



EUROPEAN PATENT SPECIFICATION

Date of publication of patent specification :
19.05.93 Bulletin 93/20

Int. Cl.⁵ : **H01T 13/39, F23Q 7/00,
C22C 29/12**

Application number : **89810563.0**

Date of filing : **24.07.89**

Electroconductive cermet compositions for ignition and heating appliances.

Priority : **28.07.88 CH 2876/88**

Date of publication of application :
31.01.90 Bulletin 90/05

Publication of the grant of the patent :
19.05.93 Bulletin 93/20

Designated Contracting States :
BE DE ES FR GB IT

References cited :
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PATENT ABSTRACTS OF JAPAN vol. 6, no. 74
(M-127)(952) 11 May 1982, & JP-A-57 12221
(HITACHI SEISAKUSHO K.K.) 22 January 1982,**

Proprietor : **CHAMPION SPARK PLUG
EUROPE S.A.
Avenue Leopold III 2a
B-7120 Binche (BE)**

Inventor : **Issartel, Jean-Paul
2, rue du Vieux Château
F-74100 Annemasse (FR)
Inventor : Richon, Dominique
Le Hameau du Léman 60 ,rue Maurice Ravel
F-74100 Ville la Grand (FR)**

Representative : **Dousse, Blasco et al
7, route de Drize
CH-1227 Carouge/Genève (CH)**

EP 0 353 196 B1

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Description

Introduction

5 The present invention relates to electrically conductive cermet compositions which can be used in the manufacture of ignition and heating appliances, inter alia spark-plugs or plasma-discharge plugs for gasoline engines, and glow-plugs for Diesel engines or external combustion engines, e.g. Stirling engines.

The distinction between electrically conductive cermets and electroconductive ceramics should be acknowledged at this stage of the disclosure: The electrically conductive cermets are binary compositions in which electroconductive particulate elements (e.g. grains of a metal powder) are intermixed with an insulating ceramic material. In contrast, electroconductive ceramics consist of electroconducting minerals such as carbides, nitrides, borides, silicides, oxides of selected metals, for instance ZrC; WC; SiC; TiN, Mo₂N; TaN; NbN; ScB₂; TiB₂; MoB; ZrB; (Y,Ca)(Cr,Mn)O₃; (La,Sr)(Cr,Mn)O₃; doped BaTiO₃, etc., either alone or in admixture with other minerals.

15 Admittedly, electrically conductive cermets may be technically and economically advantageous over electroconductive ceramics in many applications, namely because they require milder sintering conditions and demonstrate wider electrical properties versatility (due to better composition control at the formulation stage); also, in some cases, the costs of cermet starting materials may be lower than for electroconductive ceramics.

20 The prior art

The prior art is replete with electroconductive ceramics and cermet compositions useful in the field of ignition and heating appliances. Some of these compositions can actually be considered as intermediate between electroconductive cermets and ceramics as they comprise mixtures of insulating and conducting ceramic particles as well as metallic particles.

25 For instance, Japanese Patent Publication JP-A-150,579/1980 (JIDOSHA BUHIN) discloses ignition spark plugs in which the center electrode is made of cermet compositions containing insulating or conducting ceramics such as Al₂O₃, TiO₂, TiC, Cr₂O₃, NbC, WC, SiC, TaC, MoSi₂ and metal particles, e.g. Cr, Co, Fe, Al, W, Mo, and other like metals.

30 JP-A-44391/1986 (NGK) discloses ignition spark plugs whose central electrode is made in part of cermets which result from the sintering of compositions containing ceramics selected from Al₂O₃, TiO₂, Cr₂O₃, ZrO₂, SiO₂, Y₂O₃, La₂O₃, NiO, CaO, TiC, SiC, B₄C, Cr₂C₂, WC, TiN, AlN, BN and MoSi₂ together with metal particles selected from Cr, Co, Mo, Mn, Pt and Pd.

Document JP-A-44393/1986 (NGK) describes electrically conductive cermet compositions somewhat similar to that of the foregoing document, but in which the metal particles are distributed anisotropically, i.e. the concentration of said particles within the ceramic matrix varies directionally according to a given pattern.

Document US-A-4,427,915 (NGK) also describes electrically conductive cermet compositions to be used for ignition spark plugs; these compositions are very similar to that of the previously mentioned references but the metal particles further include precious metals such as Ag, Ru, Rh, Au and the like.

40 In addition to the above mentioned documents, other references disclosing ignition plugs which involve using electrically conductive ceramics and cermets include the following documents: EP-A-171,153 (GENERAL MOTORS); US-A-4,475,029 and 4,633,064 (NIPPONDENSO); US-A-4,528,121 (HITACHI); US-A-4 205 363 (CARBORUNDUM).

45 Although the electroconductive cermets and ceramics known in the art for making the electrodes or the incandescent bodies of ignition plugs have merit, it was desirable to further improve some of their working properties, inter alia the resistance to hot corrosion and the resistance to electroerosion by spark discharge.

Summary of the invention

50 In view of fulfilling the aforementioned objectives, the present inventors have developed electroconductive cermet compositions which constitute an important step in the desired direction. These compositions are summarized in claims 1 to 5.

Briefly, these electroconductive cermet compositions, which demonstrate significantly improved resistance to hot corrosion and to erosion by spark discharge comprise an alumina based ceramic and 30-60% by weight of metal particles which provide adequate electroconductivity to the compositions. The main improvement here over the achievements of the prior art is that said metal particles are in a partly oxidized state, the weight ratio oxygen/metal of these particles being in the range of 0.3 to 10% (ie. 0.003 - 0.1).

Detailed description of the invention

Although the exact reasons why the presence of partly oxidized metallic particles in the present compositions will impart thereto markedly improved working properties has not been investigated in detail (and need not be so to obtain adequate patent coverage), it has been theorized that the existence of metal oxide adhering to the metal of the particles, preferably in the form of an oxide film or layer on at least a portion of the surface thereof, will considerably increase the strength of the cermet, inter alia against wear and tear caused by abrasion, corrosion and electroerosion. Indeed, the oxide of the particulate metals, and this is particularly evident for chromium, has a degree of solubility in the ceramic phase (Al_2O_3) which reduces strongly the discontinuity barrier between the metal grains and the ceramic phase; thus, the presence of this oxide layer adherent to the metal grains and interposed between said grains and the ceramic matrix provides enhanced compatibility with the cermet body and ensures appropriate reinforcement and improved mechanical properties.

The grade or mesh-size of the metallic powders of the present cermet composition can be in the order of 0.5 to 50 μm , a grade around 1 μm being preferred. The metals suitable for making the powders are of course the metals normally used for making cermets and disclosed in the prior art, namely Cr, Ni, Co, Fe, Mo, W, Ti and the like.

In order to improve densification parameters and sintering conditions of the present compositions, the ceramic phase can be supplemented with other minerals, inter alia 1 to 20% by weight of a vitreous silicate phase. This glassy phase comprises SiO_2 and, at will, one or more oxides selected from MgO , CaO , BaO , Na_2O , K_2O , Fe_2O_3 , TiO_2 , ZrO_2 , ZnO , PbO_2 , B_2O_3 and further oxides conventionally used for making glasses. In an embodiment of the present invention, the ceramic of the cermet composition consists, at least in part, of Mullite, i.e. a mixed aluminosilicate of formula $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$.

In the method for manufacturing the cermet compositions of the present invention, a formulation is first prepared by admixing together the cermet ingredients (or precursor compounds) and adding molding or casting and sintering additives. Then the resulting blend is formed or molded into a "green" object or article which can thereafter be safely handled and heated with substantially no risk of mechanical attrition. Then the "green" article is sintered at high temperature (e.g. around 1200-1600°C) so as to furnish the article made of the desired electroconductive cermet composition.

In order that some oxide be formed at the surface of the metal particles, several routes are available; the simplest route is to use preoxidized metal particles in the cermet composition; otherwise a particle surface oxidation may take place during sintering. In this case, the oxygen required for this oxidation may arise, either from an additional oxidant added to the formulation blend before molding and which will ultimately be decomposed by heat during sintering and release its oxygen for oxidizing the metal particles, or from the atmosphere under which sintering is performed, this atmosphere containing oxygen or an oxygen containing gas.

The techniques to be used for forming or molding the green objects or articles made of, or comprising the cermet composition of the invention, are conventional. For instance, the aforementioned formulation blend can be placed in a mold and the latter is subjected to pressure (isostatic pressure or otherwise) in the order of 1 to several T/cm^2 . A dip-coating technique can also be used when it is desired to deposit a layer of electroconductive cermet on a substrate; in this case, the substrate is immersed for a given time in a slurry of the formulated cermet ingredients, withdrawn, and allowed to dry before sintering.

For doing the sintering of the molded objects, one can also use conventional sintering methods well known in the art; for instance the green article can be heated in an oven under an atmosphere of controlled composition, e.g. a neutral gas (argon, helium) or under hydrogen or nitrogen, or mixtures thereof. When it is desired that the metal grains of the composition be superficially oxidized during sintering, the latter is effected in an atmosphere having an oxygen partial pressure which can be controlled by introducing an oxygen releasing gas, for instance a 20/80 (v/v) $\text{H}_2/\text{H}_2\text{O}$ mixture. This oxidation can also be accomplished independently of the sintering operation, at lower temperatures, for instance between about 500 and 1200°C.

When the surface oxidation of the metal grains of the cermet results from the thermal decomposition of an oxidizing agent admixed with the formulation blend, this oxidation agent can be selected from organic oxidizers (which pyrolyse at sintering temperature) or mineral oxidants which release oxygen during sintering. As oxidizing agents, the following can be non-exhaustively recited: metal oxides, metal hydroxides and peroxides, e.g. $\text{Al}(\text{OH})_3$, $\text{Fe}(\text{OH})_3$, Na_2O_2 , as well as salt, for example nitrates, oxalates, carbonates, titanates, etc. The weight proportion of such oxidants in the formulation may essentially vary depending on the degree of oxidation of the metal particles which is desired; generally, this amount is between about 0.5 and 20% by weight.

When preoxidized metallic powders are used in formulating the cermets of the invention, such preoxidized powders can be obtained by oxidation techniques. For instance, for superficially oxidizing the particles of a chromium powder, the latter can be contacted with a heated oxygen flow or with a bichromate solution. Generally speaking, the techniques for superficially oxidizing metal powders are well known in the art and need

not be further developed here. The extent of oxidation of the metal powders used in the present invention, i.e. the amount by weight of oxygen incorporated to the metal grains is preferably 0.3 to 20%.

The following examples which will be better understood by means of the annexed drawing serve to illustrate the invention in more detail.

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Brief summary of the drawings

Figure 1 schematically represents an ignition spark-plug for gasoline engines in which some components are made of electroconductive cermets in conformity with the composition according to the invention.

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Figure 2 schematically represents a glow-plug for Diesel engines of which some components are made of electroconductive cermets achieved according to the invention.

Figure 3 is a microphotograph showing the internal structure of a cermet composition according to the invention.

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Figure 4 is a microphotograph which shows, comparatively, the structure of a cermet composition from the prior art.

EXPERIMENTAL

Example 1

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The following ingredients were milled for 24 hrs in an alumina ball-mill with 400 g of alumina beads of 12 mm diameter: 59.5 g of alumina powder (grade about 1 μ m) containing about 10% by weight of a glassy phase constituted by about 80% of SiO_2 , the remainder being a mixture of MgO, CaO and Na_2O ; 40.5 g of chromium powder (oxidized beforehand by an oxygen flow at 300°C and containing, by weight, about 1-3% of oxygen); 1.5 g of fish-oil (dispersing agent); 50 g of butanol (solvent); and 8 g of camphor (binder).

25

The blend was thereafter dried and sieved on a 300 μ m screen. Then the powder was molded into disks (diameter 15 mm, height 3mm) under a pressure of 1.1 T/cm².

The disks were sintered for 2 hrs at 1550°C under argon, after which they were cut (with a diamond saw) into little bars, or blocks, of 2x2x5 mm.

30

In order to test electrical and resistance properties of the cermet composition, a little bar was secured (by means of an electrically conducting silver-epoxy glue) to the central electrode of an ignition spark-plug (distance between the electrodes = 1 mm) and the bar was subjected to a succession of 150,00 spark discharges (plasma discharge; 1000 VDC; 1 joule/spark). Then the little block was unfastened by dissolving the glue in a solvent, e.g. trichloroethylene, it was cleaned and dried and the weight loss was measured on a balance. The weight loss was then converted to volume loss, using for the calculation the actual cermet density of 4.15 g/cm³ as measured by usual techniques. The volume loss consecutive to spark electroerosion is given in annexed Table 1; this is expressed in % value relative to the loss of a conventional nickel alloy in a conventional ignition spark-plug subjected to the same test.

35

For measuring the resistance to thermal corrosion (for instance mimicking that in a combustion chamber) the bars were heated for 24 hrs (1000°C) in an atmosphere obtained by burning methane containing 0,2% (v/v) of H_2S , i.e. 3 g/m³. The results are given also in Table 1 in terms of relative weight increase; This weight increase results from the oxidation of the metal.

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Example 2 (control)

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The operations reported in Example 1 were repeated, but replacing in the formulation the oxidized chromium powder by regular (non-oxidized) chromium powder of the same grade. The cermet samples which resulted from the sintering of this control composition were tested identically and the results are gathered in Table 1.

50

Example 3 (control)

The operation of the foregoing Examples were repeated by using a non-oxidized chromium powder and omitting the silicate glassy phase which was replaced by an additional quantity of Al_2O_3 and a portion of MgO (4% by weight).

55

Thus, besides the other ingredients (like in Example 1) and the operating condition which were like before (see examples 1 and 2), there were used:

Alumina 61.9 g

Pure Cr powder 38.1 g
MgO 0.25 g

The resulting cermet compositions were sintered at 1550°C as before and were tested as in example 1. Results are collected in Table 1.

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Example 4

An ignition spark-plug was constructed using the cermet composition of Example 1; this spark-plug is schematically represented in Figure 1.

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This plug comprises a conventional metal shell 1 integral with a ground electrode 4, an insulating body 2 (of vitrified alumina ceramic) and, located in a hollow axial portion of this body, the following elements : A terminal rod 9, a conducting gasket 7, an interference-suppressor resistor 8 and a center electrode 6 made of a cermet composition according to the invention. This electrode 6 was obtained by molding and sintering according to usual means under the conditions disclosed in Example 1. The several plug components were assembled together according to usual techniques of spark-plug manufacture.

15

This kind of plug was tested in an automobile engine and demonstrated a useful life much longer than that of a standard control plug in which the central electrode was of a conventional nickel alloy or that of a control plug in which the central electrode was of electroconductive cermet according to the prior art.

20

In a variant, the ground electrode 4 of the plug represented in Figure 1 can be provided, by welding or brazing, with a small bar or cap 5 made of a cermet composition which is identical with that of the center electrode. In this case the useful life of the plug is still further extended.

Example 5

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A glow-plug useful in Diesel engines was constructed using a cermet formulation like that of Example 1. A plug of this kind is schematically illustrated in Fig. 2.

30

This plug comprises a metal outer-shell 12 provided (as in the case of the plug of Example 4) with a threaded portion 13; this shell surrounds a hollow insulating body of two axially abutting parts 14 and 15. The hollow portion of insulating part 14 contains a metal terminal rod 16 which is in contact with the internal annular area of part 15 and which is retained, in part 14, by a shouldered base 17 of larger cross-section. The hollow cylindrical insulating element 15 is coated on its internal and external lateral surface with a cermet layer 18 of a composition according to the invention. This layer 18 extends without transition over the full free surface of element 15 including the external terminal face 19 of insulator 15 as shown in the drawing and hence constituting a continuous electric resistor whose respective ends are electrically in contact, on one hand with the base 17 of rod 16 and, on the other hand by its peripheral area 20, with the metal sheath 12. When an appropriate voltage is set across the sheath 12 (ground terminal) and the terminal rod 16 (plug terminal) an electric current will circulate in layer 18 which heats up and becomes incandescent. Since the cermet composition used for making this layer 18 has an improved resistance to thermal corrosion, the present glow-plug demonstrate a much extended working life when used in a Diesel engine.

40

In order to accomplish the deposit of the layer 18,19,20 on the hollow insulating body 15, one preferably uses the dip-coating technique. The formulation of Example 1 is used but containing by weight, instead of the solvent, dispersant and binder indicated, 50 g of a 1:1 mixture of trichlorethylene and ethanol (solvent); 5-10% of polyethylene-butylal (binder); 6% of a 1:1 mixture of polyethylene glycol and dioctyl phthalate; and 0,5-1% of FLUORAD (3M)(surfactant). The amount of solvent can be varied and will depend on the viscosity to be imparted to the slurry and, as a consequence, of the thickness to be given to the deposited layer of cermet 18,19,20. In the foregoing usual conditions, one dip-coating operation provides a layer of about 100-300 µm after drying. Naturally the dip-coating operation can be repeated after drying the first layer if thicker deposit are desired. The dip-coating layer is dried in air (hot or at room temperature) until the solvents have evaporated and thereafter it is sintered at about 1550°C in the conditions set up at example 1.

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The glow-plug components are assembled together conventionally, i.e. the rod 16 is inserted into insulated body 14, the base 17 of of the rod is pressed against body 15 which has been provided beforehand with the sintered cermet layer so that a good electrical contact is achieved between said cermet layer and the said base 17 (for ensuring a better contact, a soft electrically conductive gasket can be used there if desired, for instance an annealed copper washer); then the assembly is set integrally into shell 12 by crimping.

55

Example 6

A cermet formulation was prepared by milling together for 24 hrs in a ball-mill, using 200 g of alumina balls,

the following ingredients:

| | | |
|----|-------------------------------|--------|
| | Mullite powder | 28.5 g |
| 5 | Oxidized (5%) chromium powder | 21.5 g |
| | Fish oil (dispersant) | 0.75 g |
| | 1:2 mixture of tert-butanol- | |
| 10 | petroleum ether (solvent) | 50 g |
| | Camphor (molding binder) | 4,0 g |

Disks were molded with this formulation like disclosed in example 1 and the green disks were sintered for 2 hrs at 1480°C under argon. The sintered composition was then tested exactly as in the previous Examples. Results can be found in Table 1.

Example 7

The operation disclosed in Example 6 were repeated except for the following differences: to the formulation were added 0.85 g of talc powder ($4\text{SiO}_2 \cdot 3\text{MgO} \cdot \text{H}_2\text{O}$); sintering temperature 1450°C. The results of the tests are gathered in Table 1.

Example 8 (Control)

The operations of Example 7 were duplicated, the only difference being to replace the oxidized Cr powder by pure chromium powder. For the results, see Table 1.

TABLE 1

Electrical properties and resistance to thermal corrosion and to spark discharge erosion of the cermets of Exemple 1-3 and 6-8.

| Exemple (*) | Density (g/cm ³) | Resistivity ($\Omega \cdot \text{cm}$) | Comparative resistance (**) to erosion (%) | to corrosion (%) |
|----------------|---------------------------------|---|---|---------------------|
| 1 (T) | 4.15 | 0.6 | 0 | 7.9 |
| 2 (C) | 4.07 | 2.9 | 86 | 9.9 |
| 3 (C) | 4.37 | 49 | 137 | 10 |
| 6 (T) | 3.76 | 3.4 | 23 | - |
| 7 (T) | 3.72 | 2.2 | 13 | 7.9 |
| 8 (C) | 3.4 | 0.15 | 173 | - |

(*) T = test; C = control

(**) relative to a standard nickel alloy taken as showing 100% erosion (i.e. a loss of 0.38 mm³ for a 20 mm³ sample)

It can be seen from the results of Table 1, that the use of an oxidized metallic powder in electroconductive cermets, as well as the presence of a glassy phase, will improve the electroerosion and thermal corrosion resistance properties.

Figure 3 is a microscope picture of the structure of the cermet of Exemple 7, while figure 4 depicts, comparatively, the structure of the control cermet of Exemple 8.

It can be clearly seen that, in the cermet of the invention, the metal grains are intimately incorporated into the ceramic phase, no significant sharp transition borderline being visible.

In contrast, in the control sample of Example 8, a sharp line between the grains and the ceramic phase is visible.

Example 9

The following ingredients were milled for 48 hrs in a 250 ml jar with 400 g of Zircon balls.

61,9 g Al_2O_3 powder identical with that of Example 1;

40,47 g of Chromium powder, grade $\sim 1 \mu\text{m}$ containing about 3,5% by weight of Cr_2O_3 ;

1,5 g of fish-oil; 50 g of tert.butanol/petroleum ether (9:3) and 8 g of camphor.

Then the blend was dried by evaporation under reduced pressure and sieved on a 300 μm screen; then it was molded in the form of spark-plugs electrodes as indicated in Example 4 and sintered at 1560°C.

Spark plugs using the above cermet as the central electrode were tested in a RVI-Peugeot engine using fuel 98 RON, 0,15 g Pb/l. The results, in terms of erosion of the electrode (mm) with time (hrs) are given in table 2 below.

A control was prepared as indicated above, using a chromium powder with no chromium oxide or a negligible quantity (POUDNET chromium powder). The results are also in Table 2.

TABLE 2

| Time (hrs) | : | <u>25</u> | <u>50</u> | <u>75</u> | <u>100</u> |
|---------------------------|----------|------------------|------------------|------------------|-------------------|
| Electrode | | | | | |
| erosion (mm); Test | : | 0,08 | 0,13 | 0,14 | 0,18 |
| Control | : | 0,35 | 0,45 | 0,54 | 0,70 |

Example 10

Cermet electrodes were prepared as in Example 9 from the following formulation :

Al_2O_3 (same grade as in Example 1) 53,36 g

Chromium powder (3,5% O_2 as Cr_2O_3) 46.64 g

This was milled for 24 hrs with 200 g of zircon balls in the presence (as in the foregoing Examples) of 1,5 g of fish-oil, 50 g of a 1:3 mixture of Tert.BuOH/petroleum ether and 8 g of camphor. Then the mixture was treated as in Examples 1 and 8 and sintered (samples 3,50₂) under milder conditions than in Example 8 (lower temperature, shorter sintering time).

Another composition with the same proportions and same handling condition was prepared using a chromium powder with 6% by weight of oxygen (Cr_2O_3). This gave sintered electrodes labelled 60₂.

Both grades of electrodes were tested as in the previous example. Results are outlined below.

TABLE 3

| | | | | | |
|----|--------------------------------|---------------------------|------------------|------------------|------------------|
| 5 | Time (hrs) | : | <u>25</u> | <u>50</u> | <u>75</u> |
| | Electrode erosion (mm); | 3,50₂ : | 0,25 | 0,5 | - |
| 10 | | 60₂ : | 0,2 | 0,4 | 0,6 |

Claims

- 15 1. An electroconductive cermet composition having improved resistance to corrosion and/or to erosion, comprising an alumina-based ceramic and 30-60% by weight of metal particles, wherein the metal particles are partially oxidized, the weight ratio of oxygen to metal in these particles being about 0.3 to 10%.
- 20 2. The cermet composition of claim 1, wherein the oxide of the metal of the particles is in the form of an adherent film on at least part of the surface of the particles.
3. The cermet composition of claim 2, which further comprises 2-20% by weight of a silicate-based vitreous phase.
- 25 4. The cermet composition of claim 3, in which the vitreous phase comprises SiO₂ and at least one of the oxides MgO, CaO, Na₂O, Fe₂O₃, TiO₂, ZnO, PbO₂, B₂O₃.
5. The cermet composition of claim 2, wherein the ceramic phase consists, at least in part, of Mullite of formula 3Al₂O₃·2SiO₂.
- 30 6. A method for manufacturing electrically conductive cermet compositions as defined in claim 1, which comprises the steps of:
 - (1) blending together in a formulation the ingredients of the cermet composition or precursors thereof in admixture with molding and sintering additives;
 - 35 (2) forming or molding "green" objects or articles from the blended formulation; and
 - (3) sintering said "green" articles at high temperature so as to obtain articles of the desired cermet composition, the partial oxidation of the metal particles being carried out either before said blending of step (1), or during sintering.
- 40 7. The method of claim 6 including effecting the partial oxidation of the metal particles during sintering, wherein the latter results from the oxygen released by an oxidant of the blend which decomposes upon heating at sintering temperature.
8. The method of claim 6, in which the partial oxidation of the metal particles is effected during sintering, which comprises carrying out said sintering under an oxidizing atmosphere, so that said partial oxidation results from the oxidizing action of said atmosphere.
- 45 9. A process for making spark- or plasma-discharge ignition plugs for gasoline motors, which comprises realizing, at least partially, one or more of the electrodes of said ignition plugs according to the method defined in claim 6.
- 50 10. A process for making glow-plugs for Diesel engines, which comprises realizing that portion of the plugs serving as a glow element by dip-coating an insulating ceramic bait with a layer of an electroconductive cermet composition according to claim 1 and thereafter sintering said coated layer.

Patentansprüche

1. Elektrisch leitende Cermet-Zusammensetzung mit verbesserter Korrosions- und/oder Erosionsbeständigkeit, enthaltend eine auf Aluminiumoxid basierende Keramik und 30 bis 60 Gew.-% Metallteilchen, in der die Metallteilchen teilweise oxidiert sind und das Gewichts-Verhältnis von Sauerstoff zu Metall in diesen Teilchen etwa 0,3 bis 10% beträgt.
2. Cermet-Zusammensetzung nach Anspruch 1, worin das Metalloxid der Teilchen in der Form eines anhaftenden Filmes auf zumindest einem Teil der Oberfläche der Teilchen ist.
3. Cermet-Zusammensetzung nach Anspruch 2, welche weiter 2 bis 20 Gew.-% einer auf Silicat basierenden glasartigen Phase enthält.
4. Cermet-Zusammensetzung nach Anspruch 3, in welcher die glasartige Phase SiO_2 und zumindest eines der Oxide MgO , CaO , Na_2O , Fe_2O_3 , TiO_2 , ZnO , PbO_2 , B_2O_3 enthält.
5. Cermet-Zusammensetzung nach Anspruch 2, in der die keramische Phase zumindest teilweise aus Mullit der Formel $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$.
6. Verfahren zur Herstellung elektrisch leitender Cermet-Zusammensetzungen nach Anspruch 1, welches die Schritte
 - (1) des Vermischens der Bestandteile der Cermet-Zusammensetzung oder deren Precursor in einer Formulierung in Mischung mit Form- und Sinter-Zusatzstoffen,
 - (2) des Bildens oder Formens von "grünen" Gegenständen oder Erzeugnissen aus der gemischten Formulierung und
 - (3) des Sinterns der "grünen" Gegenstände bei hohen Temperaturen, um Gegenstände mit der gewünschten Cermet-Zusammensetzung zu erhalten, wobei die teilweise Oxidation der Metallteilchen entweder vor dem Mischen der Stufe (1) oder während dem Sintern durchgeführt wird, umfaßt.
7. Verfahren nach Anspruch 6 unter Einschluß der teilweisen Oxidation der Metallteilchen während dem Sintern, worin die letztere sich aus dem durch ein Oxidationsmittel der Mischung freigesetzten Sauerstoff ergibt, welches sich durch Erwärmen bei der Sintertemperatur zersetzt.
8. Verfahren nach Anspruch 6, in welchem die teilweise Oxidation der Metallteilchen während dem Sintern bewirkt wird, durch Durchführen des Sinterns in einer oxidierenden Atmosphäre, so daß die teilweise Oxidation sich aus der oxidierenden Wirkung der Atmosphäre ergibt.
9. Verfahren zum Herstellen von Funken- oder Plasma-Entladungszündkerzen für Benzinmotoren, welches zumindest teilweise die Realisierung einer oder mehrerer der Elektroden der Zündkerzen nach dem Verfahren gemäß Anspruch 6 umfaßt.
10. Verfahren zum Herstellen von Glühkerzen für Dieselmotoren, welches die Realisierung des als ein Glüh-element dienenden Kerzenteils durch Überziehen eines isolierenden keramisches Fangmittels mit einer Schicht einer elektrisch leitenden Cermet-Zusammensetzung nach Anspruch 1 und anschließendem Sintern der Überzugsschicht umfaßt.

Revendications

1. Composition de cermet conducteur électrique dont la résistance à la corrosion et/ou à l'érosion est améliorée, comprenant une céramique à base d'alumine et 30-60% en poids de particules métalliques, dans laquelle les particules de métal sont partiellement oxydées, le rapport en poids de l'oxygène au métal dans ces particules étant de l'ordre de 0,3 à 10 %.
2. Composition de cermet selon la revendication 1, dans laquelle l'oxyde du métal des particules est sous forme d'un film adhérent sur au moins une partie de la surface des particules.
3. Composition de cermet selon la revendication 2, qui comporte en plus 2-20 % en poids d'une phase vitreuse à base de silicate.

4. Composition de cermet selon la revendication 3, dans laquelle la phase vitreuse comporte du SiO_2 et au moins un des oxydes MgO , CaO , Na_2O , Fe_2O_3 , TiO_2 , ZnO , PbO_2 , B_2O_3 .
5. Composition de cermet selon la revendication 2, dans laquelle la phase céramique se compose, au moins en partie, de mullite de formule $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$.
6. Procédé de fabrication de compositions de cermet conducteur électrique selon la revendication 1, qui comporte les étapes suivantes :
 - (1) on mélange ensemble les ingrédients de la composition du cermet ou des précurseurs de celle-ci additionnée d'additifs de moulage et de frittage;
 - (2) on forme ou on moule des objets ou articles non desséchés à partir d'une formulation mélangée; et
 - (3) on fritte ces articles non desséchés à haute température pour obtenir des articles de la composition de cermet désirée, l'oxydation partielle de particules métalliques étant réalisée soit avant le mélange de l'étape (1), soit durant le frittage.
7. Procédé selon la revendication 6, selon lequel on effectue l'oxydation partielle des particules métalliques pendant le frittage, où celle-ci résulte de l'oxygène libéré par un oxydant du mélange qui se décompose lors du chauffage à la température de frittage.
8. Procédé selon la revendication 6, dans lequel l'oxydation partielle des particules métalliques est effectuée pendant le frittage, selon lequel on réalise ce frittage sous atmosphère oxydante, de sorte que l'oxydation partielle provient de l'action oxydante de cette atmosphère.
9. Procédé pour fabriquer des bougies d'allumage à étincelles ou à décharge plasma pour moteurs à essence, selon lequel on réalise, au moins partiellement, une ou plusieurs des électrodes de ces bougies d'allumage selon le procédé de la revendication 6.
10. Procédé pour fabriquer des bougies à incandescence pour moteurs Diesel, selon lequel on réalise la partie des bougies servant d'élément incandescent par revêtement par trempage d'une amorce en céramique isolante avec une couche d'un cermet conducteur électrique selon la revendication 1 et ensuite frittage de cette couche de revêtement.

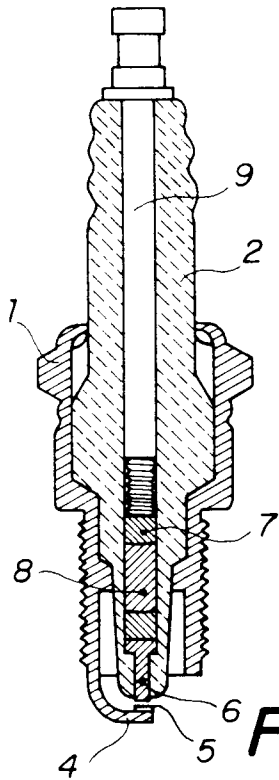


FIG. 1

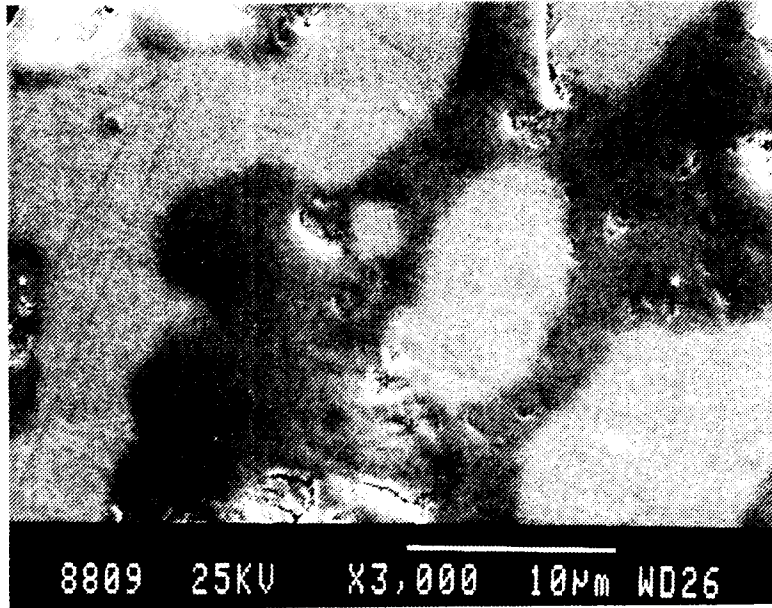


FIG. 3

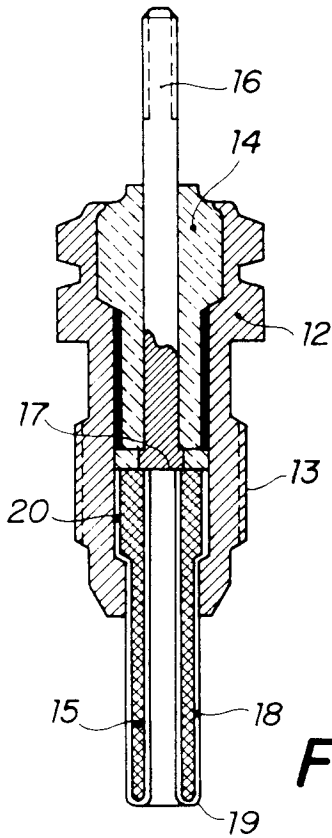


FIG. 2

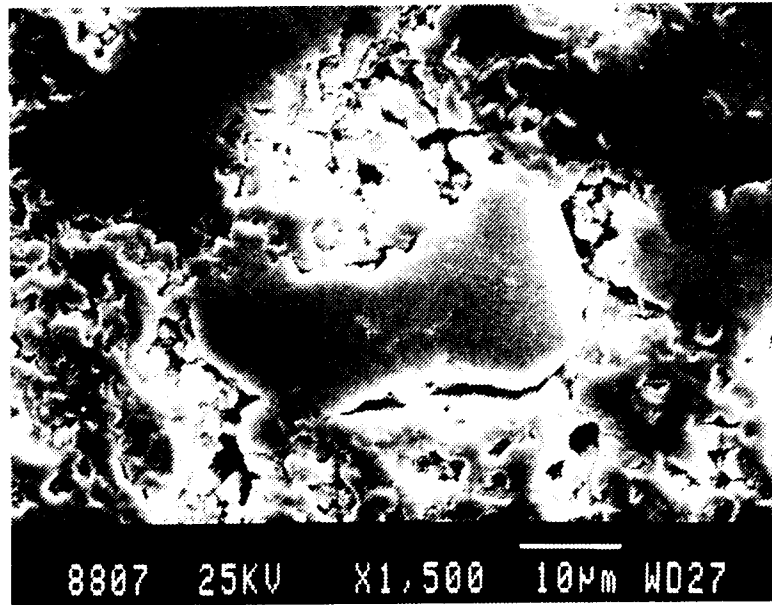


FIG. 4