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Precious-metal-base advanced materials

T. NOWICKI and C. CARBONNAUX

CLAL, Centre de Recherches, 8 rue Portefoin, 75003 Paris, France

ABSTRACT

The precious metals are basically known for their applications in jewelry, coins, bullions and catalysis. The reality is that precious metals constitute also the base of several advanced materials used in the industry in hundreds of metric tons.

Since forties, platinum alloys have been used as structural materials for equipments in the glass industry. The essential reason for this is the excellent resistance of platinum alloys to oxidation and electrolytical corrosion in molten glasses at temperatures as high as 1200-1500°C. The major drawback is a weak creep resistance. In the case of all conventional platinum alloys, the 100 h creep resistance at 1100°C is smaller than 10 MPa while the stress to cause rupture in 1000 h at 1100°C for superalloys is about 100 MPa. The unique way for significant improvement of platinum base materials creep resistance is a strengthening by an oxide dispersion (ODS). In the case of CLAL's patented "Plativer" materials, 0.05 wt% of Y_2O_3 is incorporated within the alloy matrix by the flame spraying process. The creep behaviour of such ODS materials shows a 100 times creep rate reduction comparing to conventional platinum alloys. Thanks to the fact that the mean size of oxide particles is included between 2000 and 4000 Å, the obtained materials don't exhibit any loss of plasticity in comparison of conventional Pt alloys. Further improvement of platinum base materials is related, in the authors opinion, to the development of precious metals base intermetallics.

Another interesting applications of precious metals are silver base electrical contacts. They are in fact silver matrix composites containing varying amounts of well-dispersed particles of constituents such as CdO, SnO_2 , Ni, WC or C. In the case of such materials, particular properties are required and tested : resistance to arc erosion, resistance to welding and contact resistance. Choice of the second phase depends on the specific service conditions. During last 10 years, an interesting and successful battle took place in order to replace, without alteration of the properties of conventional materials, toxic CdO by inert SnO_2 . Electrical contacts are manufactured by various powder metallurgy techniques, including coprecipitation from solution, internal oxidation, internal oxidation of atomized powders, unitary pressing and hot extrusion. A supplementary difficulty comes from the fact that in order to enable brazing or welding of contacts to supports, the parts had to be manufactured as sandwiches : silver composite/pure silver.

Many other technically fascinating precious metals base materials exist : brazing alloys for assembling metals, superconductors and ceramics ; dental materials including magnetic biocompatible alloys ; silver composites for superconductor wire jackets.

One can ask the fundamental question if the development of materials science will induce the replacement of precious metals by cheaper materials. The observation of current evolution indicate very clearly the opposed tendency : precious metals cannot be replaced by common metals because of their unique characteristics due to their atomic level properties. The relatively high cost of raw materials authorizes the use of advanced metallurgical techniques, the conversion cost being only a small portion of the total material value.

PRECIOUS METALS AND ADVANCED TECHNOLOGIES

Precious metals are basically known for their applications in jewelry and catalysis. The reality is that precious metals also constitute the base of several advanced materials used in the industry in hundreds of metric tons. The cost of precious metal is often seen as a drawback for their application. A counter argument however is that in the cases when the precious metal use is necessary the advanced metallurgical techniques are currently used, the conversion cost is only a small portion of the total material value. The result is that some of the materials science techniques known on the laboratory scale in various fields are industrially used for precious metal manufacturing.

The aim of the present paper is to present several examples of advanced precious metal base materials developed by the company to which the authors belong. This presentation is divided into three parts devoted respectively to the platinum, silver and gold base materials.

PLATINUM GROUP METAL BASE MATERIALS

Applications

Among the six platinum group metals (PGMs) Pt, Pd, Rh, Os, Ir, Ru, only platinum has found a practical application as a base for structural materials. Platinum is not used by itself very often, since it is soft. The conventional platinum alloys are solid solutions containing 5 to 20 %(wt) of rhodium or more rarely 2 to 10 %(wt) of iridium. The essential reason for the use of platinum alloys as a structural materials is their excellent resistance to oxidation and electrolytic corrosion at temperatures as high as 1200-1500°C. Since the 1940s, platinum alloys have been used on a large scale as structural materials for devices in the glass industry. More than 100 metric tons of Pt-base alloys are converted every year in the world for this purpose. Although the density of Pt alloys is high, one of the major projects envisaging the PGMs' application are parts for combustion chambers for rocket and satellite engines.

From a technical point of view, the major Achilles'heel of PGMs is their low creep resistance.

Platinum alloys creep

In the case of all conventional platinum alloys the 100H creep resistance at 1100°C is less than 10 MPa, while superalloys can resist 100 MPa stress for more than 1000H. In fact, the efficiency of solid solution alloying is low. In this situation the solution chosen by PGM manufacturers is strengthening by oxide dispersion(ODS). ODS-Pt-based materials can be classified into three types according to their methods of production :

- a) Powder metallurgy: mixing, compaction and sintering. As it is difficult to use oxide powders with the size below 1 μ m for this purpose, the oxide content has to be of order of 2000ppm in order to obtain the grain stabilization effect required.
- b) Thermal spraying: free body flame (or plasma) spraying and rolling of obtained block. In this technique, the mean size of oxides are of the order of 0.1 to 0.5 μ m, and a total amount of the order of 500ppm is sufficient
- c) Post-oxidation: internal oxidation of alloys sheets containing easily oxidizing elements such as Y or Zr in solid solution.

After oxidation the sheets are diffusion bonded in order to rebuild bulk blocks which are subsequently rolled to final thickness.

As the oxide size in this case can be as small as $0.1\mu\text{m}$ it is possible, in order to maximize flow stress, to introduce a quantity of oxide of the order of 3000 ppm without reducing the elongation of material.

The structures and properties of materials obtained using these processes are compared to those of conventional platinum alloys on Figures 1 and 2.

Platinum corrosion

The corrosion of platinum takes place by a specific mechanism [1] often different to those acting in the corrosion of common materials. The corrosion resistance of common metals, alloys, and ceramics results from the stability of compounds such as oxides and silicates [2] present respectively in the passive layers on the surface of metals and in the bulk of ceramics. The resistance of platinum alloys comes from the unique chemical inertness of the precious metals related to their noble character.

Platinum resists perfectly the majority of corrosive medias (including molten glasses), unless contaminated by individual chemical elements such as As, Sb, Bi, Si, Sn, Pb, Se, and Te arising from impurities or decomposition of their compounds takes place. The majority of platinum corrosion phenomena of practical importance are connected with the local formation of phases formed by reaction between platinum and an other chemical element. Such phases are subsequently destroyed due to their low melting point, or brittleness, or low corrosion resistance. The contamination is often related to the electrochemical phenomena of dissociation and transport of cations to the proximity of a local platinum electrode. Later, these cations react directly with platinum, or react first with glass constituents as a reducing agent, provoking platinum attack by the products of such reactions [3].

Hence, the electrochemical corrosion of platinum alloys which takes place is rather cathodic than anodic, in contrast to what it is usually met in common metals.

Economic PGM alloys

Palladium is not used practically as a structural material. The reason why, is its low creep resistance associated with limited oxidation and corrosion resistance. However, it is possible to develop alloys using palladium as the base metal. A study of about twenty different binary systems has shown that particularly interesting properties can be developed in the case of Pd-In5 % and Pd-Sn10 %. When these alloys are heated in air, a stable passive layer is developed stopping oxidation.

The further optimization of these alloy led to the design of a Pd-In-Ru-Y alloy [4] which exhibits creep properties which are equivalent at 1200°C to those of Pt-Rh10 % (see Figure 3). Specific interest for this alloy comes from the good resistance of this alloy to the corrosion by molten glasses.

Another substitute for the classic Pt-Rh alloys is the use of Pt-30 Pd-Rh alloys which presents, in specific application, sufficient creep and corrosion resistance. The difficulties connected with the refining of such alloys has reduced interest in such a solution.

Intermetallics

Limited creep resistance of precious metals conventional alloys has increased the potential interest in the development of precious metal intermetallics. The numerous precious metal base intermetallics have been identified, but very few systems have been investigated.

The systems which seems to have the most promise for advanced applications are B2 CsCl-type intermetallic compounds such as AlRu.

Multi-materials

The properties of PGMs make particularly useful the idea of multimaterials composed of different PGMs materials and ceramics and/or refractory metals.

The classical examples used basically in the glass manufacturing and chemical industry are :

Sandwiches of Pt-Rh plates stiffened by an intermediary layer of zirconia.

Mullites protected by Pt layer (with intermediary layers).

An other example are titanium electrodes clad with platinum by diffusion bonding.

SILVER BASE MATERIALS

Applications

The two classic engineering applications of silver are brazing filler alloys and electrical contacts. The latter are described in the next section. As far as brazing alloys are concerned, rapid developments were expected in order to braze metals onto ceramics. This forecast was connected with the prediction of the growth of ceramic parts used in modern thermal engines, and to the necessity of the assembling of high Tc superconductors circuits.

This development has not take place. In the problems of metals assembling to ceramics, the efforts have been focused on the process routes, rather than on the alloy development, probably because of the quite acceptable behavior of Ag-Ti and Ag-Cu-Ti brazes. As far as superconductors are concerned, it seems that the development of bulk conductors has been surpassed by thin layer applications, and the question of assembly to metals is now of minor importance.

It seems that the silver base advanced materials (eg ODS silver materials) have an unused potential. An example of a possible application for such a material is for the sheathing of superconductor wires.

Electrical contacts

In the case of electromechanical components such as relays, switches, circuit breakers, make-break contacts are used for opening and closing electrical circuits. Contacts require basic properties: erosion resistance, good electric and thermal conductivities and inhibition of welding and adhesion. Contacts are generally employed in an air environment, and hence it is necessary that films of contamination such as oxides and/or sulfides do not form readily on the material surfaces. From this standpoint, precious metals are very well suited due to their excellent corrosion resistance. In particular, silver is the basic metal most often used for contacts since it has the highest electric conductivity of the metals.

In order to enhance performance, pseudoalloys are typical materials used in silver-type contacts. They are materials composed of a silver matrix which contains insoluble constituents such as metals immiscible with silver such as nickel, molybdenum and tungsten; oxides such as CdO and SnO₂; carbon-bearing compounds such as graphite and carbides. The cross-sectional structures of some pseudoalloys are shown in Figure 4.

Electrical contacts are manufactured by various powder metallurgy techniques, including coprecipitation from solution, internal oxidation, internal oxidation of atomized powders, unitary pressing and hot extrusion.

Subsequently difficulties arise from the fact that in order to enable brazing or welding of contacts to the supports, parts have to be manufactured as sandwiches, silver composite/pure silver.

Ag-CdO is a typical material used in silver-metal oxide-type contacts, since Ag-CdO has good conductivity and an excellent welding and adhesion resistance. The dissociation of CdO arising from Joule's heat, favors arc-extinguishing and quenches the contacting surfaces. The metal oxide particles prevent the latter joining together.

The concomitant losses of cadmium and silver by vaporization in the arc prevents increase in CdO concentration in Ag-CdO, which would worsen the performance of the contact by enhancing contact resistance. In spite of the dangerous effect of cadmium on the human body which is well known, almost only CdO has been used for both medium and large currents. Twenty years of research have been required to develop cadmium free materials with properties equivalent to those of Ag-CdO.

Among metal oxides which have been investigated for the substitution of CdO, SnO₂ has been shown to be the best due to its good electrical properties. In order to improve the behavior of Ag-SnO₂, minor additions of oxides such as TeO₂, MoO₃, WO₃, Bi₂O₃, CuO have been used. The structure and properties of some Ag-SnO₂ and Ag-CdO are presented on Figure 5. Generally speaking in order to equal the properties of an Ag-CdO obtained by simple powder mixing, it is necessary to use advanced techniques such as coprecipitation, internal powder oxidation, etc.

Silver composites for superconductor wires sheath

The majority of techniques of the manufacturing of bulk superconductor wires necessitate the use of metal sheathing in contact with superconductor ceramic. The essential role of the metal jacket is to compensate for the poor mechanical properties of ceramics in use, and also to retain the superconductor during the densification of powder and the wire forming process. From the point of view of chemical properties silver base materials seem to be the more appropriated metal due to lack of interaction with ceramics and oxygen permeability which facilitate the control of oxide stoichiometry. The major drawback in using silver comes from the very low flow stress of this metal compared to flow stress of ceramics. When superconductors rods or wires coated with silver are deformed the majority of strain is concentrated in the metal. An elegant solution to this problem consist in using ODS silver based materials. In figure 6, the properties of ODS silver materials are compared with those of pure silver and silver alloys. The choice of the reinforcement phase depend on the type of superconductor ceramics. It is often favourable to use as the dispersed phase one or more of the superconductor ceramic compounds.

GOLD BASE MATERIALS

New gold alloys

For centuries, the most important gold alloys used in dentistry as well as in jewellery have been the gold alloys based on the traditional ternary Au-Ag-Cu system. The design of gold alloys based on different system will be discussed in the next sections.

Alloys for dentistry applications

Precious metal base materials find use in dentistry due to their unique blend of characteristics such high corrosion resistance, tarnish resistance, physiologically non-toxicity, biocompatibility, aesthetic aspect, high ductility and mechanical properties.

On one hand, it has been commonly known, for centuries, that gold alloys are very well suited to this purpose. As proof, the worldwide gold consumption for dentistry amounts to about 60 t/year during the past ten years. On the other hand, palladium based dental alloys have been developed in order to lower the cost of the necessary raw materials.

In fact, among the platinum group metals, only palladium is suitable as a base for dental alloys owing to its moderate melting point. The precious metal base dental alloys are divided into four groups according to their particular application : for investment casting prostheses and restorations; for stamping crowns and other parts; for bonding to porcelain and for miscellaneous restorations.

The requirements of the third group will be discussed below in more detail. In other respects, ferromagnetic noble metal alloys in combination with rare earth cobalt magnets have been applied successfully for retention of overdentures. Castable ferromagnetic alloys such as the Pd-Co and Pd-Ni binary alloys and the Pd-Ni-Co ternary alloys, embedded within the remnant root, provide a magnetic attraction which is sufficient to allow the retention of prostheses comprising permanent samarium-cobalt magnets, encapsulated by a corrosion-resistant alloy. Further developments of precious metal alloys include the Au-Cu-Zn system shape memory alloys which could offer an interesting blend of characteristics, particularly superelasticity, required for the design of an orthodontic appliance such as archwire.

Alloys for porcelain bonding. The porcelain fired onto metal (PFM) technique has occupied an important place among the modern dental restoration techniques. A metal crown or bridge modified to act as a substrate structure is prepared by the usual lost wax method, and the facing side is veneered with a tooth-simulating porcelain. Precious metal based PFM alloys must satisfy a number of requirements, the main of these being that the thermal expansion coefficient of the metal closely match those of the ceramic materials which amount to about $14 \times 10^{-6} \text{K}^{-1} \cdot \text{m}^{-1}$ within the range 20°C to 600°C . They must also form adhesive oxides in order to provide strong and durable bonding of porcelain to metal, and must not discoloration the porcelain in contact with metals and the alloy solidus at least 150°C above the temperature at which the ceramic fuses to the metal, is commonly close to 960°C .

The composition (wt.%) of DIAZERAM SF, the new high-gold based PFM alloy developed by CLAL, is given: Au 85; Pt 10; Pd 2; Others 3. Since it has good mechanical characteristics, it can be used to design large prosthetic devices such as long-span bridges. If we consider the composition of DIAZERAM SF, it can be observed that platinum is added in order to increase both the solidus temperature and the strength due respectively to its high melting temperature and the miscibility gap in the gold-platinum system. Palladium is used as an alloying element in order to raise the melting temperature without a significant broadening of the melting range, as is the case for platinum. In contrast to platinum addition, palladium has a very little effect on strength due to its mutual miscibility with gold.

The combined platinum and palladium additions serve to lower the coefficient of thermal expansion and to increase potential for precipitation hardening during an appropriate heat treatment, e.g. 550°C for 0.5 h and air cooling. Moreover, as palladium has a strong whitening effect, its content must be limited in order to obtain a yellowish alloy. As an alternative, a reactive non-precious element such as indium or tin introduced to lower the initially high melting point resulting from a high Pt content, and to promote, during an oxidizing step, the formation of an adherent external oxide layer on metal, that, good bonding will exist between the metal and the fused porcelain.

Finally, DIAZERAM SF contains a minor addition of a grain refining element such as iridium leading to a fine grain structure which provides an improvement of both mechanical properties and corrosion resistance as segregation effects are minimised.

Au-Ti

The high caratage gold-titanium alloy, Au 990 - Ti 10, is devoted to both the top segment of the jewellery market and the bonding in the electronics industry.

On one hand, the Au-1% Ti was initially developed in order to improve the durability (wear resistance and mechanical properties) of the gold used in the Far East where the millesimal fineness standard of gold jewellery must amount at least 990 (23.76 K).

For this purpose, about 20 t/y of high-carat gold are consumed annually in that region. Titanium is probably the highest hardening candidate alloying element of gold by far, in addition, titanium, often used in dental implants, is known as a non-allergy causing and physically tolerant metal. Trials have been undertaken in order to precipitation-harden gold by only one weight percent of titanium. By an appropriate heat treatment, precipitation hardening of this alloy occurs; hence its mechanical properties match those of a 9 carat alloy while still retaining the hue and brilliance of 999 fine gold [5].

On the other hand, the 990 gold-titanium alloy finds supplementary application in the field of semiconductor interconnections. One of the most widely used methods for effecting electrical connection between microchips and the terminals in the packages that house them is to use fine gold wires, typically 25 μm or less in diameter. The gold demand required for this purpose reached about 19 tons in 1990 in the Western world. There is a need for the strength of bond wires to be increased in order to reduce their section area and allow them to operate at temperatures up to 300°C, therefore, the precipitation strengthening of Au-1%Ti alloy, in the form of 25 μm diameter wire, is rather different than as mentioned above in the bulk form. When a 25 μm diameter wire is heat treated in air at 200°C, the strength is increased by precipitation but this is not followed by an expected normal softening on prolonged exposure owing to overaging. The stability of the strength must be due to dispersion strengthening.

The dispersed phase is probably an oxide which is formed by internal oxidation despite the fact that oxygen has an extremely low solubility in gold, however, oxidation is made possible either by the high density of defects in the lattice of the Au-1%Ti alloy, when cold worked by drawing down to a fine wire, might provide the necessary short-circuit path for oxygen, or by the fact that a minor addition of titanium is sufficient to enhance the diffusion of oxygen into gold along grain boundaries [6].

CONCLUSION

The fact that, in the case of precious metal products, the manufacturing costs are relatively low in comparison with the value of raw materials, gives often an opportunity for using advanced technologies in order to improve the properties of final products.

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Figure 1 - Rupture time at 1400°C under 10 MPa and Elongation at 20°C of various PGMs based materials (annealed 1150°C/30').

Pt : pure platinum

Pt + 3000 IO : Pt with 3000 ppm of ZrO_2 obtained by internal oxidation and diffusion bonding of sheets.

Pt + 500 FS : Pt with 500 ppm of Y_2O_3 obtained by free body flame spraying.

PtRh 10 + 500 FS : Pt-10 % Rh matrix with 500 ppm of Y_2O_3 obtained by free body flame spraying.

PtRh 10 + 1500 PM : Pt-10 % Rh matrix with 1500 ppm of ZrO_2 , obtained by powder metallurgy.

Pt Rh 10 : Pt - 10 % Rh.

Figure 2 - Typical microstructures of various PGMs based materials :

a) Pure Pt ; b) Pt + 3000 IO ; c) Pt + 500 FS ; d) Pt Rh 10 + 1500 PM.

Figure 3 - Creep resistance of palladium - base materials.

Figure 4 - Typical microstructures of silver-base contact materials

- a) Ag - 12 % Cd0 (internally oxidized)
- b) Ag - 4 % C (powder metallurgical) longitudinal section
- c) Ag - 20 % CW - 3 % C (powder metallurgical)
- d) Ag - 12 % Cd0 (coprecipitated powder) cross section
- e) Ag - 4 % C (powder metallurgical) cross section
- f) Ag - 40 % Ni (powder metallurgical)

Figure 5 - Properties of silver-base contact materials (a. u. : arbitrary units)

- a) Ag - 12 % Cd0 (powder metallurgical)
- b) Ag - SnO₂ (powder metallurgical)
- c) Ag - SnO₂ (coprecipitated powder)

Figure 6 - Mechanical properties of ODS silver-base materials.