Design opportunities through innovative materials

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Introduction
Mitsubishi Materials Corporation has a long history of developing highly innovative new materials. Within the field of precious metals, there is little doubt that 'Diagold', 'High-strength Pure Gold', and 'Precious Metal Clay' can be accurately described as new and exciting gold products.

Beginning with *Diagold*, this composite material of different coloured golds is made, not by lost wax casting but by special diffusion bonding. This unique patterned material gives jewellery a completely modern feeling.

High-strength Pure Gold (HPG), produced by exploiting semiconductor technology, is remarkable in terms of its purity, its strength, its hardness and also in that it is possible to roll and machine this material. Such attributes make it superior to ordinary "soft" pure gold (1) and this means that a whole new world of pure, 24 carat gold jewellery design is possible, including multi-faceted beads, wedding bands and fine and intricately designed chains.

Finally, I would like to turn to *Precious Metal Clay* (PMC), a material produced from precious metal powder and an organic binder; this unique material allows a freedom in design never previously possible. Singularly unique products can be made in much the same way as they would by hand with ordinary potter's clay. Using a special technique, it is even possible to make hollow shapes and, using specially fabricated thin sheets of PMC, we can add a twist to the ancient Japanese art of original paper folding, known as "Origami".

Diagold
Diagold is a multi-coloured carat gold material. One of its many advantages is that the pattern of the material itself can be designed according to the customer's requirements. As Diagold is produced using complete metallurgical bonding without the use of soldering, processing methods such as bending, twisting and punching can be applied as if it were an ordinary mono-metal. Diagold can be made in various patterns as listed below. Figure 1 shows the group of Diagold patterns available commercially.

- *Niji* - Rainbow pattern, a linear stripe pattern
- *Nishiki* - An old Japanese textile pattern.
- *Mokumé* - Wood grain pattern

Figure 1 - Different patterns available in Diagold

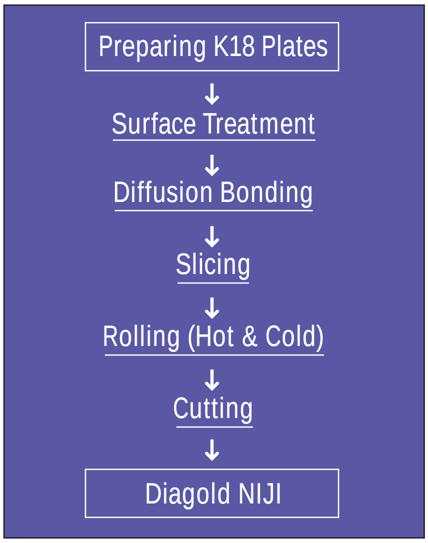

Figure 2 - The production of Diagold - schematic

The production of Diagold is shown schematically in Figure 2. 18 Carat gold plates are rolled to a specified thickness. After rolling, the bonding surface is cleaned by treating with an acid solution, the plates are stacked in a specified sequence and heated to temperatures of approximately 800°C, when a 10 ton load is placed on the plates. These conditions are maintained for about 3 hours, following which the bonded stack of plates is cut or sliced into the desired pattern and thickness. The three significant points in the production of Diagold are as follows:

1. Bonding is done under a high vacuum.
2. Cleaning of the bonding surfaces with acid.
3. Use of high pressure and high temperature to create conditions for diffusion bonding.

Figure 3 is a photo-micrograph showing the bonding surface in a cross-section of Diagold. As can be seen, a perfect bond has been achieved without any voids existing at the bonded interface. The bond strength of Diagold is demonstrated in a twist test, Figure 4, where the bond strength is maintained to an equally perfect level throughout the entire 360° revolution. Some examples of jewellery and a clock made in Diagold are shown in Figures 5 and 6.

High-Strength Pure Gold (HPG)

What is High-Strength Pure Gold (HPG)? Well, to date pure (24 carat) gold, although having the obvious advantage of purity, has been lacking in terms of strength and hardness. When used for making jewellery, there are many limitations in design brought about by the softness and lack of strength of ordinary pure gold. It was to address these shortcomings that we decided to create a new gold material and our research resulted in the development of HPG. It is a micro-alloyed metal achieved by adding a microscopic amount of chemical elements to ordinary pure gold. This exciting new material is a gold which remains exceptionally pure and has the extra strength and hardness lacking in ordinary pure gold (1).

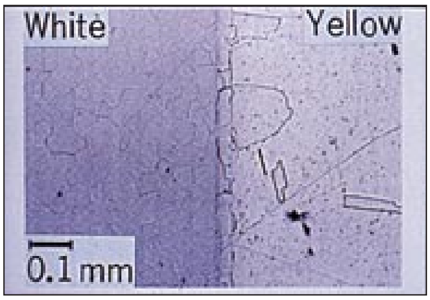

Figure 3 - Cross-section of a Diagold diffusion bonding zone showing the integrity of the interface

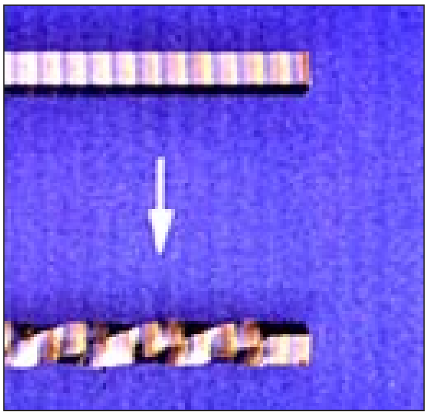

Figure 4 - The good bond strength of Diagold demonstrated by the torsional deformation of a bar through 360°

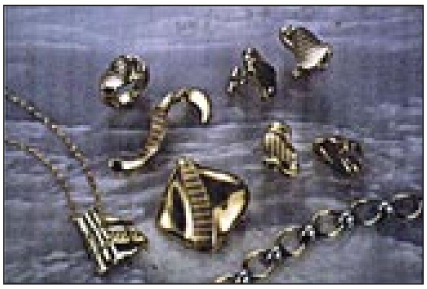

Figure 5 - Examples of jewellery in Diagold

The unique characteristics of High Strength Pure Gold at room temperature

As I have mentioned, HPG is unique because, although it is over 99.9% pure, it is both strong and hard. This does not mean it is stronger or harder than 18 carat gold but it is superior in these areas to ordinary pure 24 carat gold. A comparison of these three types of gold are shown in Table 1. As can be seen, when compared to ordinary pure gold, HPG has far greater tensile strength.

Heat resistance of High-Strength Pure Gold

HPG is very heat resistant and hardening also occurs after rolling. In Figure 7 (zero time on the left hand side), we can see the difference in hardness between ordinary pure gold and HPG at room temperature. However, the annealing curves, Figure 8, illustrate how hardness changes as the different golds are processed. The more HPG is worked, the harder it becomes and it can even achieve a Vickers hardness of 140 HV. In addition to this, even after long periods of time at a temperature of around 80°C, HPG will not fall below such levels of hardness, Figure 7. Moreover, it will not deviate much from a hardness of 100 HV even when kept at 400°C for approximately 30 minutes, Figure 8.

Figure 6 - A clock made in Diagold

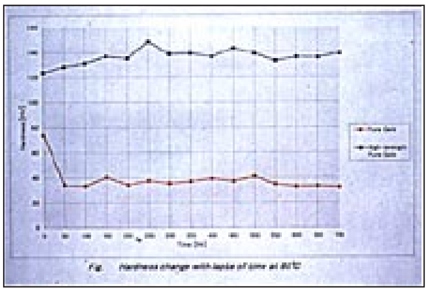

Figure 7 - Hardness change with lapse of time at 80°C for High-Strength Pure Gold

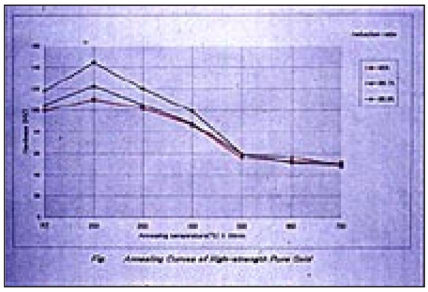

Figure 8 - Annealing curves for High-Strength Pure Gold, showing the effect of deformation by rolling on hardness

Table 1. Comparison of the strengths of golds at room temperature

	High-Strength Pure Gold		99.99% Pure Gold		18 carat Gold
	As drawn	annealed at 350° Cx30min	As drawn	annealed at 350° Cx30min	As drawn
purity (%)	99.9		99.99		75.0
Tensile Strength (kgf / mm^2)	50.2	42.1	18.5	6.3	77.4
Elongation (%)	2.1	1.8	1.1	22.2	2.1

Casting High-Strength Pure Gold

HPG can be cast in much the same way as 18 carat gold using the lost wax technique but the following two points should be borne in mind. Firstly, when casting in the air, the dopant level will be effectively reduced, depending on the length of time taken for melting. For this reason, a vacuum atmosphere or inert gas atmosphere is necessary. If the casting is carried out close to the air, then a surface seal is required.

Secondly, care should be exercised with regard to the mould. When an ordinary gypsum-bonded mould is used, the dopant contained in the HPG may cause some cracks to occur in the casting. We recommend, therefore, when casting HPG by the lost wax method that the surface of the wax is coated by such a refractory such as silicate compound.

Figure 9 describes the procedure for casting HPG. Make the shape of the desired object, for example, a ring. Coat the surface of the wax pattern with some silicate compound and place in a mould. Pour gypsum into the mould and fire it at approximately 660°C for 6 hours. Melt HPG in a carbon crucible at around 1,200°C and pour into the gypsum-bonded mould, where the gold will fill the space left by the burnt-out wax. When the item has been cast, remove from the mould and wash with sulfuric and hydrofluoric acids (see ***safety note*** at end of this paper). By coating the surface with silicate compound at the time of casting, a sound casting can be obtained.

Surface treatment for cast material in High-Strength Pure Gold

Having been drawn, rolled or otherwise worked, HPG is several times harder than ordinary pure gold. In contrast, the hardness at the time of casting is little different to ordinary gold. However, this is the only time that HPG cannot be credited with being remarkably strong. If casting is carried out in conjunction with a surface treatment, it is possible for the castings to have a surface strength hard enough for practical use.

This surface treatment is outlined in Figure 10. According to this method, the surface should be repeatedly polished and, according to the finish, the strength can be improved from 40-50 HV at the time of casting to a greater strength of around 80 to over 90 HV. The important surface treatment methods for increasing the surface strength of the HPG are polishing with a spatula or sand blasting treatment. When a spatula cannot be used due to the restrictions of the design, it will be necessary to add a sandblast treatment to the process for castings.

Table 2. The purity of High-Strength Pure Gold scrap after treatment in air, showing removal of dopant

	Au	Dopant	Others
Before treating	99.92%	760 PPM	44 PPM
After treating	99.99%	< 1 PPM	44 PPM

Handling of scrap

HPG is micro-alloyed with a unique dopant, providing the material with its unique characteristics. In order to re-use scrap pieces of HPG left over from working with material, it must be melted down and almost all of the dopant completely removed, Table 2. If the dopant is not properly removed and it is used to produce 18 carat gold, for example, it will change the characteristics of the 18 carat gold, namely the ductility and strength, and cause the formation of some cracks when heavily worked.

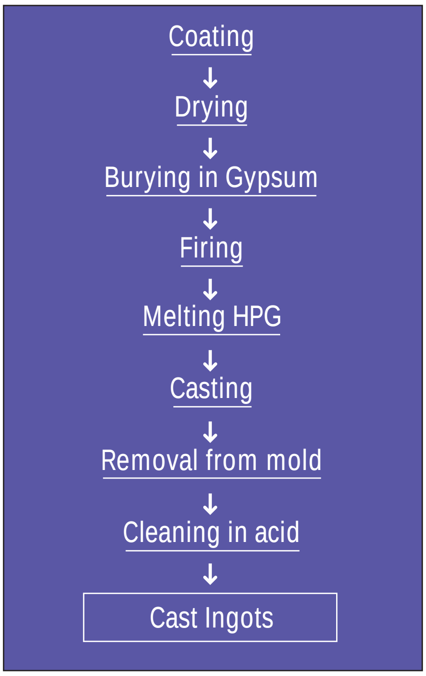

Figure 9 - Procedure for investment casting High-Strength Pure Gold

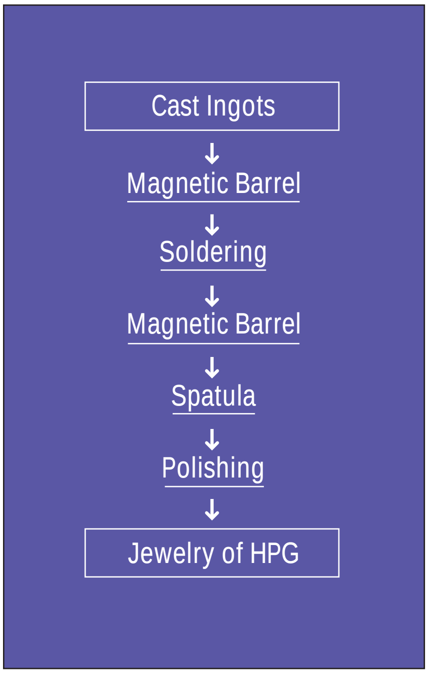

Figure 10 - Surface treatment of cast High-Strength Pure Gold

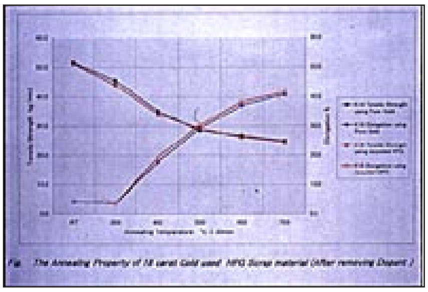

Figure 11 - Tensile properties of annealed 18 ct gold made from scrap HPG (after removing the dopant) compared to those of 18 ct gold made from ordinary fine gold stock

Thus, if scrap HPG is used untreated to make an 18 carat gold, the ductility is greatly reduced and cracks may appear as the material is being worked. If HPG is used when the dopant has been removed, the 18 carat gold will exhibit the normal elongation and hardness values, as illustrated in Figure 11. As you can see in this case, there are no problems in using treated HPG scrap to produce 18 carat gold.

Making engraved rings

There are, of course, various ways in which to make a ring shape from gold including casting, tube cutting, and bending a sheet of the metal. The method of fabricating HPG rings by using sheet metal is given in Figure 12. A shape is formed and soldered, using a solder with a melting temperature of approximately 750°C, to finish the ring shape. This heating process will, of course, weaken the ring slightly but by using the polishing techniques

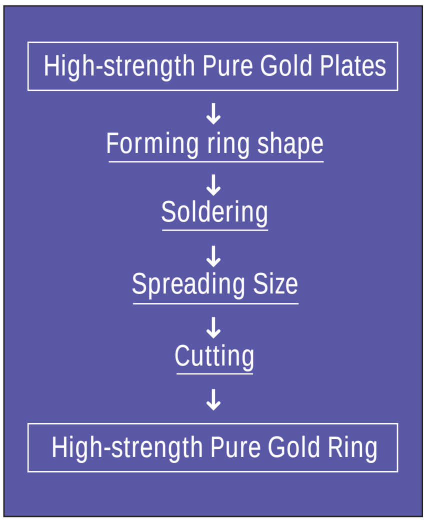

Figure 12 - Process for making a High-Strength Pure Gold ring from sheet

Figure 13 - Jewellery made in High-Strength Pure Gold

Figure 14 - Necklace chains of High-Strength Pure Gold

Figure 15 - Ornaments in HPG to adorn a Buddhist altar

described earlier, it is possible for the final ring to be as hard as 80 HV. Examples of jewellery and other items made in HPG are given in Figures 13-15.

Precious Metal Clay

Precious Metal Clay (PMC) consists of fine gold powder, with a diameter of under 20µm, and an organic binder. The organic binder is made from water soluble cellulose, surfactants, some oils and water. PMC is environmentally friendly throughout. Figure 16 shows the manufacturing process for PMC. An organic binder is added to fine gold powder, it is mixed and degassed in a vacuum. The mixing rates of the organic binder and fine gold powder are optimized in accordance with powder diameter and shape and binder type. Besides fine gold clay, fine silver clay, fine platinum clay and 18 carat gold clay (in three colours) have also been developed.

For the gold clay, after shaping, the product should be dried in the air for half a day or at around 80°C for a couple of hours. It is then placed in a kiln and heated up to around 1000°C at the rate of 15°C per minute and kept at that temperature for about 2 hours. After cooling, a sintered product is obtained. Figure 17 shows SEM photographs of PMC before and after sintering. It can be seen that this fine gold powder is fully sintered.

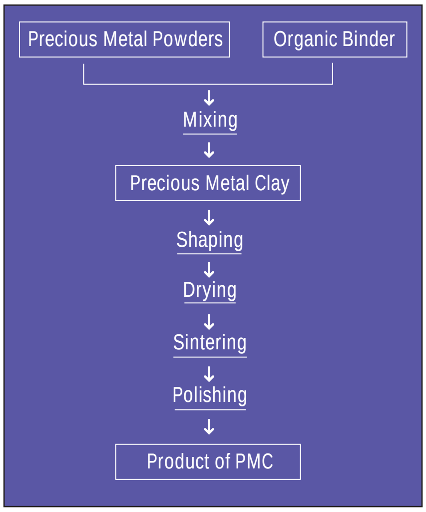

Figure 16 - Manufacturing process for Precious Metal Clay

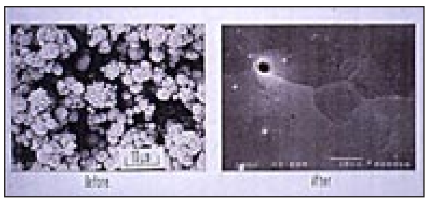

Figure 17 - Scanning Electron Micrographs (SEM) of gold clay before (left) and after (right) sintering

Figure 18 - Appearance of Precious Metal Clay before (left) and after (right) sintering showing shrinkage

Figure 19 - Necklace made of hollow beads using Precious Metal Clay

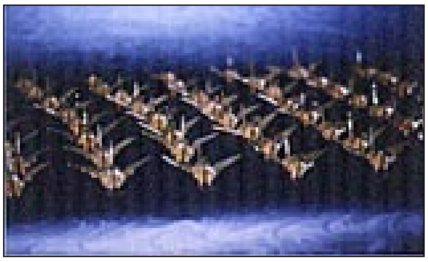

Figure 20 - Origami birds (cranes) made from PMC in sheet form

Figure 21 - Sake cup made in PMC

Figure 18 shows the appearance of PMC before and after sintering. It is found that a sintered product shrinks as the organic binder is vaporized and the metal powder sinters together during the sintering process. In general, shrinkage is about 20 to 30% in size and about 40 to 50% in volume although it depends on product size, binder type and binder content.

Hollow parts

Precious metal is very expensive and jewellery accessories should be light. Therefore, it is worth establishing a technique to make hollow parts. Using cellulose with a lower vaporization temperature as the core material, hollow parts of PMC can be produced without deformation or defects (such as indentations, blisters or bursts) and without the need to make pinholes for outgassing. Figure 19 shows a necklace made of PMC using this technique.

PMC sheets

Origami birds, cranes, made from PMC sheets are shown in Figure 20. PMC sheets can be obtained by mixing precious metal powder and organic binder although the type of binder and its composition should be adjusted. Using these PMC sheets, it is possible to fold this material as though it were paper. It is not suitable for industrial

Figure 22 - Accessory made in Precious Metal Clay (courtesy of designer Ms S Asayama)

parts because of a lack of strength, but it is satisfactory for art- and craft-works.

Art- and craft-work

The texture of PMC sintered products looks like that of unglazed pottery. Since the texture of PMC is little different from that of potter's clay, typical potter's works such as a sake cup, a tea cup, or a vase, can be made easily using clay forming techniques on a potter's wheel. A sake cup made from PMC is shown in Figure 21.

Accessories and jewellery

Figures 22-25 show accessories made from PMC. They have a feeling of softness. The good points for using PMC for making accessories are as follows:

- A particular technique is not needed to shape products
- It can be shaped without expensive moulds.
- It is possible to make light products.

It is not suitable for mass production, but products can be manufactured in considerable numbers with a low cost rubber mould.

Figure 23 - Necklace in PMC (courtesy Ms S Asayama)

Figure 24 - Accessories made in PMC (courtesy of RONAN-DOLL Association, Ms N Ohkubo)

Conclusions and future steps

Precious Metal Clay is manufactured by mixing precious metal powder and organic binder. In Japan we are promoting craft workshops where PMC is used, and we are in the process of initiating various other such activities overseas. In the future we plan to develop various other aspects of the materials, based on the user's needs.

We are now entering an age where individuality is considered increasingly important and it is, therefore, our intention to introduce to the precious metals world, materials which will enable the user to make products never previously imaginable. Continuing to produce exciting new materials is our guiding principle.

Reference

1 A. Nishio, 'The Development of High-Strength Pure Gold', *Gold Technology*, No 19, July 1996, p11.

Safety Note: Acids, particularly hydrofluoric acid, are dangerous substances and must be handled with care, using appropriate protective clothing and equipment. Adequate safety precautions must be taken in carrying out the procedures described in this paper.

Figure 25 - Accessories made in PMC (courtesy of RONAN-DOLL Association, Ms N Ohkubo)