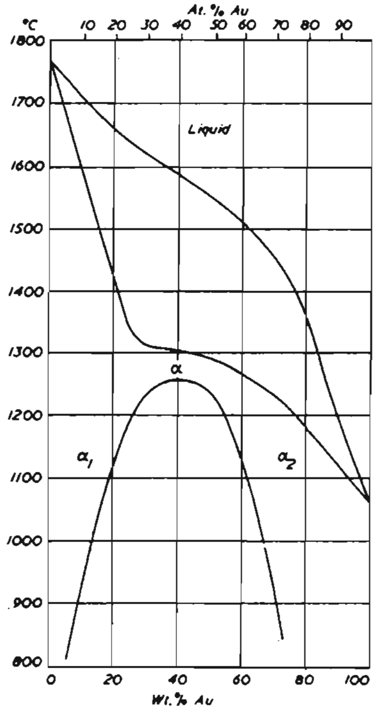
Understanding Heat Treatable Platinum Alloys

Greg Normandeau and David Ueno • Imperial Smelting & Refining Co. of Canada Ltd.

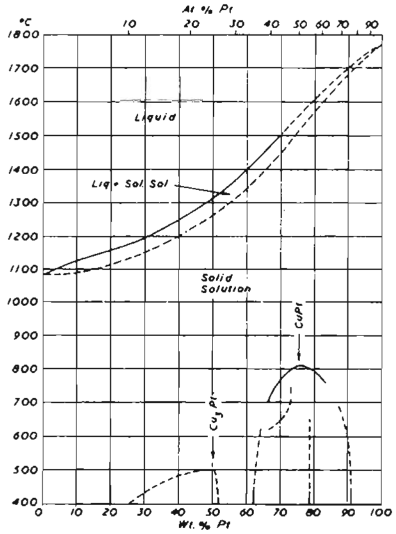
A heat treatable alloy experiences a significant change in physical properties because of a specific method of thermal processing during manufacturing procedures. Platinum alloys, generally classified as heat treatable, are based on varying additions of tungsten (W), gold (Au), gallium (Ga), indium (In) or copper (Cu) according to industry sources. (1,2,6) Information on these alloys was derived from studies in the late 1970's (3), published in the early 1990's along with certain patents regarding their application to tension setting diamonds. The response to heat treatment usually involves an increase in hardness or resistance to indentation. This affords greater wear resistance in service and an increase in yield strength, which makes the material exhibit superior spring properties. Because international hallmarking standards for jewelry require a minimum 95% Platinum content, the manipulation of physical properties available through alloying additions or combinations of cold working are limited. The simultaneous control of chemistry and thermal processing affords a means of manipulating physical properties over a greater range. After consideration of the metallurgical characteristics and physical properties, issues relating to manufacturing methods and applications will be explored with a goal of highlighting where future research should focus on these materials.



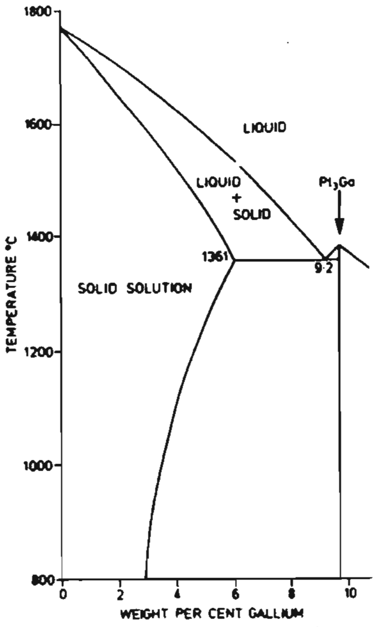
Gold Platinum Phase Diagram

Theoretical Considerations

Information in the form of phase diagrams of platinum and the various alloying additions that provide a heat treatment response is scarce and usually restricted to binary relationships. A few examples are included below. The hardening response mechanisms vary from solid state ordering in the case of copper to limited solubility resulting in two distinctly different solid solutions, in the case of gold additions. The binary relationship between gallium and platinum indicates solid solubility in the platinum rich region with the formation of brittle intermetallics possible. Solid state solubility is temperature dependent, indicating the possibility for precipitation hardening. The platinum-indium phase relationship is very similar. The ternary relationships between combinations of platinum, gold, gallium, copper and indium are not fully documented.



Platinum Copper Phase Diagram



Platinum Phase Diagram

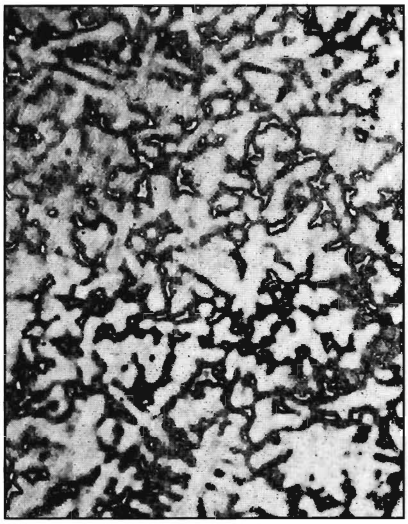


Figure 1: Overview of the investment cast microstructure. (50X)

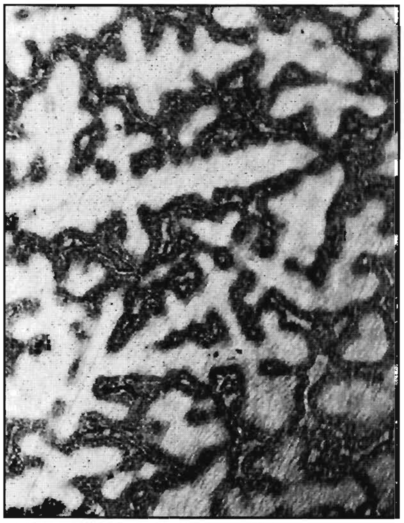


Figure 2: Detailed view of the cast microstructure. (200X)

Figure 4: View of the wrought microstructure (100X)

An overview of a typical investment cast microstructure is provided in *Figure 1 & 2.* The material is obviously heavily cored with a transition between primary dendrites of a white phase designated alpha, versus the interdendritic region containing beta phase. This microstructure is indicative of a limited solubility relationship between the elements involved. The result of energy dispersive X-ray analysis is summarized in *Figure 3.* Both phases are rich in platinum, as would be expected in a 95% alloy, while the beta phase shows a greater incidence of indium and gallium. This is typical of segregated alloys whereby the lower melting point elements concentrate in the interdendritic area. Varying the amount of each phase within the microstructure, through a specific heat treatment, can alter the physical properties. Illustrative data will be summarized in another section.

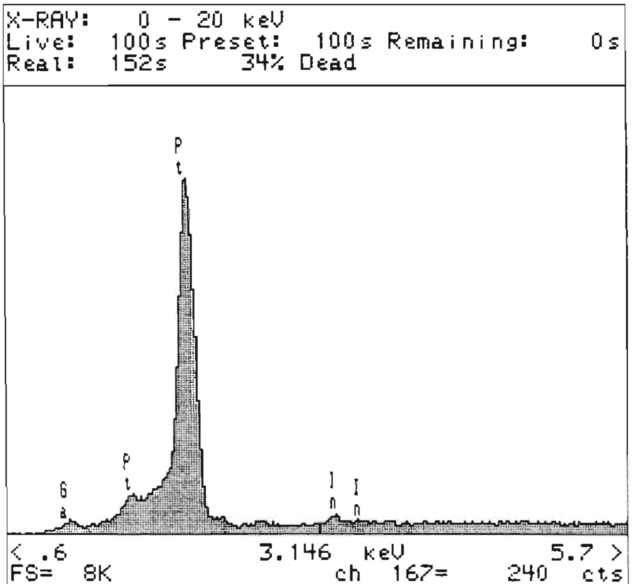


Figure 3: SEM EDAX scan of beta phase.

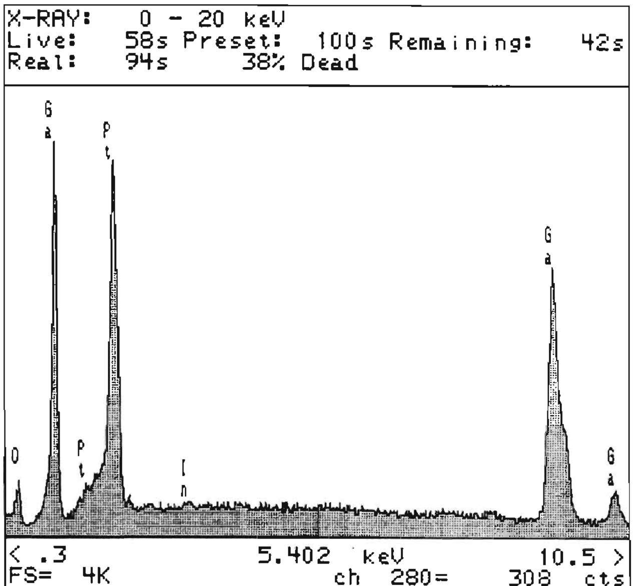


Figure 5: SEM EDAX scan of chemistry of wrought beta.

The wrought microstructure, typical of mill products such as sheet and wire, is summarized in *Figure 4*. The alloy consists of a white alpha phase equiaxed matrix with isolated beta phase particles. This transition is typical when alloys are subject to extensive section reduction followed by thermal processing, such as annealing to soften for further cold working. The SEM EDAX scan of a beta phase particle is summarized in *Figure 5*.

The size and dispersion of beta phase may control the physical properties of the wrought alloy, as is the case with two phase relationships in many other materials. Study of controlling the incidence of beta phase is just beginning.

Following the convention established in other industries with similar materials, two heat treatment terms used throughout the document are defined as follows:

Solution Treated: the phase state that exists within an alloy after treatment at an elevated temperature followed by a rapid quench to room temperature in some media. This treatment is done to reduce the quantity of a second phase and encourage the formation of a ductile solid solution amenable to further cold working. Properties such as hardness, tensile and yield strength are generally at a minimum for the alloy system, resulting in maximum workability.

Artificially Aged: the phase state that exists within an alloy after heating a solution treated material to an elevated temperature followed by relatively slow cooling in ambient air. This treatment is applied to encourage the separation of an alloy into two phases on a microscopic level. The incidence of a second phase within the alloy generally increases hardness, tensile and yield strength. Materials are not normally subjected to any forming in the aged state.

Properties of Heat Treatable Platinum

A variety of physical properties have been evaluated and are worthy of summary with comparison throughout to industry standard 95% Platinum 5% Ruthenium or 95% Platinum 5% Cobalt alloys.

Alloying additions required to impart response to heat treatment reduce the melting range of 95% Pt materials substantially (145°C). The melting range is broad at 100°C compared to the narrow 10-20°C typical of most platinum alloys.

Alloy:	Melting Temps Liquidus - Solidus		CIELAB Color Coordinates
95.2% Pt - 4.8% (Ga, In,Cu)	1650°C (3002°F)	1550°C (2822°F)	83.1 L* 0.1 a* - 4.6 b*
95.2% Pt - 4.8% Ru	1795°C (3263 F)	1780°C (3236 F)	84.2 L* 0.0 a* - 4.1 b*

This causes a large slushy range during solidification that impairs the ability to feed volumetric contraction inherent to solidification during such processes as investment casting. Compensation with larger feeding gates and sprues is normally recommended to overcome this inherent property. Color characteristics indicate a quality platinum shade. The lightness value (L*) matches well. The overall color difference vector value (DE) is 1.21 indicating a very close match in color between the standard and heat treatable materials. The human eye can barely discern color differences that approximate 1 DE value.

The abbreviation HTA, short for heat treatable alloy, is used throughout the remainder of the document to denote the base metal addition component of alloys examined.

As-cast Physical Properties:

Tests were performed on a Monsanto type "W" tensile tester with No. 12 size dumbbell investment cast pieces to determine the basic properties listed below:

Alloy/ Treatment	Hardness (HV)	Tensile Strength (psi)	Yield Strength (psi)
95.2% Pt - 4.8% HTA	280	112,000	92,000
95.2% Pt - 4.8% Ru	130	66,000	35,000[5]
95.2% Pt - 4.8% Co	135	64,000	35,000[5]
95.2% Pt - 4.8% HTA Aged @ 700C	318	125,000	104,000

The initial starting hardness of heat treatable platinum is higher than conventional materials. Both strength and hardness can be increased substantially after the completion of assembly, but before gem setting and final polish by completing the aging process. The aging process produces a slight oxidation or cloudiness on the alloy surface that does not have any specific color. No chemical treatments have been attempted to remove this oxide layer. It is easily removed through conventional polishing techniques.

Wrought Physical properties:

Tests were performed on a Monsanto type "W" tensile tester deployed stamped specimens of 0.30mm (0.014") thickness conforming closely to ASTM specification E8-89 to determine conventional wrought physical properties.

As the data indicates, heat treatable platinum has a significantly different response to cold working compared to conventional materials. Properties are also affected by thermal processing.

Alloy/ Treatment			
	Hardness (HV)	Tensile Strength (psi)	Yield Strength (psi)
95.2% Pt- 4.8% HTA Annealed = solution treated @ 1000ºC			
	190-210	105,000	75,000
95.2% Pt- 4.8% Ru Fully Annealed @1000C			
	150-160	74,000	56,000
95.2% Pt- 4.8% HTA Cold worked 50%			
	340-360	159,000	157,000
95.2% Pt- 4.8% Ru Cold worked 50%			
	220-230	104,000	102,000
95.2% Pt- 4.8% HTA Aged @ 700ºC after solution treatment			
	340-360	155,000	1125,000
95.2% Pt- 4.8% HTA Aged @700ºC after 50% CW			
	420-430	183,000	174,000
95.2% Pt- 4.8% Ru Cold worked 75%			
	250-260	116,000	115,000

In general, strengths of heat treatable platinum greatly exceed what can be obtained in conventional materials. This is especially true with the yield strength where an elevated value is critical for spring like properties. These enhanced properties can be obtained through cold working, heat treatment alone or a combination of both. Even with 75% reduction in thickness through cold work, the yield strength of standard Pt-Ru alloy cannot approach the levels attained from correct heat treatment of this specialty alloy. The elevated levels of strength attainable when cold work and aging are used in tandem are impressive.

Manufacturing Issues

Cold Working:

Platinum heat treatable alloys work harden faster than their conventional counterparts. Whereas 95%Pt-5%Ru can withstand 90% reduction in thickness during cold rolling, a heat treatable material will only accept 40-50% reduction prior to the onset of unacceptable gross fracture of the billet. The material behaves similar to a yellow gold easy solder that readily experiences edge cracking during fabrication because it's ductility has been compromised in favor of a much lower melting point. Numerous intermediate anneals (6X as many as regular material) are required to reach the same thickness. Each annealing must be done at a comparatively high temperature (1000-1100°C) preferably providing time for an extended soak (10 minutes per kg) and immediate water quench to maximize ductility for further working. All of these conditions are difficult to achieve with conventional handling equipment and 6000g (200 t.oz) billets. These conditions form a limitation towards achieving mass production volumes and economies attainable with regular platinum alloys.

These same attributes make jewelers bench handling potentially more difficult with heat treatable platinum. Hand rolling or cold forming will be hindered by the materials high stiffness and yield strength. All frequent anneals must raise the metals temperature into the bright orange to bright yellow color range, followed by a rapid quench to facilitate further forming. Purchasing the material fabricated as close as possible to final size from a supply mill will greatly reduce the effort required.

Hardening by Heat Treatment:

The material responds readily to hardening procedures over a broad range of temperatures and conditions achievable by both bench torch methods or mass production atmosphere furnaces. Both hardness and yield strength increase about 70% from fully soft values in response to a correct aging treatment. For bench work, a piece must be heated to a medium orange color (700°C) with a torch or furnace and simply allowed to cool in air until no color can be seen before quenching. The treatment can be applied to either soft or partially worked material to boost hardness and strength. It is good practice to repeat the procedure if a torch is used to ensure complete aging. A thin layer of protective flux will aid in minimizing surface oxidation or cloudiness that can occur.
The longer soak time, more thorough heating and protective atmosphere afforded by a belt furnace will also harden heat treatable platinum. Deploying conventional hydrogen-nitrogen mixed atmospheres, fixturing and belt speeds should be adjusted to allow components to soak at 700°C for 20-30 minutes. The traditional cooling experienced traveling through the water jacket cooled section of a furnace is sufficient to promote hardening.

Correctly designed heat treatable platinum alloys are very responsive to hardening procedures with minimal need for close control of conditions. The hardening procedure is fully reversible by simply heating the component to 1000°C followed by a rapid water quench to restore softness for additional work.

Melting:

Previously alloyed stock can be readily melted using all of the materials and equipment inherent to platinum investment casting. Despite the lower melting range (1650-1550°C*)* compared to conventional materials, the sluggish flow must be overcome using more superheat (200°C) than is usually required. This ensures that high temperature fused quartz crucibles and induction or oxy-hydrogen heat sources are required for small melts. The tendency towards oxidation of the alloying additives can be reduced by providing a protective cover gas of neutral argon. Avoid reducing conditions that promote the formation of brittle platinum phosphides and silicides. Primary melting and alloying practice must take care to preserve low melting point additions with protective cover gas, while casting a thin enough section to allow subsequent cold working. This is a major challenge that requires additional study.

Machining:

Preliminary machining studies indicate that heat treatable platinum exhibits substantially different behavior than conventional alloys. Equivalent speeds and feeds during lathe cutting produced large continuous swarf more indicative of machining gold than the small broken chips of platinum. Tool forces and wear appeared to be much lower despite using the same lubricants. Examination of the chips and lathe turnings on the SEM revealed the results depicted in *Figures 6 through 9.*

Figure 6: Surface profile of machined 95%Pt-5% HTA.

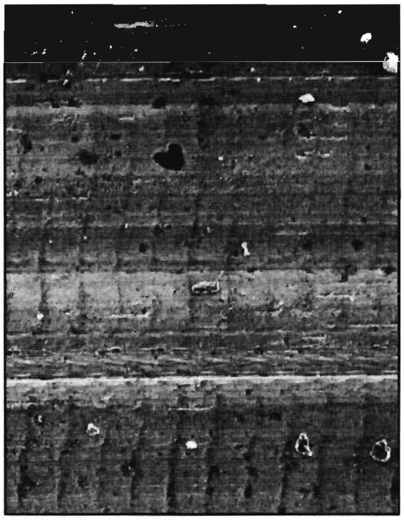


Figure 7: Surface profile of machined 95%Pt-5%Ru.

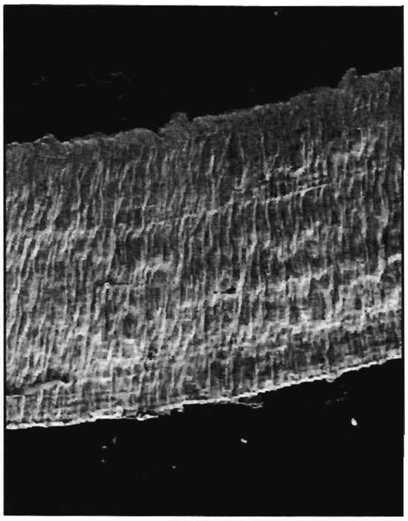


Figure 8: Lathe swarf surface of machined 95%Pt-5%HTA

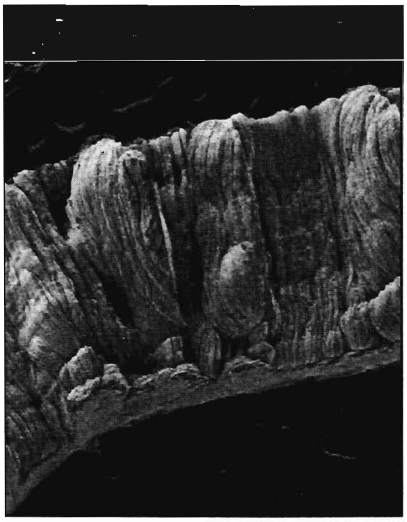


Figure 9: Lathe swarf surface of machined 95%Pt-5%Ru.

The machined surface of the heat treatable platinum is smeared with little or no tool marks, compared to the conventional material. The heat treatable platinum lathe chip also has noticeably different slip plate buildup density. The dislocated platelets of material sheared during machining are much more densely packed with the ruthenium based material. Corresponding hardness mapping of the machined face and chip cross section revealed hardness increased 15-20% from a nominal 230HV to 270HV with the heat treatable platinum. A much higher rate of work hardening in shear was noted with conventional platinum. Hardness increased from 170HV to 270HV (+50-60%). These results suggest that alloying additives in heat treatable platinum reduce the high rate of strain hardening during shear that contributes to conventional platinum alloys renowned poor machining performance. The possibility of manipulating the size and distribution of the second phase in heat treatable alloys to enhance machinability requires further research. The potential for a highly machinable soft alloy that can be subsequently hardened to the range of 350HV for superior consumer wear resistance to scratching and indentation is a very real possibility with platinum heat treatable alloys.

Figure 10: Overview of various investment cast articles.

Applications

Investment Casting:

It is possible to investment cast a broad range of jewelry articles with heat treatable platinum. *Figure 10* illustrates a range from large men's rings, through delicate sections, to 4 claw settings all investment cast with conventional platinum techniques. All surfaces are as-cast after acid pickling to remove investment residues only. As noted previously the alloy has a broad melting range that should be assisted through enlarged gates and sprues to overcome the tendency towards sluggish feeding.

Findings and Hardware:

Heat treatable platinum has significant potential where enhanced spring properties will increase holding power or the number of cycles during service. This includes bracelet closure clips, omega clips and butterfly earring clasps. *Figure 11* illustrates a typical earnut. The increased holding power of these items is substantial after correct heat treatment to increase the yield strength. In direct dead weight lift tests, regular gold earnut could lift 110g, heat treated gold 150g and heat treated platinum over 400g. Numerous other hardware applications involving the stamping of strip or the forming of wire exist. Wherever improved spring properties are required, heat treatable platinum may have an application.

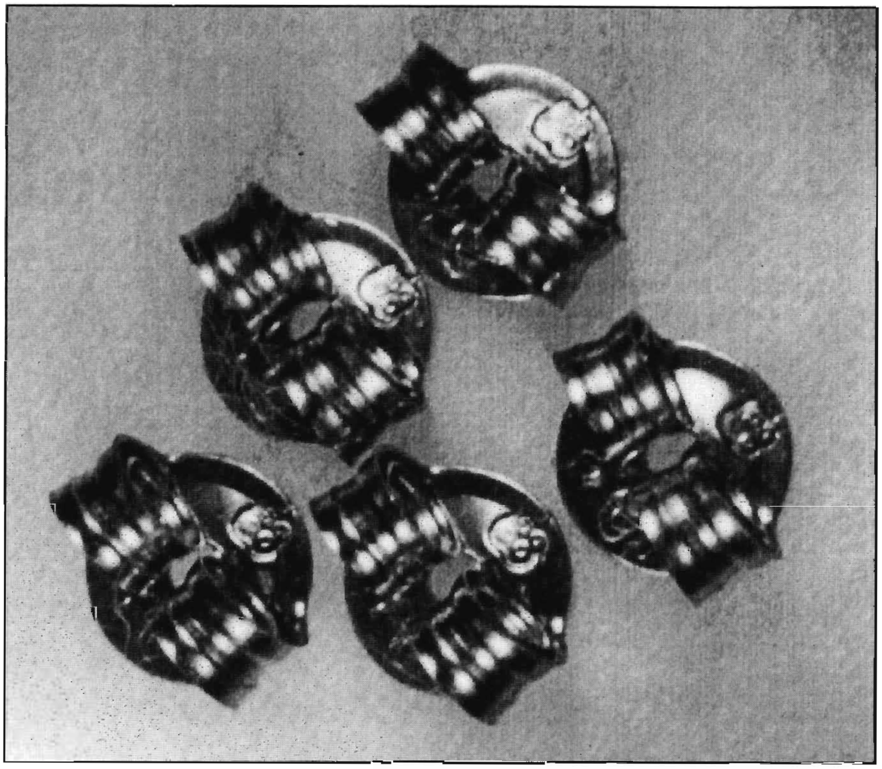


Figure 11: Overview of butterfly clasps.

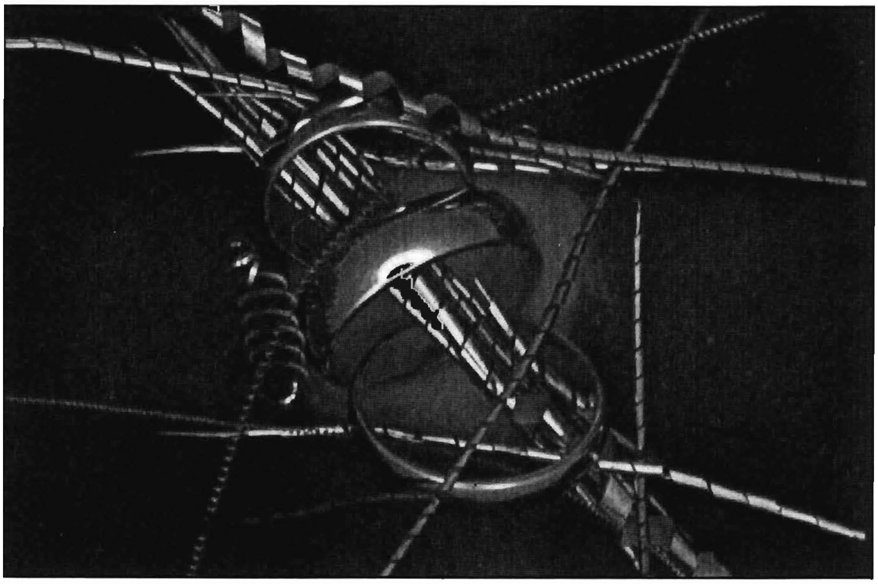


Figure 12: Overview of various seamless bands.

Seamless Bands:
Figure 12 depicts a range of machined products that exhibit a high quality surface finish. Lathe swarf consists of long thin ribbons more typical of gold machining. The potential for improved surface finish and enhanced tool life exists.

95% Platinum Braze or "solder" for Joining:

The depressed melting range of the heat treatable platinum alloy makes it an ideal candidate for joining operations where the 95% platinum content of an article cannot be compromised by conventional platinum "solders." The temperature gap between the heat treatable liquidus and 95% platinum ruthenium solidus is 130°C. This is sufficiently large for a skilled jeweler to affect a metallurgical bond. Laboratory tests hand welding 0.170" diameter tensile pieces with 0.010" heat treatable foil achieved bond strengths ranging from 75 to 90% of solid 95% ruthenium or cobalt materials. Ductility was reduced somewhat but strengths in excess of 60 ksi for a joint are more than adequate for jewelry service.

Conclusions & Areas for Further Study

- Heat treatable platinum has a higher as-cast hardness than conventional materials. This property can be increased with heating to 700°C followed by slow air cooling. Yield strength also increases in roughly the same proportion.
- Work hardening through cold working occurs at a much faster rate with heat treatable platinum alloys. They can achieve a higher hardness and yield strength than conventional alloys.
- Correct aging heat treatments increase hardness and yield strength about 60% above the fully annealed or solution treated state. Final properties are double the strength of conventional materials.
- A broad range of heat treatment conditions as simple as torch heating followed by air cooling will cause a significant increase in physical properties.
- Manufacturing procedures require extensive high temperature anneals with a rapid quench to promote softening for further cold working. These conditions are difficult to achieve with billets in excess of 6000g. This limits the size of wire and strip coils.
- Investment casting heat treatable platinum into a large variety of jewelry articles is possible.
- Performance during machining operations requires more study. The possibility that tool life can be enhanced from inherently lower strain rates during machining with heat treatable platinum requires full exploration.
- Improved methods of casting that can control solidification in large weight billets (>3000g) with a thickness of less than 9.6mm require development. Such thin sections will enhance production capabilities for thin light weight strip sizes required for stamping.
- Continued study of the microstructure, phase relationships and heat treatment parameters may improve the production methods for these difficult to handle alloys.

References

1. An Introduction to Platinum, Johnson Matthey, 1990
2. U.S Patent 5,188,679 Feb. 23, 1993 & 5,084,108 Jan. 28, 1992 Steven Kretchmer
3. Private Conversations with R. Rushforth formally of Johnson Matthey Research, May 1998
4. Metals Handbook, Desk Edition, 1-2 & 1-36, 1985, ASM International
5. Lanam, R., Pozarnik, F., Volpe C., Platinum Alloy Characteristics, Platinum Day
6. Platinum Guild International U.S.A.
7. Ainsley G., Bourne, A., Rushforth R., Platinum Investment Casting Alloys Platinum Metals Review, July 1978
8. Metals Reference Book, Smithells 8th Ed. , pg 455, 589