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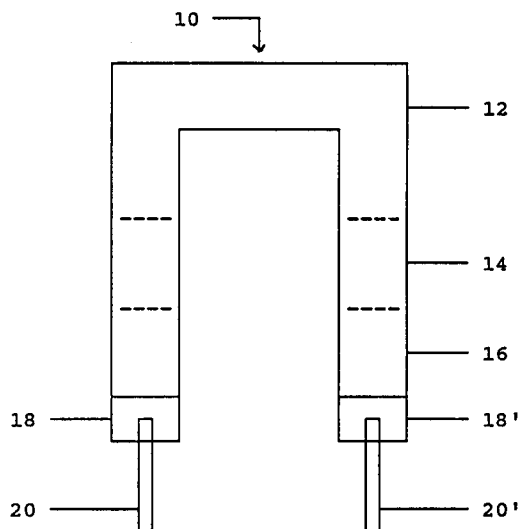
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W-8000 München 19(DE)(54) **Ceramic igniter and method of making electrical connections thereto.**

(57) Electrical connections are made to ceramic igniters which contain molybdenum disilicide, silicon carbide, and mixtures thereof as the conducting ceramic component of the igniter by forming a braze pad (18, 18') on the igniters (10) and then soldering an electrical wire (20, 20') to the braze pad with a solder having a melting temperature greater than 500 degrees C.

**FIG. 1****EP 0 486 009 A1**

This invention relates to ceramic igniters and a method of making necessary electrical connections thereto.

Although ceramic igniters have been known for many years, c.f. U.S. Pat. Nos. 3,875,477, 3,928,910 and Re. 29,853, there has been a continual problem of making electrical contacts to the ceramic bodies wherein the connections neither cause premature failure of the igniter nor substantially increase in contact resistance over the projected life of the device.

The preparation of ceramic igniters, which entail electrical conduction through a ceramic component, present substantially different problems than mere physical attachment to a ceramic body which is to be utilized only as a physical support for electrical components, i.e. in which no electrical conduction through the ceramic is required. Forming a conductive interface between a metal and a ceramic requires not only that the thermal expansion characteristics be made similar but also that an electrical path be formed which is sufficiently continuous to endure for many thousands of cycles of extreme temperature change. Furthermore, the metal and ceramic also must not react during operation so as to form an interface that would be more resistive than either the metal or the ceramic. Any chemical interaction that is used in forming the combined mechanical and electrical connection must not also form a material composition that would degrade or change during continued cyclic operations. Mechanical failure or chemical deterioration, i.e. oxidation, must both be avoided since either could cause the interface to have an increase in resistance greater than that of the metal and ceramic. The necessity of producing a combination of adhesion and a stable electrical path presents a unique problem when extended cyclic operation as is required in the igniters of this invention.

Previous attempts at making electrical connections for ceramic igniters have been varied. U.S. Pat. No. 3,875,477 discloses so doing by (i) lightly sandblasting portions of a silicon carbide igniter in the areas where the electrical contacts are to be made, (ii) coating the sandblasted terminal ends with aluminum metal or an aluminum alloy either by dipping into molten metal or by flame spraying, and (iii) using a refractory, electrically insulating cement of the high alumina type. U.S. Pat. Nos. 3,928,910 and Re. 29,853 disclose gas igniters having electrical leads bonded into physical slots of a ceramic (SiC) body by high temperature flame or plasma spraying which is not only intended to secure the inserted leads into their respective slots but also to fully and continuously encase the terminal parts of the igniter. Co-owned U.S. Appln. Ser. No. 258,307 discloses molybdenum disilicide-containing ceramic igniters in which a simple machine screw and nut assembly is placed through machined holes in the ceramic body.

Each of the above connection means has suffered from the problem of either substantially increased resistance with extended use, i.e. the resistance increases by 5, 10 or more percent after cycling through 100,000 on/off cycles, or failing to be commercially reproducible. Such large increases in resistance are a problem to the igniter industry because an igniter must be capable of igniting fuel gases throughout an extended lifetime of the appliance, at voltages which at times are as low as 85% of the standard operating voltage (20.4 instead of 24.0 v) which often occur during "brownouts" or peak electrical demand periods. Natural gas ignites at about 1050 °C. and propane gas ignites at about 960 °C. When the available voltage decreases, i.e. to 85% of the nominal voltage, an igniter temperature below that required for gas ignition could occur, particularly in older igniters in which the electrical contact has experienced severe deterioration. Thus, there is a need for an igniter which, after 100,000 cycles, does not exhibit any substantial increase in its resistance due to the electrical contact, and preferably has a low increase in total resistance, i.e. that due to both the igniter itself and the electrical connection.

U.S. Pat. No. 4,512,871 discloses an oxygen sensor with a heater in which a non-electrically conducting ceramic body is screen printed with an electrically conductive circuit which terminates in a pair of pads to which electrical contacts are made by brazing. The ceramic body is an insulator and merely functions as a physical support. Thus the problem of forming an improved electrically conductive connection is not faced by the patent.

Accordingly, it is an object of the present invention to produce an improved ceramic igniter which will have less than about a 2% change in contact resistance of the contacts after 100,000 on/off cycles and which can be reproducibly manufactured. This object is solved by the igniter according to independent claim 1 and the method of making an electrical contact to an electrically conducting ceramic material according to independent claim 9. Further advantageous features, details and aspects of the invention are evident from the dependent claims, the description, examples and drawings. The claims are intended to be interpreted as a first non-limiting approach of defining the invention in general terms.

The invention provides ceramic igniters which contain molybdenum disilicide, silicon carbide, and mixtures thereof as the conducting ceramic component of the igniter.

It is a further object to produce such an igniter having less than a about 2.5% change in contact resistance after being continuously powered at operating temperature for 2000 hours.

It is a further aspect of the invention to produce such an igniter from a ceramic composition comprising molybdenum disilicide, silicon carbide, or mixtures thereof as the conducting ceramic.

These and still further aspects will be apparent from the ensuing detailed description of the invention.

Ceramic igniters are prepared by

- 5 (i) forming a ceramic igniter body having a molybdenum disilicide content of at least about 20 volume percent at the points at which the electrical contacts are to be made,
- (ii) forming two pads of an active metal braze on the body at those points, and
- (iii) soldering electrical leads to said pads by means of a solder which melts at a temperature of greater than about 500° C.

10 Figure 1 is a top view of a preferred igniter body with connecting leads soldered to braze pads in accordance with this invention.

The ceramic igniters of the present invention comprise a non-conductive ceramic in combination with an electrically conductive ceramic. The improved electrical connections to the ceramic igniters are produced by forming a braze pad on the igniters and then soldering an electrical wire to the braze pad. The igniters 15 prepared with two such electrical connections may be reproducibly produced commercially and furthermore exhibit less than about a 2% change in contact resistance after being subjected to 100,000 on/off cycles. Also the igniters exhibit less than about a 2.5% change in contact resistance after being continuously powered at 26.4 volts at elevated temperature (1275 - 1500° C.) for 2000 hours. The conductive component of the ceramic is preferably comprised of molybdenum disilicide, silicon carbide, or a mixture thereof. More 20 preferably a mixture of molybdenum disilicide (MoSi_2) and silicon carbide (SiC), as disclosed in U.S. Pat. No. 5,045,237 of Washburn, filed October 14, 1988, is used. The disclosure and subject matter of Washburn is incorporated herein by reference.

The igniter preferably comprises about 40 to 70 volume percent of a nitride ceramic and about 30 to 60 volume percent MoSi_2 and SiC in a volume ratio of from about 1:3 to 3:1. A more preferred igniter has a 25 varying composition as described by Washburn and as indicated in Figure 1. In this case, the chemical composition of the igniter 10 is varied from a high resistive portion 12 through an intermediate portion 14 to a highly conductive portion 16. Alternatively and even more preferably the intermediate portion 14 is omitted (for ease of manufacturing). The conductive portion is provided with the two active metal braze pads 18 and 18' to which electrical leads 20 and 20' are respectively soldered in accordance with this 30 invention.

The highly resistive portion 12 of the igniter 10 is preferably comprised of about 50 to 70 volume percent nitride ceramic and about 30 to 50 volume percent MoSi_2 and SiC in a volume ratio of about 1:2. The intermediate portion 14, when present, is preferably comprised of about 50 to 70 volume percent nitride ceramic and about 30 to 50 volume percent MoSi_2 and SiC in a volume ratio of about 1:1. The highly 35 conductive portion 16 is preferably comprised of about 45 to 55 volume percent nitride ceramic and about 45 to 55 volume percent MoSi_2 and SiC in a volume ratio of from about 1:1 to about 3:2. By "highly resistive" is meant that the section has a resistivity in the temperature range of 1000 to 1600° C. of at least about 0.04 ohm-cm, preferably at least about 0.07 ohm-cm. By "highly conductive" is meant that the section has a resistivity in the temperature range of 100 to 800° C. of less than about 0.005 ohm-cm, 40 preferably less than about 0.003 ohm-cm, and most preferably less than about 0.001 ohm-cm.

Suitable nitrides for use as the resistive component of the ceramic igniter include silicon nitride, aluminum nitride, boron nitride, and mixtures thereof. Preferably the nitride is aluminum nitride.

The first step to forming the electrical connections of the present invention is to produce a braze pad or area on opposite ends of the highly conductive portions of the ceramic igniter. To obtain the high degree of 45 adhesion to the ceramic which is required, a braze which contains an active metal is utilized. A metal is considered "active" herein if it has the ability to wet and react with the ceramic materials sufficiently to provide adherence thereto by filler metals contained in the braze. Examples of specific active metals include titanium, zirconium, niobium, nickel, palladium, and gold. Preferably the active metal is titanium or zirconium. In addition to the active metal, the braze contains one or more filler metals such as silver, 50 copper, indium, tin, zinc, lead, cadmium, and phosphorous. Preferably a mixture of filler metals is used. Most preferably, the braze will comprise titanium as the active metal and a mixture of copper and silver as the filler metal.

Generally, the braze will contain in weight percent about 0.1 to about 5 weight percent active metal and about 99.9 to about 95 weight percent filler metal. Suitable such brazes are commercially available under 55 the trade name Lucanex from LucasMilhaupt, Inc. and Cusil from GTE Products Corporation. Specific brazes found useful herein include: Lucanex 721 and Cusil Braze, each of which nominally contain 70.5% silver, 27.5% copper, and 2% titanium.

Electrical wire leads are then connected to the braze pads by a solder. The solder must be able to withstand temperatures of about 450 °C. during use of the igniter without degradation and also must have a low resistivity. Generally, a solder having a melting point of greater than about 500 °C., preferably greater than about 600 °C. Suitable such solders are those which contain in weight percent about 1 to about 90% silver, about 5 to about 80% copper, about 5 to about 40% zinc, and up to about 40% of one or more metals selected from aluminum, tin, indium, phosphorous, cadmium, and nickel. Preferably, the solder will contain about 10 to 70% silver, about 10 to 70% copper, about 10 to 35% zinc, and up to 30% of the other metals. Most preferably, the solder will contain about 15 to 60% silver, about 10 to 60% copper, about 12 to 30% zinc, and up to about 30% of the other metals.

Suitable such solders are commercially available under the trade names Easy-Flo from Handy & Harmon Co. and Safety-Silv from J.W. Harris Co., Inc. A specific solder found useful herein is Easy-Flo 45 which nominally contains 45% silver, 15% copper, 16% zinc and 24% cadmium. Other specific solders which may be used include Safety-Silv 1200 which nominally contains 56% silver, 22% copper, 17% zinc, and 5% tin, and Safety-Silv 1577 which nominally contains 25% silver, 52.5% copper, and 22.5% zinc.

To perform the soldering of the wires to the braze pads, it has been found advantageous to apply the solder first to the metal wire. When the wire is placed on the braze pad on the igniter and then heated to attach it, the solder can flow from the wire to the brazed region to make the connection. This method minimizes the amount of time during which the braze is heated to above 500 °C, which will minimize/prevent oxidation of the braze pad by the air before it becomes coated with the solder. Oxidation is detrimental since it could prevent a solid chemical bond from forming and could result in mechanical failure and/or an electrical interface having a resistance higher than that of either the metal wire or ceramic igniter.

The practice of the present invention can be further appreciated from the following non-limiting examples and comparative examples in which all parts and percents are by weight unless otherwise specified.

Example 1

A double-legged triple composition hairpin or U-shaped ceramic igniter as shown in Fig. 1 is prepared from aluminum nitride, silicon carbide, and molybdenum disilicide in accordance with the teachings of U.S.S.N. 258,307, Washburn. By volume percents, the conductive portion contains 50% aluminum nitride, 30% molybdenum disilicide, and 20% silicon carbide; the intermediate portion contains 60% aluminum nitride, 20% molybdenum disilicide, and 20% silicon carbide; and the resistive portion contains 60% aluminum nitride, 13% molybdenum disilicide, and 27% silicon carbide.

To form a braze pad on each of the legs of the igniter, an active metal brazing paste, Lucenex 721, is brushed onto a 0.06" x 0.25" area of each of the legs. The paste is heated by means of a refractory metal furnace under a high vacuum to a temperature of 875 °C. for 10 minutes to form the pads.

To adhere a conventional copper electrical wire to each of the braze pads, Easy-Flo 45 Solder (45% silver, 15% copper, 16% zinc, and 24% cadmium) is used. The soldering is performed using an oxy-acetylene torch as a heat-source. A standard silver solder flux is first brushed onto the braze pad to clean the surface. Then the wire is heated and the solder introduced to the heated wire. The molten solder flows onto the wire in less than about 5 seconds. The solder containing end of the wire is placed on the pre-fluxed, braze pad of the igniter and heated with the oxy-acetylene torch, allowing the silver solder to melt and flow onto the braze pad for about less than 5 seconds and then removed. The wire is held in place for an additional 5 seconds until the solder hardens by cooling.

To evaluate the performance of the resultant electrical connection, the igniter is subjected to the standard American Gas Association test for evaluation of thermoelectric devices, ANSI Test Procedure Z 21.20, 1989, pp.12-13. The test entails cycling the igniter through 100,000 on/off sequences and determining the percent resistance changes of the total device and of the igniter body. The resistance change due to the electrical contact is then calculated by difference.

The results from duplicate samples prepared as above and having average initial igniter temperatures of 1295 ° and 1293 ° C. respectively are:

* 1 inch = 2.54 cm

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Resistance Changes, %			
Sample	Total	Igniter Only	Contact Only
A	26.8	25.6	1.2
B	21.5	20.8	0.7

Example 2

The procedure of Example 1 is repeated except that the Lucanex 721 Braze is replaced with Cusil Braze which has the same nominal composition. The results from duplicate samples having average initial igniter temperatures of 1283° and 1282° C. are:

Resistance Changes, %			
Sample	Total	Igniter Only	Contact Only
C	20.0	18.8	1.2
D	21.0	19.5	1.5

Comparative Example A

The procedure of Example 1 is repeated with a different solder, Realistic Electrical Solder which contains 60% tin and 40% lead. Attempts to solder the wires to the braze pads using an oxy-acetylene torch, a propane torch, and an electrically heated soldering iron were unsuccessful. The solder did not bond the wires to the braze.

Example 3

The procedure of Example 1 is repeated except that the intermediate portion of the ceramic igniter is omitted and the igniter is evaluated in a constant-on test at 24.0 V for 2,350 hours. Four such samples are evaluated and are found to have a percent contact resistance at the end of the test of 0.82%, 0.83%, 0.95% and 0%.

Example 4

The procedure of Example 3 is repeated except that the solder is Safety-Silv 1577. The percentage change in contact resistance after the specified number of hours during a constant-on test for multiple samples is

Resistance Changes, %				
Sample	0	840	1800	2472
1	0	1.4	1.4	0.7
2	0	1.4	2.1	0.7
3	0	1.4	2.3	0.8
4	0	1.4	2.1	0.7
5	0	2.0	2.1	0.7
6	0	1.4	2.2	1.5

Example 5

The procedure of Example 4 is repeated except that the solder is Safety-Silv 1200. The percentage change in contact resistance after the specified number of hours during a constant-on test for multiple samples is:

Resistance Changes, %					
Sample	0	768	1536	2328	3000
1	0	0.6	0	2.1	0
2	0	0	1.4	2.2	0
3	0	0.6	1.4	2.0	0.7
4	0	0.6	1.3	2.1	2.2
5	0	0.6	0	2.1	0.7

Claims

1. A ceramic igniter (10) comprising:
 - (i) a ceramic igniter body having a molybdenum disilicide content of at least about 20 volume percent at two points (16) at which electrical contacts are to be made,
 - (ii) active metal braze pads (18, 18') on the body at each of the two electrical contact points, and
 - (iii) electrical leads (20, 20') attached to said braze pads (18, 18') by means of a solder which melts at a temperature of greater than about 500 ° C.
2. The ceramic igniter of Claim 1 wherein the igniter body comprises 40 to 70 volume percent of a nitride ceramic and 30 to 60 volume percent of a combination of MoSi₂ and SiC in a volume ration of from 1:3 to 3:1.
3. The ceramic igniter of Claim 1 or 2 wherein the igniter body comprises (i) a highly resistive portion (12) containing 50 to 70 volume percent of a nitride ceramic and 30 to 50 volume percent MoSi₂ and SiC in a volume ration of about 1:2 and (ii) a highly conductive portion (16) containing 50 to 70 volume percent of a nitride ceramic and 30 to 50 volume percent MoSi₂ and SiC in a volume ratio of about 1:1.
4. The ceramic igniter of Claim 2 or 3 wherein the nitride ceramic is selected from the group consisting of silicon nitride, aluminum nitride, boron nitride, and mixtures thereof.
5. The ceramic igniter of one of the preceding Claims wherein the active metal braze pads (18, 18') comprise an active metal selected from the group consisting of titanium, zirconium, niobium, nickel, palladium, and gold.
6. The ceramic igniter of Claim 5 wherein the active metal braze pads (18, 18') further comprise at least one filler metal selected from the group consisting of silver, copper, indium, tin, zinc, lead, cadmium, and phosphorous.
7. The ceramic igniter of one of the preceding Claims wherein the active metal braze pads (18, 18') comprise titanium, copper, and silver.
8. The ceramic igniter of one of the preceding Claims wherein the solder comprises 1 to 90% silver, 5 to 80% copper, 5 to 40% zinc, and up to about 40% of at least one metal selected from the group consisting of aluminum, tin, indium, phosphorous, cadmium, and nickel.
9. A method of making an electrical contact to an electrically conducting ceramic material especially in the ceramic igniter of one of the preceding claims for use at a design operating temperature which comprises (i) forming a pad of an active metal braze on the electrically conductive ceramic material and (ii) soldering an electrical lead to said braze pad by means of a solder which melts at a temperature of at least about 50 ° C. higher than the maximum design operating temperature of the contact.

10. The method of Claim 9 wherein the active metal braze pads comprise an active metal selected from the group consisting of titanium, zirconium, niobium, nickel, palladium, and gold.

5 **11.** The method of Claim 10 wherein the active metal braze pads further comprise at least one filler metal selected from the group consisting of silver, copper, indium, tin, zinc, lead, cadmium, and phosphorous.

12. The method of one of Claims 9 to 11 wherein the active metal braze pads comprise titanium, copper, and silver.

10 **13.** The method of one of Claims 9 to 12 wherein the design operating temperature is at least about 450 ° C.

15 **14.** The method of one of Claims 9 to 13 wherein the solder comprises 1 to 90% silver, 5 to 80% copper, 5 to 40% zinc, and up to about 40% of at least one metal selected from the group consisting of aluminum, tin, indium, phosphorous, cadmium, and nickel.

15. The method of one of Claims 9 to 14 wherein the solder is placed on the electrical lead which is then placed on the braze pad and heated.

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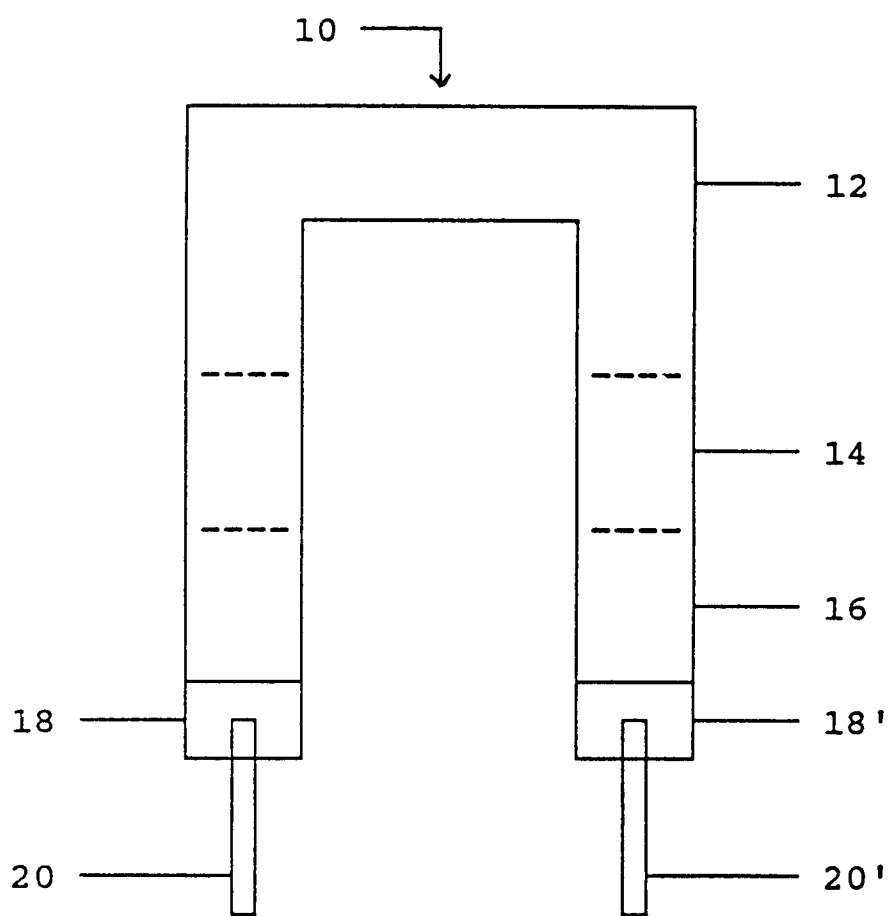


FIG. 1



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EUROPEAN SEARCH REPORT

Application Number

EP 91 11 9390

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
Y	DE-A-3 712 414 (JIDOSHA) * claims 1,2; figures *	1	F23Q7/22
A	* column 4, line 1 - line 38 * ---	8	
Y	US-A-4 486 651 (KINYA ATSUMI) * column 9, line 1 - column 10, line 40; figures 1-3 *	1	
A	---		
A	US-A-2 992 959 (SCHREWELIUS) ---		
A	US-A-3 875 476 (CRANDALL) ---		
A	PATENT ABSTRACTS OF JAPAN vol. 9, no. 152 (M-391)(1875) 27 June 1985 & JP-A-60 029 518 (HITACHI) 14 February 1985 * abstract * -----		
The present search report has been drawn up for all claims			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			F23Q H05B
Place of search THE HAGUE		Date of completion of the search 17 FEBRUARY 1992	Examiner VANHEUSDEN J.
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	