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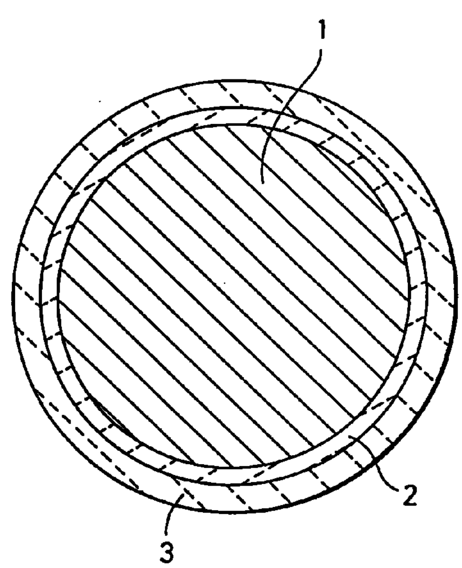
(54) Electrical conductor member such as a wire with an inorganic insulating coating

(57) An insulated electrical conductor wire has a conductor core (1, 11, 21, 31) containing Ni or Ni alloy at least in its outer surface, an oxide layer (2, 12, 22, 32) of Ni or Ni alloy formed by oxidation treatment of the outer surface of the conductor, and an insulating inorganic compound outer layer (3, 13, 23, 33) formed on the oxide layer of Ni or Ni alloy. The insulating inorganic outer layer is intimately bonded to the oxide layer and provides an improved heat resistance and insulability.

FIG. 1



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Description

BACKGROUND OF THE INVENTION

Field of the Invention

The present invention relates to an electrically conducting wire with an insulating coating made of an inorganic material. Such a wire is used for high temperature operating conditions, e.g. as an insulated lead wire or the like.

Description of the Background Art

An insulated conductor such as a wire or a member for a thermocouple is generally used in equipment such as heating equipment or fire alarm devices, which require safe operation at high operating temperatures. Such an insulated wire is also employed in an automobile in an environment which is heated to a high temperature. An insulated wire of this type is generally formed by a conductor which is coated with a heat-resistant organic resin such as polyimide, fluororesin or the like.

Such a resin-coated wire can merely withstand a temperature of about 300°C at the most. However, a wire which is employed in a high vacuum apparatus, for example, must have high heat resistance against baking, etc., a small emission characteristic as to absorbed gas and water for achieving and maintaining a high degree of vacuum, and a small emission of gases caused by thermal decomposition. It is impossible to satisfy such requirements for heat resistance and a non-outgassing property with a conventional wire which is coated with an organic material insulation.

When an insulated wire is used where a high heat resistance is required or in an environment requiring a high degree of vacuum, it is impossible to attain a sufficient heat resistance nor the required non-outgassing property with only an organic coating. In that case, therefore, an insulated wire is comprising a conductor which passes through an insulator tube of ceramics, an MI (mineral insulated) cable comprising a conductor which passes through a tube of a heat-resistant alloy, such as stainless steel alloy, that is filled with fine particles of a metal oxide such as magnesium oxide, or the like is generally used.

On the other hand, a glass braided tube insulated wire employing an insulating member of glass fiber fabric or the like is known as an insulated, heat resistant, flexible wire.

Further, wires coated with organic materials were studied. As a result, wires have been proposed, one of which is obtained by anodizing an aluminum (Aℓ) conductor for forming an Aℓ oxide layer on the outer wire surface, and another wire is obtained by mixing a frit prepared by mixing various metal oxides with each other and melting and pulverizing the as-obtained mixture for forming a slip, applying this slip to a metal conductor and heating and melting the same for forming a homogeneous composite metal oxide layer or coating on the wire surface.

However, the wire with an aluminum oxide layer is not suitable for use as a heat resistant wire since this technique is merely applicable to an aluminum conductor having a low melting point, while the as-formed film is so porous that the wire has an inferior moisture resistance and a low breakdown voltage.

On the other hand, the wire with a composite metal oxide coating is applicable to a metal conductor of copper (Cu) or nickel (Ni) having a higher heat resistance. In practice, however, this technique is merely applicable to a metal composite oxide whose melting point is lower by about 300 to 400°C than those of Cu and Ni since the metal composite oxide layer is formed through a melting process, and the heat resistance temperature is restricted below the just mentioned level. Further, the as-formed wire is inferior in flexibility since it is difficult to reduce the thickness of the film.

In the case of the MI cable, on the other hand, the overall diameter is increased as compared with the conductor diameter, leading to an inferior space factor. Thus, it is impossible to feed a high current.

In the glass braided tube insulated wire, further, fine glass powder is generated and the conductor is disadvantageously exposed due to mesh displacement.

SUMMARY OF THE INVENTION

It is an object of the present invention to provide an inorganic insulated member such as an electric conductor wire which has an excellent heat resistance and insulability.

The inorganic insulating member or electrical conductor wire according to the present invention comprises a conductor of Ni or Ni alloy, an oxide layer of an oxide of the Ni or Ni alloy on an outer surface of the conductor, said oxide layer being obtained by oxidizing the conductor in a vapor phase containing oxygen, and an oxide layer of aluminum (Aℓ) and/or silicon (Si) is provided on an outer surface of the oxide layer of Ni or Ni alloy.

According to the present invention, the oxide layer of Aℓ and/or Si is an oxide layer obtained by applying a solution prepared by hydrolyzing and polycondensing alkoxide of Aℓ and/or Si in a solvent, drying the same for allowing gelation, and thereafter heating the obtained gel.

According to the present invention, further, the oxide layer of Aℓ and/or Si has a melting point exceeding that of Ni or Ni alloy.

The inorganic insulated member according to the present invention is applied to or used as a heat resistant wire or an incombustible wire at a high temperature which does not permit using an organic insulating material, for example. However, the present invention is not restricted to such a wire, but is also applicable to another member such as a thermocouple.

The foregoing and other objects, features, aspects and advantages of the present invention will become more apparent from the following detailed description of the present invention when taken in conjunction with the accompanying drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a sectional view showing a first embodiment of the present invention with a nickel conductor core and two oxide layers;

Fig. 2 is a sectional view showing a second embodiment of the present invention with a nickel alloy core conductor and two oxide layers;

Fig. 3 is a sectional view showing a third embodiment of the present invention with a nickel core conductor and three oxide layers; and

Fig. 4 is a sectional view showing a fourth embodiment of the invention with a nickel alloy core conductor and two oxide layers.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

Fig. 1 shows an Ni core conductor 1 coated with an Ni oxide layer 2 formed around the core conductor. An Aℓ oxide layer 3 is formed around the Ni oxide layer 2. The formation of these oxide layers will be described in more detail below.

Fig. 2 shows a nickel alloy conductor 11 first coated with an Ni alloy oxide layer 12 formed around the Ni alloy conductor 11. An Si oxide layer 13 is formed around the Ni alloy oxide layer 12.

In Fig. 3 the nickel Ni core conductor 21 is first coated with an Ni oxide layer 22 formed around the Ni core conductor 21. An Si oxide layer 23 is formed around the Ni oxide layer 22. Then, an Aℓ oxide layer or Si oxide layer 24 is formed around the Si oxide layer 23.

In Fig. 4, a nickel alloy core conductor 31 is first coated with an Ni alloy oxide layer 32 formed around the Ni alloy core conductor 31. Then, an Aℓ-Si composite oxide layer 33 is formed around the Ni alloy oxide layer 32.

According to the present invention, a first oxide layer of Ni or an Ni alloy is first formed on an outer surface of a conductor of Ni or Ni alloy by oxidizing the conductor in a vapor phase containing oxygen. Then, a second oxide layer of Aℓ and/or Si is formed on the first oxide layer.

Ni or Ni alloy is an inactive metal which has an inferior affinity for a metal oxide of Aℓ or Si. When a surface of Ni or Ni alloy is directly coated with such an Aℓ or Si oxide, a rather poor adhesion is obtained and the coating is immediately separated from the Ni or Ni alloy. In order to solve this problem, the present invention teaches to first oxidize a core conductor of Ni or Ni alloy in a vapor phase containing oxygen, so as to form an oxide layer of Ni or Ni alloy. The so formed nickel oxide layer or Ni alloy oxide layer very strongly adheres to the surface of the Ni or Ni alloy. This strong bonding is due to the fact that the nickel oxide or the nickel alloy oxide has an excellent affinity for the nickel or nickel alloy. Additionally, the nickel or nickel alloy oxide has a strong affinity to aluminum oxide or silicon oxide and hence also strongly bonds to the outer layer of Aℓ or Si oxide and to the conductor core. According to the present invention, therefore, the oxide layer of Aℓ and/or Si is not separated for all practical purposes from the intermediate oxide layer, whereby an excellent flexibility is obtained when the inorganic insulating coating is applied to a wire forming a core conductor, for example.

According to the present invention, the oxide layer of Aℓ and/or Si is obtained by applying a solution prepared by hydrolyzing and polycondensing an alkoxide of Aℓ and/or Si in a solvent, drying the same for allowing gelation, and thereafter heating the so-obtained gel.

The Aℓ and/or Si oxide layer formed in the aforementioned manner has a melting point exceeding that of the Ni or Ni alloy. Additionally, the Aℓ and/or Si oxide layer is formed without any melting process.

Therefore, the critical temperature to which conductors or other members of the present invention with their inorganic insulating coatings may be exposed in operation is not restricted by the melting point of the oxide layer. Rather, the present insulating members can be heated to a temperature limited only by the melting point of the Ni core or the Ni alloy core.

Further, the oxide layer formed in the aforementioned manner has characteristics such as an extreme denseness, a smooth surface and a small adsorption of gases, e.g. steam or the like. Moreover, the present members have an excellent insulability and a high moisture resistance.

Preferred embodiments have been produced as two conductors C1 and C2 which were oxidized as follows.

(C1) An Ni wire of 0.5 mm is diameter consisting of at least 99.9 % by weight of Ni, the remainder being natural impurities was heated in the atmosphere at 950°C for 10 minutes, to form a nickel oxide layer on the surface of the wire.

(C2) An Ni alloy wire of 0.5 mm in diameter containing 15 % by weight of Cr was heated in the atmosphere at 850°C for 30 minutes, to form an oxide layer of Ni alloy on the wire surface.

The following coating solutions L1, L2 and L3 were prepared as follows:

(L1) A solution L1 was obtained by mixing tributoxy aluminum, triethanolamine, water, and isopropyl alcohol in mole ratios of 1:2:1:16. The mixture was hydrolyzed and polycondensed at 50°C for 1 hour while stirring the mixture.

(L2) A solution L2 was obtained by adding nitric acid to a mixed solution prepared by mixing tributyl orthosilicate, water, and isopropyl alcohol in mole ratios of 2:8:15 at a rate of 3/100 moles with respect to tetrabutyl orthosilicate. The mixture was hydrolyzed and polycondensed at 80°C for 2 hours while stirring the mixture.

(L3) A solution L3 was obtained by mixing the solutions L1 and L2 at a mass ratio of 80:20.

Example 1: An oxidized nickel conductor C1 was coated with the coating solution L1 and heated at 500°C for 10 minutes. The coating and heating was repeated 10 times, to form an Aℓ oxide layer of 4 µm thickness on the first nickel oxide layer.

Example 2: An oxidized nickel alloy conductor C2 was coated with the coating solution L2 and heated at 500°C for 10 minutes. The coating and heating was repeated 10 times, to form an Si oxide layer of 5 µm thickness on the first nickel alloy oxide layer.

Example 3: An oxidized nickel conductor C1 was coated with the coating solution L2 and heated at 500°C for 10 minutes.

The coating and heating was repeated 5 times to form an Si-oxide layer having a thickness of 2.5 µm. Then, a further coating operation was performed on the first formed Si-oxide layer, with the coating solution L1. The sample was again heated at 500°C for 10 minutes. The coating and heating was repeated 5 times to form an Aℓ oxide layer of 2 µm thickness on the first formed Si oxide layer of 2.5 µm thickness.

Example 4: An oxidized conductor C2 was coated with the coating solution L3 and heated at 500°C for 10 minutes. The coating and heating was repeated 10 times to form an Aℓ-Si composite oxide layer of 6 µm in thickness.

Comparative Example 1: An aluminum wire was anodized in a bath of sulfuric acid to form an Aℓ oxide layer of 10µm thickness on the aluminum surface.

Comparative Example 2: An oxidized conductor C2 was coated with a slip which was prepared by mixing a commercially available frit (composite oxide of Ba, Ca, Ti and Si: GSP220A552 sold by Toshiba Glass Co., Ltd.) with water. The wire coated with the slip was heated to 900°C to form a homogenous metal composite oxide layer of 100 µm thickness through a melted state.

All the coating operations were, for example, performed by dipping the wire into the respective coating solution.

Test Results

Example	Breakdown Voltage	Flexibility
1	500 V	6D
2	600 V	5D
3	800 V	8D
4	400 V	3D
Comparative Example 1	300 V	50D
Comparative Example 2	1200 V	1000D

The above Table shows the breakdown voltages and the flexibility values of the wires of Examples 1 to 4 of the invention and of the two Comparative Examples. The flexibility values were evaluated in terms of diameter ratios, by winding the wires on circular cylinders of a prescribed diameter D and measuring the minimum diameters causing no separation of the insulating inorganic compound coatings or layers from the conductor core. The diameter D was 0.5 mm.

The above Table shows that the wires of Examples 1 to 4 according to the present invention have a higher breakdown voltage than the first Comparative Example and a superior flexibility compared to both Comparative Examples. However, the second Comparative Example has a substantially higher breakdown voltage at the expense of being very stiff.

As hereinabove described, the inorganic insulating coating on a conductor wire according to the present invention forms an insulating inorganic compound layer which is well bonded to the conductor core and has an excellent heat resistance and insulability.

Although the present invention has been described and illustrated in detail, it is clearly understood that the same is by way of illustration and example only and is not to be taken by way of limitation, the spirit and scope of the present invention being limited only by the terms of the appended claims.

Claims

1. An insulated electrical conductor comprising a core conductor (1, 11, 21, 31) consisting essentially of a core material selected from the group consisting of Ni and Ni alloy, a first oxide layer (2, 12, 22, 32) consisting of an oxide of said core material formed on an outer surface of said core conductor (1, 11, 12, 21) by oxidizing said core conductor in a vapor phase containing oxygen, and a second oxide layer (3, 13, 23, 33) bonded to an outer surface of said first oxide layer, said second oxide layer consisting essentially of an inorganic insulating material selected from the group consisting of Aℓ-oxide and Si-oxide and combination thereof.

2. The insulated electrical conductor according to claim 1, wherein said second oxide layer (3, 13, 23, 33) has a melting temperature greater than of said core material (1, 11, 21, 31).

3. The insulated electrical conductor according to claim 1, further comprising a third oxide layer (24) on an outer surface of said second oxide layer (23), said third oxide layer (24) consisting essentially of a third oxide material selected from the group consisting of Aℓ-oxide and Si-oxide.

4. The insulated electrical conductor according to claim 3, wherein said third oxide layer (24) consists essentially of a different material than does said second oxide layer (23).

5. The insulated electrical conductor according to claim 4, wherein said third oxide layer (24) consists essentially of Aℓ-oxide and said second oxide layer (23) consists essentially of Si-oxide.

6. The insulated electrical conductor according to claim 1, wherein said core conductor (1, 11, 21, 31) consists of Ni and trace amounts of naturally occurring impurities.

7. The insulated electrical conductor according to claim 1, wherein said core conductor (1, 11, 21, 31) consists essentially of Ni and Cr.

8. The insulated electrical conductor according to claim 7, wherein said core conductor (1, 11, 21, 31) consists essentially of about 85 % Ni and about 15 % Cr.

9. A method of forming an insulated electrical conductor, comprising:

(a) preparing a core conductor (1, 11, 21, 31) of a core material selected from the group consisting of Ni and Ni alloy;
(b) forming a first oxide layer (2, 12, 22, 32) on an outer surface of said core conductor (1, 11, 21, 31) by oxidizing said core conductor in a vapor phase containing oxygen;
(c) preparing a coating solution by hydrolyzing and polycondensing an alkoxide of a member selected from the group consisting of Aℓ, Si and combinations thereof in a solvent;
(d) applying said coating solution onto said first oxide layer (2, 12, 22, 32);
(e) drying said coating solution for gelling the same; and
(f) heating said coating solution applied onto said first oxide layer (2, 12, 22, 32) to form a second oxide layer (3, 13, 23, 33) on said first oxide layer.

10. The method of claim 9, further comprising
repeating said steps (d) to (f) a plurality of times, whereby successive coating films of said coating solution are applied one on top of another to form said second oxide layer (3, 13, 23, 33).

11. The method of claim 9, wherein said step (f) does not involve a melting process.

12. The method of claim 9, further comprising preparing a second coating solution by hydrolyzing and polycondensing an alkoxide of a second member selected from said group consisting of $A\ell$, Si and combinations thereof in a solvent, applying said second coating solution onto said second oxide layer (23) and heating said second coating solution to form a third oxide layer (24) on said second oxide layer (23).

13. The method of claim 9, wherein said coating solution is prepared by forming a mixture of tributoxy aluminum, triethanolamine, water and isoppropyl alcohol, and then hydrolyzing and polycondensing said mixture.

14. The method of claim 13, wherein the respective mole ratio of said tributoxy aluminum, triethanolamine, water and isopropyl alcohol is 1:2:1:16, and said hydrolyzing and polycondensing is carried out at 50°C for 1 hour while stirring said mixture.

15. The method of claim 9, wherein said coating solution is prepared by forming a mixture of tributyl orthosilicate, water and isopropyl alcohol, adding nitric acid to said mixture, and then hydrolyzing and polycondensing said mixture with said nitric acid added thereto.

16. The method of claim 15, wherein the respective mole ratio of said tributyl orthosilicate, water and isopropyl alcohol is 2:8:15, said nitric acid is added at a rate of 3/100 moles with respect to tetrabutyl orthosilicate, and said hydrolyzing and polycondensing is carried out at 80°C for 2 hours while stirring said mixture.

17. The method of claim 9, wherein said heating step is carried out at about 500°C.

FIG. 1

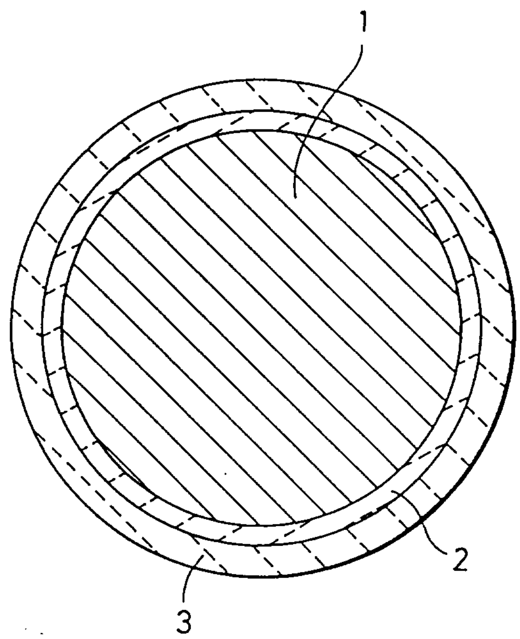


FIG. 2

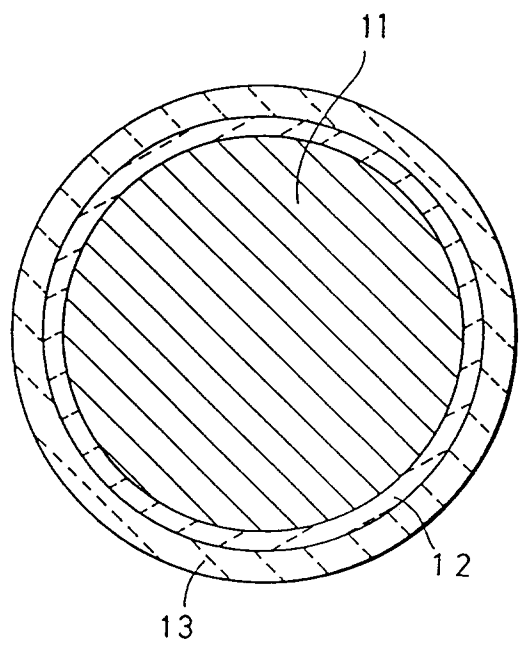


FIG. 3

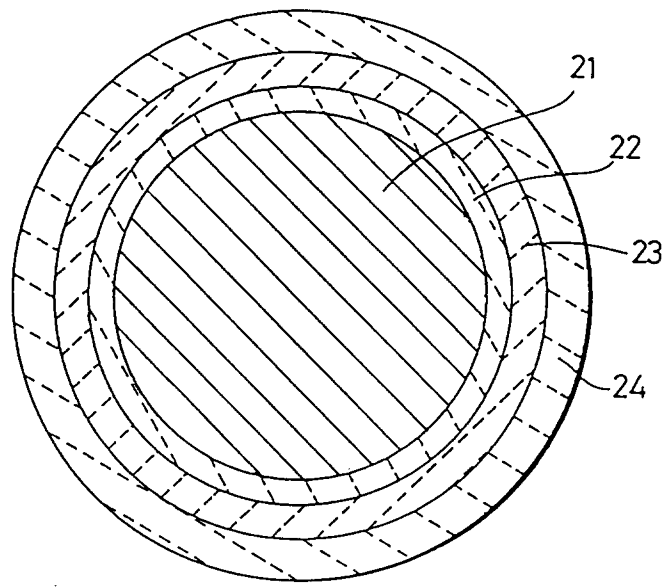
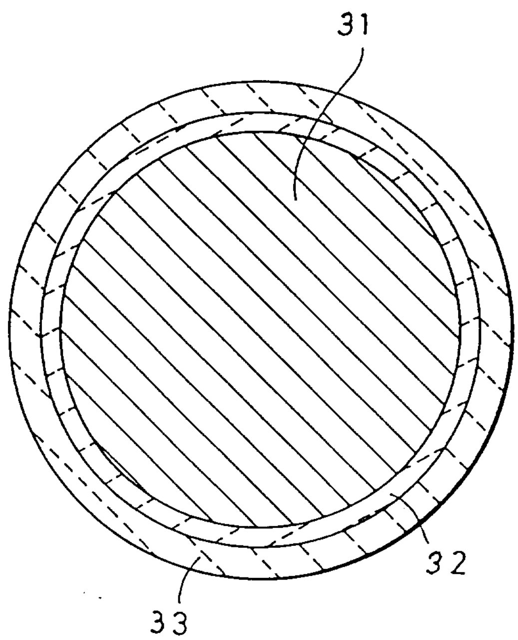


FIG. 4



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EUROPEAN SEARCH REPORT

Application Number
EP 95 10 2703

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.6)
A	EP-A-0 494 424 (SUMITOMO) * the whole document * ---	1-16	H01B7/34 H01B3/10
A	EP-A-0 416 131 (SUMITOMO) * the whole document * ---	1-16	
A	EP-A-0 292 780 (SUMITOMO) * the whole document * -----	1-16	
			TECHNICAL FIELDS SEARCHED (Int.Cl.6)
			H01B

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	28 July 1995	Drouot, M-C

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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