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(71) Applicant(s)
Saint-Gobain Ceramics and Plastics, Inc.

(72) Inventor(s)
Craig A. Willkens; Linda S. Bateman; Roger Lin

(74) Agent/Attorney
E F WELLINGTON and CO, 312 St Kilda Road, MELBOURNE VIC 3006

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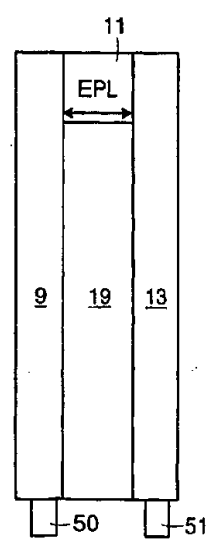
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(71) Applicant <i>Saint-Gobain Ceramics and Plastics, Inc.</i> <i>(for all designated States except US):</i> SAINT-GOBAIN INDUSTRIAL CERAMICS, INC. [US/US]; 1 New Bond Street, Box Number 15138, Worcester, MA 01615-0138 (US).	
(72) Inventors; and (75) Inventors/Applicants <i>(for US only):</i> WILLKENS, Craig, A. [US/US]; 2 East Park Road, Sterling, MA 01564 (US). BATEMAN, Linda, S. [US/US]; 19 Ledge Avenue, Spencer, MA 01562 (US). LIN, Roger [US/US]; 17 Sheridan Drive, #12, Shrewsbury, MA 01545 (US).	
(74) Agents: DI MAURO, Thomas, M. et al.; Saint-Gobain Corporation, 1 New Bond Street, Box Number 15138, Worcester, MA 01615-0138 (US).	



(54) Title: NOVEL CERAMIC IGNITER HAVING IMPROVED OXIDATION RESISTANCE, AND METHOD OF USING SAME

(57) Abstract

This invention relates to a support zone for a hairpin-style ceramic igniter, the support zone comprising AlN and SiC, and preferably alumina.



NOVEL CERAMIC IGNITER HAVING IMPROVED OXIDATION RESISTANCE,
AND METHOD OF USING SAME

Ceramic materials have enjoyed great success as igniters
5 in gas fired furnaces, stoves and clothes dryers. A ceramic
igniter typically has a hairpin or U-shape which contains
conductive end portions and a highly resistive middle portion.
When the igniter ends are connected to electrified leads, the
highly resistive middle portion (or "hot zone") rises in
10 temperature.

The art of ceramic igniters has long known of hairpin-
shaped igniters which further have an electrically non-
conductive ceramic insert disposed between their electrically
resistive legs for support. JP-A-02094282 specifically
15 discloses a ceramic igniter having SiC/ZrB₂ resistive legs and
an AlN insulating insert (or "support zone") disposed between
the resistive legs. JP-A-02094282 further teaches adding BN to
the AlN insert in order to match the coefficients of thermal
expansion ("CTE") of the two regions. Similarly, US Patent No.
20 5,191,508 ("Axelson") discloses a hairpin-shaped ceramic
igniter having an "electrically non-conductive" insert, and
teaches that the insert should be made from a single material
such as alumina, aluminum nitride, beryllium oxide, each of
which are electrically insulating materials. US Patent No.
25 4,634,837 ("Ito") discloses a ceramic igniter having a
Si₃N₄/MoSi₂-based hot zone and a Si₃N₄/Al₂O₃ insert.

The art also discloses ceramic igniters in which
conductive filaments are embedded in insulative ceramic
materials. For example, US Patent No. 4,912,305 ("Tatemasu")
30 discloses a tungsten wire embedded in a Si₃N₄/Al₂O₃/Y₂O₃
ceramic body. US Patent No. 4,804,823 ("Okuda") discloses a
ceramic igniter in which a TiN or WC conductive ceramic layer
(which also contains Si₃N₄) is disposed within a ceramic
substrate of either AlN or Si₃N₄. Okuda also discloses that
35 the substrate may further contain a sintering aid such as an

oxide, nitride, or oxynitride of Groups Iia or IIIa of the Periodic Table or Aluminum. See column 7, lines 50-55.

Although the insert material in hairpin shaped igniters is generally highly electrically insulating, there are
5 instances in which the art has disclosed inserts having some electrically conductive (such as MoSi_2) and/or semiconductive components (such as SiC). For example, JP-A-02086 ("JP '086") provides one such disclosure wherein the main constituent of the insert is silicon carbide. However, research has shown
10 that the high temperature resistivities of a first material comprising SiC and a conductive material such as aluminum and a second material comprising over 99% SiC tend to equalize at high temperatures. Therefore, if these materials were to be used respectively as a hot zone and an insert in the same
15 igniter, there would likely be electrical shorts across the insert material. In another example, US Patent No. 5,233,166 ("Maeda") discloses an igniter having a hot zone embedded in a ceramic substrate comprising silicon nitride, 8-19% rare earth oxide, 2-7% silica, and 7-20% MoSi_2 . Maeda teaches to avoid
20 producing a glass phase having alumina in an amount of more than 1 wt%.

US Patent No. 5,801,361 (Willkens '361) discloses a ceramic igniter designed for use in high voltage applications (220V-240V) in which the conventional hairpin-shaped hot zone
25 is supported by ceramic material both between its legs and outside of its legs by support zones. Willkens '361 also teaches that this support zone material should be electrically insulating (i.e., should have an electrical resistivity of at least 10^6 ohm-cm) and should preferably comprise at least 90
30 vol% of at least one of aluminum nitride, boron nitride and silicon nitride. Willkens '361 further discloses that this support zone material should not only possess thermal expansion and densification characteristics which are compatible with the hot zone, but also help protect the hot
35 zone from oxidation (i.e., less than 10% amperage decrease

over 30,000 cycles). In a WIPO publication corresponding to Willkens '361, the suggested electrical resistivity of the support zone material is 10^6 ohm-cm.

5 However, although the igniter of Willkens '361 attains the required performance specifications for voltage applications, continued use of the igniter revealed significant long-term use failures in one support zone consisting essentially of aluminum nitride (AlN). That is, the resistance of this igniter increased significantly during extended use trials. Furthermore, densification problems (likely due to thermal expansion mismatch) were encountered with these support zones during manufacture. Lastly, Willkens '361 observed that, in one example, the white-hot glow of the hot zone (which had a room temperature resistivity of about 15 0.3 ohm-cm) tended to creep downwards, and suggested that this creep was caused by current flowing through the aluminum nitride-based insert.

US Patent No. 5,786,565 (Willkens '565) discloses another ceramic igniter having a support zone (or "insert") disposed 20 between the two parallel legs of the igniter. According to Willkens '565, this insert is referred to as an "electrically insulating heat sink" or as an "electrically non-conducting heat sink", preferably has a resistivity of at least about 10^4 ohm-cm. Preferably, the composition of the 25 insert comprises at least 90 vol% of at least one of aluminum nitride, boron nitride and silicon nitride, but more preferably it consists essentially of at least one of aluminum nitride, boron nitride and silicon nitride.

However, although the igniters of Willkens '565 were 30 found to possess impressive speed, their long term use at temperatures of about 1300 °C again resulted in a significant percentages of failures.

Therefore, there is a need for a aluminum nitride-based support zone which does not alter the electrical 35 characteristics of the igniter, does not develop oxidation

problems during use, and does not pose densification nor machining problems during manufacture. In particular, there is a need for a support zone which solves these problems for the igniter disclosed in Willkens '565.

5 In an effort to discover the reason for the unacceptable oxidation of the AlN-based support zone (or "insert") material, the present inventors undertook extensive investigations, and found an extensive and incoherent layer of alumina on the surface of the AlN. Since alumina has a much
10 higher CTE than AlN, and the oxidation of AlN also produces a 6% expansion in volume, it is believed that the oxidation of the AlN insert material (that is, the production of alumina) causes cracking in the insert material and is the cause for the long term use failures.

15 Concurrently, the present inventors also examined conventional igniters possessing conventional AlN-SiC-MoSi₂ hot zone compositions which did not suffer from similar long term oxidation-related failures. It was found that, after long term use, these conventional hot zones had a coherent surface
20 layer containing a substantial amount of mullite, which has a composition of 3Al₂O₃-2SiO₂. In contrast to alumina, mullite has a CTE which is much more compatible with AlN, and produces only a small volumetric change when produced from AlN. Therefore, without wishing to be tied to a theory, it is
25 believed that the production of a mullite surface layer is critical to the success of an AlN-based insert material.

In light of the above discovery, it was believed that the desired mullite layer could be produced by adding between 2
vol% and 40 vol% silicon carbide to the AlN-based insert.

30 Subsequent manufacture and testing of this composition confirmed the presence of the desired coherent mullite layer.

Thus, it is believed that oxidation problems in AlN-based inserts can be significantly ameliorated by adding sufficient silicon carbide to produce a coherent layer of mullite on top
35 of the AlN insert.

The finding of the suitability of a AlN-SiC insert material is surprising in light of the teachings of the art respecting the known characteristics of the conventional insulator systems. In regards to AlN, it was known that an essentially AlN insulator produced unacceptable oxidation in Willkens '361. In regards to SiC, it was known that an essentially SiC support zone produced unacceptable electrical shorting at high temperatures. Accordingly, there was serious concern that a mixture containing significant amounts of both compounds would produce either unacceptable oxidation, or shorting, or both. Instead, it was found that this new support zone provided both acceptable oxidation resistance and no shorting.

Therefore, in accordance with the present invention, there is provided a ceramic igniter comprising:

- (a) a pair of conductive ends, and
- (b) a ceramic hot zone disposed between the cold ends, and
- (c) a support zone upon which the hot zone is disposed,

wherein the support comprises:

- (a) between about 50 and about 80 vol% aluminum nitride, and
- (b) between about 2 vol% and about 40 vol% silicon carbide.

Figure 1 is a preferred embodiment wherein one preferred igniter has a hairpin shape comprising two conductive legs 9 and 13 placed in electrical connection by a resistive hot zone 11, the legs 13 extending from the hot zone in the same direction, and an insert 19 is disposed between the conductive legs 13.

In general, the support zone comprises between 50 vol% and 80 vol% aluminum nitride as an insulating phase. If the support contains less than 50 vol% AlN, then the support may be too conductive and there is a danger of shorting. If the

support contains more than 80 vol% AlN, then there is typically a risk of increased oxidation.

In general, the support zone further comprises between 2 vol% and 40 vol% of an silicon carbide. If the support
5 contains less than 2 vol% of the silicon carbide, then there is insufficient reactant to form mullite and the support is too prone to oxidation. If the support contains more than 40 vol% of this phase, then there is typically a risk of shorting at high temperatures, even if the resulting ceramic support is
10 only moderately conductive (i.e., a semiconductor). Silicon carbide has a sufficient silicon content to form the desired mullite coating and is not so conductive as to cause shorting in the resulting composite insert material when present in the insert in amounts less than about 40 vol%.

15 In some preferred embodiments, the silicon carbide comprises between 10 vol% and 40 vol% of the support zone, preferably in an amount of from about 20 vol% to about 40 vol%.

In some embodiments which preferably are used with the
20 MIM design disclosed in Willkens '565, the insert comprises between 20 and 35 vol% SiC, preferably between 25 and 35 vol% SiC.

In some embodiments in which the insert material of the present invention is matched with Washburn-type conductive
25 (cold) zones and hot zones, the coefficient of thermal expansion of the insert material may be too low. For example, in one experiment, it was found that an insert material consisting essentially of 70% AlN and 30% SiC cracked when it was substantially contacting a conductive zone comprising 20%
30 AlN, 60% SiC and 20% MoSi₂. It is believed this failure was caused by a CTE mismatch between the insert and the conductive zone. When about 10% alumina was subsequently added to the insert, the densification was successful. Accordingly, in some embodiments, the support zone may further comprise between 2
35 vol% and 20 vol% of a high CTE ceramic having a thermal

expansion coefficient of at least $6 \times 10^{-6}/^{\circ}\text{C}$. Preferably, the high CTE ceramic is alumina. In some experiments in which the insert was in substantial contact with a conductive zone containing 20% AlN, 20% MoSi₂ and 60% SiC, a significant
5 number of the inserts containing 5% alumina still had cracks while essentially all the inserts having 10% alumina displayed no cracks. Therefore, in some embodiments, the insert preferably contains between 5 and 15% alumina, preferably between 8 and 15 vol% alumina. The finding that alumina
10 can be beneficial to the insert composition is surprising because Maeda teaches that more than a few percent alumina addition to the insert will cause an undesirable glass phase.

In some embodiments, in which the SiC level in the insert is relatively low (i.e., less than 25 vol% SiC), it was found
15 that a further addition of a small amount of molybdenum disilicide to the insert helped to increase oxidation resistance. Therefore, in some embodiments, the support zone may further comprises between 1 vol% and 4 vol% MoSi₂, particularly where the SiC content is relatively low. Because
20 of the desirable effect MoSi₂ has on the oxidation resistance of the support zone, it is hypothesized that, in some embodiments containing between 1-4 vol% MoSi₂, as little as 10 vol% SiC will be needed to produce the desired oxidation resistance. Therefore, in some preferred embodiments, the
25 insert comprises between 10 vol% and 25 vol% SiC (more preferably between 10 vol% and 20 vol% SiC) and between 1 vol% and 4 vol% MoSi₂. It has also been found that the addition of MoSi₂ changes of the color of the insert. Therefore, if a distinguishing color is desired, it is preferable not to use
30 MoSi₂ to do so.

In addition, it was further found that use of molybdenum disilicide produces a different type of oxide layer. In particular, the oxide produced in MoSi₂-containing support zones also contains mullite, but it is thinner and more
35 coherent than the oxide layer produced from AlN-SiC-Al₂O₃

support zones. Moreover, the layer produced by the MoSi_2 addition appears to be qualitatively more similar to that produced by the conventional Washburn hot zone.

It is further believed that tungsten disilicide may perform the same function as MoSi_2 . Therefore, in some embodiments, the support zone further comprises:

- (c) between about 1 vol% and about 4 vol% of a metallic conductor selected from the group consisting of molybdenum disilicide and tungsten disilicide, and mixtures thereof.

It is further believed that some of the support zones of the present invention may constitute novel compositions. Therefore, also in accordance with the present invention, there is provided a densified polycrystalline ceramic comprising (and preferably consisting of):

- a) between 50 and 80 vol% aluminum nitride,
- b) between 25 and 35 vol% SiC , and
- c) between 8 and 15 vol% alumina.

Also in accordance with the present invention, there is provided a densified polycrystalline ceramic comprising (and preferably consisting of):

- a) between 50 and 80 vol% aluminum nitride,
- b) between 10 and 25 vol% SiC ,
- c) between 8 and 15 vol% alumina, and
- d) between 1 and 4 vol% molybdenum disilicide.

Preferably, the conductive ceramic zone and the hot zone define a hairpin having a pair of legs, and the support zone is disposed between the legs to define a contact length, wherein the support zone contacts (i) the conductive zone substantially along the legs and (ii) the hot zone substantially at the apex. This is the design substantially disclosed in Willkens 5,786,565 (the specification of which is wholly incorporated by reference herein), and generally referred to as the MIM design. In general, the contact

between the support and the cold zone in this MIM design comprises at least 80% of the contact length.

It is further believed that using a hairpin MIM igniter design also helps ameliorate oxidation/shorting problems. In
5 conventional hairpin-insert systems, the hot zone spans a significant portion of each leg region of the hairpin and also has a relatively high resistivity in comparison to the insert disposed between the hot zone regions. Because the relative
10 resistivities of these zones was not very high (about 10 fold, or one decade), some electricity probably flowed from one hot zone through the insulator to the other hot zone. In contrast, in the MIM design, a conductive region spans essentially each entire leg. Since the relative resistivities
15 of these regions is typically much higher (about 1000 fold), much less electricity probably flows through the insulator.

In addition, because the hot zone of a MIM design is situated essentially only at the apex of the hairpin, only a relatively small portion of the insert is exposed to high temperatures, thereby reducing the chances that it will become
20 susceptible to oxidation.

Also without wishing to be tied to a theory, it is believed that using the present insert composition in systems having an operating voltage which is lower than the 24V system used by Willkens '361 contributed to the essential absence of
25 shorting through the AlN-based insert.

A low voltage drop across the igniter element helps prevent the shorting through the insulator due to the relative resistances of the insulator and the hot zone.

The hot zone provides the functional heating for gas
30 ignition. In preferred embodiments, the component fractions of aluminum nitride, molybdenum disilicide and silicon carbide disclosed in U.S. Patent No. 5,045,237, the specification of which is wholly incorporated by reference herein, are used. As indicated in the Washburn patent, the AlN-SiC-MoSi₂ system
35 is a flexible one which can produce igniters having

resistivities ranging from about 0.001 to about 100 ohm-cm. These hot zones generally have a resistivity of between 0.04 ohm-cm and 100 ohm-cm, and preferably between 0.2 ohm-cm and 100 ohm-cm in the temperature range of 1000 to 1500°C.

5 Typically, the hot zone comprises:

- (a) between about 50 and about 75 vol% aluminum nitride
- 10 (b) between about 10 and about 45 vol% of a semiconductive material selected from the group consisting of silicon carbide and boron carbide, and mixtures thereof, and
- 15 (c) between about 8.5 and about 14 vol% of a metallic conductor selected from the group consisting of molybdenum disilicide, tungsten disilicide, tungsten carbide, titanium nitride, and mixtures thereof.

In applications involving the MIM igniter disclosed in Willkens '565, the hot zone preferably comprises about 50 to 75 v/o aluminum nitride, and about 8.5-14 v/o MoSi₂, and 10-45
20 v/o SiC, and has a cross section of between 0.0015 and 0.0090 square inches, and an electrical path length of no more than 0.5 cm. More preferably, it comprises about 60 to 70 v/o aluminum nitride, and about 10-12 v/o MoSi₂, and 20-25 v/o SiC, and has a cross section of between 0.0030 and 0.0057
25 square inches, and an electrical path length of between 0.050 inches and 0.200 inches. Most preferably, it comprises about 64 v/o AlN, 11 v/o MoSi₂, and 25 v/o SiC, and has a cross section of between 0.0045 and 0.0051 square inches, and an electrical path length of between 0.075 inches and 0.125
30 inches.

Preferably, the particle sizes of both the starting powders and the grains in the densified hot zone are similar to those described in the Washburn patent. In some embodiments, the average grain size (d_{50}) of the hot zone
35 components in the densified body is as follows: a)

electrically insulative material (i.e., AlN): between about 2 and 10 microns; b) semiconductive material (i.e., SiC): between about 1 and 10 microns; c) and metallic conductor (i.e., MoSi₂): between about 1 and 10 microns.

5 Conductive ends 9 and 13 provide means for electrical connection to wire leads. Preferably, they also are comprised of AlN, SiC and MoSi₂, but have a significantly higher percentage of the conductive and semiconductive materials (i.e., SiC and MoSi₂) than do the preferred hot zone
10 compositions. Accordingly, they typically have much less resistivity than the hot zone and do not heat up to the temperatures experienced by the hot zone. The conductive ceramic zone preferably comprises:

15 (a) between about 15 vol% and about 60 vol% aluminum nitride,

 (b) between about 20 vol% and about 65 vol% of a semiconductive material selected from the group consisting of silicon carbide and boron carbide, and mixtures thereof, and

20 (c) between about 15 vol% and about 50 vol% of a metallic conductor selected from the group consisting of molybdenum disilicide, tungsten disilicide, tungsten carbide, titanium nitride, and mixtures thereof.

25 More preferably, the conductive ceramic zone comprises about 20 vol% aluminum nitride, about 60 vol% silicon carbide, and about 20 vol% molybdenum disilicide. In preferred embodiments, the dimensions of conductive ends 9 and 13 are 0.05 cm (width) x 4.2 cm (depth) x 0.1 cm (thickness). In
30 other embodiments, conductive metal can be deposited upon the heat sink material and hot zone to form the conductive legs.

 In some embodiments, the conductive ceramic zone and the hot zone define a hairpin having a pair of legs, and the support zone is disposed between the legs to define a contact
35 length, wherein the support zone contacts (i) the conductive

zone substantially along the legs and (ii) the hot zone substantially at the apex. Preferably, the contact between the support and the cold zone comprises at least 80% of the contact length.

5 The electrical path length of the hot zone, shown as EPL in Figure 1, is less than 0.5 cm. Insert material 19 is provided as an insert to contact the hot zone and substantially fill the remaining space between the conductive legs extending from the hot zone 11. When paired leads 50 and
10 51 are attached to each of the conductive ends 9 and 13 and a voltage is applied thereto, current travels from the first lead 50 to first conductive leg 9, through the hot zone 11 (thereby causing the temperature of the hot zone to rise), and then through the second conductive leg 13 where it exits
15 through the second lead 51.

In preferred embodiments, the dimensions of the inserts are 4.0 cm (depth) x 0.25 cm (width) x 0.1 cm (thickness).

The processing of the ceramic component (i.e., green body processing and sintering conditions) and the preparation of
20 the igniter from the densified ceramic can be done by any conventional method. Typically, such methods are carried out in substantial accordance with the Washburn patent. In preferred embodiments, the green laminates are densified by hot isostatic pressing in a glass media as disclosed in US
25 Patent No. 5,191,508 ("the Axelson patent"). The densification yields a ceramic body whose hot zone has a density of at least 95%, preferably at least about 99% of theoretical density.

The igniters of the present invention may be used in many applications, including gas phase fuel ignition applications
30 such as furnaces and cooking appliances, baseboard heaters, boilers and stove tops. Generally, there is provided a method of using a ceramic hot surface igniter, comprising the steps of:

- a) providing the igniter of the present invention, and

b) imparting a voltage between the conductive ceramic ends of the igniter, thereby causing resistive heating of the hot zone and forming a protective layer of mullite on the surface of the support zone.

5

EXAMPLE I

This example examines the suitability of various compositions for use as support zone inserts.

The ceramic compositions shown below in Table I were
10 created by mixing the selected powders in the appropriate proportions and compacting the mixture into green test samples. These samples were then densified to at least about 99% of theoretical density by glass-encapsulated hot isostatic pressing and finally sandblasted.

15 There were four criteria for judging suitability. The first, electrical resistivity, was measured at 25 °C. An insert having a high electrical resistivity is desirable to insure that the electrical current passing through the hairpin does not bypass the intended route through the conductive and
20 resistive zones. If a material was so resistive that its resistivity was at least 2 mega-ohm at 25 °C, then it was judged as "best". If the material had a lower resistivity of no more than 0.5 mega-ohm at 25 °C, this was judged as "poor" because its use would likely increase the chance of short
25 circuiting.

The second criterium, oxidation resistance, was measured by static oxidation testing for 18 hours at 1425 °C. An insert having an oxide film of no more than 30 um was judged to be the "best", while an insert having an oxide film of at least
30 80 um was judged to be poor.

The third criterium, coefficient of thermal expansion, was estimated for each material by a rule of mixtures calculation. A material having a CTE of between $5.3 \times 10^{-6} / ^\circ\text{C}$ and $5.5 \times 10^{-6} / ^\circ\text{C}$ was judged to be good because it would
35 likely not crack upon cooldown from densification when matched

against a typical "Washburn" conductive zone (which has a CTE of about $5.4 \times 10^{-6}/^{\circ}\text{C}$).

The fourth criterium, color match, was evaluated by visual inspection, as compared to the typical Washburn resistive zone. In some applications, it may be desirable to match the color of the insert with that of the resistive zone, while in others it may be desirable to provide a distinctly contrasting color.

Analysis of the below Table indicates a number of preferred ranges.

First, the Table demonstrates clearly that a significant alumina addition is needed in order to provide the correct CTE match with the Washburn type conductive zone. Compare examples 1-5 versus 6-10. Accordingly, it is preferred that the support zone comprises between 2 and 20 vol% alumina, more preferably between 8 and 15 vol% alumina.

TABLE I

AIN	Al ₂ O ₃	SiC	MoSi ₂	Resistivity	Oxidation	CTE (theo.)	Color match
80	5	15	0	Best	Poor	Good	No
75	5	20	0	Best	Poor	Good	No
70	5	25	0	Best	OK	Good	No
75	10	15	0	Best	Poor	Good	No
70	10	20	0	Best	Good	Good	No
80	0	20	0	Best	Poor	Bad	No
70	0	30	0	Good	Good	Bad	No
60	0	40	0	Poor	Best	Bad	No
78	0	20	2	Good	Best	Bad	Yes
76	0	20	4	Poor	Best	Bad	Yes

Second, the table shows that a molybdenum disilicide addition is good not only for color, but also for attaining the best oxidation resistance. Compare examples 9-10 versus 1-8. However, it is also clear that additions of more than 4

vol% may undesirably increase the electrical insulating feature of the insert. Therefore, in some embodiments, it is preferred that the insert have between 1 and 4 vol% molybdenum disilicide.

5 In regards to SiC, the table demonstrates a tradeoff between electrical resistivity and oxidation resistance. The oxidation resistance of the insert is generally good when there is at least 20-30 vol% SiC (suggesting the ability of SiC to form mullite), but the electrical resistivity is
10 generally good when less than 40% SiC is used. Therefore, in most embodiments, a SiC fraction of between about 20-35 vol% is desirable, preferably between 25 vol% and 35 vol%, especially if the insert consists essentially of those three components.

15 The table also shows that providing a small amount of molybdenum disilicide has a dramatic and beneficial effect upon the oxidation resistance of the insert, thereby allowing the SiC level to be lowered to lower levels and providing the desirable distinguishing color to the insert. Therefore, in
20 AlN-SiC-MoSi₂-containing systems wherein the SiC level is no more than 25% (preferably between 10 and 25 vol%), the MoSi₂ fractions is preferably between 1 and 3 vol%.

EXAMPLE II

This example demonstrates the superior oxidation
25 resistance of the igniter of the present invention.

A green laminate was constructed in substantial accordance with the design shown in Figure 5 of Willkens '565. A composite powder comprising a hot zone powder mixture of 70.8 v/o AlN, 20 v/o SiC, and 9.2 v/o MoSi₂ laid next to an
30 electrically insulating heat sink powder mixture of 60 v/o AlN, 30 v/o SiC, and 10 v/o Al₂O₃ was warm pressed to form a billet which was then sliced to form green tile 24 of that Figure 5. The hot zone portion of the warm pressed green body had a density of about 65% of theoretical density, while the
35 AlN portion had a density of about 65% of theoretical density.

The green tiles representing the conductive ends were made by warm pressing powder mixtures containing 20 v/o AlN, 60 v/o SiC, and 20 v/o MoSi₂ to form a billet having a density of about 63% of theoretical density, from which tiles 21 and 32 of Figure 5 were sliced. The green tiles were laminated as in Figure 5, and then densified by glass-encapsulated hot isostatic pressing at about 1800°C for about 1 hour to form a ceramic block having an in-situ formed second resistive section. The block was then sliced across its width to produce a plurality of hot surface elements measuring 1.5" x 0.150" x 0.030" (3.81 cm x 0.381 cm x 0.076 cm). The resulting hot zone comprised a first resistive section having a depth of about 0.125 cm, and an in-situ formed second resistive section having a depth of about 0.05 cm. The hot zone length (EPL) and thickness were about 0.25 cm and 0.076 cm, respectively.

Suitable leads were attached to the conductive portions of the hot surface element and a voltage of about 30 V was applied. The hot zone attained a temperature of about 1300 °C in less than two seconds.

To test the oxidation resistance of the new support zone, the igniter was subjected to 20,000 cycles of 18 V energy wherein each cycle consisted of a 30 second "on" phase and a 30 second "off" phase. After this test, the surface of the support zone was analyzed for oxidation by measuring oxide thickness. It was found that the oxide thickness was about 50 um. This is about 7-10 times thinner than the oxide thickness measured on the support zone disclosed in Willkens '565.

COMPARATIVE EXAMPLE I

A support zone comprising about 9 vol% silicon nitride, 10 vol% alumina and 81 vol% aluminum nitride was prepared. However, the igniter tile containing this zone and an adjacent conductive zone split during densification. It is believed this tile split because of the CTE mismatch between the support zone and adjacent conductive zone. Because silicon

nitride has a very low CTE ($3.4 \times 10^{-6}/^{\circ}\text{C}$), it was concluded that its use in the support zone lowers the overall CTE of the support zone to an undesirable level.

COMPARATIVE EXAMPLE II

- 5 A support zone comprising about 96 vol% AlN and 4 vol% alumina was prepared. However, it was found that this zone had unacceptable oxidation resistance.

We claim:

1. A ceramic igniter comprising:
 - (a) a pair of conductive ceramic ends, and
 - 5 (b) a ceramic hot zone disposed between the conductive ceramic ends, and
 - (c) a support zone upon which the hot zone is disposed, wherein the support zone comprises:
 - 10 (i) between about 50 vol% and about 80 vol% aluminum nitride, and
 - (ii) between about 2 vol% and about 40 vol% silicon carbide.
2. The igniter of claim 1 wherein the silicon carbide comprises between 10 vol% and 40 vol% of the support zone.
- 15 3. The igniter of claim 2 wherein the silicon carbide comprises between 20 and 40 vol% of the support zone.
4. The igniter of claim 2 wherein silicon carbide comprises 20-35 vol% of the support zone.
5. The igniter of claim 2 wherein the support zone further
20 comprises between about 2 vol% and about 20 vol% of a high CTE ceramic having a coefficient of thermal expansion of at least 6×10^{-6} /°C.
6. The igniter of claim 5 wherein the high CTE ceramic is alumina.
- 25 7. The igniter of claim 6 wherein alumina comprises 5-15 vol% of the support zone.
8. The igniter of claim 6 wherein alumina comprises 8-15 vol% of the support zone.
9. The igniter of claim 6 wherein the conductive ceramic
30 zone and the hot zone define a hairpin having a pair of legs, and the support zone is disposed between the legs to define a contact length, wherein the support zone contacts (i) the conductive zone substantially along the legs and (ii) the hot zone substantially at the apex.

10. The igniter of claim 9 wherein the contact between the support and the cold zone comprises at least 80% of the contact length.

11. The igniter of claim 10 wherein the conductive ceramic zone comprises:

- 5 (a) between about 15 vol% and about 60 vol% aluminum nitride,
- (b) between about 20 vol% and about 65 vol% of a semiconductive material selected from the group consisting of silicon carbide and boron carbide, and mixtures thereof, and
- 10 (c) between about 15 vol% and about 50 vol% of a metallic conductor selected from the group consisting of molybdenum disilicide, tungsten disilicide, tungsten carbide, titanium nitride, and mixtures thereof.

12. The igniter of claim 11 wherein the hot zone comprises:

- (a) between about 50 and about 75 vol% aluminum nitride
- 20 (b) between about 10 and about 45 vol% of a semiconductive material selected from the group consisting of silicon carbide and boron carbide, and mixtures thereof, and
- 25 (c) between about 8.5 and about 14 vol% of a metallic conductor selected from the group consisting of molybdenum disilicide, tungsten disilicide, tungsten carbide, titanium nitride, and mixtures thereof.

13. The igniter of claim 6 wherein the support zone further comprises between 1 and 4 vol% molybdenum disilicide.

14. The igniter of claim 1 wherein the hot zone comprises:

- (a) between about 50 and about 75 vol% aluminum nitride,
- 35 (b) between about 10 and about 45 vol% of a semiconductive material selected from the group

- consisting of silicon carbide and boron carbide, and mixtures thereof, and
- (c) between about 8.5 and about 14 vol% of a metallic conductor selected from the group
- 5 consisting of molybdenum disilicide, tungsten disilicide, tungsten carbide, titanium nitride, and mixtures thereof.
15. The igniter of claim 14 wherein the hot zone comprises:
- (a) between about 50 and about 75 vol% aluminum
- 10 nitride,
- (b) between about 10 and about 45 vol% silicon carbide, and
- (c) between about 8.5 and about 14 vol% molybdenum disilicide.
- 15 16. The igniter of claim 15 wherein the support zone comprises between 10 vol% and 40 vol% SiC.
17. The igniter of claim 16 wherein the support zone further comprises between about 2 vol% and about 20 vol% of a high CTE ceramic having a coefficient of thermal expansion of at least
- 20 $6 \times 10^{-6} / ^\circ\text{C}$.
18. The igniter of claim 17 wherein the high CTE ceramic is alumina.
19. The igniter of claim 18 wherein the alumina comprises between 8 and 15 vol% of the support zone.
- 25 20. The igniter of claim 2 wherein the support zone further comprises:
- (c) between about 1 vol% and about 4 vol% of a metallic conductor selected from the group
- 30 consisting of molybdenum disilicide and tungsten disilicide, and mixtures thereof.
21. The igniter of claim 20 wherein the metallic conductor of the support zone is molybdenum disilicide in the amount of between 1 vol% and 4 vol% of the support zone.
22. The igniter of claim 21 wherein the silicon containing
- 35 ceramic comprises silicon carbide, and the silicon carbide is

present in an amount of between 10 and 25 vol% of the support zone.

23. The igniter of claim 1 wherein the conductive ceramic zone comprises:

- 5 (a) between about 15 vol% and about 60 vol% aluminum nitride,
(b) between about 20 vol% and about 65 vol% of a
semiconductive material selected from the group
consisting of silicon carbide and boron carbide, and
10 mixtures thereof, and
(c) between about 15 vol% and about 50 vol% of a
metallic conductor selected from the group
consisting of molybdenum disilicide, tungsten
disilicide, tungsten carbide, titanium nitride, and
15 mixtures thereof.

24. The igniter of claim 23 wherein the conductive ceramic zone comprises:

- (a) about 20 vol% aluminum nitride,
(b) about 60 vol% silicon carbide, and
20 (c) about 20 vol% molybdenum disilicide.

25. A method of using a ceramic hot surface igniter, comprising the steps of:

- a) providing a ceramic igniter comprising:
(i) a pair of conductive ceramic ends, and
25 (ii) a ceramic hot zone disposed between the conductive ceramic ends, and
(iii) a support zone upon which the hot zone is disposed, wherein the support zone comprises
between about 50 vol% and about 80 vol%
30 aluminum nitride and between about 2 vol% and about 40 vol% silicon carbide, and
b) imparting a voltage between the conductive ceramic ends of the igniter, thereby causing resistive heating of the hot zone and forming a protective layer of mullite on the
35 surface of the support zone.

26. A densified polycrystalline ceramic comprising:
- a) between 50 and 80 vol% aluminum nitride,
 - b) between 25 and 35 vol% SiC, and
 - c) between 8 and 15 vol% alumina.
- 5 27. The ceramic of claim 26 consisting essentially of:
- a) between 50 and 80 vol% aluminum nitride,
 - b) between 25 and 35 vol% SiC, and
 - c) between 8 and 15 vol% alumina.
- 10 28. A densified polycrystalline ceramic comprising:
- a) between 50 and 80 vol% aluminum nitride,
 - b) between 10 and 25 vol% SiC,
 - c) between 8 and 15 vol% alumina, and
 - d) between 1 and 4 vol% molybdenum disilicide.

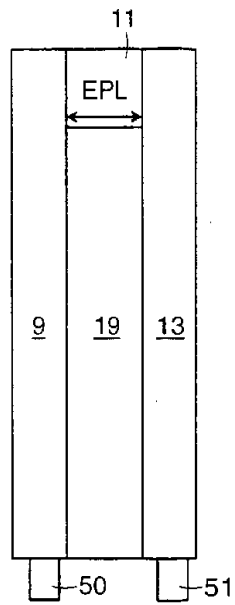


FIG. 1