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ABSTRACT

Ceramic igniter compositions are provided that contain components of conductive material and insulating material, where the insulating material component includes a relatively high concentration of metal oxide. Ceramic igniters of the invention are particularly effective for high voltage use, including throughout the range of from about 187 to 264 volts. Igniters of the invention also are useful for lower voltage such as 120 V or 102 V and sub-100 V such as 6, 8, 12 or 24 V.

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The following statement is a full description of this invention including the best method of performing it known to us.

COMPOSITIONS FOR CERAMIC IGNITERS

BACKGROUND OF THE INVENTION

1. Field of the Invention:

The invention relates to ceramic igniter compositions, and more particularly, to such compositions that contain components of a conductive material and insulating material, where the insulating material component includes a relatively high concentration of metal oxide.

2. Background.

Ceramic materials have enjoyed great success as igniters in gas fired furnaces, stoves and clothes dryers. Ceramic igniter production requires constructing an electrical circuit through a ceramic component, a portion of which is highly resistive and rises in temperature when electrified by a wire lead.

One conventional igniter, the Mini-IgniterTM, available from the Norton Igniter Products of Milford, N.H., is designed for 12 volt through 120 volt applications and has a composition comprising aluminum nitride ("AlN"), molybdenum disilicide ("MoSi₂"), and silicon carbide ("SiC"). However, while the Mini-IgniterTM is a highly effective product, certain applications require voltages in excess of 120 V.

In particular, in Europe, nominal voltages include 220 V (e.g. Italy), 230 V (e.g. France), and 240 V (e.g. U.K.). Standard igniter approval tests require operation at a range of from 85 percent to 110 percent of a specified nominal voltage. Thus, for a single igniter to be approved for use throughout Europe, the igniter must be operational from about 187 to 264 V (i.e. 85% of 220 V and 110% of 240 V). Current igniters have difficulty providing such a high and extended voltage range, particularly where a relatively short hot zone length (e.g. about 1.2 inches or less) is employed.

For instance, at higher voltage applications, current igniters may be subject to temperature runaway and thus require a transformer in the control system to step down the voltage. Use of such a transformer device is clearly less desirable. Accordingly, there is a need for relatively small igniters for high voltage applications, particularly over a range of from about 187 to 264 V, which do not require an expensive transformer but still possess the following requirements set by appliance and heating industries to anticipate variation in line voltage:

Time to temperature ("TTT")	< 5 sec
Minimum temperature at 85% of design voltage	1100°C.
Design temperature at 100% of design voltage	1300°C.
Maximum temperature at 110% of design voltage	1500°C.
Hot-zone Length	< 1.2-1.5"
Power	< 100 W.

For a given igniter geometry, one possible route to provide a higher voltage system is by increasing the igniter's resistance. The resistance of any body is generally governed by the equation

$$R_s = R_y \times L/A,$$

wherein

- R_s = Resistance;
- R_y = Resistivity;
- L = the length of the conductor; and
- A = the cross-sectional area of the conductor.

Because the single leg length of current ceramic igniters is about 1.2 inches, the leg length can not be increased significantly without reducing its commercial attractiveness. Similarly, the cross-sectional area of the smaller igniter, between about 0.0010 and 0.0025 square inches, will probably not be decreased for manufacturing reasons.

U.S. Patent 5,405,237 ("the Washburn patent") discloses compositions suitable for the hot zone of a ceramic igniter comprising (a) between 5 and 50 volume % ("v/o" or "vol%") MoSi_2 , and (b) between 50 and 95 v/o of a material selected from the group consisting of silicon carbide, silicon nitride, aluminum nitride, boron nitride, aluminum oxide, magnesium aluminate, silicon aluminum oxynitride, and mixtures thereof.

Additional highly useful ceramic compositions and systems are disclosed in U.S. Patents 5,514,630 and 5,820,789, both to Willkens et al. U.S. Patent 5,514,630 reports that hot zone compositions should not exceed 20 v/o of alumina. U.S. Patent 5,756,215 reports additional sintered compositions that include lead layers that contain up to 2% by weight of silicon carbide.

It thus would be desirable to have new ceramic hot zone igniter compositions. It would be particularly desirable to have new igniter compositions that could reliably operate at high voltages, such as from about 187 to 264 V, especially with a relatively short hot zone length.

SUMMARY OF THE INVENTION

We have now discovered new ceramic compositions that are particularly effective for high voltage use, including over a range of 187 to 264 V.

The ceramic compositions of the invention also are particularly useful for lower voltage applications, including 120 V, 102 V, 24 V, 12 V, 8 V or 6 V applications. Compositions of the invention can exhibit quite efficient power consumption and thus are highly useful for such lower voltage applications.

More specifically, in one aspect of the invention, ceramic hot zone compositions of the invention contain at least three components: 1) conductive material; 2) semiconductor material; and 3) insulating material, where the insulating material component includes a relatively high concentration of metal oxide, such as alumina.

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It has been surprisingly found that such high concentration (e.g. at least about 25 or 30 w/o of the insulating material component) of a metal oxide provides a ceramic composition that can reliably provide a high nominal voltage, including 220, 230 and 240 V.

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Moreover, ceramic hot zone compositions of the invention have been repeatedly demonstrated to reliably provide a line voltage over an extremely broad, high voltage range, including from about 187 to about 264 V. Hence, igniters of the invention can be employed throughout Europe, and reliably operate within 85 percent and 110 percent of the several distinct high voltages utilized in the various European countries. It also should be appreciated that while certain conventional hot zone compositions may provide a reliable voltage at a specified high voltage, those compositions often fail as voltage is varied over a broader range. Accordingly, the compositions of the invention that provide reliable, prolonged performance over an extended high voltage range clearly represent a significant advance.

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While hot zone compositions of the invention are particularly effective for high voltage use, as discussed above, it has been found that the compositions also are highly useful for lower voltage applications, including for 120 V or 102V or even lower voltages such as sub-100 V applications, e.g. 6, 8, 12 or 24 V applications, or yet lower voltage systems such as sub-6 V systems. For instance, igniters and hot zone compositions of the invention can be used in battery-powered ignition systems. Ceramic hot zone compositions of the invention have been shown to exhibit exceptional power consumption efficiency, thereby making the compositions and igniters particularly useful

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for such low voltage applications. See, for instance, the results of Example 6 which follows. Such enhanced power consumption efficiency also can enable use of more economical components in an ignition system, e.g. a less expensive (lower grade) transformer could be effectively employed with an igniter of the invention relative to a
 5 comparable igniter that comprised a distinct hot zone composition.

Ceramic hot zone compositions and igniters of the invention also can exhibit lower thermal diffusivity and higher specific heat than prior systems, enabling compositions of the invention to retain more thermal energy for prolonged periods. See,
 10 for instance, the results of Example 7 which follows.

Preferred ceramic igniters of the invention have a hot zone composition comprising:

(a) an electrically insulating material having a resistivity of at least about 10^{10}
 15 ohm-cm;

(b) between about 3 and about 45 v/o of a semiconductive material having a resistivity of between about 1 and about 10^8 ohm-cm,

preferably between about 5 and about 45 v/o of the hot zone composition being composed of the semiconductive material;

(c) a metallic conductor having a resistivity of less than about 10^{-2} ohm-cm,
 20 preferably between about 5 and about 25 v/o of the hot zone composition being composed of the metallic conductor,

and wherein at least about 21 v/o of the hot zone composition comprises a metal oxide insulating material. Preferably, at least about 25 v/o of the hot zone composition
 25 comprises a metal oxide insulating material such as alumina, more preferably at least about 30, 40, 50, 60, 70 or 80 of the hot zone composition comprises a metal oxide insulating material such as alumina. Preferably at least about 25 v/o of the insulating material is composed of a metal oxide such as alumina, more preferably at least about 30, 40, 50, 60, 70, 80 or 90 v/o of the insulating material being composed of a metal oxide

such as alumina. Also preferred is where the sole insulating material component is a metal oxide. Preferably the hot zone composition comprises between about 25 and about 80 v/o of the insulating material, more preferably between about 40 and about 70 v/o of the hot zone composition is composed of the insulating material.

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Additional preferred ceramic igniters of the invention have a hot zone composition comprising an electrically insulating material having a resistivity of at least about 10^{10} ohm-cm, with a substantial portion of that insulating material being composed of a metal oxide such as alumina; a semiconductor material that is a carbide such as

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silicon carbide in an amount of at least about 3, 4, 5 or 10 v/o; and a metallic conductor.

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In a further aspect of the invention, preferred ceramic igniters of the invention have a hot zone composition that is substantially free of a carbide such as SiC. Such compositions comprise a metallic conductor and an electrically insulating material having a resistivity of at least about 10^{10} ohm-cm, with a portion of that insulating material being composed of a metal oxide such as alumina, and the insulating material component also containing a further insulating material that is not an oxide, e.g. a nitride such as AlN. Such compositions may contain the same or similar amounts as discussed above for the tertiary insulating material/semiconductor material/electrically conducting material

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compositions.

Hot surface ceramic igniters of the invention can be produced with quite small hot zone lengths, e.g. about 1.5 inches or less, or even about 1.3, 1.2 or 1.0 inches or less, and reliably used at high voltages, including from about 187 to 264 V, in the absence of any type of electronic control device to meter power to the igniter. It will be understood

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herein that for multiple-leg geometry igniters (e.g. a hairpin slotted design), the hot zone length is the length of the hot zone along a single leg of the multiple-leg igniter.

Moreover, igniters of the invention can heat rapidly to operational temperatures, e.g. to about 1300°C, 1400°C or 1500°C in about 5 or 4 seconds or less, or even 3, 2.5 or 2 seconds or less.

5 Preferred hot zone compositions of the invention also can exhibit dramatic high temperature capability, i.e. repeated exposure to high temperatures without failure. The invention thus includes ignition methods that do not require renewed heating of the igniter element with each fuel ignition. Rather, the igniter can be continuously run at an elevated ignition temperature for extended periods to provide immediate ignition e.g. during a flame-out. More specifically, igniters of the invention can be run at an elevated temperature (e.g. about 800°C, 1000°C, 1100°C, 1200°C, 1300°C, 1350°C etc.) for 10 extended periods without a cooling period, e.g. at such temperatures for at least 2, 5, 10, 20, 30, 60, or 120 minutes or more.

15 Igniters of the invention may be of a variety of designs and configurations. Preferred designs include "slotted" or two-legged hairpin systems, where conductive legs are interposed by a void and are bridged by a hot zone region. Preferred for many application is a "slotless" design, which does not include a void area. Typical igniter designs have an insulator region interposed between conductive legs and contacting a 20 resistive hot zone region.

It has been found that slotless igniter designs employed in accordance with the invention (i.e. where a central igniter region comprises a non-conductor or insulator interposed between a pair of conductive regions and contacting a resistive hot zone) can 25 prematurely fail, particularly by so-called "arcing" where current traverses the central non-conductor region between the two conductor regions, rather than flowing to the resistive hot zone region. In other words, dielectric breakdown occurs through the insulator region. Such undesired "arcing" of current through an interposed non-conductor region can become more prevalent at higher voltage applications, such as above 200 V.

We have found several approaches to avoid such undesired arcing in slotless igniter systems. A preferred strategy is to increase the aluminum nitride content of the insulator region composition and correspondingly decrease the aluminum oxide content. It has been found that such an increase in AlN content can effectively avoid undesired arcing. Another approach provides for oxidation of the formed insulator region. It has been found that such oxidation (e.g. heat treating in air, treatment with chemical oxidant) can render the insulator region more resistive and electrically stable.

Other aspects of the invention are disclosed infra.

DESCRIPTION OF THE DRAWINGS

FIG. 1 shows a microstructure of a preferred tertiary hot zone composition of the invention wherein the Al_2O_3 is gray, the SiC is light gray, and the MoSi_2 is white.

FIG. 2 shows a microstructure of a prior hot zone composition that contains no metal oxide wherein AlN is gray, SiC is light gray and the MoSi_2 is white.

FIG. 3A through 3D depict preferred "slotted" and "slotless" igniter designs.

DETAILED DESCRIPTION OF THE INVENTION

As indicated above, in a first aspect, the invention provides a sintered ceramic igniter element comprising two cold zones with a hot zone disposed therebetween, the hot zone comprising a hot zone composition that comprises: (a) an electrically insulating material; (b) at least about 3 vol % of a semiconductive material; and (c) a metallic conductor having a resistivity of less than about 10^{-1} ohm-cm, wherein at least about 21 vol % of the hot zone composition comprises a metal oxide insulating material.

A sintered ceramic is also provided having a hot zone composition comprising (a) between 25 and 80 vol % of an electrically insulating material; (b) between 3 and 45 vol % of a semiconductive material; and (c) between 5 and 25 vol % of a metallic conductor having a resistivity of less than about 10^{-2} ohm-cm, wherein at least about 21 vol % of the
5 hot zone composition comprises a metal oxide insulating material.

A further sintered ceramic is provided having a hot zone composition comprising (a) an electrically insulating material, the insulating material containing a nitride and a metal oxide; and (b) a metallic conductor having a resistivity of less than about 10^{-2} ohm-cm, and the hot zone composition is substantially free of a carbide material.
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Methods of igniting gaseous fuel are also provided, which in general comprise applying an electric current across an igniter of the invention.

As discussed above, it has been unexpectedly discovered that adding a significant volume of a metal oxide to a ceramic hot zone composition can yield a ceramic igniter that can be used effectively under a high nominal voltage, including 220, 230 or 240 V. Moreover, these hot zone compositions can be useful over an extremely wide range of voltages, and thus the compositions also can be employed for lower voltage applications,
15 20 for example for 120 V or 102 V or even lower voltages such as 6 to 24 V applications.

As also discussed above and demonstrated in the examples which follow, hot zone compositions and igniters of the invention can exhibit quite good power consumption efficiency as well lower thermal diffusivity and higher specific heat than
25 prior systems.

Without being bound by any theory, it is believed that such properties, either separately or in combination, can facilitate performance of igniters of the invention at low voltage applications, such as sub-100 V applications. In particular, such efficient power

consumption and/or thermal diffusivity properties render igniters of the invention practicable for battery-powered ignitions, e.g. as may be used with outdoor or portable heating or cooking devices such as barbecue units, cooking (grills) and heating units used with recreational vehicles, and the like.

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Suitable metal oxides for use in the insulating material component include e.g. aluminum oxide, metal oxynitride such as aluminum oxynitride and silicon oxynitride, magnesium aluminum oxide and silicon aluminum oxide. For purposes of this invention, a metal oxynitride is considered a metal oxide. In some embodiments, metal oxides will be preferred that contain no nitrogen component, i.e. the metal oxide contains no nitrogen atoms. Aluminum oxide (Al_2O_3) is a generally preferred metal oxide. A mixture of distinct metal oxides also may be employed if desired, although more typically a single metal oxide is employed.

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For purposes of the present invention, the term electrically insulating material refers to a material having a room temperature resistivity of at least about 10^{10} ohm-cm. The electrically insulating material component of hot zone compositions of the invention may be comprised solely of one or more metal oxides, or alternatively, the insulating component may contain materials in addition to the metal oxide(s). For instance, the insulating material component may additionally contain a nitride such as an aluminum nitride, silicon nitride or boron nitride; a rare earth oxide (e.g., yttria); or a rare earth oxynitride. A preferred added material of the insulating component is aluminum nitride (AlN). It is believed that use of an additional insulating material such as aluminum nitride in combination with a metal oxide can provide the hot zone with desirable thermal expansion compatibility properties while maintaining desired high voltage capabilities.

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As discussed above, the insulating material component contains as a significant portion one or more metal oxides. More specifically, at least about 25 w/o of the insulating material composed is composed of one or more metal oxides, more preferably

at least about 30, 40, 50, 60, 70, 75, 80, 85, 90, 95 or 98 v/o of the insulating material is composed of one or more metal oxides such as alumina.

Preferred hot zone compositions of the invention include those that contain an insulating material component that is a combination of solely a metal oxide and a metal nitride, particularly a combination of alumina (Al_2O_3) and aluminum nitride (AlN). Preferably the metal oxide is the major portion of that combination, e.g. where the insulating component contains at least about 50, 55, 60, 70, 80, 85, 90, 95 or 98 v/o of a metal oxide such as alumina, with the balance being a metal nitride such as aluminum nitride.

Preferred hot zone compositions of the invention also include those where the insulating material component consists entirely of one or more metal oxides such as alumina.

When alumina is added to the green body of a hot zone composition, any conventional alumina powder may be selected. Typically, alumina powder having an average grain size of between about 0.1 and about 10 microns, and only about 0.2 w/o impurities, is used. Preferably, the alumina has a grain size of between about 0.3 and about 10 μm . More preferably, an Alcoa calcined alumina, available from Alcoa Industrial Chemicals of Bauxite, Ark., is used. Additionally, alumina may be introduced in forms other than a powder, including, but not limited to, alumina sol-gel approaches and hydrolysis of a portion of the aluminum nitride.

In general, preferred hot zone compositions include (a) between about 50 and about 80 v/o of an electrically insulating material having a resistivity of at least about 10^{10} ohm-cm; (b) between about 5 and about 45 v/o of a semiconductive material having a resistivity of between about 10^8 and about 10^5 ohm-cm; and (c) between about 5 and about 25 v/o of a metallic conductor having a resistivity of less than about 10^{-2} ohm-cm.

Preferably, the hot zone comprises 50-70 v/o electrically insulating ceramic, 10-45 v/o of the semiconductive ceramic, and 6-16 v/o of the conductive material.

5 If the electrically insulating ceramic component is present as more than about 80 v/o of the hot zone composition, the resulting composition can become too resistive and is unacceptably slow in achieving target temperatures at high voltages. Conversely, if it is present as less than about 50 v/o (e.g. when the conductive ceramic is present at about 8 v/o), the resulting ceramic becomes too conductive at high voltages. Clearly, when the conductive ceramic fraction is raised above 8 v/o, the hot zone is more conductive and
10 the upper and lower bounds of the insulating fraction can be suitably raised to achieve the required voltage.

As discussed above, in a further aspect of the invention, ceramic hot zone compositions are provided that are at least substantially free of a carbide such as SiC, or
15 preferably any other semiconductive material. Such compositions comprise a metallic conductor and an electrically insulating material having a resistivity of at least about 10^{10} ohm-cm, with a substantial portion of that insulating material being composed of a metal oxide such as alumina, and the insulating material component also containing a further material that is not an oxide, e.g. a nitride such as AlN. Preferably, such compositions
20 contain less than about 5 v/o of a carbide, more preferably the compositions contain less than about 2, 1, 0.5 v/o of a carbide, or even more preferably such hot zone compositions are completely free of a carbide, or other semiconductive material.

For the purposes of the present invention, a semiconductive ceramic (or
25 "semiconductor") is a ceramic having a room temperature resistivity of between about 10^4 and 10^8 ohm-cm. If the semiconductive component is present as more than about 45 v/o of the hot zone composition (when the conductive ceramic is in the range of about 6-10 v/o), the resultant composition becomes too conductive for high voltage applications (due to lack of insulator). Conversely, if it is present as less than about 10 v/o (when the

conductive ceramic is in the range of about 6-10 v/o), the resultant composition becomes too resistive (due to too much insulator). Again, at higher levels of conductor, more resistive mixes of the insulator and semiconductor fractions are needed to achieve the desired voltage. Typically, the semiconductor is a carbide selected from the group
5 consisting of silicon carbide (doped and undoped), and boron carbide. Silicon carbide is generally preferred.

For the purposes of the present invention, a conductive material is one which has a room temperature resistivity of less than about 10^{-2} ohm-cm. If the conductive
10 component is present in an amount of more than about 25 v/o of the hot zone composition, the resultant ceramic becomes too conductive for high voltage applications, resulting in an unacceptably hot igniter. Conversely, if it is present as less than about 6 v/o, the resultant ceramic becomes too resistive for high voltage applications, resulting in an unacceptably cold igniter. Typically, the conductor is selected from the group
15 consisting of molybdenum disilicide, tungsten disilicide, and nitrides such as titanium nitride, and carbides such as titanium carbide. Molybdenum disilicide is generally preferred.

Particularly preferred hot zone compositions of the invention contain aluminum
20 oxide, molybdenum disilicide and silicon carbide, with aluminum nitride optionally being employed as an additional material of the insulating material component.

The hot zone/cold zone igniter design as described in the Washburn patent (U.S. Patent 5,405,237) may be suitably used in accordance with the present invention. The hot
25 zone provides the functional heating for gas ignition. For high voltage applications (e.g. 187 to 264 V), the hot zone preferably has a resistivity of about 1-3 ohm-cm in the temperature range of 1000° to 1600°C. A specifically preferred hot zone composition comprises about 50 to 80 v/o Al_2O_3 , about 5-25 v/o $MoSi_2$ and 10-45 v/o SiC. More preferably, it comprises about 60 to 80 v/o aluminum oxide, and about 6-12 v/o $MoSi_2$.

15-30 v/o SiC. In one especially preferred embodiment, the hot zone comprises about 66 v/o Al_2O_3 , 14 v/o MoSi_2 , and 20 v/o SiC.

- In preferred embodiments the average grain size (d_{50}) of the hot zone components in the densified body is as follows:
- insulator (e.g. Al_2O_3 , AlN, etc.): between about 2 and 10 microns;
 - semiconductor (e.g., SiC): between about 1 and 10 microns; and
 - conductor (e.g., MoSi_2): between about 1 and 10 microns.

- FIG. 1 discloses a microstructure of a preferred hot zone composition of the invention that consists of a sintered blend of Al_2O_3 , SiC and MoSi_2 . As can be seen FIG. 1, the composition has a relatively homogenous arrangement of components, i.e. the components are well distributed throughout the composition and the microstructure is at least essentially devoid of any large areas (e.g. 30, 40 or 50 μm width) of a single composition component. Moreover, the conductive material (MoSi_2) component areas have coherent, defined edges and are not feathery.

- FIG. 2 shows a microstructure of a prior hot zone composition that contains no metal oxide. In FIG. 2, the conductive material (MoSi_2) component areas do not have well-defined boundaries and instead are diffuse and "feather-like".

- Igniters of the invention can have a variety of configurations. A preferred design is a slotted system, such as a horseshoe or hairpin design. A straight rod shape (slotless) also is preferred employed, with cold ends or terminal connecting ends on opposing ends of the body.

Igniters of the invention typically also contain at least one low resistivity cold zone region in electrical connection with the hot zone to allow for attachment of wire leads to the igniter. Typically, a hot zone composition is disposed between two cold

zones. Preferably, such cold zone regions are comprised of e.g. AlN and/or Al₂O₃ or other insulating material; SiC or other semiconductor material; and MoSi₂ or other conductive material. However, cold zone regions will have a significantly higher percentage of the conductive and semiconductive materials (e.g., SiC and MoSi₂) than
5 does the hot zone. Accordingly, cold zone regions typically have only about 1/5 to 1/1000 of the resistivity of the hot-zone composition and do not rise in temperature to the levels of the hot zone. A preferred cold zone composition comprises about 15 to 65 v/o aluminum oxide, aluminum nitride or other insulator material; and about 20 to 70 v/o MoSi₂ and SiC or other conductive and semiconductive material in a volume ratio of
10 from about 1:1 to about 1:3. More preferably, the cold zone comprises about 15 to 50 v/o AlN and/or Al₂O₃, 15 to 30 v/o SiC and 30 to 70 v/o MoSi₂. For ease of manufacture, preferably the cold zone composition is formed of the same materials as the hot zone composition, with the relative amounts of semiconductive and conductive materials being greater.

15 A specifically preferred cold zone compositions for use in igniters of the invention contains 60 v/o MoSi₂, 20 v/o SiC and 20 v/o Al₂O₃. A particularly preferred cold zone compositions for use in igniters of the invention contains 30 v/o MoSi₂, 20 v/o SiC and 50 v/o Al₂O₃.

20 As discussed above, slotless igniter designs preferably contain a non-conductive region interposed between two conductive legs. Preferably, a sintered insulator region has a resistivity of at least about 10¹⁴ ohm-cm at room temperature and a resistivity of at least about 10⁴ ohm-cm at operational temperatures and a strength of at least about 150
25 MPa. Preferably, the interposed insulator region of a slotless system has a resistivity at operational temperatures that is at least 2 orders of magnitude greater than the resistivity of the hot zone region. Suitable insulator compositions comprise at least 90 v/o of one or more aluminum nitride, alumina, and boron nitride. Generally preferred-insulator

compositions are a mixture of 1) AlN and/or Al_2O_3 and 2) SiC. Preferably the composition comprises at least about 90 v/o of a mixture of AlN and Al_2O_3 .

As discussed above, to avoid arcing in slotless designs, preferably the insulator composition comprises AlN in addition to other resistive materials, particularly a metal oxide such as Al_2O_3 . It has been found that addition of AlN can prevent the occurrence of such dielectric breakdown of the insulator region. We also have surprisingly found that use of AlN in an insulator composition can prevent undesired dielectric breakdown during use of an igniter, while addition of other highly resistive materials do not reduce arcing in such manner.

Preferred insulator compositions of the invention consist of AlN, Al_2O_3 and SiC. In such AlN/ Al_2O_3 /SiC insulator compositions, preferably AlN is present in an amount of at least about 10, 15, 20, 25 or 30 volume percent relative to Al_2O_3 . Generally preferred insulator compositions for use in slotless igniters of the invention contain AlN in an amount of from about 2 to 25 v/o, more preferably about 5 to 20 v/o, still more preferably about 10 to 15 v/o; Al_2O_3 in an amount of 60 to 90 v/o, more preferably 65 to 85 v/o; still more preferably 70 to 80 v/o; even more preferably 75 to 80 v/o; and SiC in an amount of 5 to 20 v/o, preferably 8 to 15 v/o. A specifically preferred insulator composition for a slotless igniter of the invention consists of 13 v/o AlN; 77 v/o Al_2O_3 ; and balance SiC.

As discussed above, it has been found that oxidative treatment of insulator regions of igniters of the invention also can prevent undesired dielectric breakdown. For instance, an igniter can be heated, e.g. about 1300-1700°C preferably about 1500 to 1600°C, in air for an extender period, e.g. 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9 or 1 hour or more to provide effective oxidative treatment of the insulator region. However, such oxidative treatment entails additional processing and requires re-preparation of the conductive legs after oxidation.

The dimensions of the igniter can affect its properties and performance. In general, the single leg length of the hot zone should be greater than about 0.5 inches (to provide enough mass so that cooling convective gas flow will not significantly affect its temperature) but less than about 1.5 inches (to provide sufficient mechanical ruggedness).
5 Its width should be greater than about 0.1 inches to provide sufficient strength and ease of manufacture. Similarly, its thickness should be more than about 0.02 inches to provide sufficient strength and ease of manufacture. Preferably, an igniter of the invention is typically between about 1.25 and about 2.00 inches in total single leg length, have a hot zone cross-section of between about 0.001 and about 0.005 square inches (more
10 preferably, less than 0.0025 square inches), and are of a two-legged hairpin design.

For a preferred two-legged hairpin igniter useful over voltages of from 187 to 264 volts, and having a hot zone composition of about 66 v/o Al_2O_3 , about 20 v/o SiC, and about 13.3 v/o $MoSi_2$, the following igniter dimensions are preferred: length of about
15 1.15 inches; individual leg width of about 0.047 inches; and thickness of about 0.030 inches. That design and composition also is useful for lower voltage applications, such as 6, 8, 12, 24, 102 or 120 V.

A preferred "slotless" igniter design has an overall length of between about 1.25
20 and 2.00 inches, a hot zone length of from about 0.1 to about 1.2 inches, and a hot zone cross-sectional area of between about 0.001 and about 0.005 square inches. For lower voltage applications, typically preferred are shorter hot zone lengths, such as less than 0.5.

FIG. 3A depicts a preferred slotted igniter system 10 having conductive (cold zone)-legs 12 and 14, U-shaped hot zone 16 and "slot" or void 18 interposed between
25 conductive legs 12 and 14. As referred to herein, the hot zone length is depicted as distance x in FIG. 3A, with an igniter length y, and a hot zone and igniter width z.

Current can be supplied to igniter 10 via leads at ends 12' and 14' of conductive zones 12 and 14 respectively.

FIG. 3B depicts a preferred slotless igniter system 20 having conductive (cold zone) legs 22 and 24, interposed insulator region 26, and U-shaped hot zone 28. As with the slotless system, as referred to herein, the hot zone length is depicted as distance x in FIG. 3B, with an igniter length y, and a hot zone and igniter width z. Current can be supplied to igniter 20 via leads at conductive zone ends 22' and 24'.

FIGS. 3C and 3D depict additional suitable slotless designs of igniters of the invention. In each of FIGS. 3C and 3D, reference numerals correspond to those of FIG. 3B, i.e. in each of FIGS. 3C and 3D the slotless igniter system has conductive legs 22 and 24 with interposed insulator region 26 and hot zone 28.

A specifically preferred hot zone composition of igniters of the invention contains about 14 percent MoSi_2 , about 20 percent SiC , balance Al_2O_3 . Such a composition is preferably employed on a slotless igniter system, suitably having a hot zone length of about 0.5 inches. A further preferred hot zone composition contains about 16 percent MoSi_2 , about 20 percent SiC , balance Al_2O_3 . Such a composition is preferably employed on a slotless igniter system, suitably having a hot zone length of about 0.1 to 1.6 inches. As mentioned above, for lower voltage applications, such as sub-100 V applications, typically preferred are shorter hot zone lengths, such as less than 0.5.

In general, hot surface ceramic igniters of the invention can be produced with quite small hot zone lengths, e.g. about 1.5 inches or less, or even about 1.4, 1.3, 1.2, 1.1, 1.0, 0.9, 0.8 inches or less, and reliably used at high voltage ranges, including from about 220 to 240 V, and in the absence of any type of electronic control device to meter power to the igniter.

An important performance property of a ceramic igniter, particularly where gas is the fuel, is time to temperature ("TTT"), i.e. the time for the igniter hot zone to rise from room temperature to the fuel (gas) ignition temperature. Igniters of the invention can heat rapidly to operational temperatures, e.g. to about 1300°C, 1400°C or 1500°C in about
5 5 or 4 seconds or less, even 3 seconds or less, or even 2.75, 2.5, 2.25 or 2 second or less.

It has been found that hot zone compositions of the invention exhibit extremely high temperature capability, e.g. up to 1750°C without serious oxidation or burnout problems. Tested conventional systems failed upon repeated exposure to 1600°C. In
10 contrast, preferred hot zone compositions of the invention survive "life testing" at such high temperatures, e.g. 50,000 cycles of 30 seconds on:30.seconds off at 1450°C. It also has been found that igniters of the invention exhibit significantly decreased amperage and temperature variations over such heating test cycles, relative to prior compositions.

15 As discussed above, the invention includes ignition methods that do not require renewed heating of a ceramic igniter. Rather, the igniter can be run for extended periods at an elevated temperature sufficient for fuel ignition, and without the need for constant on/off (i.e. heating/cooling) cycling.

20 The processing of the ceramic component (i.e., green body processing and sintering conditions) and the preparation of the igniter from the densified ceramic can be done by conventional methods. Typically, such methods are carried out in substantial accordance with the Washburn patent. See also the examples which follow, for illustrative conditions. Sintering of a hot zone composition is preferably conducted at
25 relatively high temperatures, e.g. at or slightly above about 1800°C. Sintering typically will be conducted under pressure, either under a uniaxial press (hot press) or a hot isostatic press (HIP).

It also has been surprisingly found that hot zone compositions of the inventions can be effectively densified in a single high temperature (e.g. at least about 1800 or 1850°C) uniaxial press, in contrast to prior compositions.

- 5 Prior hot zone compositions have required two separate sintering procedures, a first warm press (e.g. less than 1500°C such as 1300°C), followed by a second high temperature sintering (e.g. 1800 or 1850°C). The first warm sintering provides a densification of about 65 to 70 % relative to theoretical density, and the second higher temperature sintering provides a final densification of greater than 99 % relative to
- 10 theoretical density. Prior hot zone compositions have required a density of in excess of 99 % in order to provide acceptable electrical properties.

- The single high temperature sintering of the hot zone compositions of the invention can provide a density of at least about 95, 96 or 97 % relative to theoretical
- 15 density. Moreover, it has been found that such hot zone compositions of the invention having a density of less than 99 % relative to theoretical density (such as about 95, 96, 97 or 98 % relative to theoretical density) exhibit quite acceptable electrical properties. See, for instance, the results detailed in Example 5 which follows.

- 20 The igniters of the present invention may be used in many applications, including gas phase fuel ignition applications such as furnaces and cooking appliances, baseboard heaters, boilers, and stove tops. As mentioned above, igniters of the invention also can be employed in battery-powered systems, e.g. a cooking unit or heating unit where ignition is powered by a battery, such as 6, 8, or 24 V battery, and even lower voltage
- 25 systems such as sub-6 V system.

Igniters of the invention also may be employed in other application, including for use as a heating element in a variety of systems. In one preferred application, an igniter of the invention is utilized as an infrared radiation source (i.e. the hot zone provides an

infrared output) e.g. heating element such as in a furnace or as a glow plug, in a monitoring or detection device including spectrometer devices, and the like.

The following non-limiting examples are illustrative of the invention. All documents mentioned herein are incorporated herein by reference in their entirety.

EXAMPLE 1

An igniter of the invention was prepared and tested at high voltages as follows.

Hot zone and cold zone compositions were prepared. The hot zone composition comprised 66 parts by volume Al_2O_3 , 14 parts by volume MoSi_2 , and 20 parts by volume SiC which were blended in a high shear mixer. The cold zone composition comprised about 50 parts by volume Al_2O_3 , about 30 parts by volume MoSi_2 , and about 20 parts by volume SiC which were blended in a high shear mixer. The cold zone composition was loaded into a hot press die and the hot zone composition was loaded on top of the cold zone composition in the same die. That combination of compositions was hot pressed together at 1300°C for 1 hour in argon at 3000 psi to form a billet of about 60-70% theoretical density. The billet was then machined into tiles that were about 2.0 inches by 2.0 inches by 0.250 inches. Next, the tiles were hot isostatically pressed (HIPed) at 1790°C for 1 hour at 30,000 psi. After HIPing, the dense tiles were machined to the desired hairpin geometry. The formed igniter performed well at 230 V with good resistivity of about 1.5 ohm cm, a time to ignition temperature of about 4 seconds, and showed stability up to at least 285 V (285 V test voltage being the limit of the test equipment), thus demonstrating that the igniter was effective at high nominal voltages and over a wide range of high line voltage.

EXAMPLE 2

A further hot zone composition was prepared that contained 67 parts by volume Al_2O_3 , 13 parts by volume MoSi_2 , and 20 parts by volume SiC which were blended in a high shear mixer. The same cold zone composition was prepared as in

Example 1 above, and the hot and cold zone compositions processed, and an igniter formed, by the same procedures as described in Example 1. The formed igniter exhibited similar performance results as described for the igniter of Example 1, thus demonstrating that the igniter was effective at high nominal voltages and over a wide range of high line voltage.

EXAMPLE 3

A further hot zone composition of the invention was prepared that contained 66.7 parts by volume Al_2O_3 , 13.3 parts by volume MoSi_2 , and 20 parts by volume SiC which were blended in a high shear mixer. The same cold zone composition was prepared as in Example 1 above, and the hot and cold zone compositions processed, and an igniter formed, by the same procedures as described in Example 1. The formed igniter exhibited similar performance results as described for the igniter of Example 1, thus demonstrating that the igniter was effective at high nominal voltages and over a wide range of high line voltage.

EXAMPLE 4

A still further hot zone composition was prepared that contained 66.4 parts by volume Al_2O_3 , 13.6 parts by volume MoSi_2 , and 20 parts by volume SiC which were blended in a high shear mixer. The same cold zone composition was prepared as in Example 1 above, and the hot and cold zone compositions processed, and an igniter formed, by the same procedures as described in Example 1. The formed igniter exhibited similar performance results as described for the igniter of Example 1, thus demonstrating that the igniter was effective at high nominal voltages and over a wide range of high line voltage.

EXAMPLE 5

An additional igniter of the invention was prepared and tested at high voltages as follows.

Hot zone and cold zone compositions were prepared. The hot zone composition comprised about 66 parts by volume Al_2O_3 , about 14 parts by volume MoSi_2 , and about 20 parts by volume SiC which were blended in a high shear mixer. The cold zone composition comprised about 50 parts by volume Al_2O_3 , about 30 parts by volume MoSi_2 , and about 20 parts by volume SiC which were blended in a high shear mixer. The cold zone composition was loaded into a hot press die and the hot zone composition was loaded on top of the cold zone composition in the same die. That combination of compositions was hot pressed together at 1800°C for 1 hour in argon at 3000 psi to form a billet of about 97% theoretical density. The billet was then machined into tiles that were about 2.0 inches by 2.0 inches by 0.250 inches. Those tiles were then directly (i.e., no HIPing) machined into igniter elements having hairpin geometry. The formed igniter performed well at 230 V with good resistivity of about 1 ohm cm, a time to ignition temperature of about 5 seconds, and showed stability up to at least 285 V (285 V test voltage being the limit of the test equipment), thus demonstrating that the igniter was effective at high nominal voltages and over a wide range of high line voltage.

EXAMPLE 6

Power consumption levels of igniters of the invention were determined by measuring current at set voltage. Igniters of the invention consistently exhibited greater power efficiency relative to comparable igniters having distinct hot zone compositions.

Specifically, a slotted igniter of the invention having a hot zone composition of 65 parts by volume Al_2O_3 , about 15 parts by volume MoSi_2 and about 20 parts by volume SiC required between 0.25 A to 0.35 A at 120V.

A comparative slotted igniter of the invention having a hot zone composition of 77 parts by volume AlN , about 13 parts by volume MoSi_2 and about 10 parts by volume SiC required between 0.5 A to 0.6 A at 120V.

EXAMPLE 7

Thermal diffusivity and specific heat values were determined for igniters of the invention as well as comparable igniters having a distinct hot zone composition. Igniters of the invention consistently exhibited lower thermal diffusivity and higher specific heat than the comparable igniters having a distinct hot zone composition.

The following thermal diffusivity values at the specified temperatures were measured for a slotted igniter of the invention having a hot zone composition of 66.7 parts by volume Al_2O_3 , about 13.3 parts by volume MoSi_2 and about 20 parts by volume SiC :

	Temperatures ($^{\circ}\text{C}$)	Thermal Diffusivity (cm^2/s)
	20	0.1492
	128	0.088
15	208	0.0695
	302	0.058
	426	0.0472
	524	0.0397
	619	0.0343
20	717	0.0307
	810	0.0291
	921	0.0256
	1002	0.0242
	1114	0.0224
25	1228	0.0203
	1310	0.0195
	1428	0.0182
	1513	0.0171
	20	0.1503

The following thermal diffusivity values at the specified temperatures were measured for a comparative slotted igniter of the invention having a hot zone composition of 70 parts by volume AlN, about 10 parts by volume MoSi₂ and about 20 parts by volume SiC:

5	Temperatures (°C)	Thermal Diffusivity (cm ² /s)
	20	0.262
	126	0.183
	204	0.147
	325	0.0117
10	416	0.102
	517	0.0902
	615	0.0812
	714	0.0725
	818	0.0668
15	910	0.0593
	1005	0.0552
	1105	0.0549
	1203	0.0469
	1312	0.0425
20	1414	0.041
	1516	0.0369
	22	0.274

25 The invention has been described in detail with reference to particular embodiments thereof. However, it will be appreciated that those skilled in the art, upon consideration of this disclosure, may make modifications and improvements within the spirit and scope of the invention.

30 With reference to the use of the word(s) "comprise" or "comprises" or "comprising" in the foregoing description and/or in the following claims, unless the context requires otherwise, those words are used on the basis and clear understanding that they are to be interpreted inclusively, rather than exclusively, and that each of those words is to be so interpreted in construing the foregoing description and/or the following claims.

The claims defining the invention are as follows:

1. A sintered ceramic igniter element comprising two cold zones with a hot zone disposed therebetween, the hot zone comprising a hot zone composition that comprises:

- (a) an electrically insulating material;
- (b) at least about 3 vol % of a semiconductive material; and
- (c) a metallic conductor having a resistivity of less than about 10^{-2} ohm-cm,

wherein at least about 30 vol % of the hot zone composition comprises a metal oxide insulating material.

2. The igniter of claim 1 wherein the insulating material of the hot zone composition consists of metal oxide.

3. The igniter of claim 1 wherein the metal oxide of the hot zone composition comprises aluminum oxide.

4. The igniter of claim 1 wherein the metal oxide of the hot zone composition comprises one or more of aluminum oxide, metal oxynitride, magnesium aluminum oxide and silicon aluminum oxide.

5. The igniter of claim 1 wherein the insulating material of the hot zone composition contains one or more materials selected from the group consisting of a nitride, a rare earth oxide, and a rare earth oxynitride.

6. The igniter of claim 1 wherein the insulating material of the hot zone composition comprises aluminum nitride.

7. The igniter of any one of claims 1 to 6 wherein the semiconductive material of the hot zone composition comprises silicon carbide.

8. The igniter of any one of claims 1 to 7 wherein the metallic conductor of the hot zone composition is molybdenum, disilicide.
9. The igniter of any one of claims 1 to 8 further comprising a cold zone composition that comprises from about 15 to 50 vol % of an insulator material; 0 to 50 vol % of a semiconductive material; and 20 to 70 vol % of a metallic conductive material.
10. The igniter of claim 9 wherein the cold zone insulator material comprises aluminum nitride or aluminum oxide, or mixtures thereof; the cold zone semiconductive material comprises silicon carbide; and the cold zone conductive material comprises MoSi_2 .
11. The igniter element of any one of claims 1 to 10 wherein at least about 40 vol % of the hot zone composition comprises a metal oxide insulating material.
12. The igniter element of any one of claims 1 to 10 wherein at least about 50 vol % of the hot zone composition comprises a metal oxide insulating material.
13. The igniter element of any one of claims 1 to 10 wherein at least about 60 vol % of the hot zone composition comprises a metal oxide insulating material.
14. A sintered ceramic element comprising a cold zone and a hot zone, the hot zone comprising a hot zone composition that comprises a metal oxide in an amount of at least about 30 vol % of the hot zone composition.
15. The igniter of claim 14 wherein the metal oxide comprises aluminum oxide.
16. The igniter of claim 14 wherein the metal oxide comprises one or more of aluminum oxide, metal oxynitride, magnesium aluminum oxide and silicon aluminum oxide.
17. The igniter element of any one of claims 14 to 16 wherein at least about 40 vol % of the hot zone composition comprises a metal oxide insulating material.

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18. The igniter element of any one of claims 14 to 16 wherein at least about 50 vol % of the hot zone composition comprises a metal oxide insulating material.

19. The igniter element of any one of claims 14 to 16 wherein at least about 60 vol % of the hot zone composition comprises a metal oxide insulating material.

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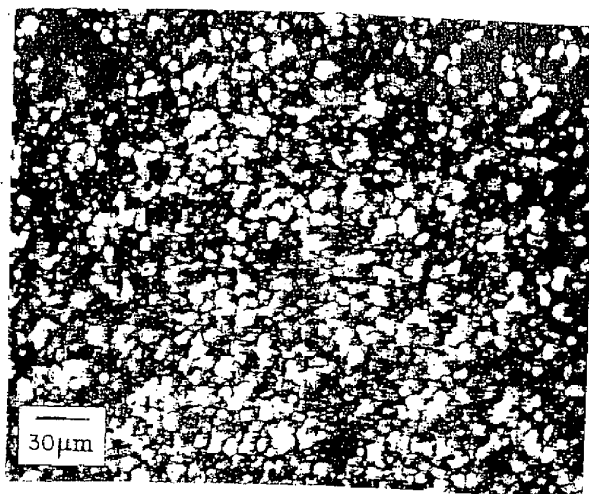


FIG. 1

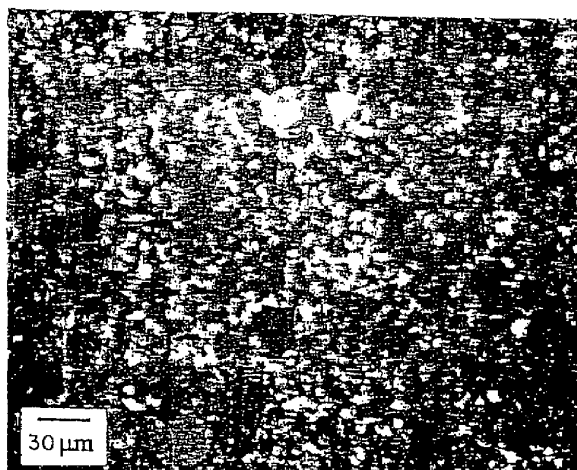


FIG. 2 PRIOR ART

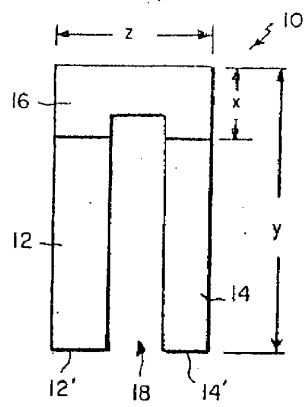


FIG. 3A

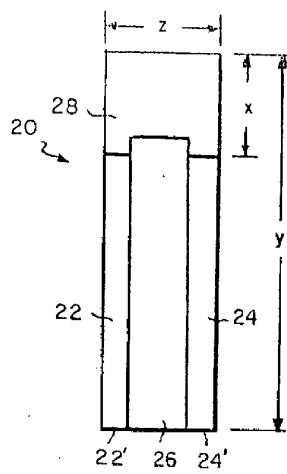


FIG. 3B

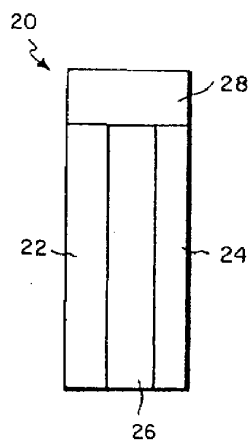


FIG. 3C

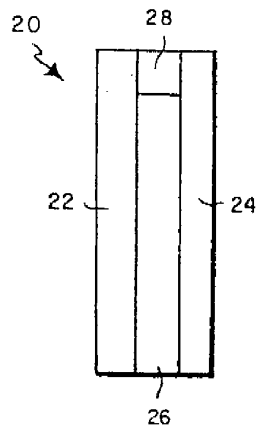


FIG. 3D