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GOLD-CHROMIUM RESISTANCE ALLOYS

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ABSTRACT

The addition of from 1.6 to 2.4 percent or more of chromium to gold produces alloys having very small temperature coefficients of electrical resistance. In particular, 2.1 percent of chromium in gold gives an alloy whose resistance has been made independent of temperature, to a few parts in 10 million, in at least the interval 20 to 30° C. These alloys are also exceptionally stable in resistance. They, however, have a thermoelectric power against copper which is 3 or 4 times as large as that of manganin. The preparation and heat treatment of some of these of laws are described. these alloys are described.

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I. INTRODUCTION

The electrical characteristics of alloys of gold with small amounts of other metals has recently been investigated by Linde.¹ As part of this investigation he prepared an alloy having 2 percent of chromium by weight and found it to have a zero temperature coefficient of resistance at about -50° C, and a slightly lower resistance at 100° C than at -50° C. These results suggested that a slightly smaller amount of chromium added to the gold might give a zero temperature coefficient of resistance at room temperatures.

An investigation of the electrical properties of pure metals ² has shown that pure gold is very stable in electrical resistance. It was thought that the addition of a small amount of chromium would have little effect upon this stability. To test this, several alloys were prepared, and the preliminary data indicated that they were very stable in resistance. It also was found possible to choose the composition and heat treatment so as to obtain a practically zero temperature coefficient of resistance.

¹ J. O. Linde, Annalen der Physik 402,52(1931); 407,219(1932). ² J. L. Thomas, BS J.Research 12,313(1934); RP657.

II. PREPARATION OF GOLD-CHROMIUM ALLOYS

No information seemed to be available as to the proper technique to be employed in alloying chromium with gold. Preliminary attempts to prepare the alloys in a vacuum or in an atmosphere of dry hydrogen were not very successful. However, it was found that they could be very readily prepared by melting the gold and chromium together in graphite crucibles, under a heavy coating of borax. The graphite crucibles were heated by means of an induction furnace. When at a temperature of about 1,200° C the alloys were poured into graphite molds.

The ingots were first hot-forged into the form of rods 5 or 6 mm square. They were then cold-rolled and swaged to a diameter of 0.75 mm, after which they were drawn down to the required size through sapphire dies. The material was annealed 4 or 5 times during the rolling and swaging, but the wire was not annealed during the drawing.

Nine of these gold-chromium alloys were prepared and investigated. They contained from 1.6 to 2.5 percent of chromium by weight, as shown by chemical analyses. With 30 grams of gold it was found that there was a loss of nearly one-fifth of the chromium in the melting. The characteristics of these alloys are given in the following sections.

III. PROPERTIES OF THE ALLOYS

1. TEMPERATURE COEFFICIENT OF RESISTANCE

For these gold-chromium alloys the relation between resistance and temperature in the interval 20 to 30° C was found to be represented with sufficient accuracy by the equation:

$R_t = R_{25} [1 + \alpha (t - 25) + \beta (t - 25)^2]$

where R_t is the resistance at t° C and R_{25} is the resistance at 25° C. Both α and β were found to be functions of the percentage of chromium, but the magnitude of α could be changed by baking at comparatively low temperatures.

The dependence of α upon the composition and the annealing is shown in figure 1. The percentages of chromium by weight were plotted as abscissas, while the values of α in the interval 20 to 30 °C were plotted as ordinates. The upper curve is for hard-drawn wire, while the lower is for wire annealed ³ in vacuo at about 500° C.

These curves suggested that a zero value for α could be obtained in either of two ways. An alloy could be prepared which contained 1.8 percent chromium by weight and annealed at 500° C, or an alloy containing more chromium could be prepared and annealed at a lower temperature. This latter procedure was tried experimentally. A 10-ohm coil of the hard-drawn wire containing 2.35 percent chromium was baked in air at 150° C for several days. The resistance and value of α were measured at frequent intervals during this baking. The results obtained are shown by figure 2. From this figure it was found that α could be made as small as was desired by properly choosing the amount of baking at 150° C. Actually this coil was baked until

³ This annealing was done in an evacuated quartz-tube furnace. About 1½ hours were required to raise the temperature to 500° C, after which the heating current was cut off and approximately the same length of time was required for the furnace to cool.

 α was made slightly negative. It was sealed in a container filled with oil, and is 10-ohm coil no. 23 for which data are given later.

Figure 2 also shows the effect of baking upon the resistance of this coil. The resistance of the coil increased as a result of the baking, while the value of α decreased. There was a linear relation between

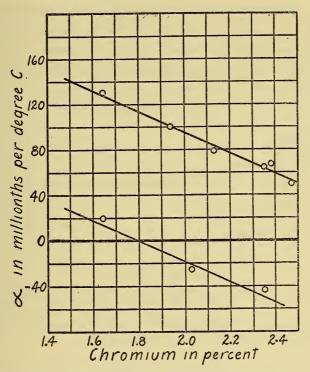


FIGURE 1.—Values of α for gold-chromium alloys.

Upper curve is for hard-drawn wire, while lower curve is for wire annealed in vacuo at 500° C.

the change in the resistance and the change in the value of α . A change of 1 percent in the resistance was accompanied by a change of 26 parts per million per degree C in α . This relation facilitated the adjustment of α to a zero value. The changes in resistance were comparatively large, and could be very readily measured, so the magnitude of α could be adjusted with a comparatively few determinations of its value.

In order to see whether the value of β was dependent upon the amount of chromium, 5 of the alloys were drawn down into wire 0.43 mm in diameter. After measuring the resistivity, 10-ohm coils were constructed from these wires and baked for a sufficient time to make α fairly small. The values of β were then determined in the interval 20 to 30° C, and plotted against the chromium content as shown in figure 3. They were again baked so as to change the values of α by small amounts. No measurable change in the β 's resulted from this second baking.

From this curve it was evident that a gold-chromium alloy having about 2.1 percent of chromium would have a zero value for β , that is to say, the temperature-resistance curve would be linear. With the proper baking the value of α , i.e., the slope of the temperature-resistance curve, could be made zero at least in the interval 20 to 30° C.

One of the alloys had a chromium content which was very nearly 2.1 percent. It was therefore investigated in detail. A 10-ohm coil

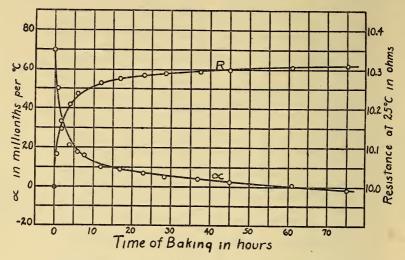


FIGURE 2.—Effects of baking at 150°C upon gold-chromium alloys containing 2.35 percent chromium.

Curve R shows how the resistance increased with time of baking, while the temperature coefficient decreased, as shown by curve marked α .

of this material was carefully baked at 200° C to bring its value of α to zero, and the following data were obtained:

Temperature	re Resistance		
° <i>C</i> . 20 22. 5 25 27. 5 30	$\begin{array}{c} 9. \ 99561_2 \\ 9. \ 99561_2 \\ 9. \ 99561_1 \\ 9. \ 99561_0 \\ 9. \ 99561_1 \end{array}$		

Within the limits of error of the resistance measurements (a few parts in 10⁷), the resistance of this coil was independent of temperature throughout the entire interval of 20 to 30° C. With manganin a minimum variation of about 10 parts per million would have been expected in this temperature interval, which is nearly 100 times that reported above. It might be pointed out that the copper lead wires contributed somewhat to the temperature coefficient of this coil. This means that for the resistance material alone, the value of α is slightly negative.

Two 100-ohm coils were made from the same melt, of wire drawn down to a diameter of 0.2 mm. Each of these 100-ohm coils required between 9 and 10 meters of wire, that is, about 6 g of the alloy. Although the value of α was not as accurately adjusted as for the above-described 10-ohm coil, no measurable curvature was found in the temperature-resistance curves. This indicated that the magnitude of β did not depend upon the size of the wire, but only upon the chromium content.

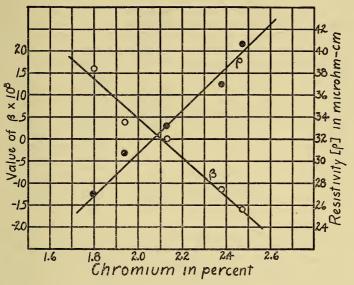


FIGURE 3.—Resistivity and curvature of temperature-resistance curves for goldchromium alloys.

Curves for which β is positive are concave upward, while if β is negative they are concave downward.

2. STABILITY

Tests of the stability of these alloys were started before the best composition from the viewpoint of temperature coefficient had been determined. Two compositions were investigated, one having more and the other less chromium than 2.1 percent. While it will require a number of years to fully test the stability of these gold-chromium resistance alloys, the results so far obtained are remarkably promising. Table 1 shows the data obtained for four resistance standards. The coils were wound with bare wire on silk-covered brass tubes, spaced with silk thread, shellacked and baked in air at comparatively low temperatures and mounted in oil-filled containers of the Rosa ⁴ type.

Items	No. 3938	No. 3937	No. 23	No. 3936
Percent chromium	1. 64	2, 35	2.35	2.35
Baking temperature, °C	140	150	150	140
Time of baking (hours)	67	21	138	20
α in millionths/°C	45	2	-4	-4

TABLE	1.—Data	on resistance	standards
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⁴ E. B. Rosa, BS Sci. Pap. 107 (1908).

Date	No. 3938	No. 3937	No. 23	No. 3936
Jan. 22, 1934	9, 99564			
Jan. 23, 1934	9, 99564			
Jan. 24, 1934				
Jan. 26, 1934	9, 99563			
Jan. 30, 1934	9, 99563			
Th.h. 5 1004	0.00504			
Feb. 5, 1934	9.99564	9, 99550		
Feb. 8, 1934			÷	99, 9533
Feb. 14, 1934 Feb. 15, 1934				99, 9534
Feb. 16, 1934		9.99550		99, 9534
Feb. 19, 1934	9,99564	9,99550		99, 9534
100.10,1001	0.00001	0.00000		00.0001
Mar. 1, 1934	9, 99563	9,99549		99, 9534
Mar. 6, 1934		9, 99550		99, 9535
Mar. 19, 1934	9. 99563	9, 99552	9.99540	99.9535
Mar. 22, 1934	9.99564	9.99551	9.99543	99.9535
Mar. 23, 1934		9. 99550	9.99544	99, 9535
Mar. 26, 1934		9. 99551	9.99545	99.9535
Apr. 3, 1934		9.99549	9.99544	99.9534
Apr. 17, 1934		9. 99549	9. 99543	99. 9535
36-1024	0.00564	0.00551	0.00540	00.0525
May 25, 1934	9, 99564	9. 99551	9. 99542	99. 9535
July 20, 1934	9, 99564	9, 99547	9, 99541	99, 9534
July 20, 1904	9. 99504	9. 99047	9. 99041	99. 9054

TABLE 1.—Data on resistance standards—Continued

RESISTANCE AT 25° C. IN OHMS

The resistances given in this table are in terms of the Washington unit as maintained since 1910 by means of a group of ten 1-ohm manganin standards. The resistances were determined by comparing with 10-ohm or 100-ohm manganin standards which in turn were occasionally compared with the reference group of 1-ohm standards. These 10- and 100-ohm standards were not entirely constant in resistance between comparisons with the reference group. Some of the changes in the values obtained for the resistances of the gold-chromium coils could be attributed to changes in the secondary manganin standards.

In considering the stability of these new alloys one must bear in mind the fact that the coils were baked at fairly low temperatures, and that they were mounted in oil-filled containers of the Rosa type. No other resistance material is known which will give a comparable stability when the coils are baked and mounted in this way, although 1-ohm manganin standards give a similar performance when coils of large-sized wire are annealed at 550° C and mounted in double-walled containers.⁵

In order to compare the stability of the gold-chromium alloys with that of manganin, the data from the preceding table are plotted in figure 4, together with typical curves obtained for manganin 10- and 100-ohm standards. The gold-chromium coils were constructed with bare wire wound on silk-insulated brass tubes, while double-silk-covered manganin wire was used. For all the curves the time is plotted beginning with the first measurements immediately after baking.

When manganin is used in the construction of resistance standards, the coils are usually kept for a year or more after they are baked in order to reach a reasonably stable condition. In the case of the coils made of gold-chromium alloys, this aging appeared to be

⁵ J. L. Thomas, BS. J. Research 5, 295(1930); RP201.

unnecessary. While it does not necessarily follow from this that the gold-chromium alloys will be stable in resistance over long periods of time, it is to be expected.

3. MISCELLANEOUS PROPERTIES

All the gold-chromium alloys were very easy to work into wire. While no hardness tests were made, all of these alloys seemed to be comparable with pure gold. The chromium oxidized slightly on the surface when the ingots were annealed and this oxide was removed

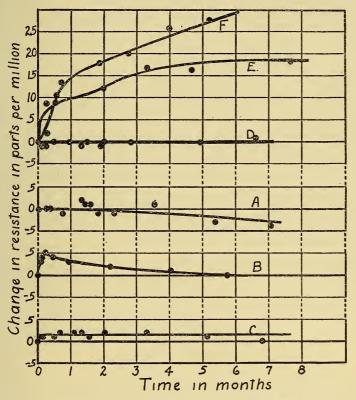


FIGURE 4.—Stability of gold-chromium resistance alloys.

Curve A for 10-ohm coil no. 3837; curve B for 10-ohm coil no. 23; curve C for 100-ohm coil no. 3938; curve D for 10-ohm coil no. 3938; curve E for 10-ohm manganin coil baked at 120° C; and curve F for 100-ohm manganin coil baked at 140° C.

by pickling in aqua-regia. Little hot working was required and the material was worked cold after a little initial forging.

The thermoelectromotive force of these gold-chromium alloys against copper was 7 or 8 microvolts per degree C at 25° C, as compared with 2 or 3 microvolts per degree C for manganin against copper. This, however, did not prevent the resistance of the coils from being measured to parts in a million when immersed in a wellstirred oil bath. It would be more troublesome in low-resistance coils, but the cost of the material probably precludes its use in constructing such coils. The resistivity of the 2.13-percent alloy was found to be about 15 times that of pure gold at 20° C. Its value is 33 microhm-cm as compared with about 45 microhm-cm for manganin. The curve marked ρ in figure 3 shows how the resistivity depends upon the percentage of chromium.

IV. CONCLUSIONS

In the preceding sections it has been shown that the addition of 2.1 percent by weight of chromium to gold produced an alloy having exceptional electrical characteristics. By baking at comparatively low temperatures the resistance of a coil made of this material was made independent of temperature over at least the interval 20 to 30° C.

While the stability of the 2.1-percent chromium alloy or the stability of its temperature coefficient was not investigated, coils made from alloys containing slightly more and slightly less chromium appeared to be exceptionally stable in resistance. A thorough investigation of the 2.1-percent alloy is to be made.

In choosing a material for the construction of standards for the maintenance of the unit of resistance, the most important factor is undoubtedly that of stability. If the gold-chromium alloys are as stable as the preliminary results indicate, they should yield valuable information about the constancy of the manganin standards used in maintaining the unit of resistance, and may even replace manganin for this purpose.

The author wishes to express his appreciation to W. F. Roeser and J. G. Thompson for their assistance in the preparation and working of the alloys described in this paper, and to R. M. Fowler for the chemical analyses.

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