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PROCESS FOR IMPROVING THE STABILITY OF BASE METAL THERMOELEMENTS

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The present invention relates to a process for improving the stability of base metal wires or rods which serve as thermoelements, such as, thermocouples, and more particularly relates to an improved process for applying a protective coating to such wires or rods.

It is known that thermoelements which are used in various furnace atmospheres at elevated temperatures, in certain circumstances, rather rapidly undergo changes in their thermoelectric properties because of chemical attack and that as a result thereof their accuracy suffers during extending use in addition to undergoing possible mechanical damage. For example, especially in sulfur containing atmospheres, base metal thermoelectric elements, such as, those of nickel, nickel-chromium or iron construction, relatively rapidly become brittle and subject to breakage. Previously, attempts have been made to overcome these difficulties by the use of protective tubes which enclose the actual measuring elements. However, the difficulty in selecting a suitable material for such tubes with reference to chemical stability, stability against changes in temperature and mechanical strength often provide new problems which prevented a satisfactory solution.

It is an object of the invention to provide a way to increase the stability of base metal wires or rods such as are used in the form of thermocouples for electrical measuring instruments so that they can be used for long periods of time without deleterious attack upon the metal of the wires or rods and the accompanying reduction in accuracy of such measuring instruments.

According to the invention, it was found that this object could be achieved by applying a special coating upon the wires or rods employed for such measuring instruments. The special coatings according to the invention are not only stable in the furnace atmospheres usually encountered, including those of oxidising, as well as of reducing nature, but also especially those containing gaseous sulfur containing compounds.

The special coatings according to the invention are produced by applying a coating of mixed silicates, which preferably is thin, upon the surfaces of the wires or rods. The mixed silicate coating according to the invention, contrary to the normal practices in applying enamel-like coatings, is applied as an essentially aqueous solution of an alkali metal silicate and of a water soluble compound of a second metal, which is built into the coating achieved in addition to the alkali metal. Advantageously, the water soluble additional metal salt is added directly to the alkali metal silicate solution applied to the wires or rods in the form of a water soluble alkali stable salt, for example, the additional metal can be in the form of an alkali stable complex salt. After application of the coatings to the surfaces of the wires or rods, such coatings are subjected to a heat treatment at a temperature above 200° C. in a non-reducing atmosphere. During such heat treatment, oxides formed from the base metal migrate into the coating and are taken up thereby in a noticeable amount and this provides for an extraordinarily strong

bond and coalescence between the coating and the base metal.

Heavy metals primarily come into consideration as the additional metal which is to be introduced into the coating as a mixed silicate with the alkali metal. Preferably, multivalent heavy metals are employed which deliver ions in aqueous solution having at least two different valences. Such metals, for example, are arsenic, bismuth, chromium, copper, iron, manganese, molybdenum, nickel, lead, antimony and, preferably, cobalt or vanadium. However, other metals which are monovalent, such as, silver or zinc, can also be used. Of course, mixtures of such additional metals can also be incorporated in the mixed silicate coating according to the invention.

Preferably, the heat treatment of the coating according to the invention is effected after it has been dried. The heat treatment can be a special heat treatment or such heat treatment can occur when the thermoelement is first put into use. It is only essential that such heat treatment is effected in a non-reducing atmosphere, as this is essential for the formation of the oxides of the base metals which are taken up by the coating and provide the excellent bond between the coating and the base metal.

The protective coating produced according to the invention can be maintained extraordinarily thin in comparison to normal enamel coatings. Expediently, the thickness of a coating according to the invention is not more than 50μ. As a result, the protective coating, which is substantially impervious to gases, is extraordinarily elastic and can be applied to long lengths of wire which can then be wound on rolls without damage to the protective coating. Furthermore, wires coated according to the invention can be welded together without removal of the coating for the production of thermocouples without causing any difficulties of contact at the weld. Of course, when the thermocouples are produced by welding precoated wires, the welded portion can subsequently also receive a protective coating according to the invention.

The coatings according to the invention can be applied to the wires or rods or thermocouples by the usual methods by dipping them in or spraying or painting them with the appropriate solution. It is essential, however, to select the coating thickness sufficiently thin that drop formation does not occur at the high temperatures at which the thermoelements coated therewith are used. After the silicate containing solutions are applied they are generally heated for one hour or more at temperatures of 200° C. and higher in a non-reducing atmosphere. The time and temperature of the heat treatment is so selected with reference to the base metal coated that a small quantity of oxide of the base metal is built into the silicate coating which is produced.

In the production of the silicate coating solutions according to the invention a portion of the water can be replaced by essentially inert water soluble organic solvents, such as, alcohols, aldehydes, ketones and the like.

Preferably, the alkali metal silicate employed in the production of the coating solution is one in which the proportion of alkali metal oxide to silicon dioxide is 1:3.3 to 3.9.

The following examples will illustrate several modifications according to the invention:

Example 1

A welded iron-constantan thermocouple was defatted and dried and then dipped into a solution of the following composition:

10 cc. commercial water glass solution (d.=1.27; $Na_2O:SiO_2=1:3.9$)
7 cc. 8% aqueous ethyl alcohol
5 cc. 1% aqueous solution of $Na_3Co(NO_2)_6$

After removing the thermocouple from the solution, it was dried in air and then heated in air for 1 hour at 200° C.

Example 2

7 cc. of a 1% aqueous solution of cobalt nitrate were mixed with 5 cc. of a 5% aqueous ammonium nitrate solution and the resulting solution then slowly stirred into 10 cc. of a water glass solution of the same composition as in Example 1. The wires which are to be protected, i. e. nickel wires and nickel chromium wires were spooled off from rolls and passed through the solution and thereafter passed through a drying oven maintained at 200 to 250° C. for a period of 15 minutes and then wound back on spools.

The following are further examples of coating solutions according to the invention which can be applied to base metal wires or rods to be used for thermocouples or to the thermocouples themselves in a manner analogous to those described in Examples 1 and 2:

Example 3

A coating solution was prepared by mixing:

10 cc. of a water glass solution (1 d.=1.33; $Na_2O:SiO_2$= 1:3.3)
10 cc. of water
6 cc. of a 1.3% aqueous lead nitrate solution
20 cc. of an 0.7% aqueous $Na_3Co(NO_2)_6$ solution

Example 4

A coating solution was prepared by mixing:

10 cc. of a water glass solution (d.=1.33)
10 cc. of a 0.05% aqueous sodium chromate solution
7 cc. of a 0.1% aqueous $Na_3Fe(CN)_6$ solution

Example 5

A coating solution was prepared by mixing:

10 cc. of a water glass solution (d.=1.33)
5 cc. of water
7 cc. of a 1% aqueous $K_2Ni(CN)_4$ solution

Example 6

A coating solution was prepared by mixing 10 cc. of a water glass solution (d.=1.33) with 5 cc. of water, dissolving 0.1 gram of V_2O_5 therein and adding 5 cc. of a 5% aqueous ethanol solution.

Example 7

A coating solution was prepared by mixing:

10 cc. of a water glass solution (d.=1.33)
5 cc. of a 7% aqueous methanol solution
10 cc. of a 0.5% aqueous $SnCl_2$ solution

I claim:

1. A process for increasing the chemical stability of base metal wires and rods employed for thermoelectric measurement of temperatures which comprises applying a thin coating of an aqueous solution of an alkali metal silicate containing a relatively small quantity of at least one water soluble heavy metal salt to the surface thereof and subsequently heating the coating to a temperature over 200° C. in a non-reducing atmosphere until oxides formed from the base metal base are taken up by such coating.

2. A process according to claim 1 in which said heavy metal salt is a salt of a multivalent heavy metal which delivers ions in aqueous solutions having at least 2 different valences.

3. A process according to claim 1 in which said heavy metal salt is a cobalt salt.

4. A process according to claim 1 in which said coating is up to 50μ thick.

5. A process for increasing the chemical stability of base metal thermocouples which comprises applying a thin coating of an aqueous solution of an alkali metal silicate containing a relatively small quantity of at least one water soluble heavy metal salt to the surface thereof and subsequently heating the coating to a temperature over 200° C. in a non-reducing atmosphere until oxides formed from the base metal base are taken up by such coating.

6. A base metal thermocouple, the surfaces of which are protected by a coating produced by the process according to claim 5.

References Cited in the file of this patent

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