United States Patent [19]

Weber

[11] **3,753,795**

[45] **Aug. 21, 1973**

[54] **SPARK PLUG ELECTRODE**

[75] Inventor: **John Herbert Weber,** Sloatsburg, N.Y.

[73] Assignee: **Westinghouse Electric Corporation,** Pittsburgh, Pa.

[22] Filed: **Aug. 2, 1971**

[21] Appl. No.: **168,364**

[52] **U.S. Cl.** **148/32,** 75/170, 75/171

[51] **Int. Cl.** **C22c 19/00**

[58] **Field of Search** ..... 75/170, 171, 128 R, 75/128 E; 148/32

[56] **References Cited**

UNITED STATES PATENTS

3,397,979	8/1968	Regester	75/170
2,071,645	2/1937	McNeil	75/170
3,323,911	6/1967	Inoue	75/128 R
3,370,942	2/1968	Inoue	75/170

Primary Examiner—Richard O. Dean

Attorney—Maurice L. Pinel

[57] **ABSTRACT**

A spark plug electrode is made of a dispersion-strengthened nickel alloy containing small amounts of aluminum and, optionally, chromium.

8 Claims, No Drawings

SPARK PLUG ELECTRODE

The present invention is directed to dispersion-strengthened nickel alloy materials for use as spark plug electrodes.

It has long been recognized that the metallic material employed as the electrodes in spark plugs used in internal combustion engines has presented a difficult metallurgical problem. It is also known that satisfactory performance of electrode material in a spark plug is a major factor in satisfactory performance of the plug in the engine and is a critical factor not only in relation to the useful life of the spark plug itself, but also with relation to satisfactory performance of the engine. In spark plugs which are subjected to exceptionally severe service, for example, in aircraft engines of high power output and even in some racing car engines, the use of platinum and platinum alloys in the electrodes has been advocated. Because of the high cost of platinum and its alloys, this solution is not available in relation to spark plugs which are used in most automotive engines. Generally speaking, present-day automotive spark plugs employ electrodes made of high-nickel alloys such as an alloy containing about 2 percent manganese, about 2 percent chromium, balance nickel or a nickel-chromium-iron alloy containing about 32.5 percent nickel, about 21 percent chromium, balance essentially iron.

In service, spark plug electrodes are subjected to a severe combination of conditions including spark erosion, attack due to the corrosive conditions existing within the engine cylinder, elevated temperatures and attack due to the presence of lead compounds in gasoline as well as other additives inserted in the gasoline. Electrode alloys are required to have relatively high thermal conductivity so as to prevent melting of electrode. Even if the conductivity of the alloy is sufficiently high to prevent actual melting, alloys having lower conductivity operate at higher temperatures due to the resistance to the passage of electricity therethrough, thereby accentuating the effects of spark erosion and the oxidation corrosion factors. It is considered that the maximum tolerable resistivity for candidate electrode materials is about 50 to 60 microhm-centimeters. It is desirable to provide alloys having resistivity of a lower level so as to provide for cooler operating temperatures at the electrode especially at the electrode tips.

The severe environment in which the electrodes must operate necessitates high corrosion resistance for candidate materials. Lead, halogens, sulfur, and vanadium in commercial fuels provide the major corrosive agents in the form of lead sulfides, halides, sulfates, and vanadium pentoxide. Depending upon engine temperatures these corrosive compounds may exist as solids, liquids, or gases; the most severe corrosion occurs when the electrodes are in contact with liquid corrosive media.

The presence of air mixed with the fuel produces an oxidizing environment. Electrode materials must have good oxidation resistance, especially under thermal cycling conditions. Another criterion is that any oxide scale formed on the electrodes should not cause significant change in the sparking characteristics. Hence, the desired oxidation behavior for an electrode is to form an adherent oxide scale which does not inhibit sparking.

The conditions encountered in spark plug electrodes represent a severe combination of factors which are destructive to metal integrity in service. Accordingly, the provision of spark plug electrode materials which will operate satisfactorily in the engine environment is not a matter of ready predictability.

With the advent of the mechanical alloying process as described, for example, in the Benjamin U.S. Pat. No. 3,591,362, it appeared that a new way had become available whereby spark plug electrode materials having satisfactory properties could be prepared. Thus, the Benjamin procedure affords a way whereby metallic material such as nickel-base alloys may be provided with an extremely finely divided and well-distributed inert dispersoid together with desired alloying elements in controlled amounts, which alloying elements are extremely difficult to incorporate in nickel or nickel-base alloys by any other means, including powder metallurgy.

The present invention is directed to the provision of special nickel alloy materials by mechanical alloying which may be employed as spark plug electrode materials.

Generally, the invention comprises providing through the mechanical alloying route dispersion-strengthened nickel alloy compositions containing, by weight, about 0.1 percent to about 2.5 percent aluminum, up to about 6 percent chromium, up to about 0.5 percent titanium, up to about 0.1 percent carbon, up to about 1 percent of a metal from the group consisting of yttrium and Rare Earth metals, at least about 0.3 volume percent and up to about 2.25 or 2.5 volume percent of a finely divided, well-distributed dispersoid oxide having a particle size of about 100 to about 1000 Angstroms from the group consisting of yttria, Rare Earth oxides, ceria and thoria. Preferably the dispersoid is yttria having a particle size to about 200 to about 500 Angstroms present in the amount of about 0.3 percent to about 2.25 percent by volume. Especially preferred compositions from the standpoints of wire drawability and resistance to cyclic oxidation contain about 0.1 percent to about 1.5 percent aluminum, up to about 4 percent chromium, and about 0.4 volume percent to about 1 volume percent yttria and the balance essentially nickel.

The special compositions are prepared by the mechanical alloying route to provide hard dense composite powders containing within each powder particle essentially the desired composition and having a particle size sufficiently coarse to resist atmospheric contamination upon exposure. Once the powder is produced it is readily converted into wire by hot compacting, for example, by hot extrusion, followed by high reduction, e.g., rolling to wire bar and hot or cold wire drawing. The material draws readily with reductions of up to 50 percent or 60 percent being readily accomplished between intermediate anneals. Intermediate anneals at temperatures in the range of about 1,800° F. to 2,100° F. for times of about 1/2 to about 1 hour may be employed as needed when cold drawing is used for wire production.

The powder may initially be prepared by mechanical alloying, i.e., a high energy dry milling process performed in a mill, such as the attritor mill or other high energy mill as described in the aforementioned Benjamin patent, provided with a grinding medium charge, e.g., balls of steel, nickel or other material. Ball-to-

powder ratios above 10 to 1 by volume preferably are employed with milling times usually exceeding about 10 hours and up to about 40 hours depending upon the size of the mill. The mill may be operated using a sealed air atmosphere although other atmospheres such as nitrogen and nitrogen-air mixtures may be employed. Raw materials employed for the mechanical alloying operation preferably include fine carbonyl nickel powder having a size range of about 4 to about 7 microns. Aluminum may be introduced into the initial powder mixture as a nickel-aluminum master alloy powder containing about 32 percent to about 46 percent aluminum. Chromium powder of high purity and having a particle size not exceeding about 200 mesh may be employed. Other desired ingredients, e.g., titanium, yttrium, cerium, mischmetal, etc., in the initial powder mix may be added directly or as master alloy powders. The powder mix is milled for a time sufficient to produce in the powder product a hardness of substantially the saturation hardness for the material. In so doing, material from the starting powders is fragmented or comminuted and by a combination of repeated comminuting and welding factors are formed into new composite powder products comprising fragments of initial starting materials bonded or welded into the form of dense metal particles wherein the dimensions across fragments of the original materials present in the composite powders becomes shorter and shorter as milling proceeds. It appears that the surface of the metal balls is the major site of the processing as material is welded to the ball surfaces and is broken away again under the influence of the milling energy in the dry environment. Properly processed powder has an internal structure which is so finely dispersed that at 250 diameters in the optical microscope it is found that little evidence of individual phases remains. In this way also, the dimension between individual particles of the hard oxide phase added to the initial powder mix becomes more and more closely spaced, e.g., with interparticle spacings of less than 2 microns, preferably less than 1 micron, or even less, e.g., 0.5 microns. The dispersoid particles themselves may be added in powder form directly to the powder mix as fine powders having a dimension not exceeding about 1,000 Angstroms. In the case of yttria, very fine material can be produced by the calcination of yttrium oxalate. It is to be appreciated that when a sealed air atmosphere is employed in the attritor, some pick-up of oxygen from the atmosphere will occur in the product powder. Thus, oxygen contents as high as about 1 percent in the product powder may result. This oxygen may be employed to produce a part or all of the required oxide dispersoid in the consolidated material produced from the powder by internal oxidation with reactive metallic elements present in the product powder, including, for example, aluminum, titanium, yttrium, cerium, or other Rare Earth metals, etc. If desired, for purposes of adjusting the total oxygen content of a product powder so as to conduct internal oxidation with the consolidated material to a desired extent, oxygen as a readily decomposable oxide, for example, nickel oxide, may be introduced in small controlled amounts into the initial mix. The short spacings created in the product powder during the mechanical alloying operation insure short distances for diffusion so that the oxygen atoms and reactive metal atoms, e.g., aluminum, yttrium, etc., can react readily in the solid matrix so as to produce an extremely finely divided dispersoid.

The powder is preferably consolidated by hot extrusion. For this purpose, the product powder can be canned in a metal can made of a metal such as mild steel or nickel and welded shut. Evacuation of the can is unnecessary. The can containing the metal powder is heated to a temperature within the range of about 1,800° F. to about 2,100° F. and extruded at an extrusion ratio between about 6 to 1 and 30 to 1 to form a consolidated bar. The can material can be moved from the extruded bar by conventional means such as pickling and the bar can then be converted to wire by conventional means.

In alloys provided in accordance with the invention, the particularly significant elements from the standpoint of oxidation resistance, including cyclic oxidation resistance, are aluminum and chromium. The amounts of these elements are correlated to the amount of dispersoid employed so as to insure drawability of the alloy. Preferably, at least about 0.1 percent aluminum is present. The aluminum content should not exceed about 2.5 percent in the interest of good cold drawability of the alloy. The chromium content does not exceed about 6 percent as otherwise the resistivity of the alloy becomes undesirably high. For alloys containing about 1.5 percent to 2.25 percent, by volume, of a refractory oxide dispersoid, chromium and aluminum should be limited to up to about 1.5 percent and up to about 0.75 percent respectively in the interest of cold drawability. When 6 percent chromium is present, the dispersoid content, e.g., yttria, should not exceed about 1 percent, by volume, in the interest of cold drawability. Carbon is not intentionally added and preferably is as low as possible to avoid deleterious effects, e.g., in relation to drawability. Since carbon in small amounts may be present in raw material powders, titanium in small amounts may be employed to fix the carbon as a carbide. The oxidation resistance of the alloy appears to be improved by retaining a small amount of a metal such as cerium or yttrium in solid solution in the alloy.

In order to show those skilled in the art the special advantages provided in accordance with the invention, the following examples are given.

EXAMPLE I

A 4.5 kilogram charge comprising carbonyl nickel powder and 0.6 parts by weight of fine yttria derived from the calcination of yttrium oxalate were charged to a 4 gallon horizontal attrition mill provided with a horizontal shaft equipped with agitator arms extending therefrom to pass through the charge and charged with 200 pounds of nickel balls with an average diameter of about 3/8 inch. The mill was run for 16 hours in a sealed air atmosphere with the agitator shaft operating at 225 rpm. The powder produced was screened through -45 mesh and sealed in a mild steel extrusion can. The resulting billet was heated to 1,950° F. and extruded at an extrusion ratio of 21.8 to 1. The resulting extruded bar stock was pickled to remove the steel can material and was drawn from an initial diameter of 0.555 inches to a final diameter of 0.093 inches. For intermediate anneals with the first being conducted at 1,900° F. and the last three being conducted at 2,000° F. each for one hour were performed during the drawing operation. The reductions before each anneal were respectively, 61.5, 64.5, 54.3 and 54.5 percent with a total reduction of 97.2 percent being accomplished. The example shows that the foregoing alloy in accor-

dance with the invention, which contained 0.34 percent aluminum, 0.32 percent titanium, 0.077 percent carbon, 3.8 percent chromium, and 0.8 percent yttria, by volume, having an average particle size of 250 Angstroms, the balance essentially nickel, was readily convertible to wire using conventional techniques. The aluminum, titanium and chromium were picked-up from the previous run in the mill.

EXAMPLE II

A 10 kilogram powder batch proportioned to provide powder nominally containing 0.12 percent aluminum, 0.24 percent titanium, 0.06 percent carbon, 2.5 percent thoria, by volume, with the balance essentially nickel comprising carbonyl nickel powder and master alloys to introduce the aluminum and titanium was charged to a 10 gallon vertical attritor mill containing 375 pounds of nickel balls of approximately 3/8 inch diameter and was milled in a sealed air atmosphere for 24 hours with the impeller operating at 132 rpm. The powder thus produced was screened to -45 mesh and sealed in a mild steel extrusion can. The can was extruded at 1,950° F. using an extrusion ratio of 16 to 1. Bar stock from this extrusion was drawn to wire by hot swaging followed by alternate drawing and annealing. It appeared that the swaging improved drawability slightly. The swaged bar which was 0.43 inches in diameter reduced from an initial diameter of 0.65 inches was then drawn to 0.093 inch diameter wire with five intermediate anneals. Reductions of 36, 34.9, 31.6, 45.1, 45.9, and 45 percent were accomplished after each anneal at 1,900° F. for one hour. A total reduction of 97.8 percent was accomplished. It was found that the drawing of this wire was limited to about 45 percent between anneals due to the dispersoid level in the alloy.

EXAMPLE III

The electrical resistivity of a number of dispersion-strengthened wires produced in accordance with procedures such as those set forth in Examples I and II were determined together with the resistivity for high purity nickel and for a nickel alloy containing 2 percent manganese and 2 percent chromium which contain no dispersoid. The compositions and resistivities of the materials are set forth in the following Table I.

TABLE I.—ELECTRICAL RESISTIVITY AT ROOM TEMPERATURE

Alloy No.	Composition (Weight Percent)* Percent				Percent (vol.)		Resistivity (micro-ohm cm.)
	Al	Ti	C	Cr	Y_2O_3	ThO_2	
1	.12	.24	.06			2.50	24.4
2	.16	.35	.062	.34		2.18	9.4
3	.0005	.13	.048	1.2	1.95		22.0
4	.52	.51	.075	6.1	0.90		48.9
5	.34	.32	.077	3.8	0.80		35.8
A**				1.6			27.8
Nickel							7-8

*Balance of alloy is essentially nickel.
**Alloy A also contained 1.9% manganese.

EXAMPLE IV

Material produced in accordance with Example II, (Alloy No. 1), together with material similarly produced and containing 0.03 percent aluminum, 0.22 percent titanium, 0.044 percent carbon, 1.91 percent chromium and 2.25 percent yttria, by volume, with the balance essentially nickel (Alloy No. 6) were subjected to a cyclic oxidation test together with material of similar dimension made of high purity nickel and made from commercially available TD nickel. The test atmosphere was air containing 5 percent water vapor and the test temperature was 900° C. The test comprised 10 cycles of 100 hours each at temperature followed by an air cool. At the conclusion of the test, samples were descaled abrasively using fine alumina powder, and were checked for weight loss with the results set forth in the following Table II.

TABLE II

Alloy No.	Descaled Wt. Loss (mg/cm^2)
High Purity Nickel	−96
TD Nickel	−157
1	−125
6	−56

It was surprisingly found that the yttriated material (Alloy No. 6) exhibited superior cyclic oxidation resistance to the thoriated material. It was also found that the Alloy No. 1 material containing thoria and small amounts of aluminum and titanium exhibited a lower weight loss than did the commercial TD nickel material which is thoriated nickel containing the same thoria content.

Although the present invention has been described in conjunction with preferred embodiments, it is to be understood that modifications and variations may be resorted to without departing from the spirit and scope of the invention, as those skilled in the art will readily understand. Such modifications and variations are considered to be within the purview and scope of the invention and appended claims.

I claim:

1. A spark plug electrode made of an oxide dispersion-strengthened, corrosion resistant, nickel-base alloy, characterized by a good combination of (a) spark erosion resistance, (b) high thermal conductivity, (c) oxidation resistance under cyclic conditions and (d) cold drawability, said alloy consisting essentially, by weight, of aluminum in an amount of about 0.1 percent with its upper limit not exceeding about 2.5 percent for purposes of cold drawability, up to about 6 percent chromium, up to about 0.5 percent titanium, up to about 0.1 percent carbon, up to about 1 percent of a metal from the group consisting of yttrium and Rare Earth metal and the balance essentially nickel.

2. A spark plug electrode in accordance with claim 1 wherein the dispersoid is a refractory oxide selected from the group consisting of yttria, Rare Earth oxides, ceria and thoria in an amount of about 0.3 percent to about 2.5 percent, by volume, said alloy being characterized in that when the volume of refractory dispersoid is within the range of 1.25 to 2.25 percent, the aluminum and chromium are controlled so as not to exceed about 0.75 percent and 1.5 percent, respectively.

3. A spark plug electrode in accordance with claim 2 wherein the alloy is produced by mechanical alloying

and the said dispersoid has a particle size of about 100 to about 1000 Angstroms.

4. A spark plug electrode in accordance with claim **2** wherein the alloy contains about 0.1 percent to about 1.5 percent aluminum, up to about 4 percent chromium, and about 0.4 volume percent to about 1 volume percent of yttria dispersoid.

5. An oxide dispersion-strengthened corrosion resistant nickel-base alloy characterized by a good combination of (a) spark erosion resistance, (b) high thermal condictivity, (c) oxidation resistance under cyclic conditions and (d) cold drawability, said alloy consisting essentially of, by weight, aluminum in an amount of about 0.1 percent with the upper limit not exceeding about 2.5 percent for purposes of good cold drawability, up to about 6 percent chromium, up to about 0.5 percent titanium, up to about 0.1 percent carbon, up to about 1 percent of a metal from ghe group consisting of yttrium and Rare Earth metal and the balance essentially nickel.

6. An alloy according to claim **5** wherein the dispersoid is a refractory oxide selected from the group consisting of yttria, Rare Earth oxides, ceria and thoria in an amount of about 0.3 percent to about 2.5 percent, by volume, said alloy being characterized in that when the volume of refractory dispersoid is within the range of 1.25 to 2.25 percent, the aluminum and chromium are controlled so as not to exceed about 0.75 percent and 1.5 percent, respectively.

7. An alloy according to claim **6** wherein the alloy is produced by mechanical alloying and the said dispersoid has a particle size of about 100 to about 1000 Angstroms.

8. An alloy according to claim **6** wherein the alloy contains about 0.1 percent to about 1.5 percent aluminum, up to about 4 percent chromium, and about 0.4 volume percent to about 1 volume percent of yttria dispersoid.

* * * * *

PO-1050
(5/69)

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,753,795 Dated August 21, 1973

Inventor(s) JOHN HERBERT WEBER

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

After "Assignee:" delete "Westinghouse Electric Corporation, Pittsburgh, Pa." and insert "The International Nickel Company, Inc., New York, N.Y."

Column 4, line 9, for "moved" read "removed"

Column 4, line 60, for "For" read "Four"

Claim 5, line 11, for "ghe" read "the"

Signed and sealed this 2nd day of July 1974.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents