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The 20th Santa Fe Symposium on Jewelry Manufacturing Technology

PALLADIUM FEATURES AS A JEWELLERY METAL FOR THE FIRST TIME

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The annual international Santa Fe Symposium® is the foremost source of the latest research and technical information on jewellery materials and manufacturing technology. Much of the industry's current state of knowledge on platinum jewellery alloys and manufacturing practice has been featured at this Symposium over the years (1–3). Breaking with tradition, the 2006 Symposium – the 20th Santa Fe Symposium – was held in Nashville, Tennessee, from 10th to 13th September 2006, rather than in Albuquerque, New Mexico, its spiritual home.

Introduction of Palladium

The 2006 Symposium was notable for featuring the new jewellery metal – palladium. This had been a very hot topic in the U.S., Chinese and European jewellery industries over the previous year, with many U.S. alloy suppliers launching new 950 palladium alloys on the market and the retail industry showing serious interest. However, a full technical appraisal has been awaited, and the three presentations on palladium ensured that a technical understanding of the metal was placed on a sound footing.

Palladium jewellery (Figure 1) is of interest as an alternative white jewellery metal because its low price and low density (compared with those of gold and platinum), coupled with its good white colour and tarnish resistance, make it a better low-cost alternative to 950 platinum than traditional cheaper options such as 18 and 14 carat white gold. In addition, retailers may be able to obtain more attractive margins.

The first presentation, 'The Working Properties for Jewelry Fabrication Using New Hard 950 Palladium Alloys', was by Professor Paolo Battaini (8853 SpA, Italy), who described progress to develop two prototype 950 palladium alloys for wrought application. The initial work was based on palladium-copper (Pd-Cu) and palladium-gallium (Pd-Ga) alloys, with indium and other alloying additions.

The annealed hardness of the Pd-Ga alloy, at HV 170, was much higher than that of the Pd-Cu alloy at HV 70, and its melting range was substantially lower. As-cast ingots were subjected to cold rolling and annealing cycles down to thin sheet. This sheet was further subjected to a number of mechanical processing operations, and the evolution of the metallurgical structure and properties was followed. For the Pd-Ga alloy, this included roll forming with continuous tungsten inert gas (TIG) welding to form seamed tube, that was further drawn down to tube of 8.5 mm diameter (easily accomplished, but dependent on good lubrication). Other processes tested were the blanking of washers, drawing and ring rolling to form ring blanks as well as square bars being rolled and then drawn to wire of 0.7 mm diameter, using diamond nibs in the dies. Good lubrication was also important here. Tensile tests were performed on the wires. Typically, a cold-worked hardness of

Fig. 1 Working a palladium alloy ring (courtesy of Mann Design Group)

HV 220 or greater was achieved before annealing to a hardness of HV 180. Good fine-grained, equiaxed microstructures were obtained.

For the Pd-Cu alloy, as-cast ingots were also cold-rolled and annealed down to thin strip, and roll-formed to square tube with continuous TIG welding, and subsequently further drawn to smaller dimension. Typical hardness after heavy cold work was HV 170, which reduced to around HV 72 on annealing.

Laser welding and brazing studies were carried out on the Pd-Ga alloy; it was found essential to establish the correct process parameters for successful laser welding, and the use of an 18 carat nickel white gold filler allowed effective brazing with an oxy-propane torch.

This work showed that the Pd-Ga alloy was the more promising of the two examined. The mechanical strength of the drawn and annealed wires was better than that of some platinum alloys, and indicated the suitability of the Pd-Ga alloy for chain manufacture.

An initial study, 'Palladium Casting: An Overview of Essential Considerations', of the investment/lost wax casting of 950 palladium alloys, was reported by Teresa Frye (Techform Advanced Casting Technology, U.S.A.). This company specialises in shell-mould casting of platinum jewellery and other high-tech metals for the aerospace and dental/medical industries. The purpose of the study was to obtain a better understanding of the casting characteristics of the new 950 palladium alloys appearing on the market, in comparison with those of the casting of platinum jewellery alloys. Frye covered several aspects: in wax sprueing, she noted that use of more auxiliary feed sprues was required for palladium thin sections to facilitate filling of the mould cavity. As in the case of platinum, investing the mould required the use of phosphate-bonded investments due to their high melting ranges (1400 to 1500ºC). Techform use ceramic face coats prior to investing the wax tree, but considered that this was not necessary. Any investment suitable for platinum should work well for palladium.

Frye found that the actual casting of palladium posed the biggest technical challenge. This was due mainly to the risk of oxidation, unlike for platinum, and so the use of protective atmospheres was essential; Frye used argon, but nitrogen is also possible. She also noted that overheating of the molten metal increased the chance of oxygen absorption with consequent defect formation (gas porosity) during solidification. Devesting of the cast metal from the mould was found to be relatively straightforward, by using boiling dilute sodium hydroxide solution followed by water blasting.

The study reported by Frye was conducted on palladium alloys selected on the basis of certain criteria, including a minimum hardness of HV 110, ductility, recyclability, melt cleanliness and fluidity. This resulted in six commercial alloys being evaluated, with casting temperature of 1600ºC, flask temperature of 950ºC, and vacuum followed by argon backfill atmosphere. Three of the test alloys resulted in brittle, defective castings, whereas the other three were ductile and crack-free. When the alloys were cast without vacuum, i.e. only argon cover, five of the alloys cast well, suggesting that vacuum was detrimental to some alloys. Scanning electron microscopy (SEM) analysis of a ductile fracture face showed the presence of low-melting gallium-rich particles on the grain boundaries.

Based on this initial evaluation, Frye selected two alloys which were subjected to form-filling casting tests using standard grid patterns and metal pour temperatures of 1590ºC, 1620ºC and 1760ºC. The latter temperature gave the best form-fill for Hoover & Strong's 'TruPd' and similar good fills were obtained in comparative trials on a 950 Pt-Ru alloy, cast at 1980ºC. Examination of cast rings in 'TruPd' under the same conditions showed a lack of porosity.

Frye concluded that there is still much work to be done on casting of palladium alloys, which present unique challenges compared with other precious metals. Recyclability of palladium alloy scraps is of particular concern.

Barrie-John Williams (Johnson Matthey, New York) gave the third presentation on palladium jewellery alloys, 'Palladium – Light, Bright and Precious – a World View', in which he reviewed palladium as a jewellery metal. The presentation included a potted history of palladium, discovered by Wollaston (4) in 1803, and some basic statistics on supply and demand, with particular reference to the U.S. source of supply – the Stillwater mine. Williams noted that recent interest in palladium as a jewellery metal in its own right (as opposed to its use in white gold) started in China in 2003, and that the Swiss began to use it for watches in 2005 as an alternative to white gold.

Williams noted that pure palladium is too soft for jewellery use, so alloys of 95% palladium have been developed (i.e. 950 fineness) that are harder and better wearing. The qualities of palladium as a jewellery metal include its preciousness as a member of the platinum group metals, its natural bright white colour, good lustre and lack of tarnishing as well as its lower density than that of gold and platinum. Like platinum it is rare, and its high purity at 950 fineness is attractive in the market.

Current ISO standards of purity (ISO 9202:1991 Jewellery – Fineness of precious metal alloys) are 950 and 500 finenesses. China has adopted 950 and 990, and in the U.S.A., 950 is favoured, as it is also in Germany and Switzerland. The U.K. assay offices have applied to have palladium recognised as a hallmarkable jewellery metal.

Williams noted that many 950 alloys are being developed and introduced to the market by alloy manufacturers, including Johnson Matthey, for both wrought and casting applications. Most are based on the Pd-Ru system with other alloying additions. He remarked that one of the disadvantages is the high cost of refining palladium alloy scrap.

Platinum Alloys

Platinum was also discussed at the Symposium. John McCloskey (Stuller Inc, U.S.A.) presented results of a study of two common 950 platinum alloys, 'Microsegregation in Platinum-Cobalt and Platinum-Ruthenium Alloys'. Based on the respective phase diagrams and using the Gulliver-Scheil equation to calculate the partition coefficient, McCloskey and his coworkers calculated the degree of microsegregation to be expected in cast alloys. Measurements on cropped sections of cast ingots by microprobe analysis showed that localised concentrations of ruthenium from centre to edge of the primary dendrites varied between 2 and 6% in an alloy containing 4.8% ruthenium. For the 4.8% cobalt alloy, the cobalt values varied between 4.3% minimum and 5.8% maximum. McCloskey used these data to calculate the partition coefficients, and found broad agreement with those calculated from the phase diagrams. He noted that in the Pt-Ru alloy, the last liquid to freeze is depleted in ruthenium and is almost pure platinum (98% measured), whereas in the Pt-Co alloy, the cobalt concentration of the liquid increases during solidification.

He concluded that the non-equilibrium freezing characteristics of the two alloys were distinctly different and that this, together with the wider freezing range, may explain the better casting characteristics of Pt-Co alloys.

The investment casting of platinum was investigated by Appolonius Nooten-Boom II (Hean Studios, U.K.), and reported in a presentation (by John Wright (Consultant, U.K.)), 'Dynamics of the Restricted Feed Tree'. Nooten-Boom showed how metal flowed into the mould during casting, and how improved fill can be obtained by use of a restricted feed system, which slows the feed of molten metal into the mould. This is contrary to conventional wisdom in the jewellery industry, although not in the engineering industry.

Technical Information

Andrea Basso's (Legor Srl, Italy) 'Jewelry and Health: Recent Updates' was a study on contact dermatitis in which 920 individuals were tested for allergies to metals commonly found in jewellery by skin patch tests using metal salts and metal discs (made of gold alloys of various carats). The patch tests using metal salts showed positive reactions to several metals in the order (maximum number first): nickel, cobalt, palladium, potassium, gold, copper, mercury and silver, with platinum and zinc showing no positive reactions. Of the 266 patients positive to nickel, some 53% were not positive to other metals. The other 47% were also sensitive to cobalt chloride, palladium chloride and gold thiosulfate in that order. In the patch tests with metal discs, no type of allergic reaction was found in subjects not sensitised to nickel. However, it was noted that where nickel release values were below those limits of the EU Directive (5), some sensitised patients still showed allergic reaction.

In his presentation '"Where Can I Find What I Want to Know?" Sources of Technical Information for Jewellers', Chris Corti (COReGOLD, U.K.) discussed various sources and reference books giving technical information. This included The PGM Database (6), various handbooks and manuals by Platinum Guild International, Johnson Matthey, the World Gold Council and others, as well as jewellery journals and websites. Corti's survey revealed a lack of up-to-date reference books on the metallurgy and properties of jewellery metals and their manufacturing technology. The Proceedings of the Santa Fe Symposium® were considered important sources.

Jewellery Manufacturing Techniques

Stewart Grice (Hoover & Strong, U.S.A.) discussed the diffusion bonding of difficult alloy combinations related to *mokumé gane* jewellery, and focused on carat Au-Pt and Au-Pd combinations. A goldsmith's experience in TIG welding of jewellery was presented by Kevin Lindsey (Lindsey Jewelers, U.S.A.) and showed its effective use in both small workshops and factories.

Martin Moser (OTEC Präzisionsfinish GmbH, Germany) discussed the effect of machine finishing parameters on polishing of jewellery, and how these can be used to optimise the finishing process. The investment casting of titanium jewellery was reviewed by Hubert Schuster (Jewellery Technology Institute, Italy) and the fundamentals of shotting and graining were reviewed by Joseph Strauss (HJE Company Inc, U.S.A.). Klaus Weisner (EVE GmbH, Germany) discussed the specifications of semi-finished jewellery materials and the problems that can arise if orders are placed with non-realistic expectations, drawing on his experience as an alloy supplier. The design aspect of jewellery was discussed by the designer Barbara Berk (Barbara Berk Designs, U.S.A.) who spoke about textile techniques such as weaving of wires, basketry and braiding in precious metals.

20th Anniversary of the Santa Fe Symposium®

Valerio Faccenda (Consultant, Italy) summed up the achievements of the last 20 years of the Santa Fe Symposium® in terms of its contributions to the jewellery industry: a fitting review of a unique resource that has made a major impact.

To mark the 20th anniversary of the Santa Fe Symposium®, a special tribute was paid to Eddie Bell, the co-founder, by many delegates past and present, by way of recognition of his vision and commitment to the industry. The highlight was the presentation of a 'concho' belt to Eddie. The 11 concho discs were crafted by skilled delegates, and included both platinum and palladium (donated by Johnson Matthey) as well as gold, silver and titanium. This belt was a feast of goldsmiths' skills. A fitting tribute!

Conclusion

The many questions to speakers at this Symposium confirmed the wide technical interest in palladium as a jewellery metal. The Santa Fe Symposium® proceedings are published as a book and PowerPoint® presentations on CD-ROM. They can be obtained from the organisers *via* www.santafesymposium.org. The 21st Symposium will be held in Albuquerque, New Mexico, U.S.A., from 20th to 23rd May 2007.

References

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5 European Directive, 76/769/EEC – 12th Amendment (94/27/EC)

6 The PGM Database, http://www.platinummetalsreview.com/jmpgm/index.jsp

The Reviewer

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