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ALLOY

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My invention relates to alloys of metals in the iron group of the periodic table and particularly to ferrous base alloys of four or five components.

5 One object of my invention is to provide an alloy having a predetermined coefficient of expansion over a temperature range from substantially room temperature to the annealing temperature of certain glasses, particularly boro-silicate glass and ordinary lead glass.

10 Another object of my invention is to provide an alloy having a smaller coefficient of expansion than the nickel-steel alloys.

15 Another object of my invention is to provide an alloy adapted to form a vacuum-tight seal through boro-silicate glass.

Another object of my invention is to provide an alloy adapted to form a vacuum-tight seal through lead glass.

20 Another object of my invention is to provide an improved method of sealing electrical conductors through glass.

A further object of my invention is to provide a method for producing a vacuum-tight seal of electrical conductors, having only a limited range of expansivity substantially equal to that of ordinary glasses, through the latter without causing breakage of the seals in cooling to room temperature.

30 Other objects of my invention will become apparent on reading the following specification.

In connection with the manufacture of vacuum-tight electrical-discharge devices in glass containers the problem arises of making vacuum-tight seals of metals through the glass walls. In forming such seals, a small hole is melted in the glass wall of the container; the metal lead is inserted and the molten glass squeezed around the lead and fused thoroughly in contact therewith. In order that the resulting seal shall not crack or leak after it has cooled, it is necessary that the metal and the glass shall have substantially the same expansivity with temperature over the range from the annealing temperature of glass down to room temperature; and that the metal be one which the glass will "wet". Platinum metal has the foregoing properties, when used in combination with ordinary lead glass, and the first successful

seals through glass were made with platinum leads.

However, for certain purposes, it is desirable to use higher-melting glass than the ordinary lead glass just referred to; and hence, the use of boro-silicate glass in electrical apparatus has become fairly common. The boro-silicate glass, however, has a materially lower coefficient of expansion than lead glass and, consequently, platinum seals could not be used in it. However, tungsten and molybdenum were found to have coefficients of expansion of the right order of magnitude and to form vacuum-tight seals with boro-silicate glass. Such seals are, however, rather expensive and not entirely satisfactory.

Platinum, likewise, is an extremely expensive metal and, consequently, composite conductors having cores of nickel-steel covered by thin jackets of copper were developed, and thus cheaper but equally satisfactory, seals through ordinary lead glass were obtained. The coefficient of expansion of copper is higher than that of lead glass; and, since the jacket of copper is relatively thin, the nickel-steel alloy employed is one which has a coefficient of expansion nearly equal to that of lead glass. Copper is a metal which lead glass "wets" readily; and the expansivity of nickel-steel is slightly less than that of glass over the range of approximately 400° C. between the temperature at which strains readily relieve themselves in lead glass and room temperature.

However, when the attempt was made to find nickel-steels of the low expansivity corresponding to that of boro-silicate glass, it was found that, while this low expansivity existed up to a certain critical temperature, this temperature, herein called the inflection temperature, was considerably lower than the temperature of above 300° C. encountered with boro-silicate glass, and even lower than that of the nickel-steel alloys suitable for lead glass; and that, consequently, there was a range of temperature just below the proper annealing temperature of the glass in which the expansivity was so great that vacuum-tight seals could not be produced.

In accordance with the present invention, I have made discoveries concerning regulated addition of manganese and carbon in meeting complications introduced, by substituting cobalt

for a certain part of the nickel in the nickel-steels previously employed. This avoids deleterious modification of the iron base metal and yet controls the expansivity and the inflection temperatures in a manner to obtain alloys useful at high temperatures and having sufficiently low coefficients of expansion throughout the entire range below the necessary annealing temperature of boro-silicate glass. Such alloys are "wet" by the boro-silicate glass.

Thus, as one benefit of this invention, it becomes possible to produce satisfactory vacuum-tight seals with this alloy in either boro-silicate glass or in lead glass. Certain description and specific applications of the alloys of this invention are found also in my application, Serial No. 376,291, filed July 5, 1929.

In manufacturing Fe-Ni-Co alloys commercially, any manganese and carbon present create the very complex conditions involved in a quinary alloy. Manganese is desirable for mechanical reasons, but it also lowers the Ar₃ temperature at which the undesirable gamma to alpha transformation of iron occurs; it raises the expansivity of the alloy; and it complicates the effects of each of the other components. Carbon also influences the Ar₃ temperature, alters the expansivity as well as the inflection temperature, and indirectly affects each of the other components.

I have found that low expansion nickel cobalt steels can be regulated in compounding the alloys so as to avoid interference from the Ar₃ transformation temperature, and so as to retain low expansivity up to a higher inflection temperature than heretofore. In this invention, increase of inflection temperature to the high range of 300° C. and above is accomplished by increasing the sum of nickel and cobalt with the individual percentages of these two elements related to the desired inflection temperature, in a manner to be explained. Further, in this invention, the Ar₃ temperature, at which the deleterious form of iron appears, is depressed by regulating the amounts of manganese and carbon to the nickel and iron according to the following relationship:—

$$\frac{\% \text{ Ni} + 2.5(\% \text{ Mn}) + 18(\% \text{ C})}{\% \text{ Fe}} = 0.50 \text{ to } 0.60,$$

the ratio 0.55 being preferable. This relationship refers to carbon in solid solution and is independent of the cobalt content, but is useful in checking the amount of cobalt by difference of the sums of these four elements from 100%.

I have found that manganese is for certain purposes detrimental to the expansion properties and prefer to keep it below 0.2% though it may be as high as about one percent. On the other hand carbon in solid solution is for many purposes of distinct advantage in that it permits the use of a higher cobalt content than otherwise possible and does not seriously harm the expansion properties. Its content, with strict reproducibility of expansion between heating and cooling, is limited to a maximum of about 0.3%. I, therefore, specify these maximum contents with the knowledge, however, that higher contents can be used to advantage under certain conditions. Various lead glasses are known to be representative of the softer glasses that are annealed at the lower temperatures, while of the boro-silicate glasses representative of those annealed at temperatures above 300° C., that known as G80 has an annealing temperature of about

565° C. For sealing low expansion metal in glass, it is sought to obtain the inflection temperature of the metal at least as high as the annealing temperature to be encountered, so as to avoid marked change of expansivity of the metal.

I have found that the mean expansivity A per degree centigrade between 0° C. and the inflection temperature (upper limit of low expansivity), T, may be expressed with considerable accuracy by the following equation:

$$A = (0.024 T - 5.5) \times 10^{-6}$$

The preferred percentages of nickel and cobalt are connected with the inflection temperature, T, (expressed in degrees centigrade) by the equations

$$\% \text{ Nickel} = 41.2 - 0.0282 T$$

$$\% \text{ Cobalt} = 0.0795 T - 17.1$$

for alloys having 0.2% manganese and 0.0% carbon; and by the equations

$$\% \text{ Nickel} = 38.2 - 0.0282 T$$

$$\% \text{ Cobalt} = 0.0795 T - 13.8$$

for alloys having 0.5% manganese and 0.1% carbon.

Thus a value of inflection temperature, T, having been determined, as by the annealing temperature of the glass to be employed, the percentage composition of the preferred alloy is determinable by the foregoing equations and likewise its mean expansivity. The cobalt may range from about 6%, or preferably about 12%, in a nickel plus cobalt sum as low as 40 for inflection temperatures of about 300° C. to as high as 40% in a nickel plus cobalt sum of about 55 for high inflection temperatures of about 565° corresponding to that of G80 boro-silicate glass.

Preferably, the sum of nickel plus cobalt is brought within the range of about 43 to 55, with manganese present to a maximum of about 0.5% and carbon to a maximum of about 0.3%. For example, an iron base alloy of 23.7% nickel, 21.9% cobalt, 0.2% manganese and 0.3% carbon shows the sum of nickel and cobalt as 45.6%, and has an inflection above 300° C., and has the Ar₃ transformation temperature of the iron so far depressed that the alloy remains useful at atmospheric temperature. Sufficient cobalt is present to counteract the effect of carbon on the coefficient of expansion. Another suitable alloy contains 25.0% nickel, 23.6% cobalt, 0.5% manganese, 0.1% carbon. Here the sum of nickel and cobalt, 48.6%, assures an inflection temperature above 300° C., and the relatively higher cobalt content counteracts the effect of the increased manganese on the Ar₃ point. It may be added that the sum of 55 above corresponds to an inflection temperature of about 565° C.

It is evident from the formulas that the sum of nickel plus cobalt regulates the inflection temperature, with the percentage of nickel decreasing and the percentage of cobalt increasing in this sum as the inflection temperature increases. Cobalt tends to raise the Ar₃ point; but, by regulating the composition within the limits of this invention, the Ar₃ point is depressed safely below room temperature, while a low coefficient of expansion is retained to inflection temperatures above 300° C.

While I have, in the foregoing, described certain particular embodiments of my invention, it will be understood that these are for purposes of illustration only, and that the broad principles may be otherwise utilized, as will be readily apparent to those skilled in the art. I, accordingly,

desire that the following claims shall be accorded the broadest construction of which their terms are susceptible in view of the limitations imposed by the prior art.

5 I claim as my invention:

1. An alloy of low thermal expansivity essentially of iron base containing nickel and cobalt in a sum of about 43 to 55 per cent to obtain inflection temperatures above approximately 300° C., with the cobalt at least about 12 per cent to obtain low expansivity, and nickel at least 15 per cent, the balance of the alloy being substantially iron.

2. An alloy of low and reversible thermal mean expansivity below the order of 8×10^{-6} composed of iron base containing essentially nickel and cobalt in a sum of about 40 to 55 percent to obtain inflection temperatures above approximately 300° C., with carbon in small amount up to the order of 0.5%, and with the cobalt ranging from about 6.75 percent, corresponding to 300° C. inflection temperature, in the lower sum to about 33 percent with 22 percent nickel to obtain low expansivity, the balance of the alloy being substantially iron.

3. An alloy of low thermal expansivity composed essentially of iron base containing nickel and cobalt in a sum about 40 to 55 percent to obtain inflection temperatures from approximately 300° to 565° C., with the cobalt ranging correspondingly from about 12 to 33 percent to obtain low expansivity, the balance of the alloy being substantially iron.

4. An alloy of low thermal expansivity composed essentially of iron base containing nickel and cobalt in a sum of about 40 to 50 percent, with the cobalt from about 12 percent with about 29 percent nickel to about 25 percent with about 25 percent nickel to obtain low expansivity, the balance of the alloy being substantially iron.

5. An alloy of low thermal expansivity composed essentially of iron base containing nickel and cobalt in a sum of about 45 to 50 percent, with the cobalt about 20 to 25 percent to obtain low expansivity with elevated inflection temperature the balance of the alloy being substantially iron.

6. An alloy of low thermal expansivity composed of iron base containing essentially nickel and cobalt in a sum of about 43 to 55 percent to obtain inflection temperatures above approximately 300° C., with the cobalt ranging from about 10 percent in the lower sum to about 33 percent with 22 percent nickel to obtain low expansivity, the percentage of nickel in proportion to the iron being about 0.5 to 0.6 the balance of the alloy being substantially iron.

7. An alloy of low thermal expansivity composed essentially of iron base containing nickel and cobalt in a sum of about 43 to 55 percent to obtain inflection temperatures from approximately 300° to 570° C. with the cobalt ranging from about 10 percent with 33 percent nickel to about 33 percent with 22 percent nickel to obtain low expansivity, and containing amounts of manganese less than about one percent, the percentage of nickel plus 2.5 times the percentage of

manganese being in proportion to the iron about 0.5 to 0.6 the balance of the alloy being substantially iron.

8. An alloy of low thermal expansivity composed essentially of iron base containing nickel and cobalt in a sum of about 43 to 55 percent to obtain inflection temperatures above approximately 300° C. with the cobalt ranging from about 10 percent with 33 percent nickel to about 33 percent with 22 percent nickel to obtain low expansivity, and containing amounts of dissolved carbon less than 0.5 percent, the percentage of nickel plus 18 times the percentage of dissolved carbon being in proportion to the iron about 0.5 to 0.6 the balance of the alloy being substantially iron.

9. An alloy of low thermal expansivity composed essentially of iron base containing nickel and cobalt in a sum of about 43 to 55 percent to obtain inflection temperatures above approximately 300° C. with the cobalt ranging from about 10 percent with 33 percent nickel to about 33 percent with 22 percent nickel to obtain low expansivity, and containing amounts of manganese less than about one percent and of dissolved carbon less than 0.5 percent, the percentage of nickel plus 2.5 times the percentage of manganese plus 18 times the percentage of dissolved carbon being in proportion to the iron about 0.5 to 0.6 the balance of the alloy being substantially iron.

10. An alloy of low thermal expansivity composed essentially of iron base containing nickel and cobalt in a sum of about 43 to 55 percent to obtain inflection temperatures above approximately 300° C. with the cobalt ranging from about 10 percent with 33 percent nickel to about 33 percent with 22 percent nickel to obtain low expansivity, and containing amounts of dissolved carbon less than 0.5 percent, the percentage of nickel plus 18 times the percentage of dissolved carbon being in proportion to the iron about 0.55 the balance of the alloy being substantially iron.

11. An alloy of low thermal expansivity composed essentially of iron base containing nickel and cobalt in a sum of about 43 to 55 percent to obtain inflection temperatures above approximately 300° C. with the cobalt ranging from about 10 percent with 33 percent nickel to about 33 percent with 22 percent nickel to obtain low expansivity, and containing amounts of manganese less than about 0.5 percent and of dissolved carbon less than about 0.3 percent, the percentage of nickel plus 2.5 times the percentage of manganese plus 18 times the percentage of dissolved carbon being in proportion to the iron about 0.55 the balance of the alloy being substantially iron.

12. An alloy of low thermal expansivity composed essentially of iron base containing about 23 to 25 percent nickel, 21 to 25 percent cobalt, 0.2 to 0.5 percent manganese and less than 0.3 percent carbon the balance of the alloy being substantially iron.

HOWARD SCOTT. 140