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METAL ARTICLE

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The present application is in part a continuation of our copending application 561,986, filed September 10, 1931. The invention of the present application relates to effecting improvements in the metals platinum, palladium and gold, and certain alloys of these metals, which include all alloys consisting of the said three metals, and also alloys consisting of two of these metals, and also alloys consisting substantially of one or more of these metals, together with iridium, osmium, rhodium or ruthenium, or mixtures of these, in which the amount of said added material is relatively low, usually not over 5 to 10%, and also certain alloys containing one or more of the first mentioned group of metals, together with small amounts (i. e. not over 10–15%) of such metals as copper, nickel, silver, cobalt, tungsten, chromium, tantalum, molybdenum or the like, which alloys are in general rather soft and hence are easily worked mechanically as by milling, boring, turning, rolling or die pressing, and similar mechanical operations.

It is well known that the metals palladium, platinum and gold are soft and are very easily worked. It has many times been proposed to make these metals harder by the addition of the highly expensive materials iridium, osmium, rhodium or ruthenium or mixtures of the same, in amounts up to 5 to 10%. The metals iridium, osmium, rhodium and ruthenium, and mixtures of these, are hereinafter included in the expression "hardening metal". It has also been proposed to add other metals, which may have more or less hardening effect.

In accordance with the present invention, we preferably do not add the expensive metals above referred to, although they are capable of producing a certain degree of natural hardness in the alloys. The amount of the iridium, rhodium, ruthenium or osmium may in some cases constitute up to 40% of the entire alloy, but even such additions do not produce the degree of hardness which is desired in the present invention, and furthermore it is not possible to mechanically work the alloys of the principal metals with these expensive metals, as readily as the principal metals by themselves or alloys consisting wholly of these principal metals.

In accordance with the present invention, the "principal metals" namely platinum, palladium, gold and alloys consisting of the three or two of these, which of course may also contain small amounts (i. e. not over 5 to 15%) of other materials (metals) as impurities, constitute the starting material. The metal or alloy is first worked or fashioned into the proper mechanical shape, which may be a dish, or a crucible or a ring or a spinnerette, and preferably without adding the expensive metals above mentioned (iridium, rhodium, ruthenium and osmium) and preferably without adding any substantial amounts of hardening metals. Silver is not to be regarded as a metal suitable for the hardening process for the reason that it does not produce substantial hardening of the principal metal, but for most purposes silver if present in the alloy is not present to the extent of more than 20 or 25%, and never more than 40%. Also we preferably do not add copper or nickel, in any considerable amount, since these would act as hardening agents. However we do not exclude the presence of small quantities of copper or nickel, which might be present as impurities in the precious metal.

It is well known that some of the metals platinum, palladium and gold and alloys consisting of two or all of these are lacking in hardness, and for certain purposes are unsuitable, on account of not possessing sufficient hardness and strength. These metals and some of their alloys have attractive colors and are used in making jewelry, but the jewelry made from these materials alone is, in many cases, objectionably soft so that the same does not last well. Also in some cases the jewelry does not retain its luster well.

These metals are also well known to be highly resistant to various chemicals, including strong acids at the boiling point, solutions of alkali metal sulphides and polysulphides, and if the said metals could be given a sufficient degree of hardness and sufficient degree of strength, they would be rendered more suitable for certain purposes in the chemical industries.

The present invention is based upon our observation that it is possible to form an article out of platinum, palladium or gold or alloys consisting essentially of these, and to carry out the mechanical treating or fashioning operations such as turning, milling, boring, die pressing, drawing, bending, and the like, during the manufacture of the article while the material is relatively soft, and then, when the mechanical work has been completed or substantially completed, to harden the article very substantially, by causing the same to take up and to more or less completely diffuse through the said article, certain metalloid elements, notably silicon, boron, or mixtures of the same. It is important that

such metalloid elements should be delivered to the metal article, which is to absorb the said metalloid, in a non-oxidized condition, and in many cases we find it advantageous to apply the said metalloid hardening agent, in elemental condition, or as a compound free from oxygen, mixed with carbonaceous material such as charcoal or coal, and in a reducing (rather than oxidizing) atmosphere, although in many cases it could be applied as a vapor (non-oxidized), in an atmosphere of some inert gas.

Boron appears to give more satisfactory hardening results than silicon, but the latter can also be used in many cases.

We give the following examples, but it is to be understood that the invention is not restricted to these examples:

A spinnerette, for use in the artificial silk industry is manufactured from pure platinum. The platinum being a soft metal and easily worked, and very malleable and very easily rolled, stamped, pressed, and bored, the manufacture of the platinum spinnerette presents no technical difficulties. The platinum spinnerette (having the minute holes bored therein) is then painted on one or both sides with a paste containing charcoal 12 parts, boron 3 parts, diphenyl 1 part and propyl alcohol 6 parts. The coating applied to the said spinnerette may be about 1 to 2 millimeters thick, more or less. The coated article is then wrapped up in copper foil, in order to exclude the atmosphere, and is then heated to a temperature of about 900° C., which temperature may be maintained for about an hour to an hour and a half. The heating is preferably conducted under reducing conditions, that is to say the article may be heated in a muffle furnace in which the muffle is heated by a reducing flame or a current of combustible gas may pass through the muffle. At any event care must be taken not to oxidize the coating material. If the heating is conducted in an atmosphere which is devoid of free oxygen, which constitutes the preferred condition, it is immaterial whether the temperature is constant or fluctuates more or less. If on the contrary the atmosphere of the muffle contains free oxygen (even in small amount), then it is very advisable not to allow the temperature to fluctuate very much because such a condition would be likely to produce an oxidizing atmosphere within the copper foil wrapping (at times), which would cause burning (oxidation) of the boron.

The muffle is well closed and it is advisable to pass a reducing gas through the same, for example fuel gas, particularly during the cooling operation. The article is then allowed to cool, without removing it from the muffle, or from the copper foil wrapping, the cooling being preferably under strongly reducing conditions, and when the device is cold, or has cooled sufficiently so that it can be readily handled, it is removed from the muffle. The copper foil may be found to be somewhat discolored from the heat, but it should not be thoroughly oxidized, or unsatisfactory results will probably be produced. The copper foil wrapper is taken off, and the residue of the paste is brushed off, (and can be used for making up the next batch of paste, more of the boron being added thereto). The treated spinnerette will then be subjected to polishing in the usual manner, and will be found to be very greatly hardened.

We have referred above to using a thin copper foil for wrapping the coated article during the heat treatment. Other metal foils which are stable at the temperatures encountered can be used, so long as they are inert with respect to the boron, silicon and carbon.

The hardness of the finished article in this particular case, may be far above 250 kilograms per square millimeter (Brinell hardness). The elasticity may be about equal to that of a good grade of steel, and the tensile strength may be about equal to that of medium quality of steel.

An alloy of platinum and palladium, containing 98% of platinum and 2% of palladium, or various alloys containing platinum and palladium up to 20% of the latter, can be likewise used for the preparation of spinnerettes by the procedure as given above.

If it is desired to harden the material less, in the case of platinum or the above mentioned platinum-palladium alloys, a temperature of say 870° C. can be maintained for one and a half hours, and for hardening material still less, temperatures of 850 to 870° C. can be maintained from half an hour to one hour or an hour and a half. Some hardening can be produced at temperatures down to about 815 to 825° C., with platinum or palladium alloys of platinum, as given above.

The above example can be further modified by using alloys of platinum, palladium and silver. Thus an alloy containing 35% platinum, 40% palladium and 25% silver can be hardened in a similar manner, at about the same temperatures as given above.

Platinum-copper alloys can be similarly hardened, such alloys being highly suitable for use in jewelry, to produce alloys having about the same hardness as iridium, which alloys would cost only a fraction as much as iridium.

In some cases it is possible to omit the propyl alcohol and the diphenyl from the above mixture and to carry on the heating in an atmosphere of hydrogen, producing very satisfactory results.

Instead of wrapping the article in copper foil, after applying the coating, the article can be embedded in a powdery mixture of boron, carbon and diphenyl, and placed in a nickel-chromium alloy box having a tight-fitting cover, and heated as above indicated. Here also it is advisable to conduct the heating operation in a somewhat reducing atmosphere, rather than an oxidizing atmosphere.

It is possible to use the powder (carbon and boron) four or five times, if care is taken, before it has lost most of its boron. If desired it can be used over many times, by adding a small amount of boron after each use or after each two or three uses, depending upon the care exercised to prevent oxidizing gases coming in contact with the powder at a high temperature.

For "platinum tooth alloy", i. e. alloys suitable for dental purposes such as movable bridges, etc., consisting of 40% Pd, 50% Ag, 6% Au, 4% Sn or of 40% Pd, 36% Ag, 10% Au, 4% Co, 10% Cu, a temperature of 925° C., maintained for about 75 to 80 minutes has been found to be very satisfactory for producing the hardening with the aid of the boron or other hardening agent as explained above. A temperature fluctuation up to about 50° C. is permissible.

The above alloys can also be hardened somewhat with the aid of the boron or other hardening agent as explained above by heating for

about 45 minutes up to temperatures around 725° C., with a permissible temperature fluctuation of 25°. When applying the process to objects which are soldered it is advisable to observe that the temperature used in the hardening operation should be somewhat below the melting temperature of the solder.

The solder should have a melting point of at least 950° C. and preferably substantially above this. It is inadvisable to heat to within about 100° of the melting point of the solder, since the latter may soften somewhat to allow distortion of the article.

Reference was made above to cooling the metal or metal alloy article after the heat treatment. It is advisable to allow the furnace to cool off slowly, rather than to quench the hot articles. For removing the uncombined residue of hardening substance, some of which may, after the brushing above referred to, cling to the surface of the hardened article, it is advantageous to brush the article with a little hydrochloric acid or with an aqueous potassium permanganate solution. A solution of sodium peroxide in aqueous caustic potash solution is extremely good for washing the said article. The article can then be polished (in well known maner) and is ready for use. Prior to the initial coating operation, it is advisable to thoroughly cleanse the article, to remove grease, and the like, remaining from various mechanical operations.

It may be noted that after the hardening operation, the article can be subsequently heated for a long time up to glowing temperatures, (i. e. up to 500° to 800° C.) without any appreciable diminution of the hardness of the allow. If the said heating were at a higher temperature and under conditions to permit the oxidation of the boron, the latter would be oxidized and the article would thereby be softened, after a long time.

In addition to the metalloids boron and silicon, it is also possible to use zirconium metal, in a very finely divided condition, with the production of satisfactory results.

If desired, treatment of the articles with silicon can be carried out in accordance with the above examples, the temperatures being 800° C. when using a powder of 5 parts of silicon mixed with one part of charcoal. The best time was found to be one hour, when using hydrogen as the deoxidizing gas at a temperature of 50 to 75° C. lower than the temperature above referred to for using boron.

Instead of applying the boron or other element as above described, in the form of a paste, it is also possible to fume the surface of the article with boron, in a reducing atmosphere. It would also be possible to heat the article in an atmosphere composed of hydrogen and hydride of boron.

The silicon can also be applied in the form of vapors of silicon chloride or silicic chloroform ($SiCl_4$ or $SiHCl_3$). These compounds, in the vapor form will decompose at temperatures around 600° C., whereby elementary silicon will be separated, the latter depositing upon the platinum metal article.

Other alloys which are particularly applicable for treatment under the present invention include the following—platinum-nickel alloys, palladium-nickel alloys (all containing not over 10 to 20% of nickel, for best results).

A particularly useful alloy for some purposes is 90% palladium and 10% gold. This has an initial hardness of 50 kilograms per square millimeter (according to Brinell) and after treatment of this material by elementary silicon deposited upon the said palladium-gold alloy and after being subsequently heated to about 800° C., for about 45 minutes, and cooled (all under reducing conditions) the resulting alloy was found to have increased in hardness about tenfold, the said material of course being shaped before the treatment with silicon.

For jewelry purposes silicon is found to be a very suitable hardening metal for an alloy, consisting of 96% Pt and 4% expensive platinum metals at a temperature as mentioned above. The hardness thereby reaches values similar to those of an alloy of platinum with 25% iridium.

In applying this silicon to gold rings for jewelry purposes the best results were found at a temperature of 700° C. applied during 45 minutes. The hardness thereby reached values of 150 kg. per square millimeter.

The dental industry is using palladium with 3 to 20% of other platinum metals, gold or silver as a material suitable for movable bridges or the like. In this case it is recommended to use boron as a hardening metal under the conditions as referred to above, viz. 825° C. during 45 minutes. When hardening injection needles consisting of 60% palladium, 30% gold and 10% platinum, excellent results in hardening were reached at a temperature of 850° C. during one hour using a hardening powder consisting of 4 parts of charcoal and one part of boron in a hydrogen atmosphere.

In the place of the powder of diphenyl and propyl alcohol other organic compounds can be used which decompose at about 500° C. into hydrogen and soot in order to remove the oxygen. For instance:

C_6H_6 (benzol)
$C_6H_4(CH)_2C_6H_4$ (anthracene)
$(CH_3)_2C_6H_4$ (xylol)
$C_6H_5CH_3$ (toluol or the like)

Also the absorptive qualities of the charcoal in the above mentioned hardening powder can be used. If the charcoal is heated to about 500° C. in an ammonia atmosphere and cooled down ammonia is absorbed in large quantities. If this charcoal is mixed with the boron in the above mentioned proportion a powder is obtained with which excellent results in the hardening process were reached without any further organic compounds and without forming any annoying soot.

The hardening powder with the absorbed ammonia is particularly recommended in using zirconium in the above mentioned powder in the place of silicon. In this case the hardening temperature should be 50 to 100° C. higher than when using boron.

The silicon, boron and the like enter the metal article through its surface, by a process of diffusion, and the depth of the said diffusion into the body of the metal will depend upon the amount of time and temperature of the heating operation. With shaped articles, having a thickness not over 5 millimeters, the times as stated above, are sufficient to cause diffusion of the hardening agent substantially to the core, and with articles of a much greater thickness, a longer period would be necessary. It is not necessary however (in most cases) that the heating should be continued until the whole material is uniform in composition, since if the

surface portion of the article is hardened, the article itself is thereby strengthened, even if the material still contains a core of the soft metal in an unhardened or partly hardened state.

The amount of boron, silicon or zirconium to be taken up by the metal of the platinum-palladium-gold group, will depend upon the results desired. When an amount of silicon or boron equal to 1 or 2% of the platinum group metal has been absorbed, a very considerable hardening is produced. In some cases the amount of the boron or silicon may be up to 5% or even 10% of the platinum group metal.

From the standpoint of the jeweler, the platinum metal articles, although they are hardened, have not substantially altered in appearance, in other words the color and appearance of the platinum metal is substantially the same as before treatment. This is also true of palladium and gold.

In many cases, a large number of the articles to be hardened can be packed into the powdery composition as above referred to, composed of carbon and silicon or boron, with or without diphenyl or similar reducing agent, in a graphite crucible, which is covered and then put into a furnace and heated to the temperatures as indicated above.

For many purposes the platinum group metal can be hardened, for instance a body made of an alloy of 96% platinum and 4% palladium can be hardened by the process above described, to produce a body having a hardness corresponding approximately with that of an alloy of 80% platinum and 20% iridium, which alloy is also highly chemically resistant and very strong and tough.

With regard to the use of the expensive metals osmium, iridium, rhodium and ruthenium, the distribution of a small percentage 2 to 20%) of any one or more of these four in the metal consisting of platinum, palladium, or gold, or of an alloy of two or all of these three, causes some hardening. The alloys so formed can then be mechanically worked, and then treated with the boron, silicon or zirconium, producing a further hardening. Except where a very great hardness is desired, we do not recommend the use of these expensive metals.

The above alloys can further be improved—after the case hardening at 925° C.—by heating them afterwards in a reducing atmosphere for about 45 minutes up to temperatures around 725° C., with a permissible temperature fluctuation of 25° C. Through this secondary annealing at 725° C. an aging effect results in addition to the hardening effect resulting from the case hardening process. The hard-surfaced articles produced as described above are completely shaped or, in other words, permanently fashioned; that is to say, they have their final shape, and are not subjected to any further treatment altering their shape.

Where in the appended claims we speak of an element selected from the group consisting of boron, silicon, and zirconium, it is to be understood that we desire this to be interpreted as covering the equivalent mentioned in this specification, namely a mixture of two or all the elements of such group.

We claim:—

1. A permanently fashioned article made of a material consisting at least in major part of at least two metals of the group consisting of platinum, palladium, and gold, said article having a hardened surface formed by an alloy of said material with an element selected from the group consisting of boron, silicon and zirconium.

2. A permanently fashioned article made of a material consisting at least in major part of at least two metals of the group consisting of platinum, palladium, and gold, said article having a hardened surface formed by an alloy of said material with an element selected from the group consisting of boron, silicon and zirconium, while the interior of said article consists of said material in a relatively soft state.

3. A permanently fashioned article composed of a core of soft material consisting at least in major part of at least two metals of the group consisting of platinum, palladium, and gold, and a hard surface envelope surrounding said core and consisting of an alloy of said material with an element selected from the group consisting of boron, silicon, and zirconium.

4. A permanently fashioned article made of a material consisting at least in major part of at least two metals of the group consisting of platinum, palladium, and gold, said article having a hardened surface formed by an alloy of said material with boron.

5. A permanently fashioned article made of a material consisting at least in major part of at least two metals of the group consisting of platinum, palladium, and gold, said article having a hardened surface formed by an alloy of said material with silicon.

6. A permanently fashioned article made of a material consisting at least in major part of at least two metals of the group consisting of platinum, palladium, and gold, said article having a hardened surface formed by an alloy of said material with zirconium.

7. A permanently fashioned article made of a precious metallic material hardenable by alloying it with an element selected from the group consisting of boron, silicon, and zirconium, said article having a hardened surface formed by an alloy of said material with such element.

8. A permanently fashioned article made of a precious metallic material hardenable by alloying it with an element selected from the group consisting of boron, silicon, and zirconium, said article having a hardened surface formed by an alloy of said material with such element, while the interior of said article consists of said hardenable material in a relatively soft state.

9. A permanently fashioned article made of a precious metallic material hardenable by alloying it with an element selected from the group consisting of boron, silicon, and zirconium, said article having a hardened surface of substantially the same color and appearance as said material and formed by an alloy of said material with such element.

10. A permanently fashioned article made of a precious metallic material hardenable by alloying it with an element selected from the group consisting of boron, silicon, and zirconium, said article having a hardened surface of substantially the same color and appearance as said material and formed by an alloy of said material with such element, while the interior of said article consists of said hardenable material in a relatively soft state.

11. A permanently fashioned article made of a precious metallic material hardenable by alloying it with an element selected from the group

consisting of boron, silicon, and zirconium, said article having a hardened surface formed by the diffusion of said element into said material.

12. A permanently fashioned article made of a precious metallic material hardenable by alloying it with an element selected from the group consisting of boron, silicon, and zirconium, said article having a hardened surface formed by the diffusion of said element into said material, while the interior of said article consists of said hardenable material in a relatively soft state.

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