June 9, 1964 G. ZWINGMANN 3,136,634

NOBLE METAL ALLOYS HAVING A HIGH SPECIFIC ELECTRIC RESISTANCE

Filed Jan. 30, 1963 3 Sheets-Sheet 1

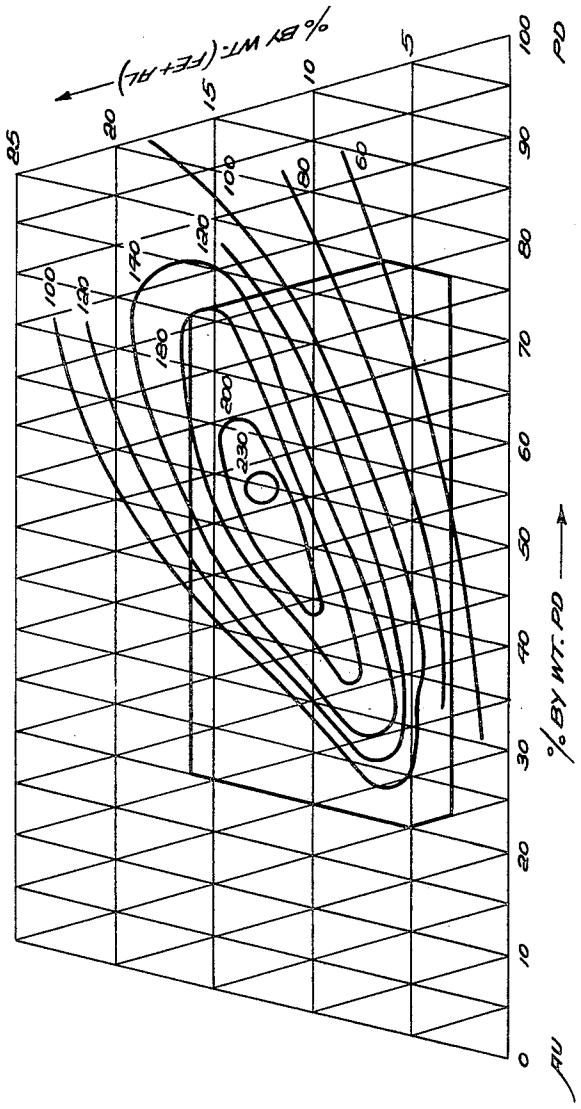


Fig. 1.

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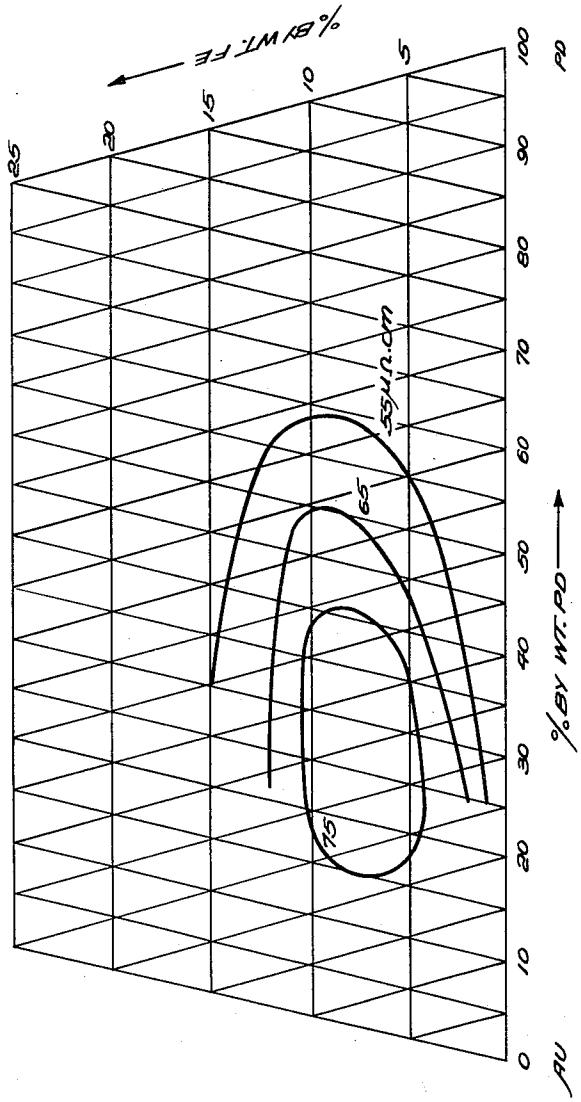
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Fig. 2.



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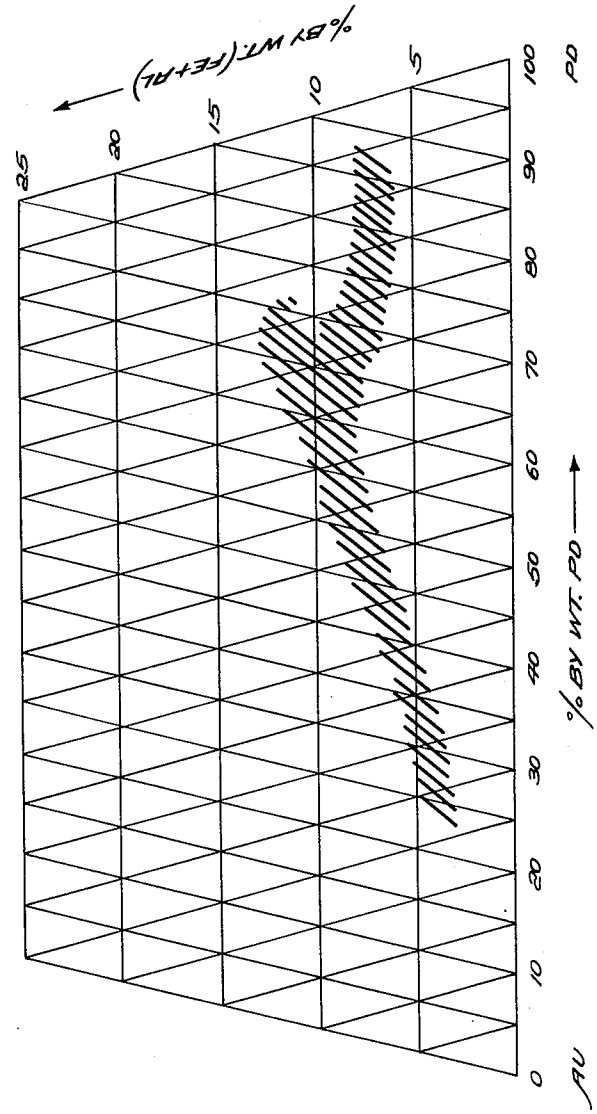


Fig. 3.

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NOBLE METAL ALLOYS HAVING A HIGH SPECIFIC ELECTRIC RESISTANCE

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6 Claims. (Cl. 75—165)

The present invention relates to an improved noble metal alloy of high specific electrical resistance with a low temperature coefficient and low thermoelectric potential against copper.

In the process of miniaturizing parts of electric and electronic equipment the endeavor is made, for example, in the production of potentiometers and similar electrical apparatus, to employ alloys which have as high a specific electrical resistance as possible. In addition, such alloys should also exhibit other desirable properties, such as, low temperature coefficients for the specific electric resistance, high resistance to abrasion, low thermoelectric potential against copper, corrosion resistance, constant resistance under long periods of operation, as well as a low and constant transfer resistance.

Some of these requirements are excellently fulfilled by alloys consisting only of noble metals. However, previously no base metal free alloy is known which has a specific electrical resistance greater than about 50 $\mu\Omega\cdot$cm. As a consequence, in order to achieve higher specific resistances, base metals were alloyed therewith. A number of alloys of this type are already known which in addition to one or more noble metals, such as, platinum, gold, palladium and the like, contain most varied additions of base metals, for example, Pd/W, Pd/Mo, Pt/Cu/Ni, Pd/V, Pd/Ti and like alloys, have been described for this purpose.

In addition, alloys of the three component system Au/Pd/Fe have also become known, particularly because after a special heat treatment some of them achieve very high specific resistance values. Such alloys, however, without such heat treatment exhibit only relatively low specific resistances between about 40 and 80 $\mu\Omega\cdot$cm. The special heat treatment consists in that after soft annealing at 750° C. they are tempered at temperatures between 300 and 600° C. for up to 24 hours. The highest specific resistance which can be achieved with such special heat treatment is 191 $\mu\Omega\cdot$cm. and is achieved with a 49.5% Au/40.5% Pd/10% Fe alloy. The numerical percentages given herein and in the following are by weight.

In practice, however, such specially heat treated alloys are little suited for potentiometer wires as the high specific resistance values achieved with such heat treatment would change when the potentiometer becomes warm in use.

According to the invention it was found that alloys with 18 to 75% Au, 75 to 20% Pd, 2 to 15% Fe and 0.4 to 5% Al, B, Ga or In possess the desired high specific resistance and therefore are suited for use in resistance wires, for example, for potentiometers. The alloys according to the invention differentiate from the known Au/Pd/Fe alloys primarily in that they contain small quantities of Al, B, Ga or In, such as, for example, 0.4

to 1.2% of Al. These seemingly small additions have the unexpected and surprising effect that they render the tempering treatment, which is decisively important for the known Au/Pd/Fe alloys, superfluous.

In the production of the alloys according to the invention a final anneal of only, for example, 30 minutes at 800–900° C. with subsequent cooling of almost any desired nature suffices. It was found that upon cooling in the furnace from 900° C. to room temperature over a period of 10 hours, upon cooling through the same temperature range in 10 minutes and upon normal cooling in air by removing the samples from the oven at 900° C. (cooling time 10 seconds) practically in every instance the same specific electric resistance was attained for each individual alloy. Even with sharp quenching in ice water the specific electrical resistance only changes 3–5%. A further increase in specific electrical resistance by tempering at 400 to 500° C. is not possible as is the case with Au/Pd/Fe alloys not containing the small additions according to the invention.

A further advantage of the alloys according to the invention resides in that specific electrical resistances can be achieved therein which are even higher than those attained in the Au/Pd/Fe alloys in the tempered state. The highest specific electric resistance found in an alloy according to the invention is 230 $\mu\Omega\cdot$cm. with an alloy of 50% Pd, 38% Au, 11% Fe and 1% Al.

This maximum specific resistance is not only higher than that achieved in the corresponding Au/Pd/Fe not containing additions such as Al, but also is achieved with an alloy with a lower gold content. This provides two advantages, namely, that a part of the gold is replaced by the cheaper palladium and that the specific weight of the alloy is less so that a larger quantity of wire can be produced per unit of weight.

The specific electric resistance of the alloys according to the invention passed through a rather flat maximum with changing content of the additional metals which, for example, in the case of aluminum is at about 1%. It was, for example, found that with additions of 0.9 to 1.1% of aluminum practically the same specific electric resistance is obtained. This circumstance is of advantage in the production of the alloys as up to 10% of the aluminum supplied can be lost by oxidation during the melting of the alloy and still the alloys obtained will exhibit great uniformity in their specific electric resistance.

The alloys exhibit their maximum resistance in soft annealed form rather than in wrought form. They therefore exhibit exceptional constance of resistance over long periods of use and even on warming over the normal temperatures of use.

In the accompanying drawings:

FIG. 1 shows a diagram of Au/Pd/Fe/Al alloys containing 1% of Al and demarks such alloys according to the invention containing 18–75% of Au, 75–20% of Pd, 2–15% of Fe and 1% Al and in addition gives the lines of equal specific electric resistance;

FIG. 2 shows a diagram of Au/Pd/Fe alloys and gives the lines of equal specific electric resistance of such alloys without an addition of Al and without tempering; and

FIG. 3 shows a diagram of Au/Pd/Fe/Al alloys containing 1% of Al, the hatched area being the range in

which the thermoelectric potential against copper is zero or only weakly negative or positive.

Table 1 gives several examples of the specific electric resistances of the alloys according to the invention containing additions of Al, Ga and In:

Table 1

Au	Pd	In percent		Ga	In	Spec. electr. resistance soft annealed 0.5 h./800° C. in μΩ·cm.
		Fe	Al			
65.8	30	3.5	0.7	-------	-----	85
65.5	30	3.5	1	-------	-----	90
65.3	30	3.5	1.2	-------	-----	89
62	29.5	7.5	1	-------	-----	130
58	34.5	6.5	1	-------	-----	160
47	42	10	1	-------	-----	190
44.5	45	9.5	1	-------	-----	205
38	50	11	1	-------	-----	230
30	55	14	1	-------	-----	194
30	58	11	1	-------	-----	206
20	72.5	6.5	1	-------	-----	75
44.8	44.7	9.4	-------	1.1	-----	188
55.9	36.2	6.4	-------	1.5	-----	139
59	33.4	5.6	-------	2	-----	121
57.1	35.6	6.3	-------	-------	1	119
56.1	35.6	6.3	-------	-------	2	132

Practically the same resistance values are obtained with Ga and In as with Al but in addition the processing properties of the Ga and In containing alloys are improved. The hardness of the Ga and In containing alloys is lower than that of the corresponding Al containing alloys. Furthermore, a certain tendency for the alloys produced with Al to undergo transcrystallization is suppressed by additions of Ga or In.

If desired, it is possible to employ two metal additions, such as, Ga and In simultaneously rather than only one metal addition.

When calculated in atom percent the quantity of the metal addition is practically the same for the metal additions indicated but in view of the different atomic weights of such metal different ranges in percent by weight come into consideration.

Preferably the alloys according to the invention consist of 18–70% of Au, 70–23% of Pd, 4–11.5% of Fe and 0.4–1.2% of Al or 0.4–3% of Ga or 1–5% of In. Also, preferably the sum of the Fe and Al, B, Ga or In contents is at least 5% and not more than one quarter of the Pd content in percent by weight.

In suited instances it is also expedient to employ B as the metal addition, especially when the quantity of Pd in the alloy is relatively high. All of the metal additions employed according to the invention are elements of Group III of the periodic system.

The average temperature coefficient of the specific electric resistance of the alloys according to the invention between 0° C. and 100° C. in general is very near to zero or it is even negative. The maximum negative value found was $-0.265\times10^{-3/°}$ C. On the other hand, there are alloys within the range according to the invention which still have a specific electric resistance around 100 μΩ·cm. and have temperature coefficients of over $+4\cdot10^{-3/°}$ C. in view of ferromagnetic influences.

The thermoelectric potential of the alloys according to the invention against copper runs with increasing Fe content from negative values through zero, weakly positive values and then again to negative values. The hatched area shown in FIG. 3 is the range in alloys according to the invention containing Al in which the thermoelectric potential against copper is zero or only weakly negative or positive. Similar groups of curves are also obtained with the other metal additions according to the invention.

I claim:

1. An alloy consisting essentially of 18 to 75% by weight of Au, 75 to 20% by weight of Pd, 2 to 15% by weight of Fe and 0.4 to 5% by weight of at least one component selected from the group consisting of Al, Ga, In and B.

2. An alloy consisting essentially of 18 to 70% by weight of Au, 70 to 23% by weight of Pd, 4 to 11.5% by weight of Fe and 0.4 to 1.2% by weight of Al.

3. An alloy consisting essentially of about 38% by weight of Au, about 50% by weight of Pd, about 11% by weight of Fe and about 1% by weight of Al.

4. An alloy consisting essentially of 18 to 70% by weight of Au, 70 to 23% by weight of Pd, 4 to 11.5% by weight of Fe and 0.4 to 3% by weight of Ga.

5. An alloy consisting essentially of 18 to 70% by weight of Au, 70 to 23% by weight of Pd, 4 to 11.5% by weight of Fe and 1 to 5% by weight of In.

6. An alloy according to claim 1 in which the sum of Fe and component contents is at least 5% by weight and does not amount to more than one-fourth of the Pd content in percent by weight.

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