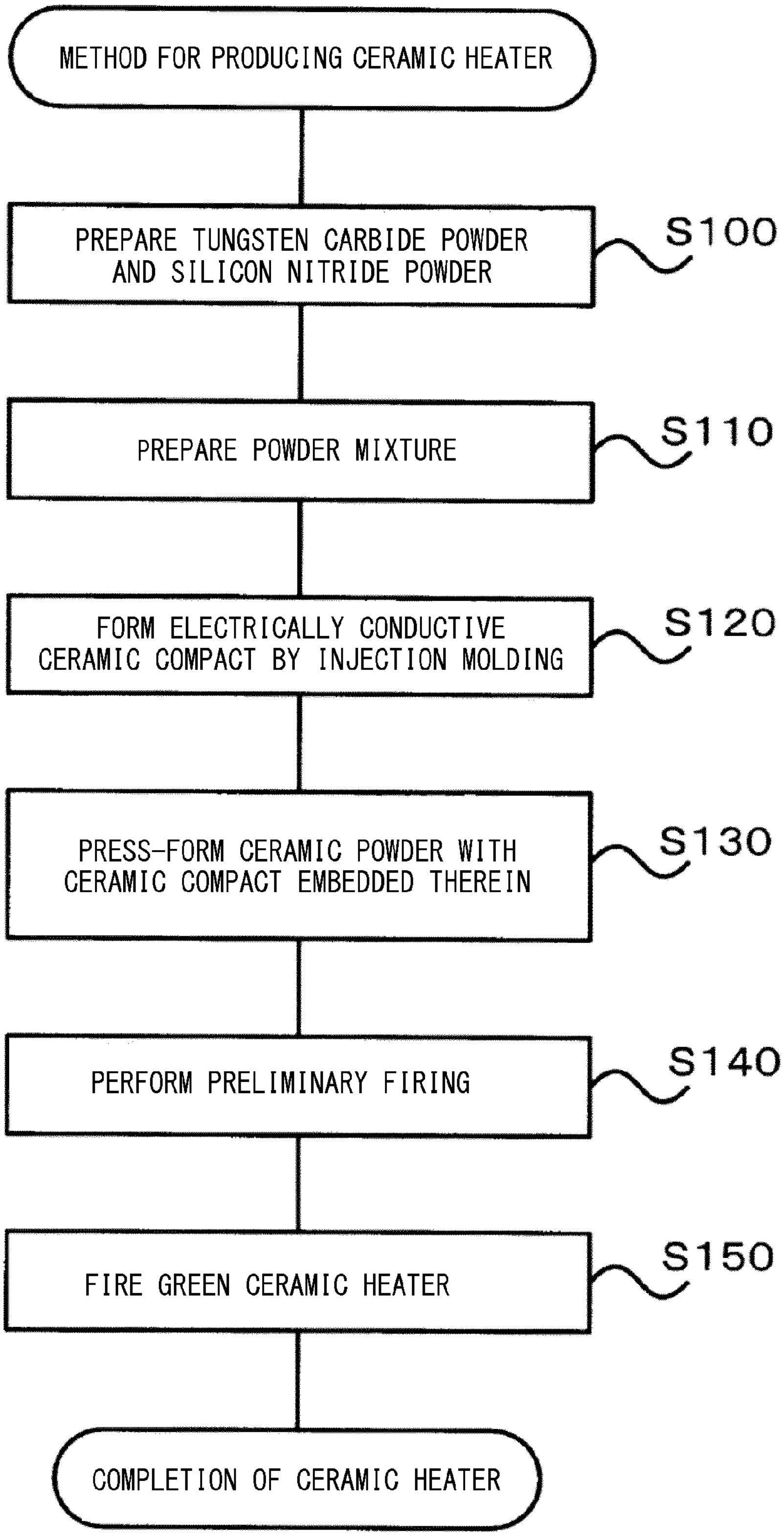
METHOD FOR PRODUCING CERAMIC HEATER
PREPARE TUNGSTEN CARBIDE POWDER AND SILICON NITRIDE POWDER
S100
PREPARE POWDER MIXTURE
S110
FORM ELECTRICALLY CONDUCTIVE CERAMIC COMPACT BY INJECTION MOLDING
S120
PRESS-FORM CERAMIC POWDER WITH CERAMIC COMPACT EMBEDDED THEREIN
S130
PERFORM PRELIMINARY FIRING
S140
FIRE GREEN CERAMIC HEATER
S150
COMPLETION OF CERAMIC HEATER

FIG. 3

	WC (mass%)	Diameter of WC raw material particles (μm)	Firing time (min.)	Area ratio of WC (%)	Diameter of WC aggregates (μm)	Diameter of silicon nitride particles (μm)	Specific resistance	Component strength	Crack occurrence rate	Overall rating
Sample 1	67	0.7	60	28	1.4	1.1	C	A	AA	C
Sample 2	73	0.5	60	33	1.1	1.1	A	A	B	B
Sample 3		0.7	60		1.4	1.0	A	A	AA	AA
Sample 4			120			4.5	A	A	A	A
Sample 5		2.5	60		3.5	1.4	A	A	AA	AA
Sample 6			120			4.5	A	A	A	A
Sample 7		3.5	90		7.0	2.9	A	A	AA	AA
Sample 8			150			7.4	A	A	A	A
Sample 9		5.1	150		8.9	7.4	A	C	A	C
Sample 10	77	0.5	60	50	1.0	1.2	A	A	C	C
Sample 11		0.7	60		1.4	1.2	A	A	AA	AA
Sample 12			90			3.1	A	A	A	A
Sample 13		2.5	60		3.5	1.4	A	A	AA	AA
Sample 14			120			5.0	A	A	A	A
Sample 15		3.5	60		7.0	1.7	A	A	AA	AA
Sample 16			150			7.5	A	A	A	A
Sample 17		5.1	150		10	8.0	A	C	A	C
Sample 18	85	0.7	90	67	1.4	2.1	A	A	AA	AA
Sample 19			120			5.6	A	A	A	A
Sample 20		2.5	60		3.5	1.4	A	A	AA	AA
Sample 21			120			5.0	A	A	A	A
Sample 22		3.5	90		7.0	2.9	A	A	AA	AA
Sample 23			150			7.3	A	A	A	A
Sample 24		5.1	180		11	9.1	A	C	A	C
Sample 25	90	3.0	120	72	7.0	4.5	A	C	C	C

FIG. 4

REFERENCES CITED IN THE DESCRIPTION

Patent documents cited in the description

- JP 2006127995 A **[0004]**
- JP 2002220285 A **[0004]**
- JP 2007335397 A **[0004]**