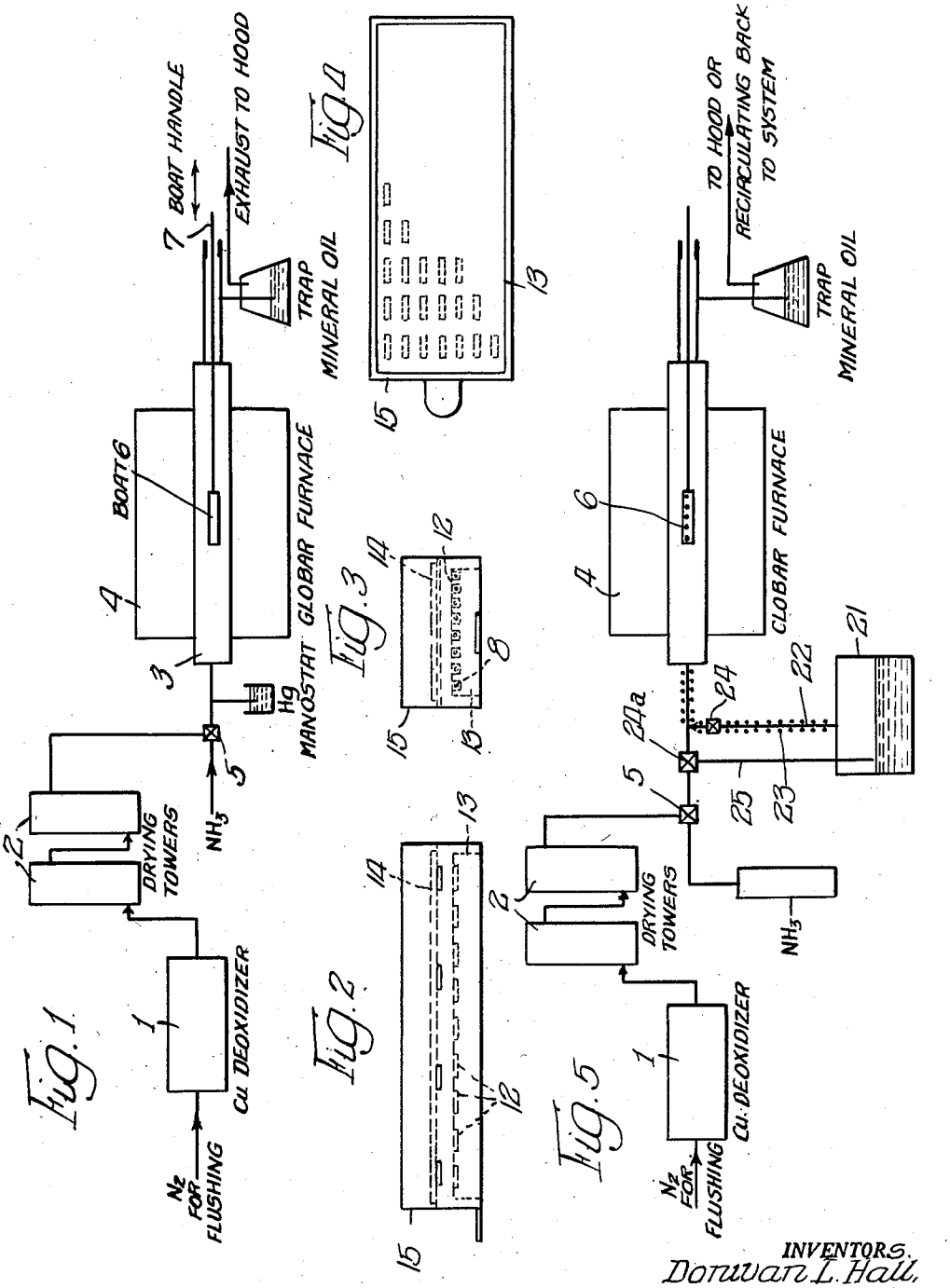
April 2, 1957 D. L. HALL ET AL 2,787,688

CONTACT MATERIAL

Filed July 10, 1951 5 Sheets-Sheet 1



INVENTORS.
Donavan L. Hall,
Arthur E. Middleton,
Earl R. Olson,

By Brown, Jackson, Boettcher & Dienner Attys.

April 2, 1957 D. L. HALL ET AL 2,787,688

CONTACT MATERIAL

Filed July 10, 1951 5 Sheets-Sheet 2

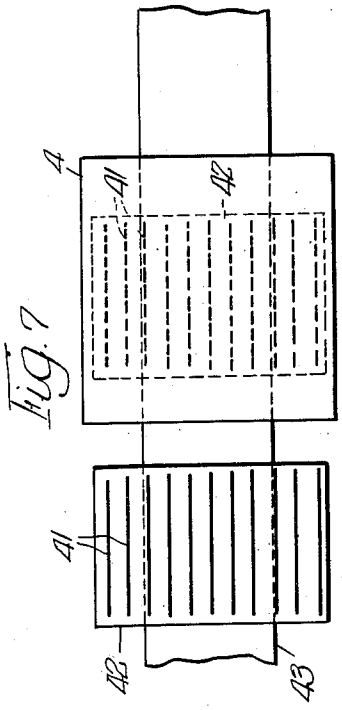


Fig. 7

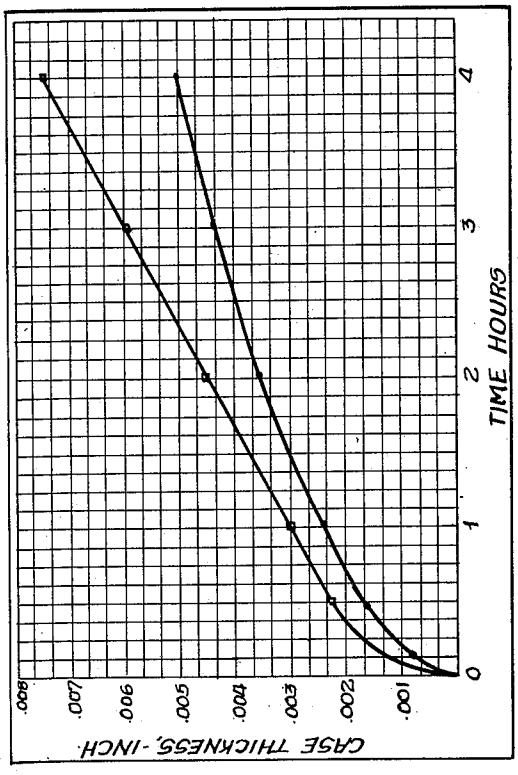


Fig. 9

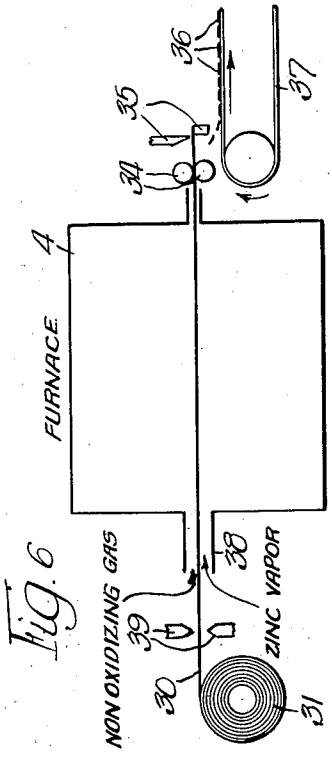


Fig. 6

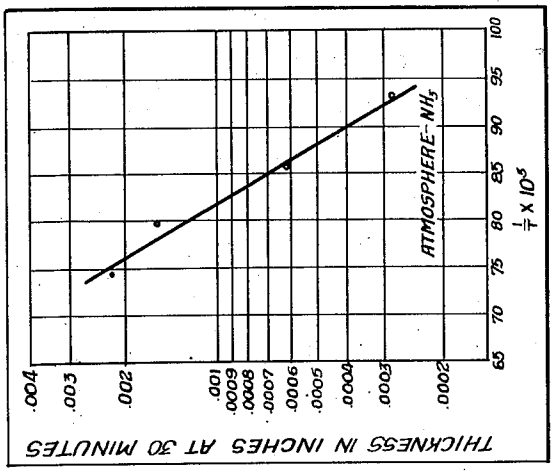


Fig. 8

INVENTORS.
Donavan L. Hall,
Arthur E. Middleton,
Earl R. Olson,
By Browne, Jackson, Boettcher & Dienner attys.

April 2, 1957 D. L. HALL ET AL 2,787,688

CONTACT MATERIAL

Filed July 10, 1951 5 Sheets-Sheet 3

Fig. 10

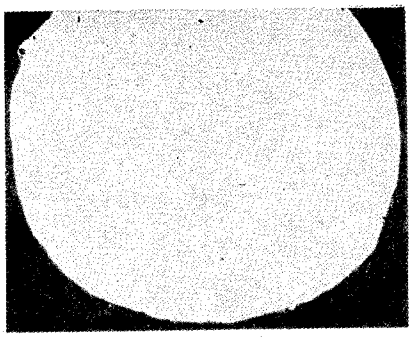


Fig. 11

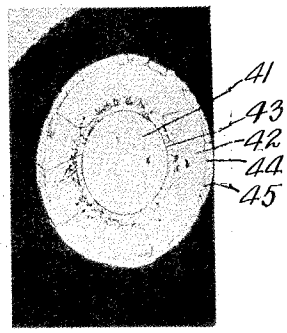


Fig. 12

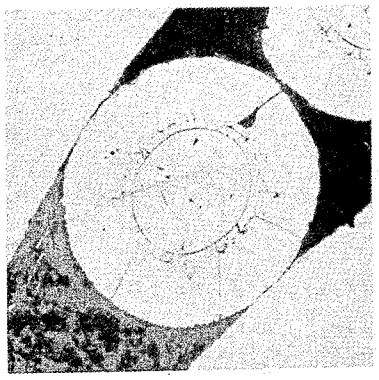
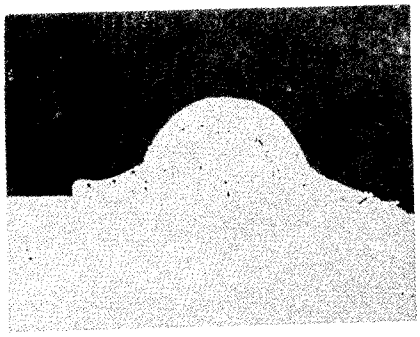
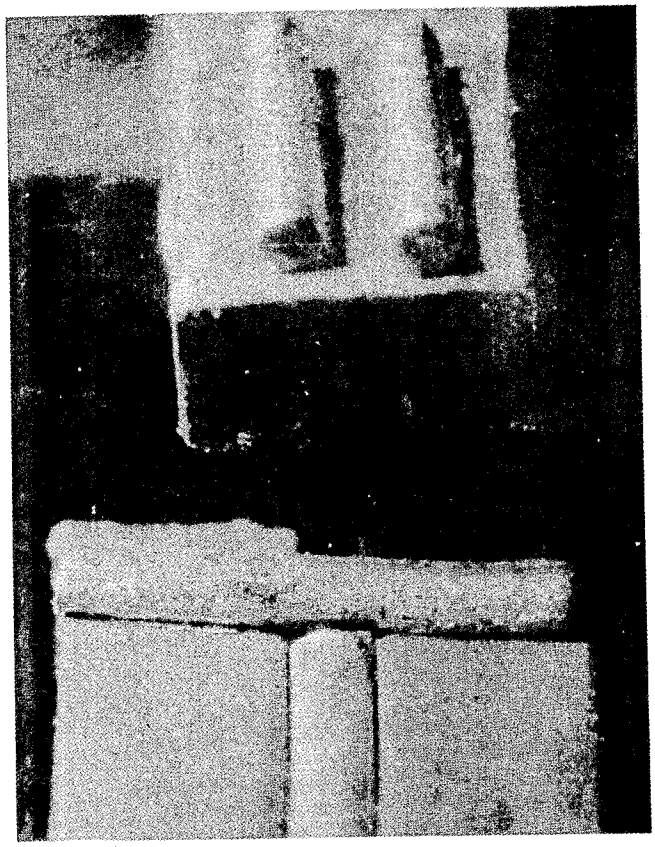


Fig. 13



Inventors:
Donivan L. Hall
Arthur E. Middleton
Earl R. Olson
By Brown, Jackson, Boettcher & Dienner
Atty's.

Fig 14.



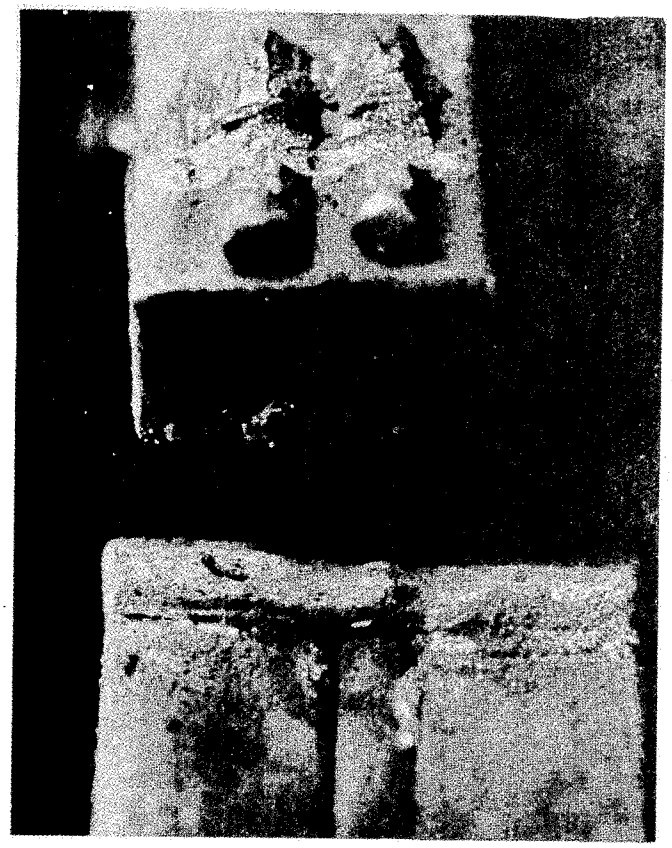
Inventors:
Donivan L. Hall
Arthur E. Middleton
Earl R Olson
By Brown, Jackson, Boettcher & Dienner
Attys.

April 2, 1957 D. L. HALL ET AL 2,787,688

CONTACT MATERIAL

Filed July 10, 1951 5 Sheets-Sheet 5

Fig 15



Inventors:
Donivan L. Hall
Arthur E. Middleton
Earl R. Olson
By Brown, Jackson, Boettcher & Dienner
Attys.

United States Patent Office 2,787,688 Patented Apr. 2, 1957

2,787,688

CONTACT MATERIAL

Donivan L. Hall, Galion, and Arthur E. Middleton and Earl R. Olson, Columbus, Ohio, assignors, by direct and mesne assignments, to The North Electric Company, a corporation of Ohio

Application July 10, 1951, Serial No. 235,948

15 Claims. (Cl. 200—166)

The present invention relates to a new and novel alloy or composition which is particularly adapted for use with electrical equipment, to a method for making same, and to an electrical member made therefrom. In particular, the present invention relates to novel electrical contact members which are especially adapted for use in telephony, telegraphy and other co-related fields.

With the rapid growth of industry in recent years there has been a corresponding diversification and increase in the use of electrical equipment in the various fields. In these new uses and applications, greater demands were constantly made of the electrical equipment, and as a result the existing equipment in many of these fields became outmoded. The newer systems of control, for example, operated at greatly accelerated speeds and demanded electrical equipment which was capable of withstanding the greater mechanical stresses which accompanied the accelerated speeds; automatic switching in its new form meant more frequent operation of the equipment and required equipment which was capable of withstanding increased physical wear; the more complex circuits which were developed introduced unusual electrical load conditions which required equipment capable of withstanding destruction resulting from these causes. These and many other severe operating conditions which tended to shorten the life of the equipment were continually encountered in the rapidly advancing field, and it was soon evident that the development of new materials was necessary to prevent repeated equipment failures.

Primary among the causes of failures of electrical equipment in their new application was the inability of the known electrical contact members (which form an integral part of all electrical equipment) to withstand these varied load conditions. As a specific example of the problems that arose therefrom in one field alone, reference is made to the telephone art, this field being exemplary of the exacting conditions in most other fields which utilize electrical equipment in their operations.

In the early days of the telephone art a single manual telephone board which was adapted to extend connections between one hundred subscribers lines included only a limited number of so-called circuit controlling members, and each of these members was operated, at most, a comparatively few times a day. With the development of automatic telephone exchanges in which each of the subscribers controls a series of automatic switches in extending a connection to another exchange subscriber, a similar one hundred line exchange now utilizes tens of thousands of these circuit controlling contact members, some of which are operated at an extremely high frequency rate. For example, one set of contacts alone (the contacts on the conventional dialling relay in a telephone exchange) will be operated as many as two million times a year. Moreover the operations of these contacts are effected under varied and severe electrical and mechanical conditions which quickly promote contact destruction.

In the use of conventional materials in such applications, it was not uncommon to have equipment failures in less than a year, such failures being in the nature of deterioration due to mechanical wear, fusing and sticking of contact points, extreme pitting of contact surfaces, and contact transfers. As a result of these continued failures a large amount of time and research were expended in an effort to provide materials which would operate under these adverse conditions.

The extensive development which has been conducted in the past resulted in the advancement of such materials as gold, palladium, platinum, and silver, as well as cadmium, copper iridium, nickel, rhodium, osmium, and ruthenium. Most of these metals have been employed singly, and others have been combined in an attempt to improve their properties to the point that successful operation may be consistently established therewith. Even today however, after years of development and research, the known contact materials used with dialling relays in automatic telephone exchanges exhibit an incurable type of failure resulting from inductive voltage surges and electrical discharges and usually have a life expectancy of only one to two years.

The excessive maintenance and operation costs which result from these failures in a system having thousands of these contacts is immediately apparent. The cost of the maintenance moreover is further aggravated by the reduced quality of service which is frequently afforded to the subscribers as a result of these failures.

There is a need therefore in industry today, and particularly in the telephone industry, for an improved material which will provide satisfactory service over long periods of time when subjected to use under even the most adverse operating conditions, and it is an object of the present invention to provide a new and novel alloy or composition for use in electrical contacts which are particularly adapted to fill this need. It is also an object of the invention to provide a novel method for making articles from this alloy, and particularly, to provide a method for making improved contact members for use in electrical equipment.

These, and other objects and advantages of the present invention, will become more apparent from the following detailed description, examples, and drawings, wherein:

Figure 1 is a schematic diagram of an apparatus arrangement for producing the new and novel composition of the present invention;

Figure 2 is a diagrammatic side elevation view of a device showing an arrangement of elements on a tray for high production purposes;

Figure 3 is an end view of the device shown in Figure 2;

Figure 4 is a plan view of the device shown in Figure 2;

Figure 5 is a schematic diagram of another apparatus arrangement, similar to that shown in Figure 1, for effecting the purpose of the present invention;

Figure 6 is another schematic diagram of an apparatus arrangement, similar to Figure 1, but designed for continuous operation;

Figure 7 is a diagram of a system arranged for continuous batch operation;

Figure 8 is a diagram showing the effect on the casing of the temperature used;

Figure 9 is a diagram showing the rate of the growth of the casing with time at different temperatures;

Figure 10 is a polished, cross-sectional enlarged view of the untreated base material, palladium wire;

Figure 11 is an enlarged polished and etched cross-sectional microphotographic view of a novel composition of the present invention showing the casing and phases obtained with a given treatment;

Figure 12 is an enlarged, polished and etched, cross-

sectional view of the new and novel material of the present invention, heated to a high temperature and then quenched to bring out beta phase on the surface;

Figure 13 is an enlarged, polished, cross-sectional view showing a contact element of the present invention mounted on a ferrous base and showing the fillet which forms between the contact and base;

Figure 14 is a view showing the result of operating the contact of the present invention for one type of life test under specified conditions; and

Figure 15 is a view similar to Figure 14, and shows the result of running a prior-art contact material for the same life test under the same conditions.

It his now been discovered that by treating palladium in the presence of an adequate concentration of zinc vapor at a given temperature and for given periods of time, the zinc is caused to diffuse into the palladium to form a composition of matter which is characterized by remarkable wear and endurance properties. The resulting material may take the form of a casing on a palladium rich core, a number of several phases exhibited in the thickness; or a material of a single phase. Each phase exhibits given characteristics whereby each of the various phases may have preferred applications in keeping with its characteristics. One phase for example which is particularly well suited for electrical contact work is the beta phase, it having been proven by comparative tests that a member having as little as 25% beta phase by volume has a life expectancy of twenty years as compared to two years for contacts of known materials. Other phases of the novel alloy, as for example the alpha phase, have remarkable properties of endurance and wear in their application as electrical contact members. The delta phase exhibits other equally desirable wear characteristics, having an extremely high Knoop hardness number rating. This new and novel material has good electrical and thermal conductivity in each phase, is readily secured to current carrying members or armatures, and is as resistant to the formation of chlorides, hydroxides, oxides and sulfides as most materials now commonly used in electrical equipment.

Palladium and zinc have harnesses of 55 to 100 and 40 to 50 Knoop numbers respectively. However the alloy of palladium and zinc in any of its phases has a Knoop number of greater value than the palladium and zinc have individually. For example, the alloy in its first or alpha phase contains up to 15% by weight of zinc, the balance palladium, and has a hardness of 55–150 Knoop numbers; in its second or beta phase, comprises a body centered, cubic form of palladium and zinc alloy containing from about 22 to about 27% by weight of zinc and having a hardness of 275–325 Knoop numbers; in an intermediate stage comprising the alpha and beta phases, contains a total of less than 27% by weight of zinc; in a fourth or gamma phase has a hardness of a 100–150 Knoop numbers containing from 28 to 41% by weight of zinc and has a tetragonal lattice structure; in a fifth or intermediate stage comprises a mixture of beta and gamma containing less than 41% by weight of zinc; and in a further phase known as delta and including the alloy identified as Pd_5Zn_{21}, has a portion of up to 75% zinc and a Knoop hardness of from 400 to 470 numbers.

A member made of the alloy in one, several or all of the aforegoing phases may be provided by varying the process or by varying the treating process to convert the existing phases of the alloy to other phases thereof as desired and as more fully described hereinafter.

The novel method by which the noble metal palladium is alloyed with zinc to provide the alloy of the preferred phases, and the method of providing an electrical contact of that material is now set forth hereat.

In general, the new and novel contact of the present invention is prepared by diffusing zinc into palladium at high tempratures in the presence of a nonoxidizing gas. One system and method are set forth in Figure 1 of the drawings, it being understood that variations of the system will effect corresponding changes of time, temperature, etc., and are considered to be within the scope of this invention. As there shown, the system is first flushed with nitrogen which is passed through a copper deoxidizer 1 and drying towers 2—2 and into a quartz reaction tube 3 of a globar furnace 4, and thence to the hood. After flushing, a valve 5 between the drying towers in the tube is turned on to introduce a continuous stream of ammonia gas into the system while the nitrogen is cut off. A vycor or metal boat having a long handle, schematically indicated at 7, and containing palladium contacts and an excess of a source of zinc, is then pushed into the hot zone of the quartz tube 3 of the furnace. It is not necessary that the zinc source be placed in physical contact with the palladium.

The system is operated at elevated temperatures for periods of less than an hour to several hours, at the end of which time the contact members are composed of the novel palladium zinc alloy. The contacts are then permitted to air cool therein and upon removal are ready for immediate use as electrical contact members without further treatment.

Any source of zinc in which the zinc very readily violatilizes therefrom at the temperatures employed may be used in the system. It is not necessary that the contacts be rotated or that their positions be changed in the process, or that the zinc source be piled around the palladium contacts, for the zinc vapor appears to very readily diffuse through all the surfaces of the palladium to provide even and uniform penetration thereof. As shown in Figures 2, 3 and 4 one method of producing the contacts in quantity may comprise placement of the palladium contacts 8 in slots 12—12 of a ceramic tray 13 in a boat or holder 15 with a sheet 14 being inserted thereabove as the zinc source.

In Figure 5 there is shown another apparatus similar to that shown in Figure 1 except that the zinc vapor from the zinc retort distiller 21 is led through piping 22 surrounded by heating elements 23 to maintain the zinc in a vaporized form, to a mixing valve 24, where it is fed into the hot zone of the globar furnace 4 to contact the palladium elements supported in the holder 6. The amount of the zinc vapor entering the system and in contact with the palladium, as well as the gas flow rate, can be very easily controlled by means of the valves, such as 5, 24, 24*a*, in the lines leading to the furnace. A back pressure line 25 supplies gas under pressure to force the zinc vapor toward the furnace. It is to be understood that means for collecting the excess zinc at the exit of the tube can be employed so that the zinc may be re-used in lieu of the zinc vapor re-circulating system.

A method for continuously treating a palladium wire or strip 30 is illustrated in Figure 6 and, as there shown, the palladium wire or strip is passed from a roll 31 into the furnace 4 and is pulled through the furnace by means of rollers 34—34 where a knife or other cutting means 35—35 cuts it into the desired lengths 36, which fall on conveyor 37. The speed with which the wire passes through the furnace may be varied to vary the time of treatment of the passing metal. The zinc vapor and nonoxidizing gas may be led into the furnace through the same port 38 or through separate control means. The wire may be serrated by suitable notching means 39—39 at predetermined intervals along its length prior to entry into the furnace 4 and, as a result of the thinness of the material at the point of the serration, the casing will form on a greater portion of the contact surface. That is, as the wire emerges from the furnace and is cut by the knife 35, substantial portions of the ends of the individual pieces will have a casing similar to that of the major portion of the contact.

In Figure 7 there is shown a schematic sketch which illustrates generally a method of providing a continuous batch treatment of palladium wire or strips 41, in which

a series of strips are mounted on each of the frameworks 42 of ceramic or other suitable materials which is carried by a conveyor 43. At predetermined timed intervals the conveyor 43 operates to move a prepared batch of wires 41 into the furnace 4 and a treated batch of wires 41 out of the furnace 4. Suitable automatic means for loading the conveyor and for removing the alloyed strips from the framework and cutting same into the desired lengths may be used with the illustrated system in an obvious manner. Other systems for diffusing the zinc into palladium metal at high temperatures in the presence of nonoxidizing gas which may be used are considered to be within the scope of this invention.

The palladium members to be coated may be of any form, shape or thickness, the illustrated sheets and wires being merely shown herein for purposes of example.

The source of zinc in this method is placed within the furnace closely adjacent the palladium, or alternatively, the zinc vapor is supplied in a high concentration from an outside source of supply. Differences in the quantity of zinc required will obviously be dependent upon times, temperatures, thicknesses of coating desired and its design and efficiency, an excess of zinc being generally supplied to the system in most instances to insure thorough penetration. The use of a source of zinc in a ratio of 10 to 1 (zinc to palladium) has been found to be satisfactory.

A very good source of zinc vapor from which the evolution of zinc is not too rapid is an alloy of copper, nickel and zinc (called nickel silver) containing 14 to 37% zinc, which is placed in short strips about the palladium. For example, "nickel silver 18% A" contains 65% copper, 18% nickel and 17% zinc and "nickel silver 18% B" contains 55% copper, 18% nickel and 27% zinc. Any alloy which will furnish zinc as a vapor by diffusion therefrom, as for example German silver, or a compound such as zinc carbonyl, cyanide, or nitrate are satisfactory materials for use in the process. Pure zinc may also be used, the zinc in such case being volatilized in the furnace or in a separate still and then piped thereto. Obviously a material which contains little zinc or furnishes only a small amount will have to be used in larger quantities and vice versa.

The atmosphere which is used in the furnace should not be deleterious with respect to zinc, palladium, or the resulting alloy. The gas apparently acts as a carrier for the zinc and appears to have desirable cleansing and fluxing properties. Gases which have been found to be acceptable include any nonoxidizing or essentially oxygen free gas which also includes gases which are inert or reducing. By way of example, gases which have proven satisfactory in the process include ammonia, argon, helium, hydrogen, and nitrogen. Other gases having similar nonoxidizing characteristics may be used, these gases being merely exemplary for purposes of disclosure. Certain of these gases but not all, may form inclusions at various points in the cross section of the resulting contacts. However, such inclusions in very minor amounts do not apparently effect the properties of the resulting alloys.

The useful gases can be used singly or mixed together, or in any order. In the process, the passage of the gas through the system when effected at a rate of about one to five liters per minute has been found to be very efficient in causing proper zinc diffusion and concentration.

The temperature range in providing the novel palladium zinc contact alloys of the invention will vary from 500 to about 1000 degrees centigrade with the apparatus utilized in the test. Designed variation of the described system will, of course, cause variations in the temperatures which are within the scope of the invention.

Figure 8 shows the correlation between the case thickness and temperature. The characteristics of a substitutional diffusion process are shown by the practically straight-line function of log of thickness vs. the reciprocal of the absolute temperature. In other words, the thickness of the case will be found to vary with temperature according to the diffusion laws, i. e., the log of the case thickness is proportional to the reciprocal of the absolute temperature. The law governing temperature dependence of diffusion in metals is expressed by the equation

$$D = Ae^{-\frac{Q}{RT}}$$

where D is the diffusion coefficient of Zn in Pd, A is a constant dependent upon the metals involved, and Q provides a measure of the activation energy of the reaction required to cause diffusion. Both A and Q are practically independent of temperature. R is the gas constant, and T is the absolute temperature. It can also be shown that D is approximately proportional to x^2 where x is the displacement of particles across an area of unity. It can be seen, therefore, that a log plot of D, or a log plot of case thickness, as a function of $1/T$ yields a straight line. Further, some change in phases is noted as the temperature or the time, or both, are continued at higher rates for longer periods. For example, Figure 9 shows that thicker cases are obtained at higher temperatures for the same time and concentration of zinc.

The process can be carried out for any length of time to vary the casing or phase being produced. A treating period of more than 12 hours in the described system, for example, provides an alloy of higher zinc content, such as the gamma and delta phases. As soon as the process starts, that is, within a very few minutes, zinc will begin to diffuse into the Pd so that the lower time limit is almost negligible. However, to obtain a satisfactory casing, phase, or alloy having the desired wear properties, it is considered desirable to treat for at least one half-hour. The best results, as to case thickness, hardness, efficiency of method, etc., have been obtained utilizing a period of time of from 1 to 4 hours so that this represents a preferred range with the given system.

For a given amount of available zinc vapor and at a given temperature, the case or phase will grow with increased time of treatment. Table A, below, shows the diameter increase caused by the zinc diffusion into palladium wire (15 mil) using a "nickel silver 18 percent B" source for the zinc at 1,000° C. in an ammonia atmosphere.

TABLE A

Time of Treatment, Hours	Diameter Increase, Percent
½	11.5
1	15
2	20
3	24
4	27½
6	30
8	32
12	33½

Table B, below, shows the thickness and weight increases caused by the diffusion of the zinc into a 10 mil palladium sheet under an ammonia atmosphere at 1,000° C. using the same type of zinc source. It will be noted that the thickness increase is somewhat proportional to the resulting weight increase:

TABLE B

Time, Hours	Diameter Increase, Percent	Weight Increase, Percent
1½	20	15
3	28½	18
3½	32	24
4½	36	26
5½	42½	29
7	51	32

A satisfactory casing of 1.2 mil beta phase constitutes approximately 25% by volume of alloy or about 5% total weight zinc.

Quenching may be performed immediately following the diffusion treatment to prevent some zinc volatilization from the contact, although in the manufacture of articles such as telephone contacts, which are small in weight and volume, the air cooling is quickly effected as the contacts pass through the cool end of the furnace and air quenching appears to be sufficient.

Past or subsequent treatments, such as heating and quenching in an inert gas or reheating in zinc vapors at a lower temperature can be used to change the phases of the material or to produce one solid phase.

For example, subsequent heat-treatment for continued periods at high temperatures but below about 1000° C. may show grain consolidation, or growth of the alpha, beta, with a loss of some of the mixed phases, a reduction in the sharp interface between the core and the casing, and loss of gamma. However, heating at or above 1000° C. for any appreciable length of time in an atmosphere void of zinc, causes loss of zinc through volatilization and resulting pitting of the surface of the material.

The following examples will serve to illustrate a method of providing an alloy of palladium and zinc and the manner of providing individual phases thereof, the manner of providing alloys having several of the phases thereof, and particularly the manner of providing an alloy including the beta phase, which has proven extremely satisfactory for use in certain electrical contact applications.

Example I

Palladium wire, 0.015 inch in diameter, was heated at 1,000° C. for five hours in the presence of an excess 30 parts "nickel silver," an alloy containing 55% Cu—18% Ni—27% Zn, 1 part of Pd, under an atmosphere of nitrogen in a furnace utilizing the apparatus set-up shown in Figure 1. The gas flow rate was 3,000 cc./min. The wire increased in diameter about 20% and the zinc had apparently diffused completely throughout the palladium. The same experiment was performed on a palladium sheet, 0.010 inch thick, except that it was treated for only 3 hours. The sheet was observed to have been penetrated through about 80% of its thickness by the zinc. Presence of zinc in sheet and wire was determined by X-rays, and microchemical and spectrographical analyses. The sheet increased about 30% in volume, and 18.4% in weight. On the basis of the new volume and weight, the density was observed to be about 10.7 grams per cc. as compared to 11.7 grams per cc. for the sheets prior to treatment. This corresponds to a diffusion of about 16% zinc. The sample calculations following indicate that the changed density and volume can be explained by substitutional diffusion:

The weight increase, as observed, was 18.4 percent, the volume increase, as observed, was 28.2 percent and the density, as observed, was 10.7 grams per cc. Assuming a 100 gram specimen of untreated palladium, 100 divided by 11.67 is equal to 8.575 cc. of palladium, where 11.67 was the observed density of untreated palladium. Also, 18.4/7.14=2.575 cc. of zinc where 7.14 is its density.

Total volume=2.575+8.575=

$$11.15 \text{ cc.} \frac{100+18.4}{11.15}=10.6 \text{ gr./cc./—}$$

calculated density of Pd-Zn alloy

Further

$$\frac{2.575}{8.575}=30\%$$

where 30% is the calculated volume increase. Thus, the observed volume increase corresponds with that calculated for a direct substitution of zinc atoms for palladium within the limits of accuracy of the measurement. The atom size is not conducive to interstitial diffusion, and these calculations, thus, are an attempt to show that substitutional rather than interstitial diffusion occurs. The hardness of the treated wire was 290 Knoop numbers and of the treated sheet was 305 Knoop numbers. Both wire and sheet showed slightly less film formation after exposure for 0.5 hour at 450° F. to an atmosphere of 90% chlorine than pure palladium treated under similar conditions.

Figure 11, 100X, shows a sample of the material as produced by the process of this example, which has been sectioned, polished, and etched, to show a varying grain structure. In the figure the central core 41 is Pd in which some zinc has dissolved and is described as alpha palladium phase. The second phase, 42, which is the thickest, is considered beta phase, a body centered cubic compound of Pd and Zn. The area or zone designated as 43 is a mixture of the alpha and beta phases. The portion indicated by the number 44 is a thin outer coating on the casing, really a portion of the casing itself, and is designated as gamma phase, PdZn. The lamellar structure indicated at 45 is apparently a mixture of beta and gamma phases.

Contacts made by this process and subjected to given test conditions along with the control palladium contact which did not have the treatment (Figure 10) indicated that an increase in life span of at least six times may be expected.

Example II

Additional palladium wires were treated according to the method described in Example I, except that the temperature and times were varied. The samples were microchemically and spectrographically analysed and tested with X-rays. The results of the increased temperature have been indicated generally in Figure 8, it being observed that when magnified 500 times, the samples indicated a definite change in grain size, the size increasing with temperature increases and the case thickness also increased in given proportional amounts with the temperature increases.

Example III

Additional experiments were performed similar to that described in Example I, the source of the zinc to be disfused was "nickel silver," an alloy thirty times weight of palladium of 55% copper, 18% nickel and 27% zinc. The palladium contacts were treated at 950° C. for thirty minutes under certain tests in a vacuum and under other tests using different carrier gases.

Only a small effect was indicated with the vacuum treatment (10^{-5} mm. Hg pressure), the method producing a layer of flat, irregular grains, rather than a case as was formed on the surface in the previous methods. A sample treated in hydrogen, magnified 250 times, showed a casing on the top surface having a hardness of 325 Knoop numbers. Casings formed on palladium sheet in helium and nitrogen provide a case having Knoop numbers of 290 and 310, respectively. The magnification 500 times indicated that a fine lamellar structure is provided near the surface of the palladium zinc casing when treated with helium and nitrogen respectively. Although the surface of the casing of the alloy may vary slightly in physical appearance, the overall properties of the material are quite similar.

Example IV

The alloy was also post heat-treated. Palladium wire was treated in close proximity to an excess of "nickel silver" (27% Zn) under an atmosphere of ammonia for 4 hours at 940° C. Subsequently, the resulting contact was treated in air at 982° C. for 10 minutes, and then given a water quench. The material was then sec-

tioned and polished and finally etched with a solution containing a 1 to 1 to 3 ratio of 20 percent KCN, 20 percent $(NR_4)_2S_2O_8$, and 3 percent KI. The results therefrom are shown in Figure 12 (150X) where the major portion of the contact is beta phase. It will be noted that the outer phases have absorbed some of the inner mixed phase and that there has been some loss of zinc from the outer casing as evidenced by the rough, irregular, porous surface and the absence of the lamellar structure.

The resistivity and temperature coefficient of resistivity were determined for a sample treated for a period longer than that required to alloy the center of the palladium sheet with the diffusing Zn (1,000° C.—7 hours—ammonia atmosphere). A resistivity of about 5.8×10^{-5} ohm.-cm. was observed. The temperature coefficient of resistivity was 2.8×10^{-4} per °C. for temperatures from room to 320° C. Measurements were made potentiometrically using a type K potentiometer. Pure Pd and Zn have resistivities of 11×10^{-6} and 6×10^{-6} ohm.-cm., respectively. Both exhibit a temperature coefficient of about 3.5×10^{-3}. These comparisons reveal the alloy has a higher resistivity and lower temperature coefficient of resistivity than palladium or zinc. At higher temperatures the resistivity is not objectionable and is comparable to palladium. Thus, the element is not subject to adverse burning or melting.

As shown in Figure 13, 100X, the novel contact materials of the present invention are easily attached to base contact or current-carrying members, in this case a nickel-iron magnetic type base, by spot welding. In such cases they readily form large fillets between the contact itself and the current-carrying member. Such fillets apparently materially aid in securing the contact to the current-carrying base.

Tests were conducted utilizing the novel contact material in a conventional telephone relay of the well known McBerty type. As shown in the microphotograph, Figure 14, the contacts of the present invention, mounted on each electrode as wires perpendicular to each other (which is the preferred form), are practically unaffected after a long period of operation—in the present case 3,029,600 operations (150 ma. load, ¼ mfd., 150 ohms). Gold alloy contacts under the same conditions of loading and operation are shown in Figure 15 where it is to be observed that the contacts have been entirely worn away. Life tests on the alloy of the present invention under conditions involving low value currents and frequent operation such as are commonly experienced in the telephone and telegraph fields, indicate that a life span in the order of twenty years may be expected as compared to two years for known materials.

The alloy may be used in both polarities of a contact set or in different combinations. The use of the palladium zinc alloy as the cathode element against a pure palladium anode has been particularly successful in elementary tests. The use of other metals with the palladium zinc alloy as the cathode has proven successful.

CONCLUSION

In summary, it is readily seen that the present invention teaches that a new and novel alloy or composition can be readily prepared by treating palladium with zinc vapors at a temperature and for a period of time sufficient to cause the zinc to disperse into the palladium to form a new palladium-zinc alloy. The times, temperatures of treatment, and concentrations of zinc can be varied over a considerable range to produce a variety of palladium-zinc alloys of various phases to provide the alloys having the desirable properties set forth herein. These alloys, compositions or articles are characterized in many instances by the development of a hard case or phase of palladium and zinc on the base material, which also exhibits concentrations of zinc, although by other treatments the member can be formed of a single phase or a plurality of phases. The contact alloy of the present invention has a higher hardness and resistance to deformation than conventional materials and withstands material transfer much better than other contact materials. These alloys are especially suitable for use as contacts in low current applications and can be used in both polarities or on either polarity, or in different combinations working against refractory metals or refractory compounds with metals, such as carbide materials, or with nonrefractory metals, such as gold and silver or their alloys, or other contact metals and alloys.

The results obtained with the new palladium-zinc alloy show that it welds more readily to electrical components than presently used metals or alloys, such as those of palladium, platinum, or gold. Further, the contacts of the present invention have good electrical and thermal conductivity and resistance to the formation of surface films or corrosion.

We claim:

1. An electrical contact member formed of an alloy consisting essentially of palladium and zinc.

2. An electrical contact member formed of an alloy consisting essentially of palladium and zinc characterized by the presence of zinc in an amount effective to provide a substantial increase in resistance to wear in contact use.

3. In an electrical contact member, the combination of a current conducting base and a solid state alloy surface consisting essentially of palladium and zinc.

4. An electrical contact member comprised of a solid state alloy consisting essentially of palladium and zinc in at least one of the phases alpha, beta, and gamma.

5. An electrical contact member for use with electrical equipment in circuit breaking and making functions consisting of a solid state palladium-zinc alloy in which the atoms of said zinc have diffused into said palladium and substitutionally replaced said palladium atoms.

6. An electrical contact member for use with electrical equipment consisting of a palladium-zinc alloy of the beta phase having a Knoop hardness of from 275 to 325 numbers and having from 22 to 27 percent by weight of zinc.

7. An electrical contact member consisting essentially of up to 75 percent by weight of zinc and the balance palladium having the phases alpha, beta and gamma singly and alternatively in combinations thereof, the atoms of said zinc having diffused into said palladium and substitutionally replaced said palladium atoms.

8. The method of producing an alloy which comprises subjecting a noble metal to zinc vapors in the presence of an inert non-oxidizing gas for a period of time and at a temperature to cause said zinc to diffuse into said noble metal.

9. The method of producing a palladium-base alloy which comprises subjecting a palladium member to zinc vapors in the presence of a non-oxidizing gas for a period of time and at a temperature sufficient to cause said zinc to diffuse into said palladium.

10. The method of producing a palladium-base alloy which comprises subjecting palladium to zinc vapors in the presence of a non-oxidizing gas for a period of time and at a temperature sufficient to cause the zinc to diffuse into said palladium to form a palladium-zinc alloy having a hardness substantially greater than both said palladium and said zinc.

11. The method of producing a hard casing on a palladium-base by diffusing zinc into palladium which comprises placing a source from which zinc is to be vaporized in close proximity to palladium in a furnace, continuously passing a non-oxidizing gas therethrough, and heating said furnace to a temperature for a period of time sufficient to cause said zinc to vaporize and to diffuse into said palladium.

12. The method of producing a hard casing on a pal-

ladium-base by diffusing zinc into palladium which comprises placing a source from which zinc is to be vaporized in close proximity to palladium in a furnace and continuously passing a non-oxidizing gas therethrough, heating said furnace to a temperature for a period of time sufficient to cause said zinc to vaporize and to diffuse into said palladium to form at least one of the phases alpha, beta, gamma and delta in an amount sufficient to provide increased wear.

13. The method of producing a hard encased electrical contact member of zinc and palladium which comprises placing a contact of palladium with a mixture of zinc vapors and at least one non-oxidizing gas selected from the group consisting of ammonia, argon, helium, hydrogen and nitrogen at a rate of one to five liters per minute and at a temperature of from five hundred to one thousand degrees centigrade for one-half to twelve hours to form a hard casing on said palladium.

14. The method of providing a palladium member having a case suitable for electrical circuit make-break functions which comprises placing an excessive amount of zinc in the form of an alloy comprising essentially copper, nickel and zinc in close proximity to a palladium member, and then, in the presence of a non-oxidizing gas, heating said alloy to a temperature and for a period of time sufficient to cause said zinc to diffuse from said alloy into said palladium and replace said palladium atoms by substitution without rediffusing from said palladium, to thereby form an encased material consisting of up to seventy-five percent by weight of zinc and the balance palladium, said material exhibiting at least one of the phases alpha, beta, gamma and delta.

15. The method of providing a palladium contact member having a case suitable for use in electrical circuit make-break operations according to claim 14 including the additional steps of heating the formed contact to a relatively high temperature for a short time, and then quenching in order to provide a larger amount of a desired phase therein.

References Cited in the file of this patent

UNITED STATES PATENTS

1,832,307	Kingsbury	Nov. 17, 1931
1,935,897	Wise	Nov. 21, 1933
2,300,286	Gwyn	Oct. 27, 1942
2,303,405	Sivil	Dec. 1, 1942
2,379,641	Keitel	July 3, 1945
2,384,501	Streicher	Sept. 11, 1945
2,413,604	Colbert et al.	Dec. 31, 1946
2,428,959	Boyle	Oct. 14, 1947
2,432,657	Colbert et al.	Dec. 16, 1947
2,501,164	Durat	Mar. 21, 1950
2,545,352	Gibbs	Mar. 13, 1951

OTHER REFERENCES

Zeitschrift für Physikalische Chemie, AB. B Band 12, 1931, published in 1931 by Akademische-Verlagsgesellschaft m. b. H., pages 57–78.

Hansen: Aufbau der Zweistofflegieningen, printed in Berlin, 1936; reproduction by Edwards Bros., Inc., Ann Arbor, Michigan, 1943; page 1016.