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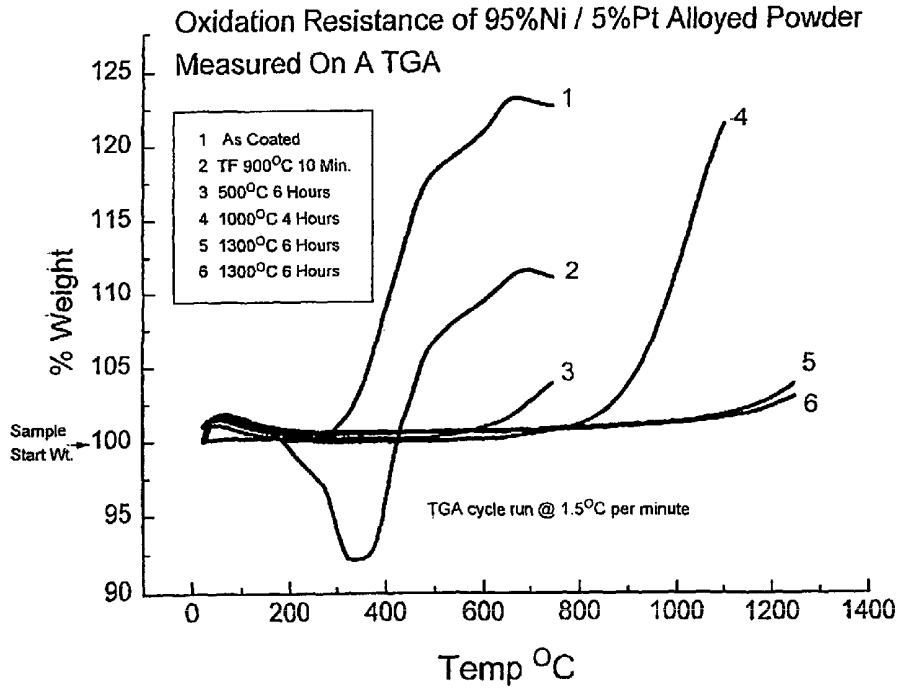
(54) **Title:** METHOD OF SUPPRESSING THE OXIDATION CHARACTERISTICS OF NICKEL



(57) **Abstract:** A method of providing a resistance to oxidation of Nickel at high temperatures by combining Ni powder with five percent Pt resinate, and heating the same to a temperature of 500 °C to 1300 °C. Electro-conductive components serving as electrodes and the like comprise a Ni/Pt powder subjected to temperature of between 500 °C and the respective melting points of Ni and Pt.

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For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

TITLE: METHOD OF SUPPRESSING THE OXIDATION CHARACTERISTICS OF NICKEL

BACKGROUND OF THE INVENTION

One of the major problems for using nickel (Ni) in an air firing ceramic system in the capacitor industry is that this element will oxidize, before the ceramic components in the system have matured, to form a multilayer capacitor consisting of alternating layers of Ni as the conductive plates to form a capacitor. This resultant Ni oxidation can stress the capacitor during the heating cycle, which creates physical defects, such as cracks in the ceramic body. One way to overcome this, which has become very well known in the industry is to use a ceramic capacitor system, which can be fired under an inert or reducing atmosphere, thus not allowing the Ni to oxidize through the thermal processing. Unfortunately, this requires the use of reduction resistant ceramics dielectric materials that are typically formulated with expensive high purity oxides and carbonates. Furthermore the firing process requires expensive kilns with very critical controls for gas flow.

It has been known in various literatures that platinum (Pt) has the capability to suppress oxidation on various metals. It has also been known that Pt suppresses the oxidation characteristics on palladium (Pd). Heretofore, Pt has not been used to suppress the oxidation characteristics of Ni.

It is therefore a principal object of this invention to provide a method for suppressing the high temperature oxidation resistance of Ni through the use of Pt.

A further object of the invention is to produce an alloy of Ni powder and Pt resinate wherein the two ingredients are heated to a temperature of between 500°C and the respective melting points thereof to create an Ni/Pt alloy.

These and other objects will be apparent to those skilled in the art.

SUMMARY OF THE INVENTION

A method of providing a resistance to oxidation of Ni at high temperatures by combining Ni powder with five percent Pt resinate, and heating the same to a temperature of 500°C to the respective melting points of Ni and Pt to create a Ni/Pt alloy. Electro-conductive components serving as electrodes and the like comprise an Ni/Pt alloy created by subjecting the above components to the above temperature range.

DESCRIPTION OF THE DRAWING

Fig. 1 is a graph showing the oxidation of Ni Powder (95%) mixed with (5%) by weight of Pt and subjected to various concentrations of heat.

DESCRIPTION OF THE PREFERRED EMBODIMENT

An experiment was conducted with coating a Ni powder using a Pt resinate. Ten grams of Ni powder and Pt resinate (liquid) which when reduced to pure metal would be 5% of the total metal sample weight, were milled in a glass jar with a ZrO_2 media in alcohol. The sample was dried and screened through a 100 mesh sieve. One gram of Ni/Pt powder was mixed with one gram of electrode medium to form a paste, which was painted onto an Al_2O_3 substrate.

The Al_2O_3 substrate, with the Ni/Pt sample painted thereon, was heat treated through a nitrogen atmosphere thick film firing furnace, using a 900°C peak temperature profile, under the nitrogen atmosphere so that the sample would not oxidize during the cycle. The resulting Ni/Pt alloy was then removed from the substrate and tested with the DTA/TGA along with the control Ni/Pt alloy, to measure it's oxidation resistance. No difference in the oxidation characteristic of the control Ni/Pt alloy and this quick heat treated alloy was seen.

It should be understood that the use of Pt resinate (a liquid) was used as a convenience. Pt powder in the same proportions can be mixed with Ni powder and then heat treated as described herein to achieve the same

resulting alloy. Several samples of this Ni/Pt powder were prepared in the manner described above and heat treated at various different temperature and time to determine if this system might require more heat energy to allow the Pt to alloy with the Ni. The heat treatment profiles were as follows: 500°C for 4 hours, 1000°C for 6 hours and 1300°C for 6 hours.

Each of the samples was heat treated in a high temperature nitrogen and form gas capable furnace, in an atmosphere of forming gas (1% hydrogen, balance nitrogen). The samples were tested with the DTA/TGA for oxidation characteristics. (See Fig. 1).

The 500°C heat treat sample clearly showed the Ni powder oxidation start point had shifted to 500°C. The oxidation point of the 1000°C heat treat samples shifted further to between 700°C and 800°C. The 1300°C heat treat samples performed even better, shifting the oxidation start point to over 1000°C. A repeat sample was prepared and heat treated at 1300°C and it performed similar to the previous run.

It was determined that the resistance to oxidation of the Ni was favorable from 500°C up to the melting points of Ni and Pt (which are approximately 1453 and 1772°C, respectively).

Fig. 1 shows 5 curves on a graph which show the oxidation rate of the 95/5% mixture of Ni and Pt subjected to different temperatures. The increase in weight is caused by the additional weight of NiO produced by the oxidation of the Ni.

This result has shown that Pt resinate mixed with Ni at 5% by weight of Pt resinate (or the same proportions of Ni and Pt powder), when heat treated properly is capable of suppressing the oxidation characteristics of Ni, so that it can function as air-fireable electrode, with significant cost savings. (The resulting alloy from a mixture of Ni and Pt resinate is comprised of Ni and Pt for the "resinate" is vaporized in the heating process.)

Aside from the capability for multilayer ceramic capacitor conductive plates or electrodes described above, other uses of the Ni/Pt combination are possible: As an air-fireable end termination for an electronic component which

requires metallization to make the component circuit broad mountable as a SMT (Surface Mount Technology) product; or as a thick film screen printable air-fireable conductor material. The production of the Ni/Pt alloy is the most significant aspect of this invention.

It is therefore seen that this invention will achieve its stated objectives.

What is claimed is:

1. An alloy comprised of Ni and Pt subjected to a heat treatment of between 500°C to the melting point of Pt.

2. The alloy of claim 1 wherein the alloy is produced by the heat treatment of Ni powder and Pt powder.

3. The alloy of claim 1 wherein the Ni and Pt are present in the proportions of 95% to 5% by weight, respectively.

4. The alloy of claim 2 wherein the Ni and Pt are present in the proportions of 95% to 5% by weight, respectively.

5. An alloy comprised of Ni powder and a Pt resinate subjected to a heat treatment of between 500°C to the respective melting points of the ingredients.

6. A method of suppressing the oxidation characteristics of nickel, comprising, combining Ni with Pt in a ratio of approximately 95% Ni powder and 5% Pt by weight, and heat treating the Ni/Pt mixture to a temperature of between 500°C and the melting point of Pt.

7. The method of claim 6 wherein the heat treating takes place in a nitrogen atmosphere.

8. The method of claim 6 wherein the heat treating atmosphere also comprises about 1% hydrogen.

9. A method of creating an air-fireable and termination element for electronic components which requires metallization, comprising, making an air-fireable end termination element from a combination of Ni powder with Pt

in a ratio of approximately 95% Ni powder and 5% Pt by weight, and heat treating the Ni/Pt mixture to a temperature of between 500°C and the melting point of Pt.

10. An air-fireable end termination element comprised of Ni and a Pt alloyed product heat treated to a temperature between 500°C and the melting point of Pt.

11. The device of claim 9 wherein the proportion by weight of Ni to Pt are approximately 95% - 5%, respectively.

12. An air-fireable conductor plate for capacitors comprised of Ni powder and Pt heat treated to a temperature between 500°C and the melting point of Pt.

13. The device of claim 12 wherein the proportion by weight of Ni to Pt is approximately 95% - 5%, respectively.

14. A thick film screen printable fireable conductor material comprised of Ni powder and Pt heat treated to a temperature between 500°C and the melting point of Pt.

15. The device of claim 14 wherein the proportion by weight of Ni to Pt are approximately 95% - 5%, respectively.

16. The method of making an alloy of Ni and Pt, comprising, combining Ni powder with Pt, subjecting the same to a temperature of 500°C to the melting point of Pt, to create an alloy of Ni and Pt.

17. The method of claim 16 wherein the Ni powder is mixed with the Pt in a ratio of 95-5%, respectively, by weight.

AMENDED CLAIMS

[received by the International Bureau on 12 February 2002 (12.02.02);
original claims 1-17 replaced by new claims 1-12 (2 pages)]

1. (Amended)

A method of creating an air-fireable end termination element for electronic components comprising:

making an air-fireable end termination element from a combination of Ni powder with Pt in a ratio of approximately 95 % Ni powder and 5 % Pt by weight, and

heat treating the Ni/Pt mixture to a temperature of between 500°C and the melting point of Pt.

2. (Amended)

An air-fireable end termination element comprised of a Ni and Pt alloyed product heat treated to a temperature between 500°C and the melting point of Pt.

3. (Amended)

The device of claim 2 wherein the proportion by weight of Ni to Pt is approximately 95 % - 5 %, respectively.

4. (Amended)

An air-fireable conductor plate for capacitors comprised of Ni powder and Pt heat treated to a temperature between 500°C and the melting point of Pt.

5. (Amended)

The device of claim 4 wherein the proportion by weight of Ni to Pt is approximately 95 % - 5 %, respectively.

6. (Amended)

A thick film screen printable fireable conductor material comprised of Ni powder and Pt heat treated to a temperature between 500°C and the melting point of Pt.

7. (Amended)

The device of claim 6 wherein the proportion by weight of Ni to Pt is approximately 95 % - 5 %, respectively.

8. (Amended)

An air-fireable capacitor comprising:

a first Ni and Pt conductive plate alloyed between 500°C and the melting point of Pt;

a ceramic dielectric; and

a second Ni and Pt conductive plate alloyed between 500°C and the melting point of Pt.

9. (Amended)

The capacitor of claim 8 wherein the proportion by weight of Ni to Pt is approximately 95 % - 5 %, respectively.

10. (Amended)

An air-fireable capacitor comprising:

a plurality of alternating layers of Ni and Pt conductive plates alloyed between 500°C and the melting point of Pt; and

a plurality of alternating layers of a ceramic dielectric.

11. (Amended)

The capacitor of claim 10 wherein the proportion by weight of Ni to Pt is approximately 95 % - 5 %, respectively.

12. (Amended)

A method of creating an air-fireable capacitor comprising:

(a) mixing Ni and Pt powders with an electrode medium to form a paste,

(b) painting the paste onto a ceramic dielectric, and

(c) firing in air from between 500°C and the melting point of Pt.

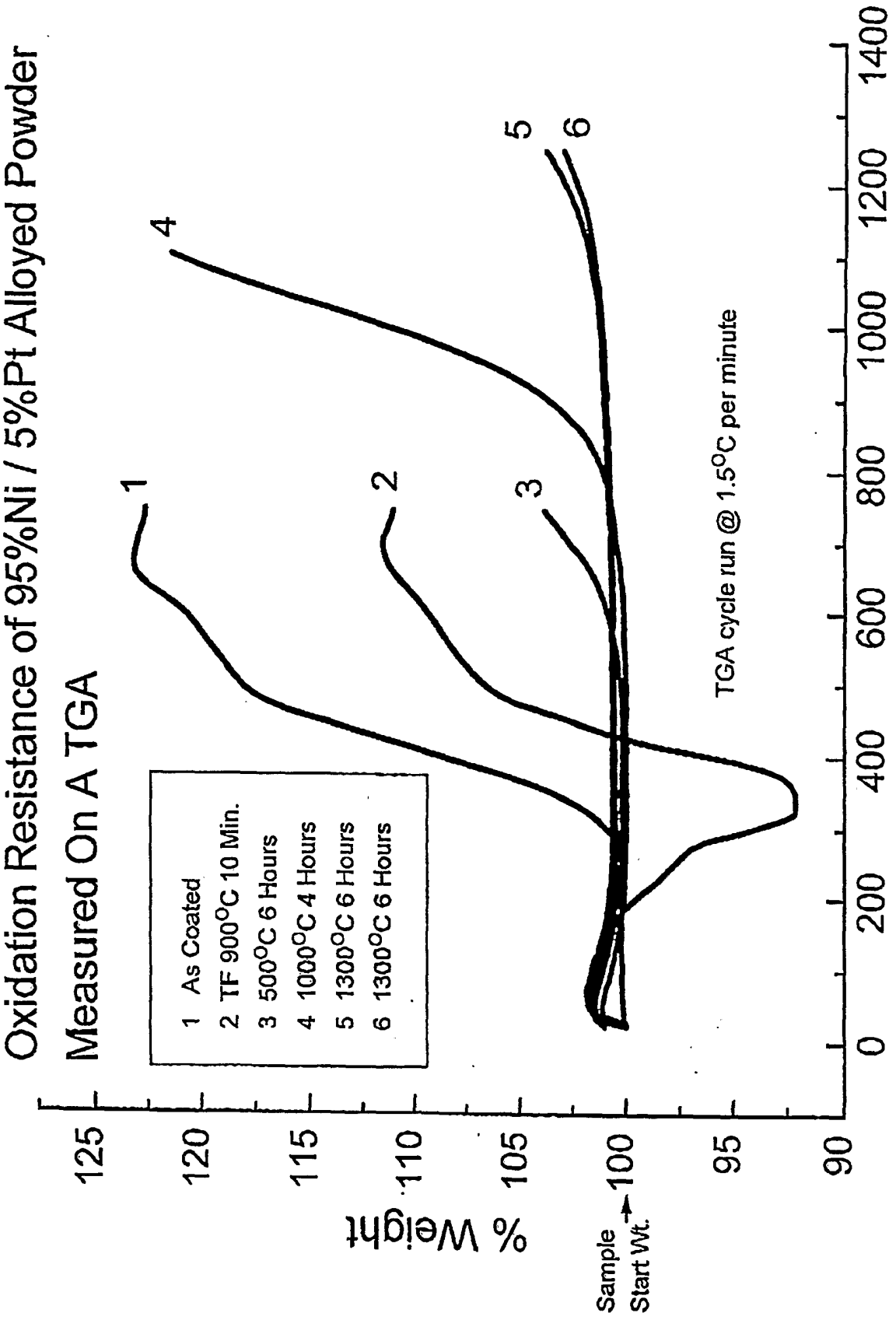
Oxidation Resistance of 95%Ni / 5%Pt Alloyed Powder
Measured On A TGA
1 As Coated
2 TF 900°C 10 Min.
3 500°C 6 Hours
4 1000°C 4 Hours
5 1300°C 6 Hours
6 1300°C 6 Hours
TGA cycle run @ 1.5°C per minute
% Weight
Sample Start Wt.
Temp °C
125
120
115
110
105
100
95
90
0
200
400
600
800
1000
1200
1400

FIG 1

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 01/10897

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C22C19/03 C22C1/04 H01G4/228

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 H01G C22C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
EPO-Internal, PAJ, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	GB 1 507 031 A (STANDARD TELEPHONES CABLES LTD) 12 April 1978 (1978-04-12) page 1, line 48 - line 91 ---	1,2,10
X	PATENT ABSTRACTS OF JAPAN vol. 016, no. 219 (C-0943), 22 May 1992 (1992-05-22) -& JP 04 041676 A (TANAKA KIKINZOKU KOGYO KK), 12 February 1992 (1992-02-12) abstract ---	1-8
X	PATENT ABSTRACTS OF JAPAN vol. 012, no. 242 (C-510), 8 July 1988 (1988-07-08) -& JP 63 033563 A (TANAKA KIKINZOKU KOGYO KK), 13 February 1988 (1988-02-13) abstract ---	1-5

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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
14 December 2001	20/12/2001

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31–70) 340–2040, Tx. 31 651 epo nl, Fax: (+31–70) 340–3016	Gregg, N

Form PCT/ISA/210 (second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 01/10897

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication,where appropriate, of the relevant passages	Relevant to claim No.
X	GB 2 242 203 A (JOHNSON MATTHEY PLC) 25 September 1991 (1991-09-25) example 2	1-5
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INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
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