

UNITED STATES PATENT OFFICE

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CONSTANT RESISTIVITY ALLOY

No Drawing.

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This invention relates to alloys which exhibit a substantially constant electrical resistivity over a wide range of temperature, and particularly to alloys of the copper base type.

Objects of the invention are to provide alloys of the copper-manganese type which, as compared with known compositions, show a marked improvement in the constancy of their electrical resistance. A further object is to provide an alloy of the copper-manganese type which includes an additional element or elements for improving the resistivity characteristics of the alloy. More specifically, an object is to provide a constant resistivity alloy consisting of or comprising copper, manganese and aluminum. The invention also contemplates the provision of methods of preparing such alloys to improve the uniformity of their temperature-resistance characteristics.

It is well recognized that certain copper-manganese alloys exhibit an approximately constant electrical resistivity over a wide range of temperature, and such alloys are sold commercially under the name "Manganin". My investigations on the nature and properties of manganin have led me to believe that the peculiar temperature-resistance characteristics of such copper base alloys are due to the combination of two influences. In one respect, these alloys behave substantially like other copper base alloys for which the product of electrical resistivity by the temperature factor oscillates closely around a constant figure. On the other hand, a certain process is always taking place when these alloys are subjected to temperature changes, which process may be described, in a hypothetical way, as a formation of and dissociation of additional bonds between the atoms of copper and manganese. This process may be imagined, for purposes of illustration, as the formation of a compound such as Cu_2Mn at lower temperatures, and the dissociation of this compound at higher temperatures. I visualize this process as taking place in a single homogeneous phase and not being characterized, as in other processes taking place in metallic alloys, by the precipitation

out of the formed compound as a separate phase.

An increase in the dissociation of this compound, like the ionic dissociation of a solute within a solvent, tends to increase the conductivity of the whole system and consequently it counteracts the increase in resistivity due to the increase in temperature. The constant of the chemical process involved increases with the temperature as a function of a higher order and for that reason the increase in conductivity due to temperature increase becomes ever stronger. As long as the alloy is in the domain of temperatures much lower than the normal room temperature, the second process does not completely balance the natural increase in resistivity and the alloy has a positive temperature factor. When certain temperatures are reached, these influences almost balance each other and the temperature factor of resistivity becomes practically equal to zero. At higher temperatures, the second process begins to predominate and the temperature factor becomes negative, continuously increasing in its absolute value up to the moment when the total amount of the compound still left becomes so small that its dissociation does not add any more to the conductivity of the alloy, and the resulting temperature factor becomes more positive until at very high temperatures the alloy behaves again in a normal way.

This feature is encountered in practically every composition in the copper manganese series but the total amount of the compound present and the rate of its decomposition with the increase in temperature depend upon the amount of manganese present. In alloys low in manganese the natural temperature coefficient is high and its decrease due to the chemical process involved so small that a curve representing the actual change of resistivity with temperature shows only a strong bend. With the increase in the content of manganese this bend becomes more pronounced and the tendency for it to go through a maximum and to become negative beyond it increases. The more manganese is present, the closer the maximum approaches the nor-

mal temperatures and alloys containing from 10.5 to 18% manganese have this maximum located between 60° and 0° C., respectively.

However, straight binary copper manganese alloys tend to oxidize easily, particularly on annealing, and this oxidation eliminates nearly the whole of the manganese at the surface of the sample to a depth depending upon circumstances of time and temperature. In this way, a highly conductive outside layer is formed and, for a given alloy, instead of a definite, predetermined curve for the resistivity-temperature changes one obtains most variable curves for different specimens, sometimes with a highly positive factor. Alloy samples characterized by such curves cannot be regarded as reliable for the construction of instruments of precision.

It is doubtful whether this feature was ever described before but in an empirical way it was counteracted to an extent by adding to the alloy another element which stays in solid solution in copper and cannot be easily burned away. Such element as usually encountered is nickel. The regular manganin of commerce contains about 12% manganese and 4% nickel, the balance being copper.

The addition of the nickel gives rise to another effect. It evidently changes the dissociation constant of the copper manganese compound present; in fact, it increases the dissociation constant. For that reason these commercial manganins have a range of high constancy which, as compared with the binary alloys, is shifted down very closely to normal or atmospheric temperature. On the other hand, the increase in dissociation beyond normal temperature becomes so strong that even the best manganin of commerce shows about .2% of change in the negative direction when approaching 100° C.

In accordance with the present invention, the temperature-resistance characteristics of copper-manganese alloys are stabilized and improved by the addition of an element or elements which do not give rise to the undesired effects of nickel.

I have discovered that aluminum, either alone or in association with a smaller quantity of iron, is far superior to nickel as an additional element in alloys of the copper-manganese type. Aluminum decreases the natural temperature coefficient of the alloys considerably more than nickel does, and therefore makes it easier to balance the natural positive temperature coefficient of the alloy by the relatively small dissociation which takes place at low temperatures. Like nickel, aluminum increases the dissociation at higher temperatures, but to a somewhat lower degree. Furthermore, the aluminum prevents the formation, even in an oxidized alloy, of an outer layer of such high conductivity as obtains in binary copper-manganese alloys and,

to a lesser extent, in manganin containing nickel.

For best results, smaller amounts of manganese can and should be used when aluminum is present.

As compared with the usual 12 to 14% of manganese which has been used in a commercial manganin, the manganese may be reduced to from 7 to 11% when aluminum is present to the extent of from 3 to 4.5%. A further flattening of the temperature-resistivity curve may be effected by the addition of from .2 to 1% of iron, although for many uses this further improvement in constancy may not be important.

One particular alloy which exhibits very high constancy of electrical resistivity consists of 9.5% manganese, 3.5% aluminum, 0.5% iron, and the balance copper.

A further advantage accompanying the use of aluminum in copper base alloys is the lowering of the thermo-electric voltage developed between copper and the alloy. The potential developed between a commercial manganin and copper may run from about 0.7 to 1.5 microvolts per degree, while an alloy including, for example, 9% manganese and 4% aluminum will develop only from 0.1 to 0.5 microvolts.

I have also found that the addition of tin to the aluminium-containing alloys is advantageous, particularly in ameliorating other physical properties of the alloys. For instance, the capacity of the alloy for taking solder is advantageously affected by the addition of tin. An alloy of the following composition has been found, for example, to have very desirable characteristics:

	Per cent
Manganese -----	10
Aluminum -----	3
Tin -----	2

the balance being copper.

Although the addition of aluminum reduces those variations in resistivity which arise from surface oxidation of the alloy, I have found that the resistivity curves of specimens of like composition will coincide when the annealing is carried out under non-oxidizing conditions, such as obtained by a high vacuum. Except in the case of thin bars, strips or wires, the preliminary annealing operations may be performed in air or under charcoal, if the specimens are then carefully pickled. The last anneal should be carried out, however, under high vacuum or equivalent non-oxidizing conditions. Temperatures of from 500-550° C. are appropriate for the annealing of the copper base alloys.

Alloys such as contemplated by this invention may, of course, be made up in the usual manner in the form of bars, ribbons, strands or wire.

What I claim is:

1. An alloy of constant resistivity type comprising copper, manganese 7 to 11% and aluminum 3 to 4.5%.

2. An alloy of constant resistivity type comprising copper, manganese 7 to 11%, aluminum 3 to 4.5% and iron 0.2 to 1%.

3. An alloy of constant resistivity type consisting of copper, manganese 7 to 11%, aluminum 3 to 4.5% and tin about 2%.

4. A constant electrical resistivity alloy comprising 9.5% manganese, 3.5% aluminum, and the balance copper.

5. A constant electrical resistivity alloy comprising 9.5% manganese, 3.5% aluminum, 0.5% iron and the balance copper.

6. A constant electrical resistivity alloy comprising 10% manganese, 3% aluminum, 2% tin and the balance copper.

In testimony whereof, I affix my signature.
MICHAEL G. CORSON.