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SPARK PLUG ELECTRODE

Max Joseph Stumbock, South Orange, and Ross Bayes, Basking Ridge, N. J., assignors to Baker & Company, Inc., Newark, N. J., a corporation of New Jersey

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This invention relates to sparkplugs and is concerned more particularly with sparkplug electrodes.

The construction material of sparkplug electrodes must be a metal having a suitably high melting point and be a good conductor of heat and electricity, and must possess a number of other favorable characteristics—such as strength and resistance to erosion in the presence of the fuel—required for satisfactory performance in operation.

Sparkplug electrodes may consist, therefore, of base metals or precious metals. Electrodes of such metals as platinum or alloys thereof are far superior to electrodes of base metal such as nickel or tungsten or alloys of such metals, but are too expensive for general use, as, for instance, in internal combustion engines of automobiles, and are, therefore, restricted in use to more critical uses such as in internal combustion engines of airplanes.

Silver has excellent resistance to corrosion by the fuels of internal combustion engines and is a good conductor of heat and electricity and in theory would be an excellent construction material for sparking plug electrodes. Unfortunately, however, silver which has a melting point of about 960° C. is not adapted to withstand the high temperatures, up to about 800° C. and more, to which it would be subjected during the arcing of the electrodes, with the result that sparkplug electrodes made of silver deteriorate fast. The fine grain crystal structure, considerable hardness and tensile strength which characterize silver in the cold-worked state persist only at low temperatures when silver and silver alloys are subjected to temperatures in excess of 200° C., graingrowth sets in and hardness and tensile strength are lowered, tendencies which become especially marked at higher temperatures, in particular at about 800° C., resulting in ultimate failure of the silver sparkplug electrode at an early state, and erosion under the corrosive influence of the vaporized fuel at elevated temperature is quite rapid. Another disadvantage of silver, and its alloys, is that sparkplug electrodes must be cleaned from time to time and silver, after having been exposed to elevated temperatures, is not sufficiently hard to withstand the blast of the customarily used sand blast method.

It is one object of this invention to produce a sparkplug electrode which shall have high electrical conductivity and high heat conductivity. It is another object of this invention to provide such a sparkplug electrode of silver. It is a further object of this invention to produce a silver sparkplug electrode which shall be capable of operating at elevated temperatures and which shall have substantial hardness and ability to retain a high degree of hardness at elevated temperatures even in excess of 800° C. Other objects and advantages of our invention will appear from the description thereof hereinafter following.

Sparkplugs and the arrangement of the electrodes therein, such e. g. as a center electrode provided within a mass of insulation material, with or without a metal core, in operative position with a side electrode secured to a metal shell, or other arrangements, are well known in the art and our invention is not concerned with such structural features or arrangement, but is concerned merely with the metal or metal composition of which the electrode, or at least one electrode such as the center electrode, consists.

This application is a continuation-in-part of our co-pending application, Serial No. 691,170, filed August 16, 1946, now abandoned.

The electrode of the present invention is formed of silver and alloys of silver, e. g. with copper, in the form of a compacted heated, i. e. sintered, mass containing a refractory oxide distributed uniformly and in fine divided state throughout the mass of silver along the crystal boundaries of such silver and silver alloys.

The "refractory oxide" may be any one or more of the oxides commonly known as refractory oxides, including oxides of the alkaline earth metals of group II *a* of the periodic table, e. g. beryllium, strontium, barium, or of metals of group III *b* of the periodic table, e. g. aluminum, scandium, yttrium and rare earth metals (Atomic Nos. 57–71) e. g. lanthanum, cerium or neodymium, or of metals of group IV *b* of the periodic table, e. g. zirconium, thorium, or of metals of group V *b* of the periodic table, e. g. vanadium or colombium, or the sesquioxide of chromium in group VI *b* of the periodic table. The enumeration of the specific refractory oxides above referred to is illustrative of refractory oxides but is not meant to exclude other oxides commonly included in the term "refractory oxide."

Among the refractory oxides we have found that the most suitable ones are the oxides of thorium, beryllium and aluminum.

The constituents of the mass are provided in finely divided condition which may be produced in any suitable manner. Thus, the silver or alloying metal may be provided, for instance, by mechanical disintegration, granulation or the like, or by chemical means such as by precipitation or by decomposition and reduction of metal compounds. The refractory oxide may be provided, for instance, in the form of dry powder or paste or in the form of a solution of a salt adapted to be decomposed to the oxide by heating. The constituents are mixed in such finely divided condition, i. e. either in their final form of metal and oxide, respectively, or in any of the preparatory phases or in the final form of one constituent, e. g. solution of silver compound with solution of salt adapted to be decomposed to the oxide or with refractory oxide, or otherwise.

The mixture is then subjected to heat during or after the compacting process, as by hot pressing or by pressing and sintering, whereafter the compacted mass can be worked, as by swaging, rolling, drawing and so forth, to form the mass into the desired shape, such as, for instance, wire which may then be converted into the desired shape, such as wire, used to form the sparkplug electrode. In order to obtain best results, the material should be hard worked to give the silver a highly fibrous structure.

The amount of refractory oxides may be as low as 0.01% or as high as 10%, but in order to retain without substantial impairment the high electrical and heat conductivity of the silver, while yet obtaining the retention of the fine or fibrous crystal structure on continuous exposure to elevated temperatures, e. g. 800° C., and conveying to the silver a special hardness, the content of refractory oxide should not exceed about 1.5%. Hence, we prefer to use from about 0.1% to 1% refractory oxide in the silver sparkplug electrodes of this invention, with 3% to 5% generally as the maximum limit.

The following example will illustrate one suitable and advantageous method of producing the improved silver according to the invention. 622 grams silver powder were covered with distilled water to make a heavy paste. 6.23 grams thorium oxide were added in the form of thorium nitrate. The materials were mixed and the mixture stirred while drying over a water bath. The mixture was finally dried completely at 180° C. The dry powder mixture passed through a 100 mesh sieve. The powder mixture was then pressed into a bar, 4'' x 1'' x 1'', for instance at 12.5 tons pressure per square inch and was then sintered for approximately one hour at 800° C. to 900° C., during which process the material is converted into a compacted finely grained crystalline structure and the thorium nitrate becomes decomposed to thorium oxide. The sintered bar was then swaged with intermediate anneals down to .300'' and cold worked from thereon.

The refractory oxide is distributed throughout the silver mass of the electrode, along the boundaries of the silver crystals. Care is, therefore, taken, as to the temperature of processing the material and, where necessary, as to avoidance of reducing conditions, that the refractory oxide is not decomposed to metal, since in the metallic state, as distinguished from the oxide state, the material would alloy with the silver.

The silver sparkplug electrodes of this invention withstand the high temperatures occurring in the continuous arcing operation. Recrystallization of the silver, and consequent deterioration, is resisted, so that erosion in the presence of the fuel vapors is substantially avoided. Even at 850° C. and more, the silver retains a fine crystal structure, characteristic of cold worked fine silver at lower temperatures. The tensile strength and hardness of the electrode material are far greater than the tensile strength and hardness of silver as such at such elevated temperatures. For instance, referring to the specific example hereinabove stated, the wire when annealed at 0.060 inch for 30 minutes at 550° F. shows a Rockwell hardness of 15 T 40 against a Rockwell hardness of 15 T 30 for regular fine silver, that is the silver of our electrode has a hardness one-third greater at such temperature than fine silver.

One interesting characteristic of the electrodes of the invention is their uniformity of wear, or erosion, as distinguished from the irregular erosion of other types of electrodes. In the conventional nickel alloy sparkplug electrode used in automotive internal combustion engines, such as 95% nickel alloy electrodes, the center electrodes are eroded faster at the corners, leaving a conically shaped end. In the electrodes of the invention, the wear across the end of the electrode is uniform and the customary initially flat surface of the center electrode is maintained substantially uniform, so that the initial configuration is retained intact, thus contributing further to increased life and efficient operation of these electrodes.

Sparkplug electrodes, i. e. the center electrode as well as the earthed side electrode or electrodes, in accordance with our invention, exhibit a much longer useful life than like electrodes of regular silver. They possess the low electrical resistivity and high resistance to oxidation and corrosion which are characteristic of fine silver but also possess fine crystal grain structure and great hardness and strength at elevated temperatures, characteristics not heretofore exhibited by silver sparkplug electrodes. The electrodes are thus more efficient and long lived and, furthermore, are capable of being cleaned by the customary sand blasting method. The additional favorable properties thus possessed by sparkplug electrodes in accordance with this invention make it possible to utilize such silver sparkplug electrodes where heretofore it was thought impossible to use such electrodes.

The invention is, of course, applicable to electrodes of alloys of silver, i. e. alloys containing a major proportion of silver and a minor proportion of other suitable alloying elements which may be taken from the group of precious metals, for instance gold or platinum group metals, e. g. platinum, palladium and ruthenium or the like, or from the group of base metals, for instance copper, although, in general, the admixtures of such other alloying elements should not exceed about 20% of the silver content. The term "silver" as used in the appended claims shall include such silver alloys, and the term "refractory oxide" as used in the appended claims shall mean one or more refractory oxides.

While the electrode consisting of the sintered mixture will normally be of wire or the like composed in its entirety of the mixture specified, we do mean to include also structures in which the arcing surface body is composed of such mixtures or where the compacted heated mixture of silver and refractory oxide described forms the core of the electrode surrounded by an integral shell of silver, or other suitable metal.

What we claim is:

1. A spark plug comprising a pair of electrodes electrically insulated from each other and at least one electrode formed of a compacted heated

mixture of silver and refractory oxide, the constituents being initially in finely divided condition, wherein the refractory oxide is distributed throughout the body of said silver along the grain boundaries of the crystals thereof, said refractory oxide constituting from 0.01% to 1.5% of said mixture.

2. A spark plug comprising a pair of electrodes electrically insulated from each other and formed of a sintered material of silver and thorium oxide, the constituents being initially in finely divided condition wherein said thorium oxide is distributed throughout the body of said silver along the grain boundaries of the crystals thereof, said thorium oxide constituting from 0.01% to 10% of said material.

3. A spark plug comprising a pair of electrodes electrically insulated from each other and formed of a sintered material of silver and aluminum

oxide, the constituents being initially in finely divided condition wherein said aluminum oxide is distributed throughout the body of said silver along the grain boundaries of the crystals thereof, said aluminum oxide constituting from 0.01% to 10% of said material.

MAX JOSEPH STUMBOCK.
ROSS BAYES.

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