UNDERSTANDING HEAT TREATABLE PLATINUM ALLOYS

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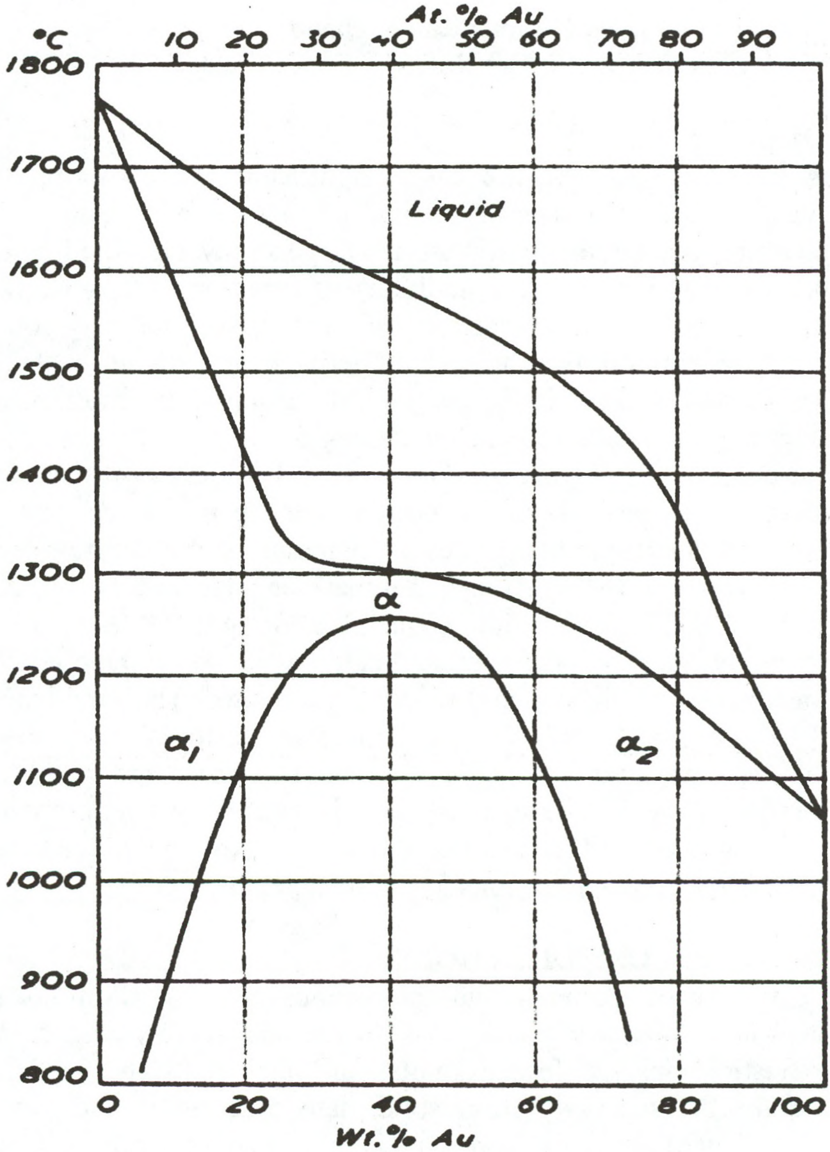
INTRODUCTION:

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), and 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 which affords greater wear resistance in service, and an increase in yield strength that makes the material exhibit superior spring properties. Based on international hallmarking standards requiring a minimum of 95% content for unqualified designation as platinum jewelry, the physical properties manipulation 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 will be explored with a goal of highlighting potential applications for these materials.

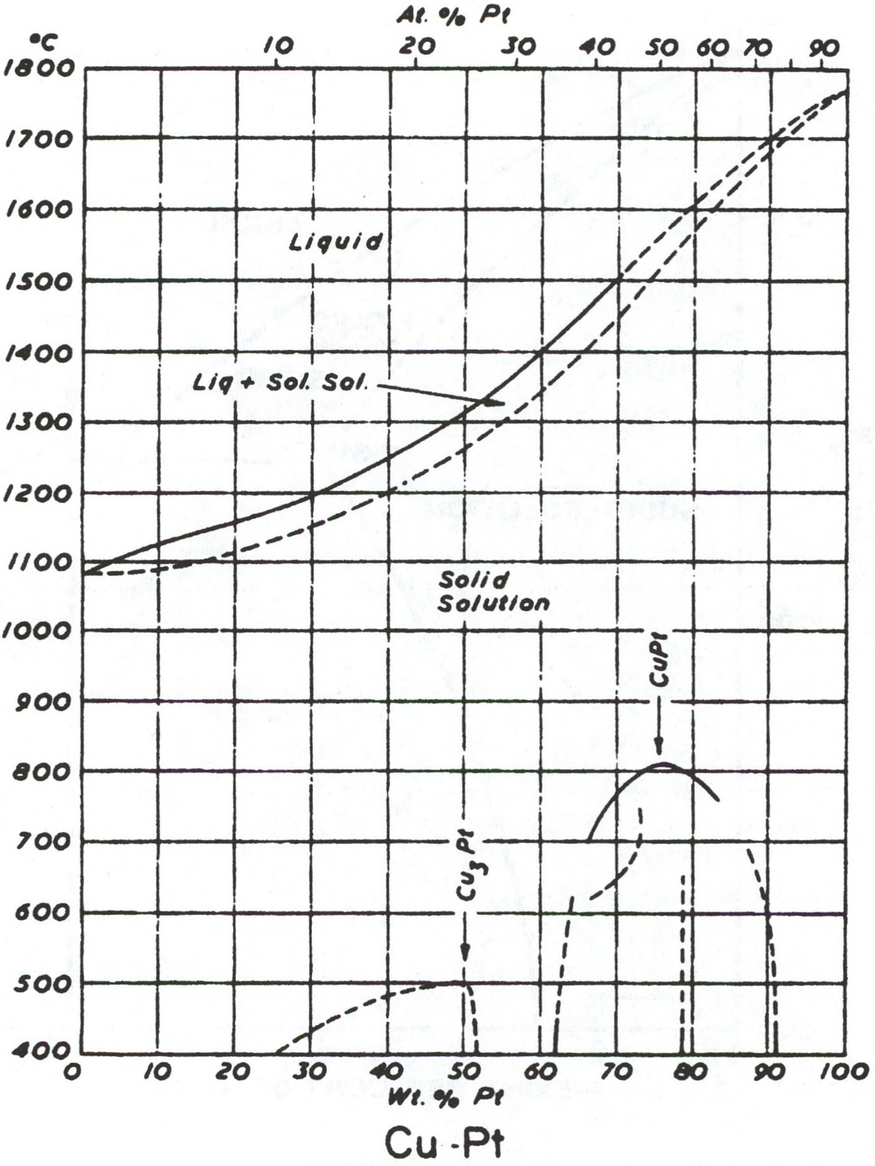
THEORETICAL CONSIDERATIONS:

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. The hardening response mechanisms vary from solid state ordering in the case of copper to limited solubility resulting in two distinctly different solid solutions as in the case of gold additions. The binary relationship between gallium and platinum indicates solid solubility in the platinum rich region with the possible formation of brittle intermetallics. Solid

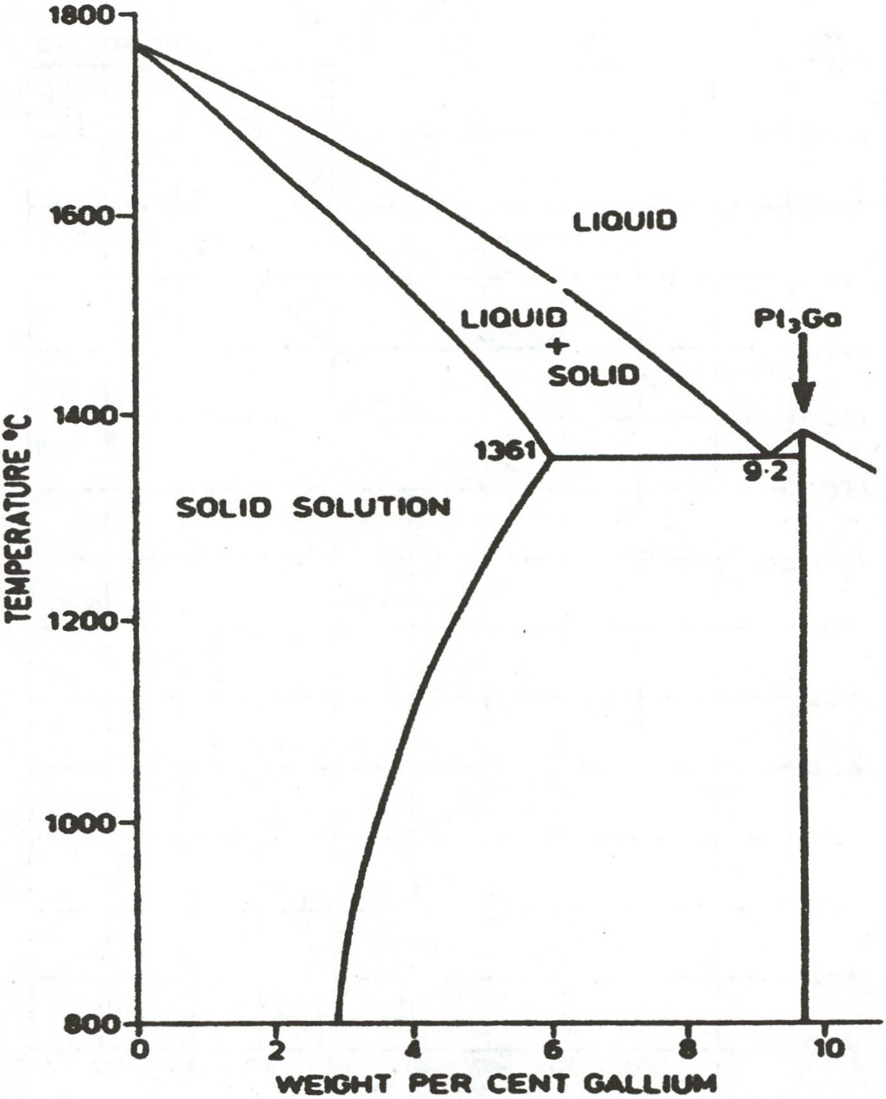


Au-Pt

Gold Platinum Phase Diagram (Ref. 7)



Platinum – Copper Phase Diagram (Ref. 7)



Portion of the Platinum –Gallium Phase Diagram 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.

An overview of a typical investment cast microstructure is provided in figure 1. The material is obviously heavily cored with a transition between primary dendrites of a white phase designated alpha, versus the interdendritic region containing the 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 2. 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.

A wrought mill product is typically deployed for sheet and wire. The SEM EDAX scan of a beta phase particle is summarized in figure 3 with the microstructure depicted in figure 4. The alloy consists of a white alpha phase equiaxed matrix with isolated beta phase particles. This transition from the cast state is typical when alloys which are subjected to extensive section reduction followed by thermal processing, such as annealing to soften for further cold working. The size and dispersion of beta phase can control the physical properties of the wrought alloy, as is the case with two phase relationships in many other materials.

Following the convention established in other industries with similar materials, 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

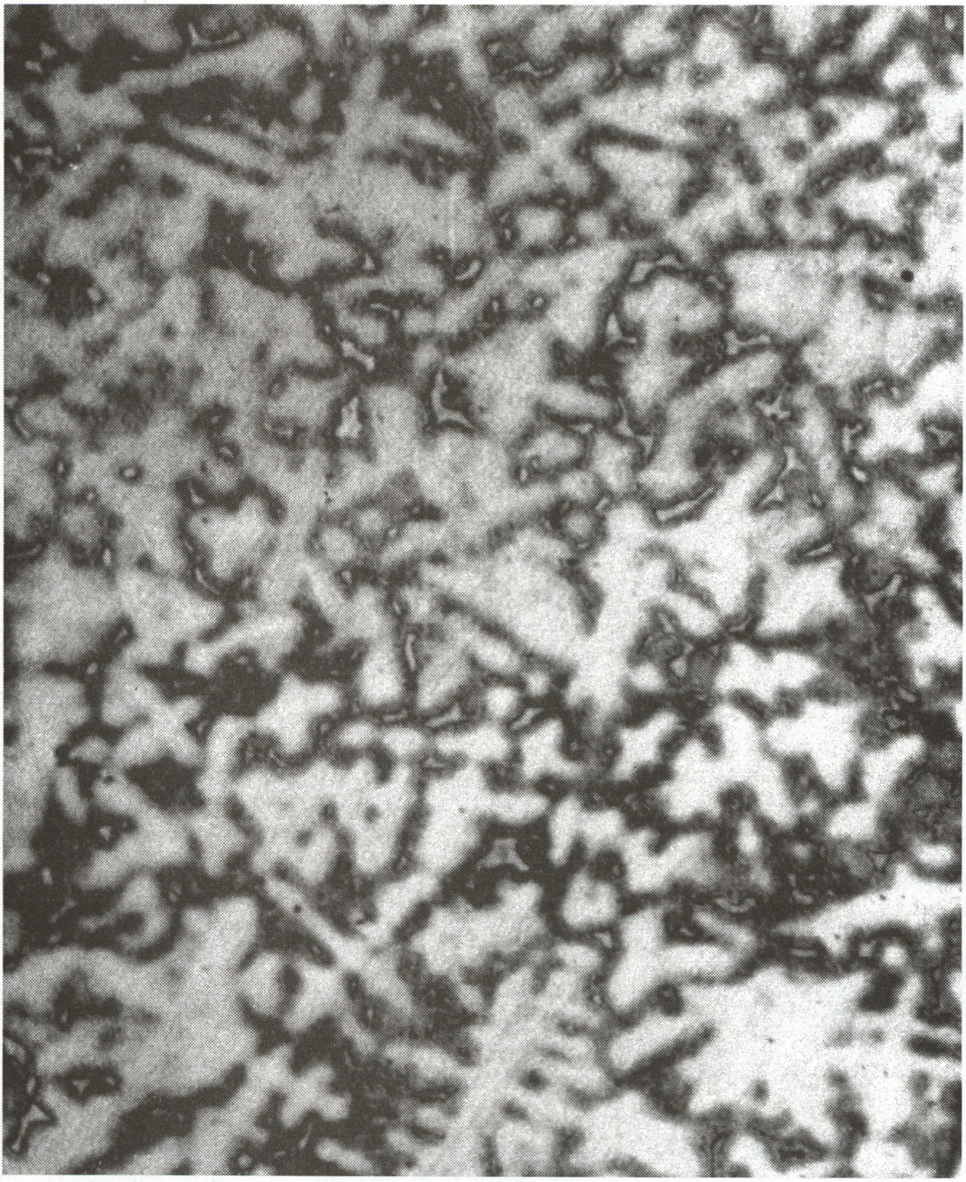


Figure 1. Overview of investment cast microstructure (50X)

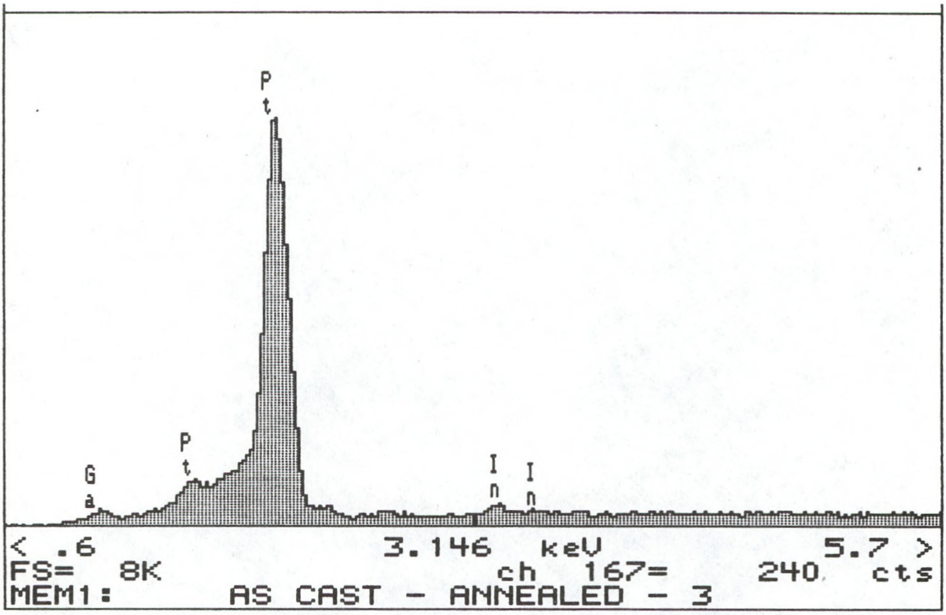


Figure 2: SEM EDAX scan of beta phase

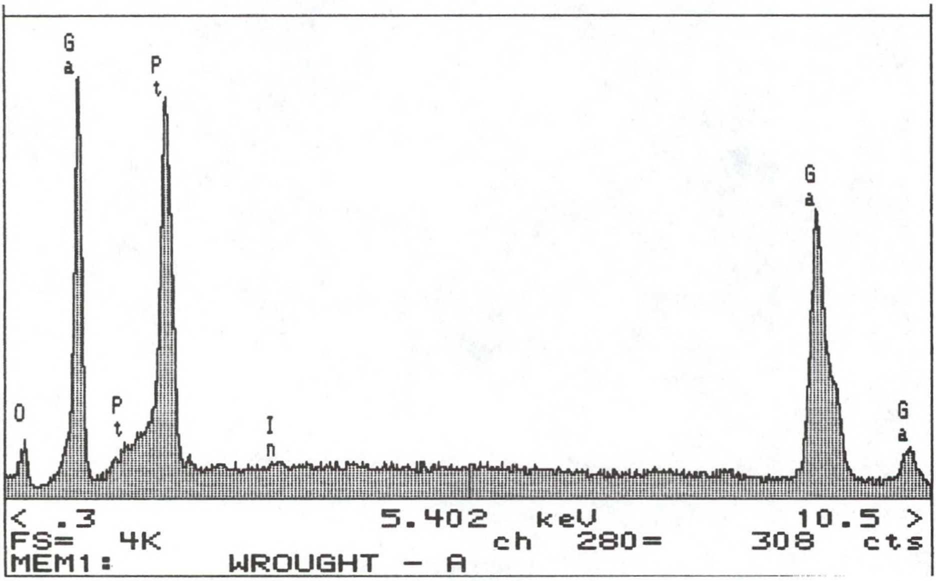


Figure 3: SEM EDAX scan of wrought beta phase

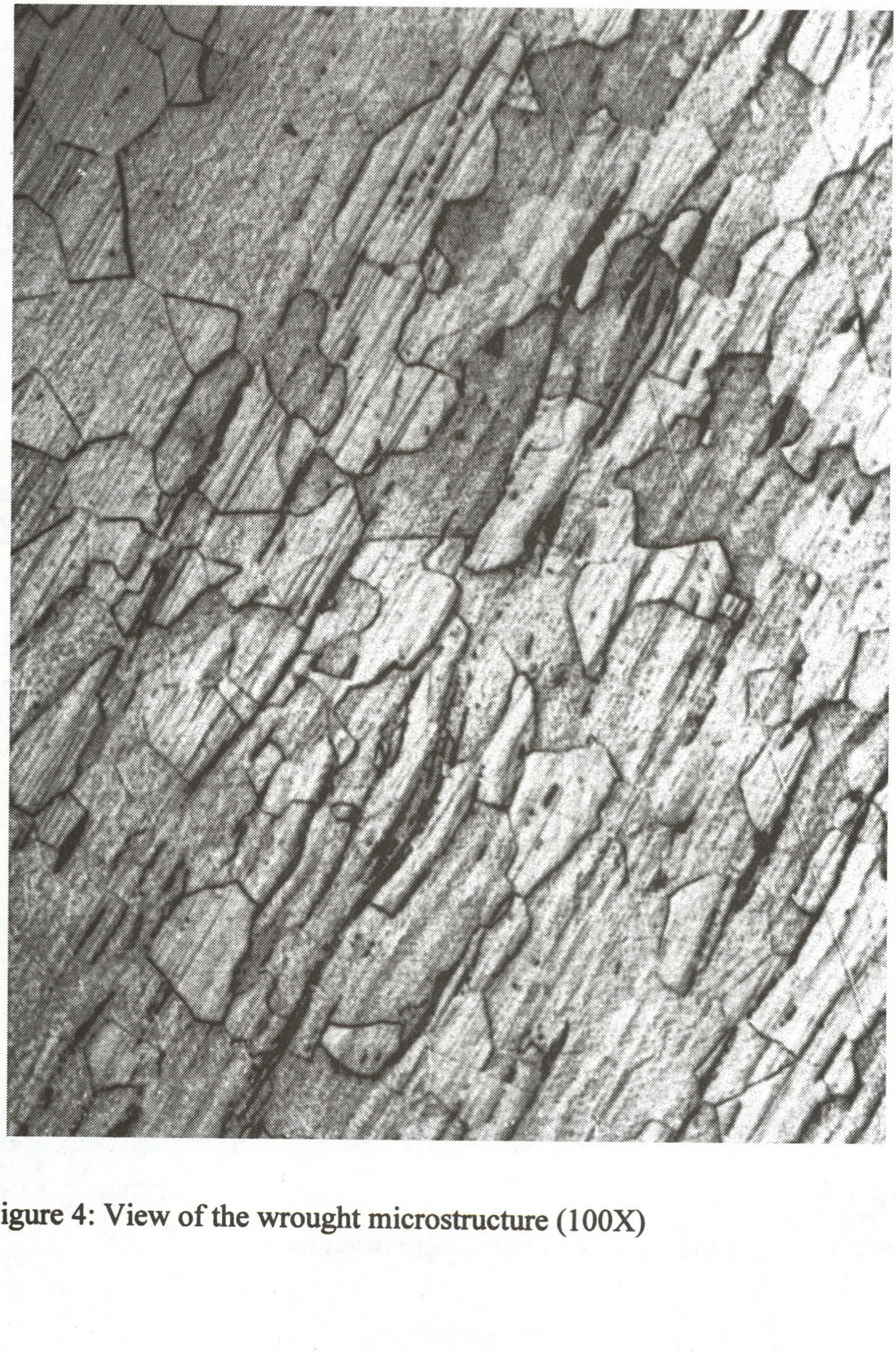


Figure 4: View of the wrought microstructure (100X)

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.

Over Aged: the structure of coarse second phase aggregates that occurs when thermal processing during aging is continued over an extended period of time. A measure of ductility is restored while hardness decreases towards the solution treated 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.

MELTING TEMPERATURES & COLOUR
Alloy: 95.2% Pt - 4.8% (Ga, In,Cu)
Liquidus: 1650 C (3002 F) Solidus: 1550 C (2822 F)
CIELAB colour coordinates: 83.1 L* - 0.1 a* - 4.6 b*

Alloy: 95.2% Pt - 4.8% Ru
Liquidus: 1795 (3263 F) Solidus: 1780C (3236 F)
CIELAB colour co-ordinates: 84.2 L* - 0.0 a* - 4.1 b*

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

Colour characteristics indicate a quality platinum shade. The lightness value (L*) matches well. The overall colour difference vector value (DE) is 1.21 indicating a very close match in colour between the standard and heat treatable materials. The human eye can barely discern colour 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 colour. 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.

Alloy/ Treatment	Hardness (HV)	Tensile Strength (psi)	Yield Strength (psi)
95.2% Pt- 4.8% HTA *Annealed = solution treated @1100C*	175-185	115,000	83,000
95.2% Pt- 4.8% Ru Fully Annealed @1100C	120-130	70,000	50,000
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 @ 700C* *After sol'n treat*	340-360	145,000	117,000
95.2% Pt- 4.8% HTA *Aged @700C* *After 50% CW*	420-430	183,000	174,000
95.2% Pt- 4.8% Ru *Cold worked 75%*	250-260	116,000	115,000

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.

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 either cold working, or heat treating, 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 (174,000psi @ 425HV). The same size section of heat treatable platinum will absorb 70% more load and still deform elastically compared to 95%Pt-5%Ru material.

MANUFACTURING ISSUES:

Cold Working:
Platinum heat treatable alloys work harden faster than their conventional counterparts. 95%Pt-5%Ru can withstand 90% reduction in thickness during cold rolling, while 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 favour 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 (1000-1100C) and provide 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 metal temperature into the bright orange to bright yellow colour 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 colour (700C) with a torch or furnace and simply allowed to cool in air until no colour 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. Conventional hydrogen-nitrogen mixed atmospheres, fixturing with belt speeds adjusted to allow components to soak at 700C for 20-30 minutes summarizes acceptable practice. The traditional cooling experienced while travelling 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 1100C followed by a rapid water quench to restore softness for additional work. This provides a basis for design modifications after the completion of assembly or heat treatment.

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 (1550-1650C) compared to conventional materials, the sluggish flow must be overcome using more superheat (200C) than is usually required. This requires high temperature fused quartz crucibles and induction or oxy-hydrogen heat sources 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:

Detailed studies indicate that heat treatable platinum exhibits substantially different behavior than ruthenium alloyed platinum. Equivalent speeds and feeds during lathe cutting or drilling produced large continuous swarf more indicative of machining gold than the small broken chips of platinum. Examination of drill chips and lathe turnings on the SEM revealed the results depicted in figures 5 through 14. Comparison of the machined surface, depicted in figures 5 & 6, showed a distinct difference in appearance. The heat treatable material appeared to smear during cutting without chatter. The heat treatable platinum lathe chip had a noticeably different slip plate buildup density. The material sheared during machining is much more densely packed with the ruthenium based material. Compare figures 7 & 8.

A series of drilling tests were conducted to compare and quantify tool life for each material. Both drill press hand feed and CNC vertical milling machine tests were executed on 1” wide by 0.080” thick sheet without lubrication until the tool broke in two. The conditions were not chosen to optimize tool life. Breakage failure was considered a simple indicator of performance that was not open to interpretation. The number of successfully completed holes prior to failure was recorded.

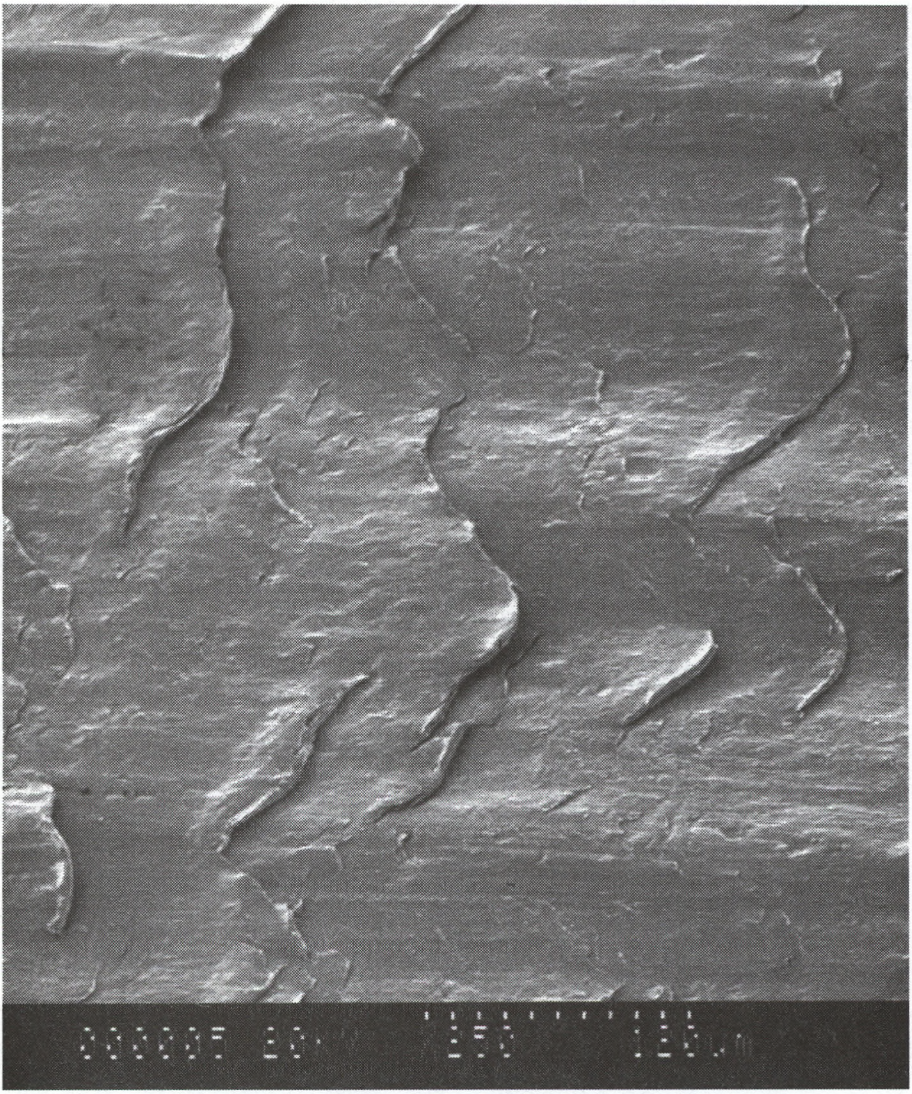


Figure 5: SEM surface profile of machined 95% Pt – 5% HTA

Figure 6: SEM surface profile of machined 95% Pt – 5% Ru

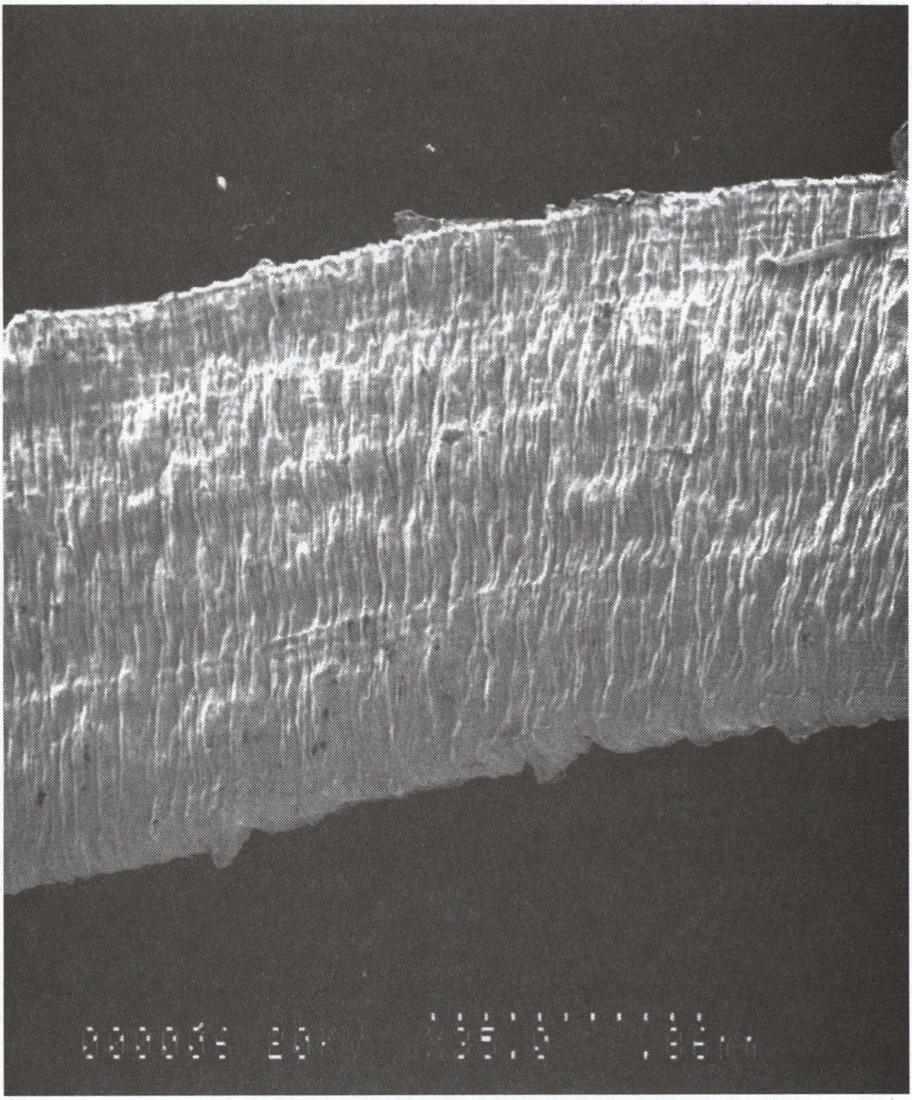


Figure 7: Lathe Swarf surface of machined 95%Pt-5%HTA

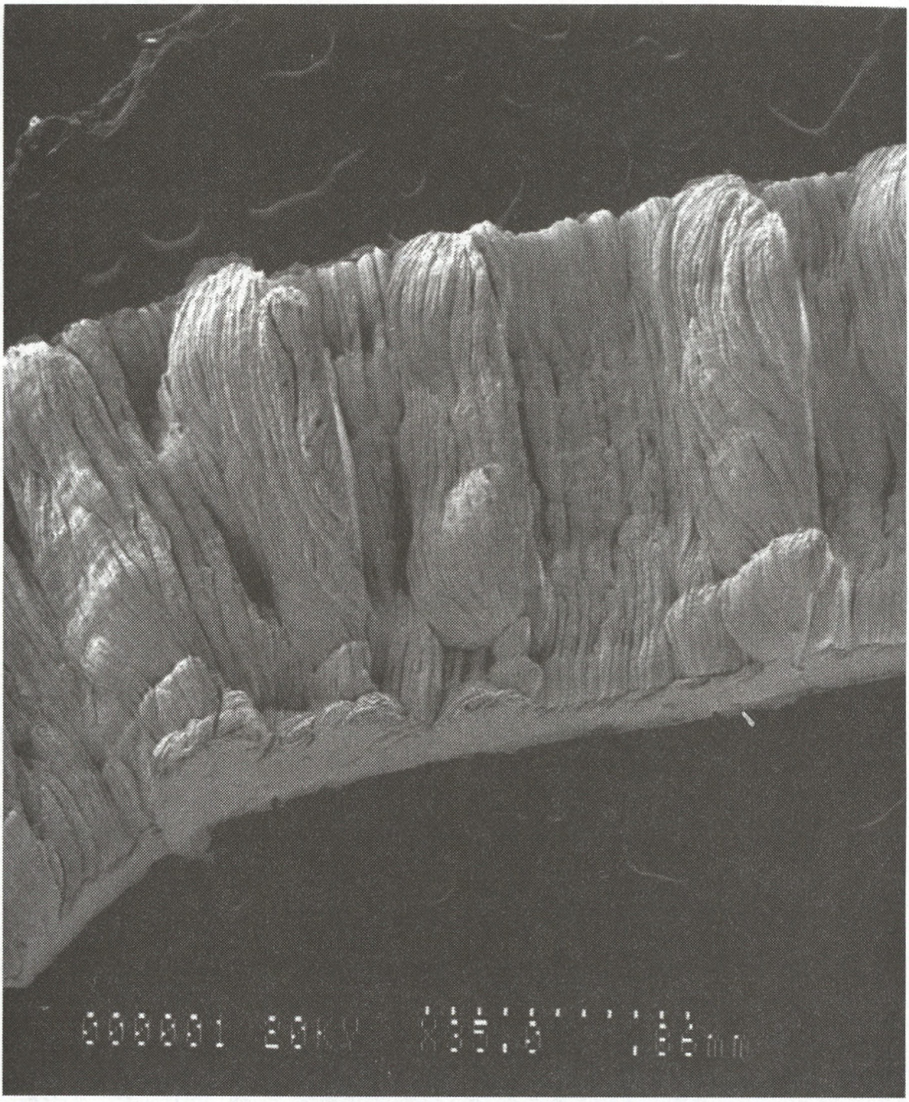


Figure 8: Lathe Swarf surface of machined 95%Pt-5%Ru

Test #1:

Material	Drill Size	Tool RPM	Feed Rate	Hardness
95PtRu	0.0625”	~430	~1.0-1.5”/m	HV130
# Holes Until Failure:		Note: Average:18	Note: Hand Feed	Dead Soft
2	2	22	5	60

Test #2:

Material	Drill Size	Tool RPM	Feed Rate	Hardness
95Pt HTA	0.0625”	~430	~1.0-1.5”/m	HV230
# Holes Until Failure:		Note: Ave: 165	Note: Hand Feed	Free Machining
297	76	65	221	>100

Test # 3:

Material	Drill Size	Tool RPM	Feed Rate	Hardness
95Pt5Ru	0.0625”	1000	1.5”/m	HV130
# Holes Until Failure:		Note: Ave: 10	Note: CNC	Dead Soft
15	5	5	5	19

Test #4:

Material	Drill Size	Tool RPM	Feed Rate	Hardness
95Pt-HTA	0.0625”	1000	1.5”/min	HV230
#Holes Until Failure			Note: CNC	Free Machining
>707				

The results of hand drilling tests (1 vs. 2) showed that the free machining over-aged microstructure contributed to a substantially better average tool life prior to failure. CNC tests to replicate the results under more controlled conditions of feed and alignment provided surprising results when a single drill lasted through 707 holes without breaking in free machining platinum compared to 5 drills that produced 49 holes in

Figure 9: SEM image of 95%Pt HTA first dilled hole

Figure10: SEM image of 95%Pt-5%HTA last drilled hole

conventional platinum (test 3vs.4). Figures 9&10 show the drilled surface of the heat treatable platinum. The same smeared appearance was found on the first through last cuts. Also noteworthy, the chips of heat treatable platinum measured 0.004" thick compared to 0.012" for 95%Pt-5%Ru. Figures 11 & 12 show the same distinctly different appearance found during lathe turning trials. The machined 95%Pt-5%Ru surface started out with a clean cut (figure 13), but degenerated to the point that small fragments were bonded back onto the surface (figure 14) by the end of the trial.

Hardness mapping of lathe machined face and chip cross sections revealed a hardness increase of 15-20% from a nominal 230 HV to 270 HV 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%).

Results from this series of experiments 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. This is a significant advantage that should lead to reduced tool wear and improved productivity in machining operations when heat treatable platinum is used.

APPLICATIONS:

Investment Casting:

It is possible to investment cast a broad range of jewelry articles with heat treatable platinum. Figure 15 illustrates this range from large mens 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.

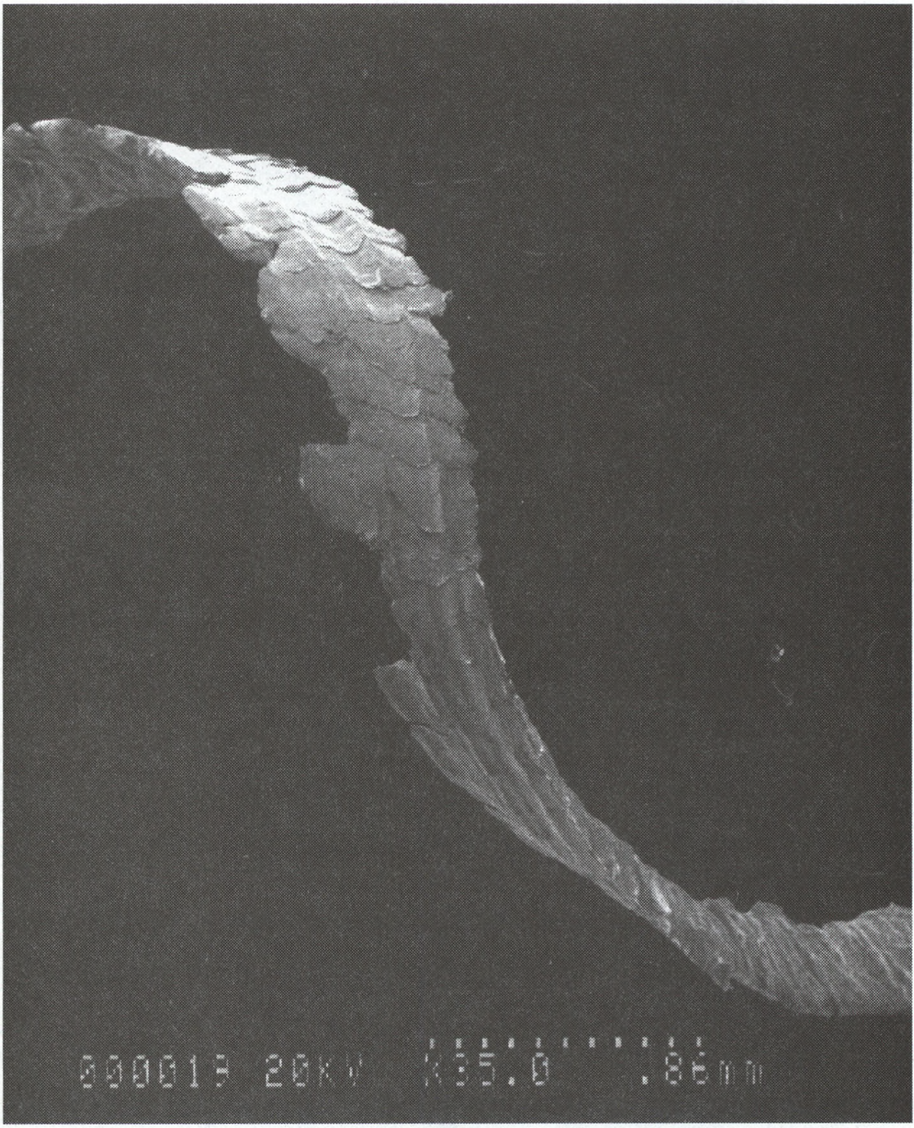


Figure 11: SEM image of 95%Pt-5% HTA drill chip

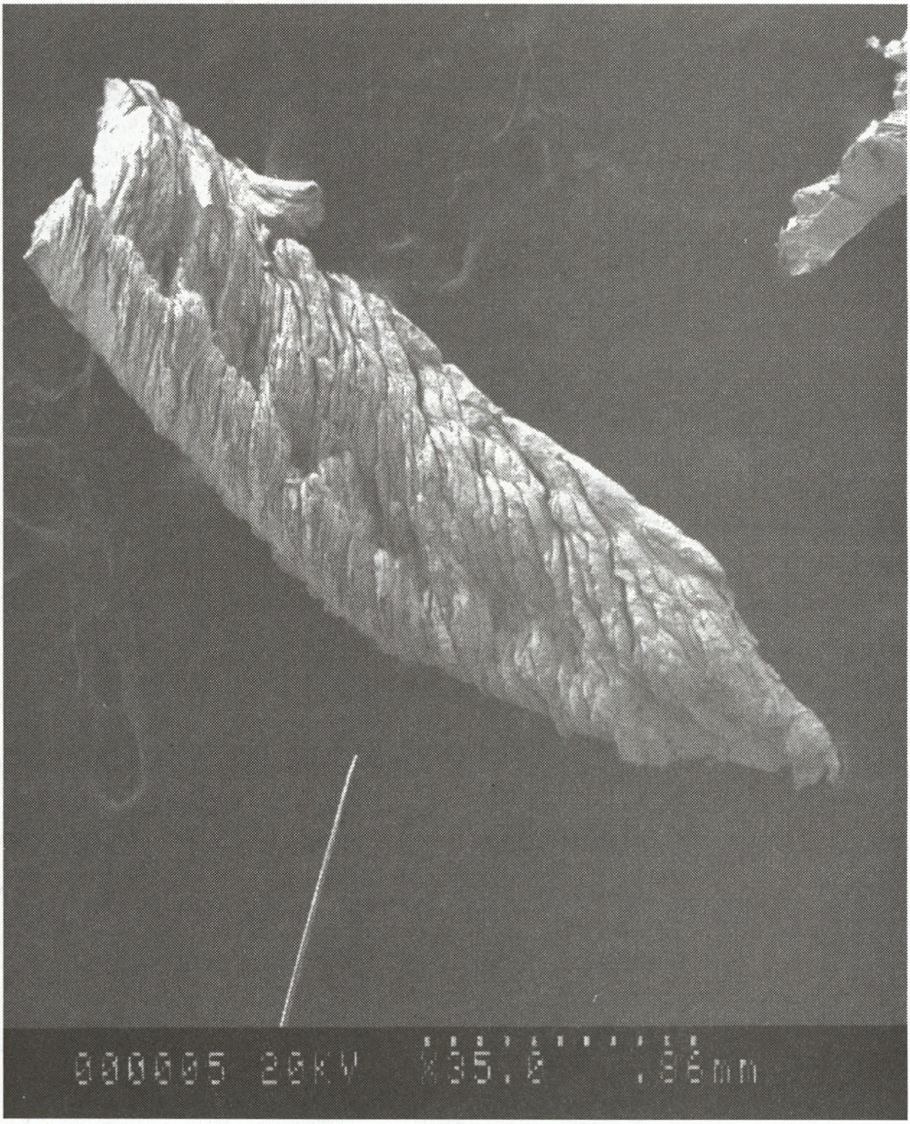


Figure 12: 95%Pt-5%Ru drill chip; note rough surface

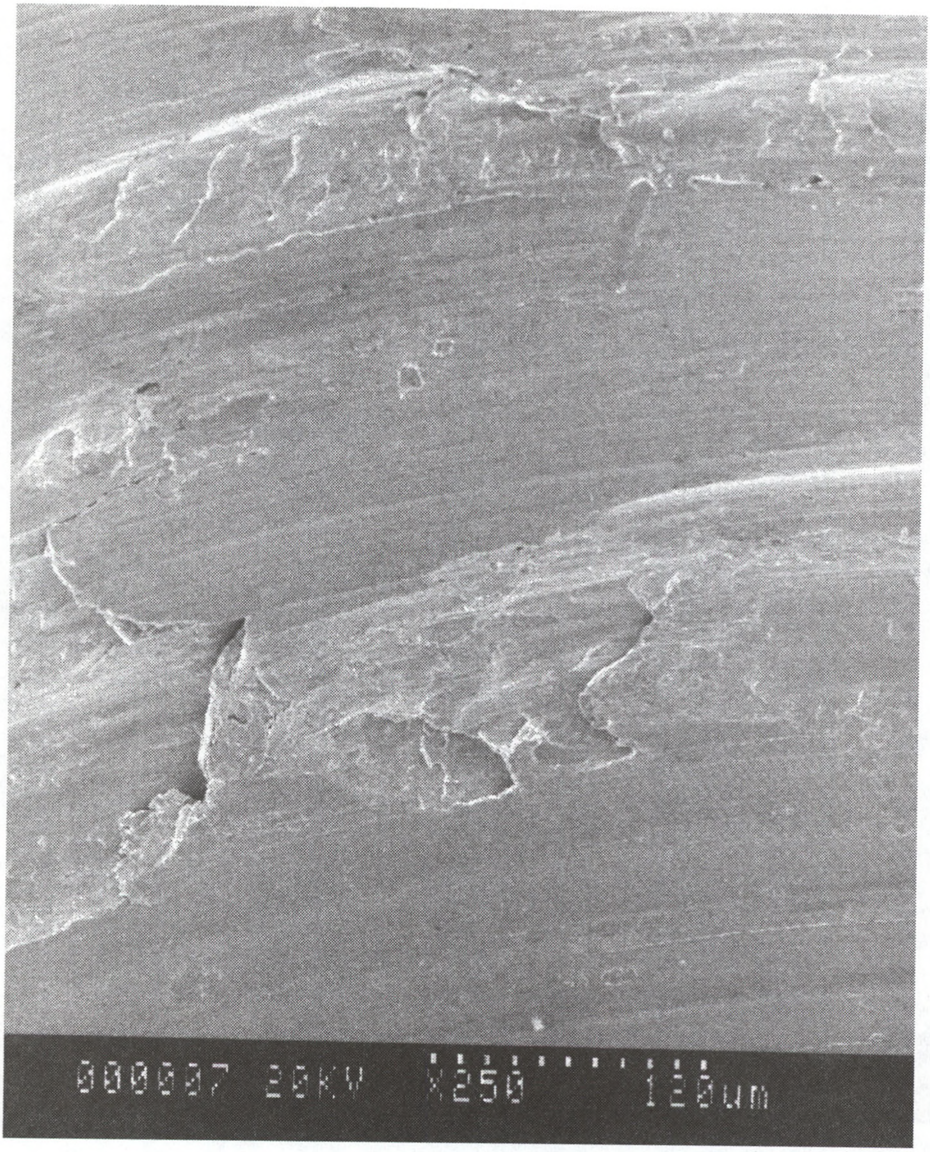


Figure 13: 95%Pt-5%Ru drilled surface first hole

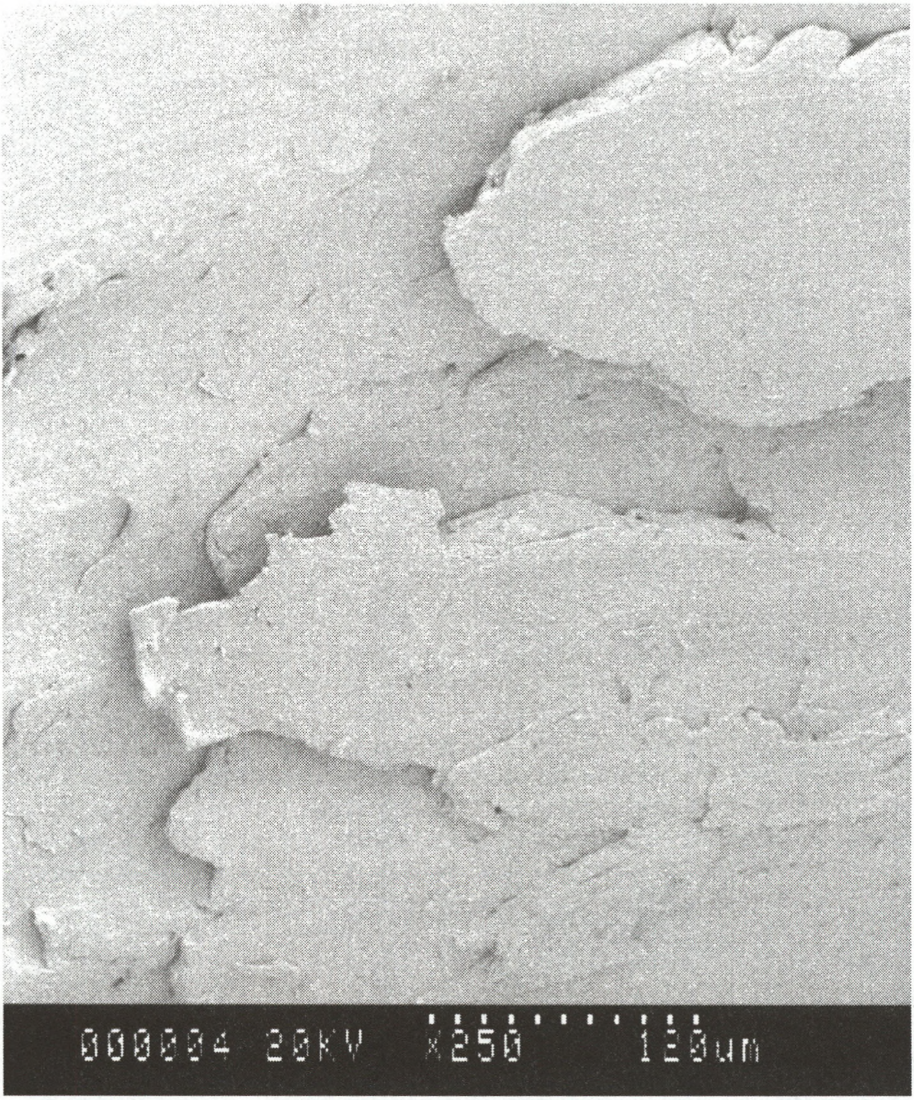


Figure 14: 95%Pt-5%Ru surface of last hole drilled prior to failure

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 earnut clasps. Figure 16 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, the same size regular gold earnut could lift 110g, heat treatable gold 150g and heat treatable 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.

Seamless Bands:

Figure 17 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 key to material performance is the correct heat treatment. Manipulating the size and distribution of the second phase to create the so called 'free machining' structure enhances machinability substantially. The microstructure composed of an alpha matrix with finely dispersed beta phase is essentially over-aged. The material exhibits ductile bulk properties for plastic deformation such as ring sizing. The free-machining structure can be converted back to a single phase solid solution that can be hardened in the final product form after finishing operations. This ensures optimum properties during machining operations followed by heat treatment to maximize consumer wear performance (340HV). Conventional platinum alloys cannot be manipulated in this fashion.

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 130C. This is sufficiently large for a skilled jeweller to affect a metallurgical bond. Laboratory tests hand

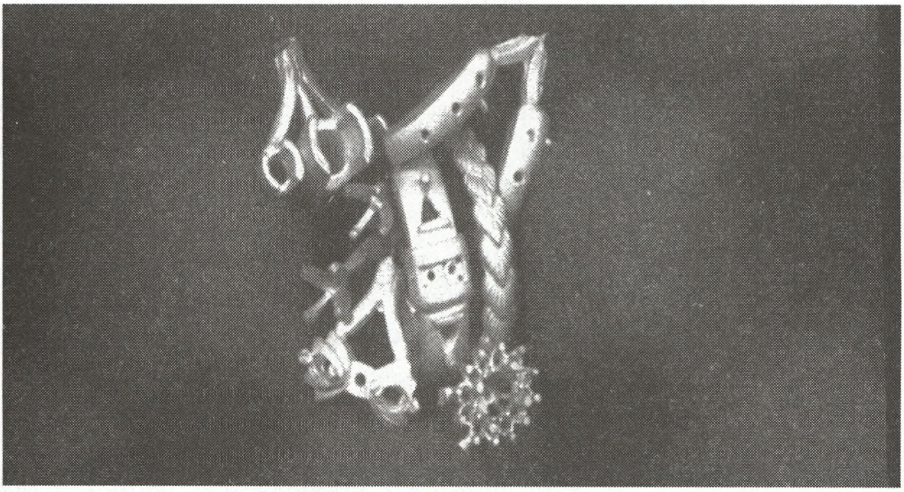


Figure 15: Overview of assorted investment cast pieces

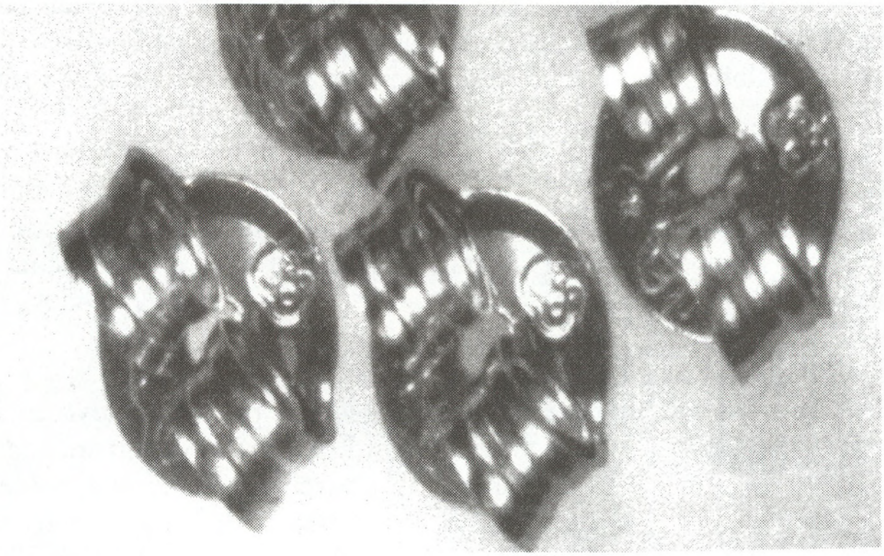


Figure 16: Overview of earnuts

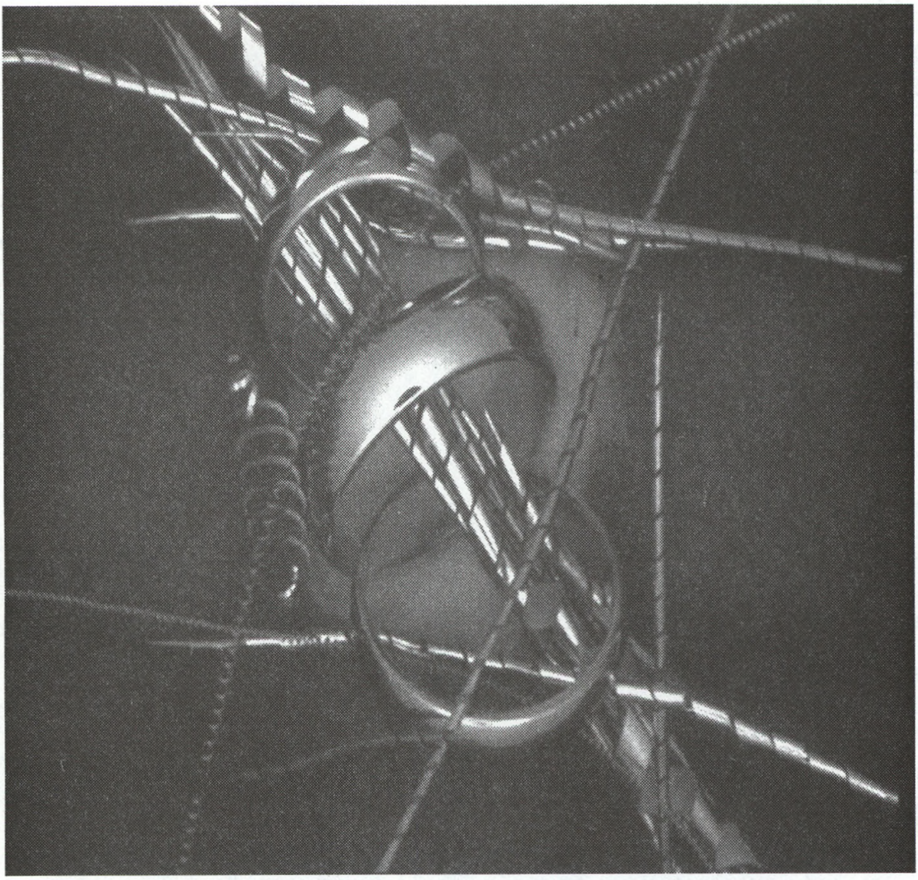


Figure 17: Overview of various wrought seamless bands

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 jewellery 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 700C followed by slow air cooling. Yield strength also increases substantially.
- 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 about 90% and yield strength about 40% 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 is substantially better with the free machining microstructure compared to conventional materials. Tool life can be enhanced from inherently lower strain rates during machining. Optimizing conditions of heat treatment microstructure and machine operation require continued study.
- Heat treatment provides a basis for controlling alloy physical properties for optimizing performance during manufacturing and jewellery service. A ductile structure required during forming can be hardened for wear. A free machining structure which is optimum for machining can be hardened for better consumer performance.

- 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.
- The reduced melting range of heat treatable platinum provides a basis for application as a brazing material. Unqualified hallmarking with 95% platinum content can be accomplished with high strength joints.
- Continued study of the microstructure, phase relationships and heat treatment parameters may improve the production methods for these difficult to handle alloys.

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