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(54) **INSULATED WIRE**

ISOLIERTER DRAHT
CABLE ISOLE

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(56) References cited:
EP-A- 0 292 780 **JP-A- 0 238 585**
JP-A- 2 123 618 **JP-A- 5 818 809**
JP-A- 53 136 009

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Description

Technical Field

[0001] The present invention relates to an insulated wire, and more particularly, it relates to an insulated wire, a fireproof wire or the like, which can be used under high-temperature or high-vacuum environment.

Background Art

[0002] In general, an insulated wire whose conductor is coated with heat resistant organic resin such as polyimide, fluororesin or the like has been employed in equipment such as heating equipment or a fire alarm, for which safety under a high temperature is required, or environment in an automobile, which is heated to a high temperature.

[0003] In general, further, an insulated wire whose conductor is passed through a ceramic insulator tube, or an MI cable (Mineral Insulated Cable) whose conductor is passed through a heat resistant alloy tube of a stainless steel alloy which is filled up with metal oxide particulates of magnesium oxide or the like, etc. has been employed in a case for which particularly high heat resistance is required or in environment for which a high degree of vacuum is required.

[0004] On the other hand, a fiber-glass braided insulated wire employing textile of glass fiber as an insulating member or the like can be mentioned as an insulated wire having flexibility, which can be used under high-temperature environment. As an insulated wire which is excellent in heat resistance, insulation and heat dissipativity, there exists the so-called alumite wire, which is prepared by anodizing a wire of an aluminum alloy.

[0005] Further, there has also been proposed an insulated wire which is prepared by employing a material such as a metal alkoxide or a metal organic acid salt, being changeable to a ceramics state, and forming a ceramics film around a conductor.

[0006] In the aforementioned insulated wire whose conductor is coated with heat resistant organic resin, a temperature under which insulation can be maintained is about 300°C at the most. Therefore, it has been impossible to apply such an insulated wire to a use for which insulation is required even under a higher temperature.

[0007] On the other hand, the aforementioned insulated wire whose conductor is passed through a ceramics insulator tube has had such a disadvantage that the same is inferior in flexibility although its insulation can be maintained under a high temperature. Further, although the aforementioned MI cable can maintain insulation under a high temperature and is flexible as compared with the aforementioned wire whose conductor is passed through a ceramics insulator tube, difficulty is caused when the same is bent with large

curvature.

[0008] Further, the aforementioned fiber-glass braided insulated wire can maintain insulation even under a high temperature, and is excellent in flexibility. However, it has been impossible to use this wire under environment for which a high degree of vacuum is required, since the same easily discharges dust.

[0009] On the other hand, the aforementioned alumite wire can maintain insulation even under a high temperature, and has some flexibility. However, application of the wire has been restricted since the conductor employed for the wire is restricted to aluminum alone.

[0010] As to the aforementioned insulated wire which is prepared by forming a ceramics layer around a conductor, further, the ceramics layer is mostly a single layer having a small layer thickness, and it has been difficult to increase the breakdown voltage, although the wire is excellent in flexibility.

[0011] Document D1, being JP 63-195 283, discloses an electric wire which comprises a conductor insulated by two ceramic layers. The coat according to the wire of D1 is prepared by a liquid phase (sol-gel process) step and a vapor phase step.

[0012] The first layer of the wire according to document D1 is formed of ceramics produced by a reaction of alkoxide. However, the thickness of the first layer specifically disclosed by D1 is 0.3 μm (Embodiment 1) and 0.5 μm (Embodiment 2). D1 does not disclose a wire with a thickness of the first layer which falls within the range from 1 to 10 μm.

[0013] D2 is directed to an electric wire which has a coating of a gel film which is formed by applying a solution obtained by hydrolyzing and dehydrating/condensing alkoxide onto an outer part of a conductor and thereafter leaving the same. The content of this document is specifically directed to forming a gel coat, and it is not an object of this document to form a highly adhesive ceramics coat.

Disclosure of the Invention

[0014] An object of the present invention is to solve the aforementioned problems of the conventional insulated wires, and to provide an insulated wire which has the following properties:

- (a) Capability of maintaining insulation even under a high temperature.
- (b) Superiority in flexibility.
- (c) No emission of gas.
- (d) Capability of employing various types of conductors.
- (e) Possession of a high breakdown voltage.

[0015] The object is solved by the features of claim 1 and 6.

[0016] The insulated wire according to the present invention comprises a conductor, a first insulating metal

oxide layer which is formed around the conductor, and a second insulating metal oxide layer, containing ceramics particles mixed by addition, which is formed around the first insulating metal oxide layer.

[0017] The first insulating metal oxide layer and/or the second insulating metal oxide layer can be formed by applying a precursor of a metal oxide containing at least one compound which is selected from a group of alkoxides or organic acid salts of Si, Zr, Al and Ti to the periphery of a conductor and changing the same to a ceramics state by heating, using a method such as a sol-gel method, a thermal decomposition method or the like.

[0018] A more preferable insulated wire is implemented if the ceramics particles contained in the second insulating metal oxide layer of the present invention are in the form of fine plates.

[0019] Further, an insulated wire having further superior flexibility is obtained when the layer thickness of the first insulating metal oxide layer is 5 to 10 μm .

[0020] In addition, it is also possible to provide an insulated wire comprising a protective coat, by coating the outer side of the second insulating metal oxide layer with an insulating material containing an organic material.

[0021] The conductor is not particularly restricted so far as the same has conductivity, and the configuration, the material etc. thereof may be selected in response to its application such as a thermocouple or a flexible printed circuit, for example.

[0022] Since the insulated wire according to the present invention comprises insulating layers of metal oxides having extremely high melting points around the conductor, it is possible to maintain insulation even under a high temperature, as compared with the conventional insulated wire which is coated with heat resistant organic resin.

[0023] Further, the insulated wire according to the present invention can be used also under high-vacuum environment, since the same emits no gas.

[0024] In the present invention, further, the insulating metal oxide layer can be increased in thickness since the ceramics particles are contained in the insulating metal oxide layer by addition, whereby it is possible to obtain an insulated wire having a high breakdown voltage.

[0025] It is difficult to increase the first insulating metal oxide layer in thickness, and an insulated wire which comprises only the first layer has a low breakdown voltage. However, since the first insulating metal oxide layer is in close contact with the conductor, it is excellent in flexibility and can maintain insulation even if the same is extremely deformed in bending or the like.

[0026] On the other hand, the second insulating metal oxide layer has high insulability since the same can be easily increased in thickness by applying a substance obtained by adding ceramics particles to a precursor of ceramics to the conductor and baking the

same. If this layer alone is formed around the conductor, however, it may not be possible to maintain good insulation due to fine cracks caused in the layer when the same is extremely deformed in bending or the like, since the layer is inferior in adhesion with the conductor as well as bonding property of particles within the layer to the first insulating metal oxide layer.

[0027] Therefore, the aforementioned first layer is formed around the conductor and the aforementioned second layer is further formed around the first layer, so that fine cracks, that may be caused in the second layer by extreme deformation resulting from bending or the like, are prevented by the first layer, and it is possible to maintain high insulability over the entire insulating layers.

[0028] When alkoxides or organic acid salts of Si, Zr, Al and Ti are employed as materials for the first and/or second insulating metal oxide layer, it is possible to form homogeneous insulating layer(s) by preparing a precursor of an oxide from these solutions using a method such as a sol-gel method or a thermal decomposition method, applying this precursor to the periphery of the conductor, and further carrying out baking.

[0029] Further, when the ceramics particles which are contained in the second insulating metal oxide layer by addition in advance of application are in the form of a fine plate, it is possible to obtain an insulated wire having a higher breakdown voltage.

[0030] Further, since the thickness of the first insulating metal oxide layer is 5 to 10 μm , it is possible to obtain an insulated wire having further superior flexibility.

[0031] In addition, it is also possible to use the wire as a fireproof wire by providing a protective coat which contains an organic material on the outer side of the second insulating metal oxide layer.

Brief Description of the Drawings

[0032] Fig. 1 is a sectional view of an insulated wire in which a first insulating silicon oxide layer of 5 μm in thickness and a second insulating metal oxide layer of 35 μm in thickness are formed around a nickel-plated copper wire of 1 mm in diameter according to the present invention.

[0033] Fig. 2 is a sectional view of an insulated wire which is obtained by coating three insulated wires shown in Fig. 1 with polyolefine resin mixed with magnesium hydroxide.

Best Modes for Carrying Out the Invention

Example 1

[0034] A nickel-plated copper wire of 1 mm in diameter was employed as a conductor.

[0035] 1 mole percent of nitric acid was added to a mixed solution of 4 mole percent of tetraethoxysilane,

24 mole percent of water and 71 mole percent of ethyl alcohol. This solution was applied to the aforementioned nickel-plated copper wire, and thereafter baking was continuously carried out at a temperature of 500°C, to form a first insulating silicon oxide layer of 5 µm in thickness.

[0036] Further, a substance, which was obtained by mixing 2 parts of mica of about 2 µm in mean particle diameter to 10 parts of a mixed solution of 4 mole percent of tetraethoxysilane, 1 mole percent of tetraethoxyzirconium, 1 mole percent of water and 94 mole percent of ethyl alcohol as ceramics particles, was applied to the periphery of the aforementioned first insulating silicon oxide layer, and thereafter baking was continuously carried out at a temperature of 600°C, to form a second insulating metal oxide layer of 35 µm in thickness.

[0037] Fig. 1 is a sectional view of an insulated wire formed by the aforementioned process.

[0038] A first insulating metal oxide layer 13 is formed around a conductor comprising a nickel-plated layer 12 which is formed around copper 11, and a second insulating metal oxide layer 14 containing ceramics particles is further formed around the same.

[0039] As to a material which was provided with only the first insulating metal oxide layer, a breakdown voltage was measured in the process of formation of such an insulated wire, whereby the result was about 500 V. Further, a breakdown voltage of an insulated wire which was provided with the second insulating metal oxide layer containing ceramics particles was measured, whereby the result was at least 1200 V.

[0040] Thus, it has been clarified that an insulated wire having a high breakdown voltage can be obtained according to the present invention.

[0041] Even if the insulated wire formed by the aforementioned process was held under a temperature of 850°C for 30 minutes, insulation was maintained. Thus, it has been clarified that the insulated wire obtained according to the present invention can maintain insulation even under a high temperature.

Example 2 (comparative)

[0042] Three insulated wires obtained in Example 1 were employed, and these three wires were coated with polyolefine resin mixed with magnesium hydroxide, to obtain a single wire.

[0043] Fig. 2 is a sectional view of the wire thus obtained. Three insulated wires 21 are gathered and respectively coated with polyolefine resin 22 mixed with magnesium hydroxide, to form a single wire.

[0044] This wire continuously served as a wire even if the same was held under a temperature of 850 degrees for 30 minutes.

Industrial Applicability

[0045] As hereinabove described, the insulated wire according to the present invention can maintain insulation even under a high temperature, is excellent in flexibility, emits no gas, can use various types of conductors, and is advantageously applicable to an insulated wire, a fireproof wire, a thermocouple and a flexible printed circuit etc., for which a high breakdown voltage is required.

Claims

1. An insulated wire comprising a conductor, a first insulating ceramic layer being formed around said conductor, and a second insulating ceramic layer, containing ceramics particles added to the precursor of ceramics, being formed around said first insulating ceramic layer, wherein said first insulating ceramic layer and/or said second insulating ceramic layer is formed by baking a precursor containing at least one compound selected from a group of alkoxides or organic acid salts of Si, Zr, Al and Ti, wherein said second layer is thicker than said first layer, and wherein said first layer has a thickness of 5 to 10 µm.
2. The insulated wire according to claim 1, wherein said ceramic particles have a plate like structure.
3. The insulated wire according to one of claims 1 to 2, further comprising a protective coat, containing an organic material, on the outer side of said second layer.
4. The insulated wire according to one of claims 1 to 3, wherein said electrical conductor consists nickel-plated copper.
5. The insulated wire according to one of claims 1 to 4, wherein said first layer consists of silicon oxide, and said ceramic phase from said precursor of ceramic in said second layer comprises silicon oxide.
6. A method of manufacturing an insulated wire, comprising the steps of :
 - (a) providing an electrical conductor;
 - (b) forming a first insulating ceramic layer around said conductor;
 - (c) forming a second insulating ceramic layer containing ceramics particles added to the precursor of ceramics around said first insulating ceramic layer, wherein

said first insulating ceramic layer and/or said sec-

ond insulating ceramic layer is formed by baking a precursor containing at least one compound selected from a group of alkoxides or organic acid salts of Si, Zr, Al and Ti, wherein said second layer is thicker than said first layer, and wherein said first layer has a thickness of 5 to 10 μm .

7. The method according to claim 6, wherein said ceramic particles have a plate like structure. 10
8. The method according to one of claims 6 or 7, further comprising a step of forming a protective coat, containing an organic material, on the outer side of said second layer. 15
9. The method according to one of claims 6 to 8 wherein said electrical conductor consists of nickel-plated copper. 20
10. The method according to one of claims 6 to 9, wherein silicon oxide is generated in said step of forming said first layer, and silicon oxide is generated in said step of forming said second layer. 25

Patentansprüche

1. Isolierter Draht, umfassend einen Leiter, eine erste isolierende Keramikschicht, welche um den Leiter gebildet ist, und eine zweite isolierende Keramikschicht, welche keramische Partikel enthält, die dem Precursor von Keramik zugefügt sind, der um die erste isolierende Keramikschicht gebildet ist, wobei die erste isolierende Keramikschicht und/oder die zweite isolierende Keramikschicht durch Backen eines Precursors gebildet ist, der wenigstens eine Komponente enthält, die aus einer Gruppe von Alkoxiden oder, organischen Säuresalzen von Si, Zr, Al und Ti ausgewählt ist, wobei die zweite Schicht dicker ist als die erste Schicht und wobei die erste Schicht eine Dicke von 5 bis 10 μm aufweist. 30
2. Isolierter Draht nach Anspruch 1, worin die keramischen Partikel eine plattenartige Struktur aufweisen. 45
3. Isolierter Draht nach Anspruch 1 bis 2, ferner umfassend einen ein organisches Material enthaltenden Schutzmantel auf der Außenseite der zweiten Schicht. 50
4. Isolierter Draht nach einem der Ansprüche 1 bis 3, worin der elektrische Leiter aus nickel-platiertem Kupfer besteht. 55
5. Isolierter Draht nach einem der Ansprüche 1 bis 4,

worin der erste Leiter aus Siliziumoxid besteht und die keramische Phase aus dem Precursor von Keramik in der zweiten Schicht Siliziumoxid umfaßt.

6. Verfahren zum Herstellen eines isolierten Drahts, umfassend die Schritte:
 - (a) Bereitstellen eines elektrischen Leiters;
 - (b) Bilden einer ersten isolierenden keramischen Schicht um den Leiter;
 - (c) Bilden einer zweiten isolierenden Schicht, welche dem Precursor von Keramik zugefügte keramische Teilchen enthält, um die erste isolierende Keramikschicht, wobei

die erste isolierende keramische Schicht und/oder die zweite isolierende keramische Schicht durch Backen eines Precursors gebildet ist, welcher wenigstens eine Komponente enthält, die aus einer Gruppe von Alkoxiden oder organischen Säuresalzen von Si, Zr, Al und Ti ausgewählt ist, wobei die zweite Schicht dicker ist als die erste Schicht und wobei die erste Schicht eine Dicke von 5 bis 10 μm aufweist.

7. Verfahren nach Anspruch 6, worin die keramischen Partikel eine plattenartige Struktur aufweisen.
8. Verfahren nach einem der Ansprüche 6 oder 7, ferner umfassend einen Schritt zum Bilden eines ein organisches Material enthaltenden Schutzmantels auf der Außenseite der zweiten Schicht.
9. Verfahren nach einem der Ansprüche 6 bis 8, worin der elektrische Leiter aus nickel-platiertem Kupfer besteht.
10. Verfahren nach einem der Ansprüche 6 bis 9, worin Siliziumoxid in dem Schritt zum Bilden der ersten Schicht erzeugt wird, und wobei Siliziumoxid in dem Schritt zum Bilden der zweiten Schicht erzeugt wird.

Revendications

1. Fil isolé comprenant un conducteur, une première couche céramique isolante formée autour du conducteur, et une seconde couche céramique isolante contenant des particules céramiques ajoutées au précurseur de la céramique, mises en forme autour de la première couche céramique isolante, dans lequel la première couche céramique isolante et/ou la seconde couche céramique isolante sont formées par cuisson d'un précurseur contenant au moins un composé choisi dans le groupe des alcoxydes ou sels d'acide organique de Si, Zr, Al et Ti, la seconde couche étant plus épaisse que la première couche et la première couche ayant une

épaisseur comprise entre 5 et 10 μm .

2. Fil isolé selon la revendication 1, dans lequel les particules céramiques ont une structure analogue à des plaquettes. 5
3. Fil isolé selon l'une des revendications 1 et 2, comprenant en outre une couche protectrice contenant un matériau organique à la face externe de la seconde couche. 10
4. Fil isolé selon l'une des revendications 1 à 3, dans lequel le conducteur électrique est constitué d'un cuivre nickelé. 15
5. Fil isolé selon l'une des revendications 1 à 4, dans lequel la première couche est constituée d'oxyde de silicium, et la phase céramique provenant du précurseur de céramique de la seconde couche est l'oxyde de silicium. 20
6. Procédé de fabrication d'un fil isolé, comprenant les étapes suivantes :
 - (a) la disposition d'un conducteur électrique, 25
 - (b) la formation d'une première couche céramique isolante autour du conducteur, et
 - (c) la formation d'une seconde couche céramique isolante contenant des particules céramiques ajoutées au précurseur de la céramique 30

autour de la première couche céramique isolante, dans lequel :

la première couche céramique isolante et/ou la seconde couche céramique isolante sont formées par cuisson d'un précurseur contenant au moins un composé choisi dans le groupe des alcoxydes ou sels d'acide organique de Si, Zr, Al et Ti, dans lequel 35

la seconde couche est plus épaisse que la première couche, et dans lequel 40

la première couche a une épaisseur comprise entre 5 et 10 μm .
7. Procédé selon la revendication 6, dans lequel les particules céramiques ont une structure analogue à des plaquettes. 45
8. Procédé selon l'une des revendications 6 et 7, comprenant en outre une étape de formation d'une couche protectrice, contenant un matériau organique, à la face externe de la seconde couche. 50
9. Procédé selon l'une des revendications 6 à 8, dans lequel le conducteur électrique est constitué de cuivre nickelé. 55
10. Procédé selon l'une des revendications 6 à 9, dans lequel l'oxyde de silicium est créé dans l'étape de

formation de la première couche, et l'oxyde de silicium est créé dans l'étape de formation de la seconde couche.

FIG. 1

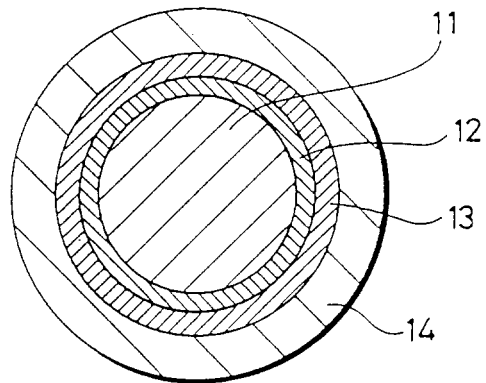


FIG. 2

