

Platinum Alloy Characteristics: A Comparison of Existing Platinum Casting Alloys with Pt-Cu-Co

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The growing interest in and demand for platinum jewelry can be viewed as a renaissance of the 1920's for the metal in the United States. The jewelry industry uses four main classes of platinum alloys. These classes are:

- Pt 1000
- Pt950-Ru, Cu, Co, W, Ir
- Pt-900-Pd, Cu, Ru, Ir
- Pt850-Pd, Cu, Ru, Ir

This paper will focus on the Pt 950 class of alloys - alloys with a minimum of 95% weight platinum. This class is used due to the fact that pure platinum is soft and does not have the mechanical strength for most jewelry applications. The mechanical strength of platinum is increased by alloying a second element with the platinum. Different alloying elements have varying degrees of effect on the mechanical and chemical properties of platinum. The amount of various alloying additions in weight percent are plotted versus the annealed hardness of the resulting alloys in fig. 1. Palladium and rhodium have the least effect, while iridium, copper and gold have a stronger effect. Ruthenium and nickel have the

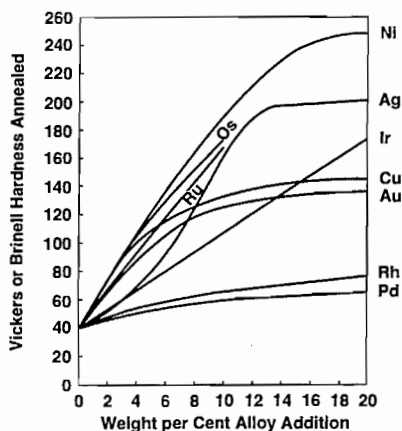


Figure 1: The graph shows the effect of increasing additions of selected alloying elements on the hardness of Platinum alloys.

greatest effect in increasing the hardness of the resulting platinum alloys. The alloying of the elements with platinum is usually achieved in the liquid phase because the diffusion is 100 times greater in liquids than in solids. Once a homogeneous mixture of the platinum alloy is achieved in the liquid state, there are three

main type of mixtures that can result as the alloy is cooled to the solid state:

- Complete solubility - the atoms of metal a and metal b form a random mixture that cannot separate (like water and wine).
- Partial solubility - the metal a can absorb only a limited quantity of the atoms of metal b and, likewise, b absorbs only a limited quantity of a. These maximum quantities are called the limit of solubility (like sugar and water).
- Total insolubility - the two metals cannot be mixed. Even if they are miscible in the liquid state at a very high temperature, the atoms of each metal separate when the temperature decreases and they reach the solid state. The microstructure is a juxtaposition of pure a particles and pure b particles (like an emulsion of oil and water).

Therefore, it is important to know the behavior of the mixture

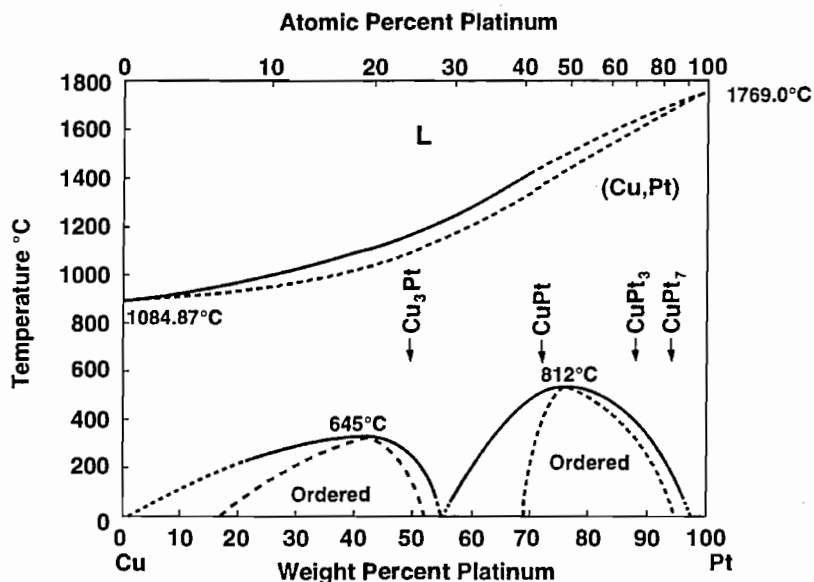


Figure 2: The Platinum-Copper binary phase diagram.

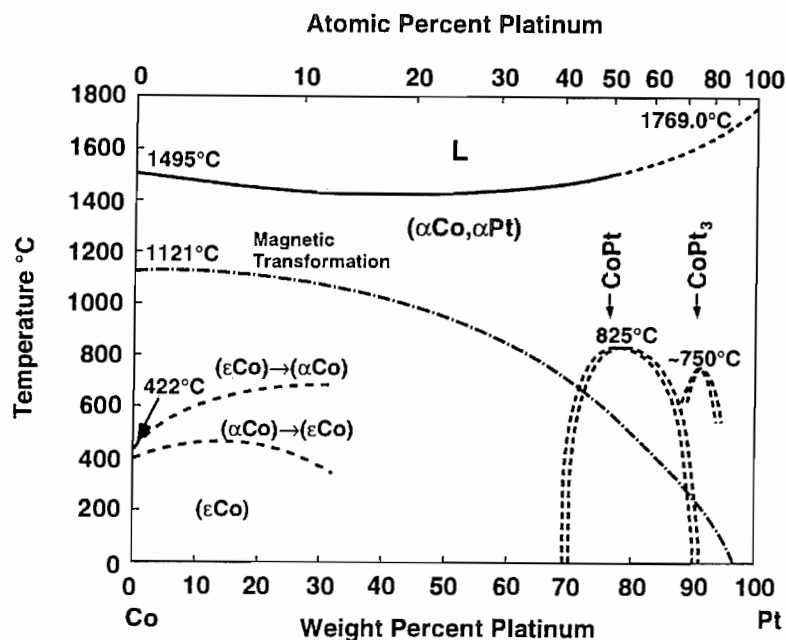


Figure 3: The Platinum-Cobalt binary phase diagram.

of the alloying elements with platinum. Maps of the types of mixtures that occur are called binary phase diagrams (when just two elements are alloyed). The phase diagrams of two of the elements that are alloyed with platinum are displayed in figs. 2 and 3. fig. 2 illustrates Pt-Cu and fig. 3 illustrates Pt-Co. These two elements are highlighted at this time because they will be important later.

The phase diagrams of figs. 2 and 3 show that copper and cobalt both have complete solubility in platinum. A single, homogeneous alloy of the type platinum formed with either of these elements has more predictable and consistent properties than those that are multi-phase. These alloys can be easily rolled or fabricated to form the desired final shape and size. The Pt-Cu and Pt-Co phase diagrams also suggest that changes occur in the solid state in

these two-alloy systems. The solid state reactions are referred to as age hardening or ordering reactions. An understanding of these reactions and the temperatures at which they occur can aid the jeweler in producing a superior finished product. Annealing of the alloy should be done at a temperature above where the ordered phase is stable. Alloys should also be cooled rapidly through this temperature range. However, the final product can be made harder by heating within the temperature region where the ordering takes place.

There is another piece of information that can be gleaned from examination of the Pt-Co phase diagram that is of interest to the jeweler. The magnetic transformation, or Curie temperature, are shown on the diagram. There are four ferromagnetic elements that are common: iron, cobalt, nickel and gadolinium.

Alloying with these elements can result in a magnetic material at least over part of the alloy range. The magnetic transformation curve indicates the range extends to approximately 3.5% Co.

Therefore, the phase diagram predicts the magnetic properties of the Pt950 Co alloy. When choosing an element for alloying with platinum, many properties must be taken into account. The reactivity of the element is very important. If the element is oxidizable, it can be a source of defects in the final product, not only during the melting but also during the casting or brazing of the final piece. Factors that must be kept in mind in choosing an alloying element are the recycling of the alloy, whether the scrap can be reused and the effect of contaminants, the availability of investments and crucibles that will not react with the components, and so on. One very important property for jewelry is its castability, which is the key to good quality for lost-wax pieces. The elements used to improve the castability of karat gold (cadmium and zinc) have boiling points far too low: 767° C (1412° F) and 907° C (1667° F), compared with the casting temperature. They will evaporate and will not be effective.

Each system must be tested and its flowability and castability measured. As a rule, it is not usually possible to find an alloy that can meet every requirement: color, hardness, castability, weldability, ductility, small grain size. The jeweler also wants to use the same alloy for cast and fabricated pieces to be sure they have the same color. When the properties of an alloy have been determined, the jeweler has to decide on the

best compromise to satisfy the design and the functionality of the final piece. For instance, a ring or bracelet must be more wear-resistant, hence, have a greater hardness than a pendant or a necklace. One must also be aware of other steps in making the jewelry. If the joining of a platinum and gold piece is required, it is important to make sure that the brazing alloy does not contain elements which will embrittle the platinum. Cadmium, indium, tin and zinc are elements used in brazing alloys for gold which will embrittle platinum.

Gold and platinum pieces that are to be joined should be finished separately. The temperatures used for annealing platinum are too high for gold and polishing platinum is more difficult than polishing gold. Gold must be polished first so it does not lose its color. The main problem when joining these two materials is the different coefficient of expansion (see table 1). The difference in thermal expansion can result in cracking from the stresses generated. However, the cracking can be prevented by using the proper stress-relieve anneal. Carbon and silicon are two other contaminants to be avoided. However, silicon is often the basic component of the investment materials. Thus, the reuse of metal from the casting tree must be done with the knowledge that this is a potential source of casting defects which can lead to poor quality castings. There are many other sources of these elements in the workshop, for example, the dust in the air, the reducing flame of the torch (this is why induction melting under argon protection is recommended), the polishing material, and the

Property	Pt	Au	Ag
Density (g/cm ³)	21.5	19.3	10.5
Boiling Point °C °F	3825 6917	2853 5167	2162 3923
Melting Point °C °F	1768 3214	1064 1947	963 1765
Heat of Fusion (J/g)	113.6	63.7	104.8
Young Modulus (GPa)	171	78.5	82
Thermal Conductivity (W/m.K)	75	318	435
Coefficient of Thermal Expansion (10 ⁻⁶ K ⁻¹)	9.1	14.1	19.1

Table 1: Precious Metal Data

solder blocks. Each step of the process must be carefully examined and analyzed to avoid contamination. Alloy usage is different all over the world depending on the local customs and the hallmark rules. In Japan, alloys are acceptable with 85% platinum. In Europe, only 95% platinum (or greater) alloys are allowed. The first platinum alloys were made with the precious elements iridium and palladium, because of their oxidation resistance. But the iridium alloys have a high melting point and Pd, as has been indicated, has a small effect on the hardness. So non-precious

metals were tested. The properties of the most common precious and non-precious alloys are summarized in table 2. The recommended use of the alloys and a ranking of how they perform is presented in table 3. The traditional alloy in Europe is 950Pt-50Cu. (The actual content of the platinum alloy is a little higher because no platinum brazing alloys are available and the total platinum content must be kept above 95% in weight. The excess platinum compensates for the brazing alloy in those cases where brazing is required.) This alloy (Pt-Cu) has poor casting qualities and an

	Melting Range (°C)	Extension (%)	Hardness (HV) When Annealed	Density	Applications in Jewellery Making
Fine Pt	1,768	37	40	21.45	Base Metal for Alloys
Pt 955 Co	1,750-1,765	20	135	20.8	Casting Ingots, Lost Wax Process
Pt 955 Cu Chains,	1,725-1,745	29	60	20.6	Medium Properties, Chains, Watch Cases
Pt 955 Pd	1,755-1,765	22	60	20.6	Chains, Mechanical Applications (Mountings, Frames)
Pt Rh 5%	1,810-1,820	35	75	20.65	Forming
Pt Ru 5%	1,780-1,795	32	130	20.7	Machine-Tooled/ Beaten Rings
Pt Ir 5%	1,780-1,790	30	80	21.45	Pieces for Welding Machine-Tooling Possible
Pt W 5%	1,830-1,845	20	140	21.3	Mechanical Parts

Table 2: Platinum Alloys

	Welding	Pressing	Die Stamping	Lost Wax Casting	Beating	Brazing	Setting	Chains	Findings	Hinges
Pt-Co	●	●	●	●●●	●	●	●	●	●	●
Pt-Cu	●●●	●●●	●●●	●●	●●	●●●	●●	●●●	●	●●●
Pt-Pd	●●	●●●	●●●	●	●●	●●●	●●●	●●	●●	●●●
Pt-Rh	●●	●●	●●	●	●●	●●	●●	●●	●●	●●
Pt-Ru	●●	●●	●●	●	●●	●	●	●●	●●	●
Pt Ir	●●●	●●	●●	●●	●	●●●	●	●●●	●●	●●●
Pt-W	●●●	●●	●●●	●	●	●●●	●	●●	●●●	●●●

●●● Recommended
 ●● Satisfactory
 ● Difficult

Table 3: The main applications of Platinum Alloys in Jewelry

Alloy	Hardness	Grain Size
Pt-Cu-Co	119	1 to 4
Pt-Cu	106	1 to 4 (Area >1)
Pt-Ru	130	3 to 6 (Area from -1 to 3)
Pt-Co	135	-1 to 2

Table 4: Hardness (Hv5) and Grain size measured on rings cast by lost wax technique

Alloy	Vickers Hardness	Tensile Strength (MPa)	Yield Strength (MPa)	Elongation (%)
Pt-Cu-Co	110	369	182	23
Pt-Cu	127	398	227	20
Pt-Ru	127	456	246	25
Pt-Co	126	441	243	26

Table 5: Mechanical Properties measured on tensile sample. (Lost wax technique)

undesirable color. To overcome these deficiencies, a Pt-Co alloy was developed. However, as was seen in examining the phase diagram, this alloy is weakly magnetic. So, when sorting minute pieces of scrap by magnetic separation, a large amount of the

platinum alloy may be lost.

The remainder of this paper will focus on a new alloy that has been developed in order to retain the good properties of both the Pt-Cu and Pt-Co systems and yet overcome their deficiencies. The new alloy is a 950Pt-Cu-Co alloy

that is non-magnetic. First, laboratory data will be presented and then the results of a jeweler's evaluation done at Tiffany will be presented by Costantino Volpe.

Experimental Procedure

A comparison is made between four 950Pt alloys: Pt-Cu, Pt-Co, Pt-Ru and Pt-Cu-Co. Rings and tensile samples were cast to compare the as-cast mechanical properties and the microstructures. The casting was done using a Plativast investment from Ransom. The burnout was done at 1000° C. The cooling rate was different for the rings and the tensile samples due to the variation in geometry. The casting temperature was not measured. The grain determination and microstructured evaluation was done on the rings. The CIELAB colors were measured on a diamond-polished specimen using a Minolta spectrophotometer. This device gives more reliable data than a simple colorimeter on a shiny surface.

Results

The as-cast hardness and grain size measured on the rings is summarized in table 4. In this test, the Pt-Cu-Co alloy had a hardness intermediate between Pt-Cu and the harder alloys, Pt-Ru and Pt-Co. The Pt-Ru ring had the finest grain size, with the other three alloys being similar. The microstructure will be discussed in more detail later. The mechanical properties for the four alloys measured using as-cast tensile specimens are presented in table 5. The Pt-Cu-Co alloy has the lowest hardness, tensile strength and yield strength of the four alloys in this series of tests.

State	Vickers Hardness	Tensile Strength (MPa)	Yield Strength (MPa)	Elongation (%)
Annealing Treatment (1000°C-30 mn Cold-Water Quench)	121	441	287	32
50% Cold Rolled	210	558	469	12
100% Cold Rolled	221	652	615	8
400% Cold Rolled	239	774	747	8

Table 6: Mechanical characteristics of Pt-Co-Cu

Additional hardness, tensile strength, yield strength and elongation data are reported in table 6 for the Pt-Cu-Co alloy. This material was cast, cold rolled, annealed and cold worked. Hardness and tensile tests were done on the resulting material. The

hardness of the annealed material is similar to the ring material. The tensile properties and elongation are significantly higher than the as-cast tensile bars. The conclusion is that the Pt-Cu-Co alloy has sufficient strength and ductility for most jewelry applications,

whether cast or fabricated.

The microstructures of the four alloys cast as rings are shown in figs. 4 through 7. The Pt-Ru has a fine grain structure but a large quantity of intergranular porosity. The Pt-Co is nearly porosity free but the grain size is very heterogeneous (the lower magnification was used to show this phenomenon). The grain size of the Pt-Cu is larger than the Pt-Ru and has only a small amount of intergranular porosity. The new Pt-Cu-Co alloy is quite porosity free and has a more homogeneous microstructure than the Pt-Co alloy. Therefore, the microstructure of the new alloy appears to be more sound, based on labo-

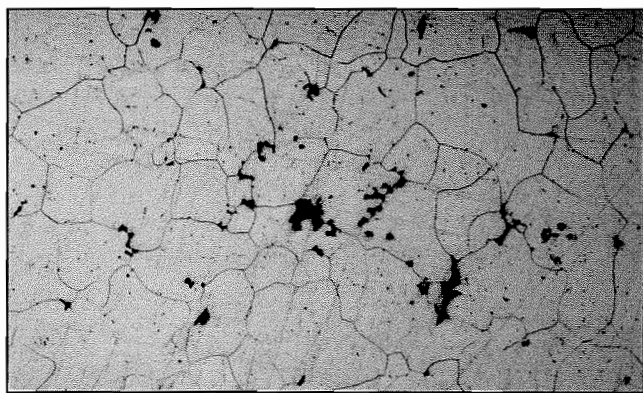


Figure 4: A Photomicrograph of the as-cast microstructure of a ring cast from 950 Pt-Ru. Magnification 80X

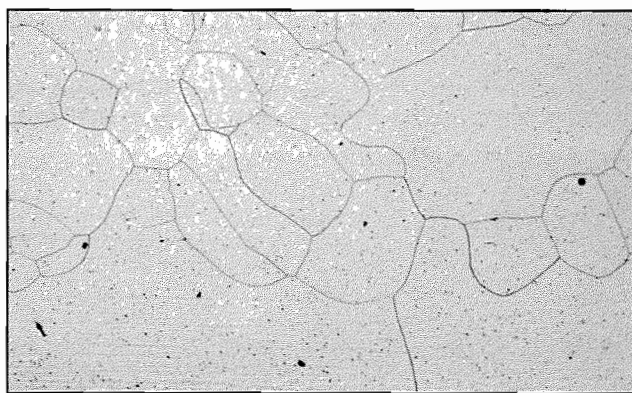


Figure 5: The Photomicrograph of the as-cast microstructure of a ring cast from 950 Pt-Co. Magnification is 50X

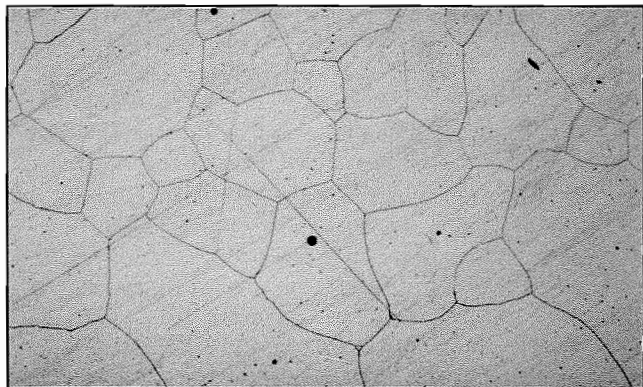


Figure 6: The Photomicrograph of the as-cast microstructure of a ring cast from 950 Pt-Cu. Magnification is 80X

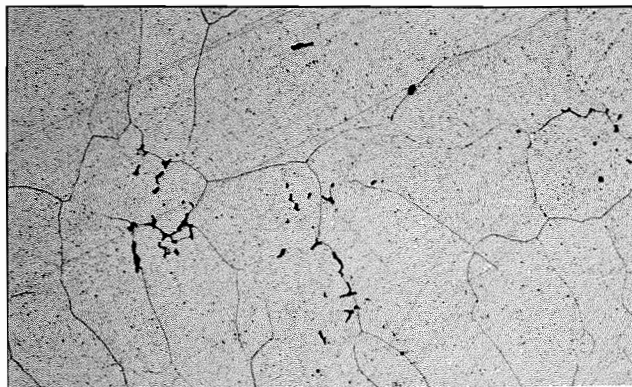


Figure 7: The Photomicrograph of the as-cast structure of a ring cast from 950 Pt-Cu-Co. Magnification is 80X

Alloy	L*	a*	b*
950 Pt-Co-Cu	87.28	0.55	4.26
950 Pt-Cu	87.89	0.49	3.83
950 Pt-Ru	87.25	0.50	4.01
950 Pt-Co	86.64	0.52	4.45

Table 7: CIELAB colors. (Spectrocolorimetry measurements)

ratory tests, than Pt-Ru. The quality is nearly the same as Pt-Co but the new alloy is not magnetic, simplifying scrap recovery.

The color measurements (see table 7) show that the four alloys have nearly the same color, the Pt-Cu being slightly whiter (L*) and the Pt-Co a little darker. The red component (a*) is close to the same and the yellow (b*) component is higher for the Pt-Co alloy. The naked eye would have a difficult time differentiating the color of these four alloys. The initial data generated in the laboratory indicates the new alloy has promising properties. Costantino Volpe's report on additional casting and jewelry trials that were done at Tiffany to further evaluate the Pt-Cu-Co alloy versus Pt-Ru, follows.

Comparison of Pt-5Ru and Pt-Co-Cu Platinum Casting Alloys, Part II

In the world of metal and alloy production, platinum is not necessarily a difficult metal to work with. It is fairly soft, yet holds a nice polish. It is one of the few elements that has no oxidation properties, so in fact it is a

pleasant metal to cast in that respect, no cover gas or vacuum is needed. Although it has a high melting point, induction machines today have more than enough power to melt it.

The problems that arise when casting platinum jewelry are the result of restrictions that are inherent to the industry. In other industries when alloys are designed for various usage, there is usually more freedom in terms of the alloying elements added and to what degree. This allows an alloy to be designed that has all the necessary properties, including good manufacturing properties. However, in our industry, we are constrained by the fact that our platinum alloy must be at least 95% platinum. This allows us only 5% to work with in terms of adding other elements to give us desired properties. An example of this is melting range. Looking at phase diagrams we can see that at 95% platinum we cannot reduce the melting point enough to have a significant impact. Pure platinum melts at 3224° F (1773° C). Varying 50 degrees one way or the other doesn't help our cause much. 950 platinum has a very narrow gap between the solidus

and liquidus and this causes very quick freezing. This fact forces us to go to high superheats and casting speeds to get the metal into the mold and achieve good filling. Unfortunately these two acts will contribute to shrinkage porosity. The other constraint that we place on ourselves is that of design. Jewelry is designed to look good, not necessarily for ease of manufacture. Therefore, what property can we change that will make casting these 950 alloys easier?

Pure platinum and platinum-ruthenium alloys tend to have a fairly high surface tension. Metals with high surface tension require more force and time to get into cavities. We can observe this phenomenon very easily in gold casting where the addition of small amounts of zinc produce very good improvements in castability due to the fact that zinc reduces the surface tension of the alloy. A lower surface tension allows the metal to flow against mold cavity walls with less friction, meaning the flow will be quicker and the cavity will fill with less force. The result is we don't have to apply as much superheat or throw it as hard. The tradeoff here is that better wetting of the mold could result in quicker heat loss and without proper mold temperature we can negate the effects of the lower surface tension.

Theoretically, if we can find an element or combination of elements that will reduce the surface tension, then we can increase the castability of the alloy.

Unfortunately, surface tension measurements are very difficult to perform, especially on high-melting metals. One can try to melt a drop of platinum on a flat surface and then look at its

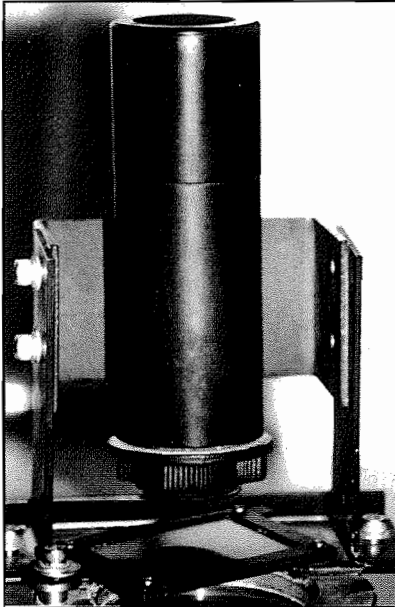


Figure 8: Optical Pyrometer

cross-sectional profile, but even this is difficult and not exact because one actually wants to observe the profile in the liquid state. It is therefore easier to measure it qualitatively. This is what we have done by way of these casting studies. Under identical conditions we can compare how various shapes fill for different alloys. It is important to have as few variables as possible. This means that the pieces have



Figure 9: Casting Machine

to be placed on the button in exactly the same manner, the flasks should be invested with the same batch of investment, burnout should be in the same oven and cast at the same temperature and speed. Casting at the same temperature and speed can only be accomplished using a modern casting machine with a pyrometer. Trying to judge the temperature by eye can be very difficult, especially when using a new alloy,

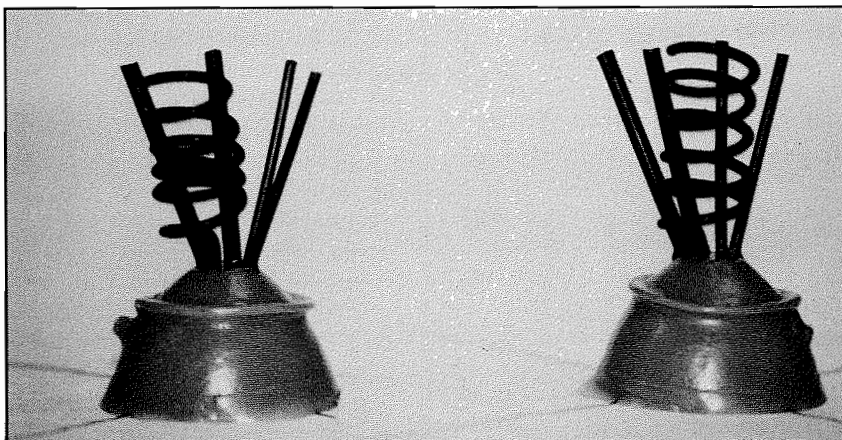


Figure 10: Wax button showing rods and coils.

which may have a different look when molten. The only way to tell with any kind of accuracy is to use an instrument such as an optical pyrometer (fig. 8).

Experimental Procedure

Our casting studies were done in a commercially available centrifugal induction casting machines (fig. 9), incorporating typical production processes for platinum alloys. Side-by-side comparisons were done between two alloys, Pt-Ru and a new alloy, Pt-Co-Cu.

To determine castability, wax grids were prepared. Four sets of two grids were prepared, with each set scheduled to be cast at a different speed. The first set was cast at 100% acceleration, the second at 90% acceleration, the third at 80% and the fourth at 70%. Each set had one casting done with Pt-Ru; the other was done with Pt-Co-Cu.

Wax coils of 12-gauge thickness having 10 turns in them were also prepared as a more critical test of castability. Two flasks each, containing a 10-turn coil, two 8-gauge rods, two 14-gauge rods, and a .25-inch-diameter rod were prepared and invested (fig. 10). Two flasks were also prepared containing two ring shanks and a flat plate 5cm by 1cm wide. The plate had a thickness of .048cm.

All flasks were invested with a commercial platinum investment following manufacturers' instruction. Burnout was done in an electric oven (fig. 11), once again following manufacturers' instructions. For our experiments, only virgin metal was used. The process would be repeated in the second round with a 50/50 mixture of

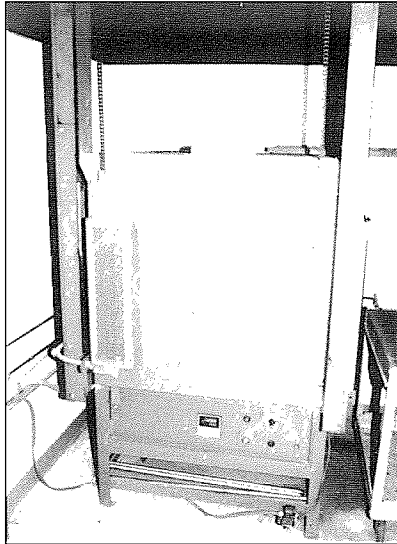


Figure 11: Electric Oven

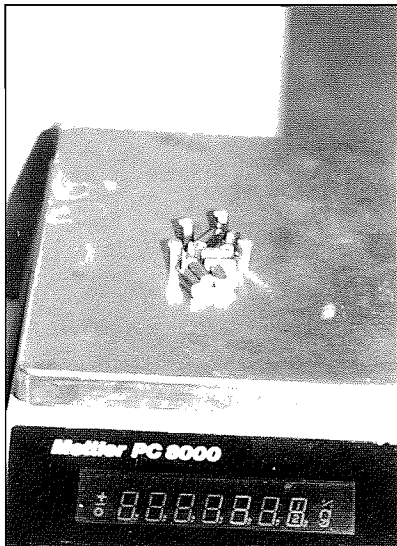


Figure 12: Metal on Scale

scrap to pure metal. Alloy was received in hexagonal rod form, which melts quicker than other forms and is more convenient to handle (fig. 12). In its raw state, Pt-Co-Cu cannot be distinguished from Pt-Ru, so care must be taken that alloys are not mixed. Our casting machine utilized a double broken arm configuration that provides an extra kick on initial

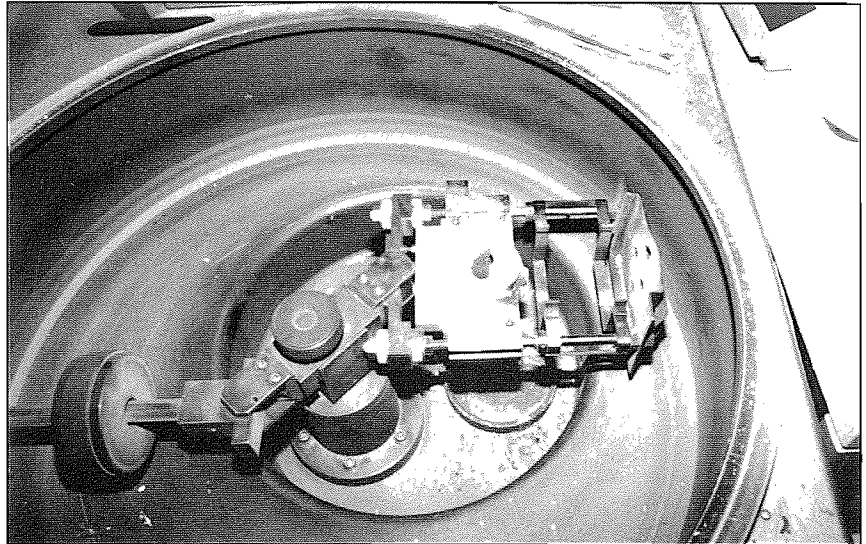


Figure 13: Broken Arm of Casting Machine

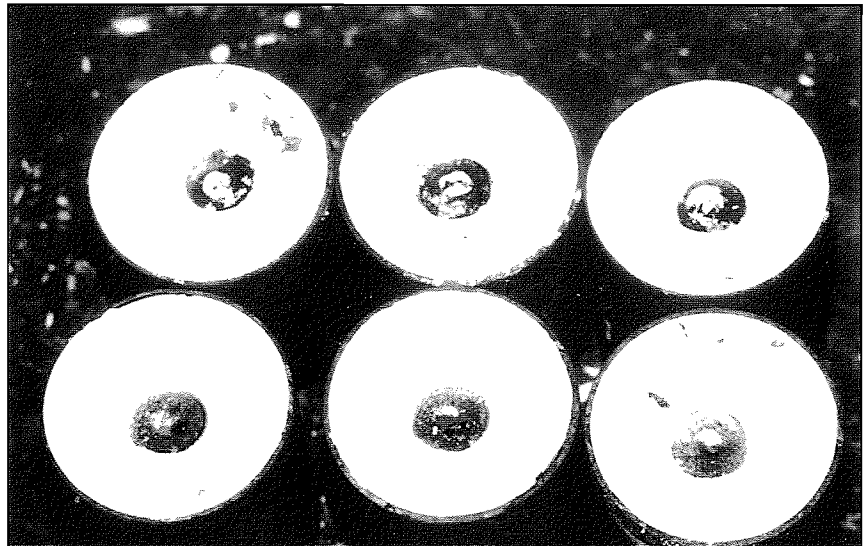


Figure 14: Cast flasks showing Buttons

acceleration (fig. 13). This extra kick compensates for the fact that in most induction casting machines there is a slight delay between the time the heat is removed as the coil drops away and when the arm begins its spin.

Burnout was at 1600°F. The alloy was melted and cast at 3500°F. The acceleration and

speed were kept constant for all flasks. All melts were done in air, without gas or vacuum. The melt characteristics of the two alloys were very similar except that the Pt-Co-Cu alloy produced more smoke than the Pt-Ru. This may present a problem when optical pyrometers are used for temperature sensing since smoking the lens can give false temperature

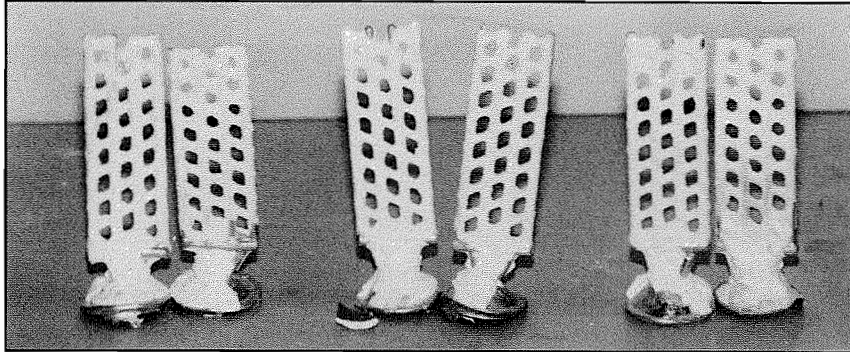


Figure 15: Cast grids with investment attached

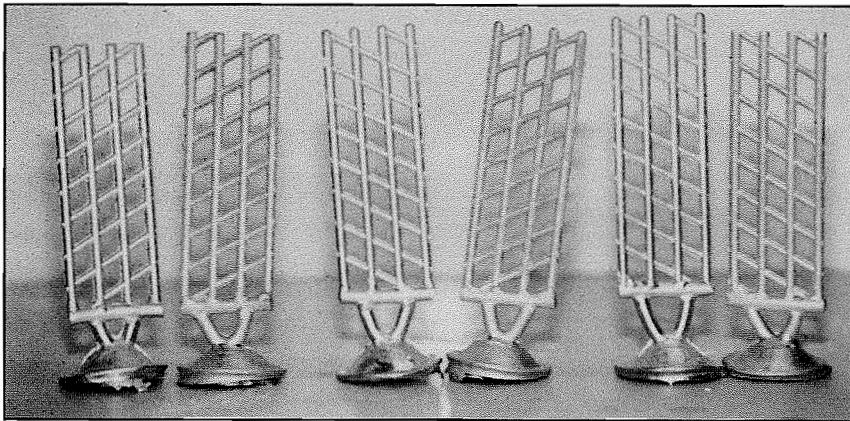


Figure 16: Cast grids after cleaning

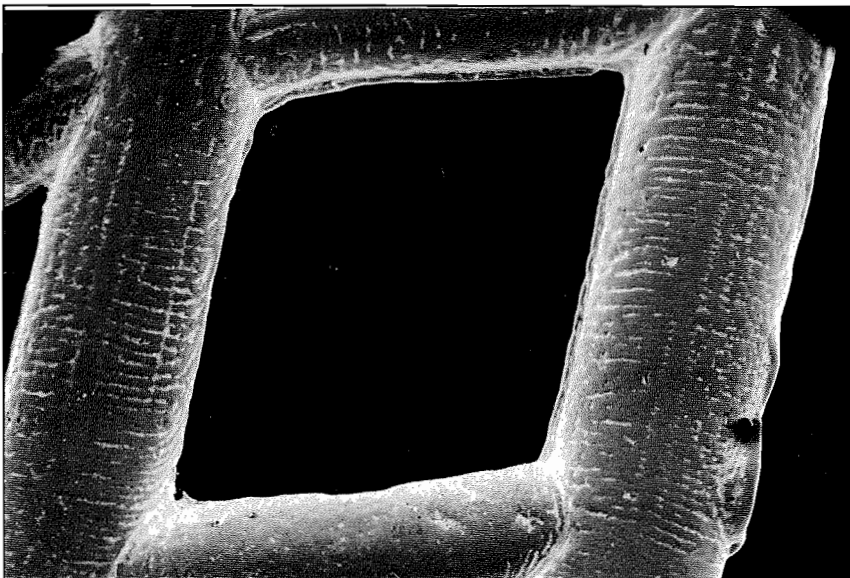


Figure 17: SEM of Pt-Ru grid showing flow lines

readings. Otherwise, the alloys melted smoothly and cast well, leaving no metal behind in the crucible. The Pt-Co-Cu alloy was easily identified as it had a slight oxidation to it, in the form of a faint bluish tinge on the button and surrounding investment. (fig.14) After cooling, the castings were broken out of the flasks with an air hammer. The breakout characteristics were about the same for both metals. (fig. 15)

The castings were immersed in hydrofluoric acid for 24 hours to remove all traces of investment. The castings were then examined for fill and other general characteristics such as surface roughness, color and porosity. Simple bend tests were also conducted to determine ductility.

Results

Filling

All grids filled, which was unexpected (fig. 16). However at close examination under 10X power, it can be seen that at 80% and 70% acceleration the Pt-Ru shows flow lines on the surface, an indication that the metal was at the freezing point as it made contact with the mold wall (fig. 17). The Pt-Co-Cu did not show this characteristic (fig. 18). On the other hand our coils showed a definite difference in fill characteristics. The coil test was repeated twice and in both cases the Pt-Co-Cu alloy showed more filling than the Pt-Ru.(fig. 19) The test was repeated and in both cases the coil showed greater filling with the Pt-Co-Cu alloy.

When the gauge size was increased to 10, both alloys filled the coil completely. This could lead us to conclude that the thinner and finer the piece, the more advantageous the Pt-Co-Cu alloy will be.

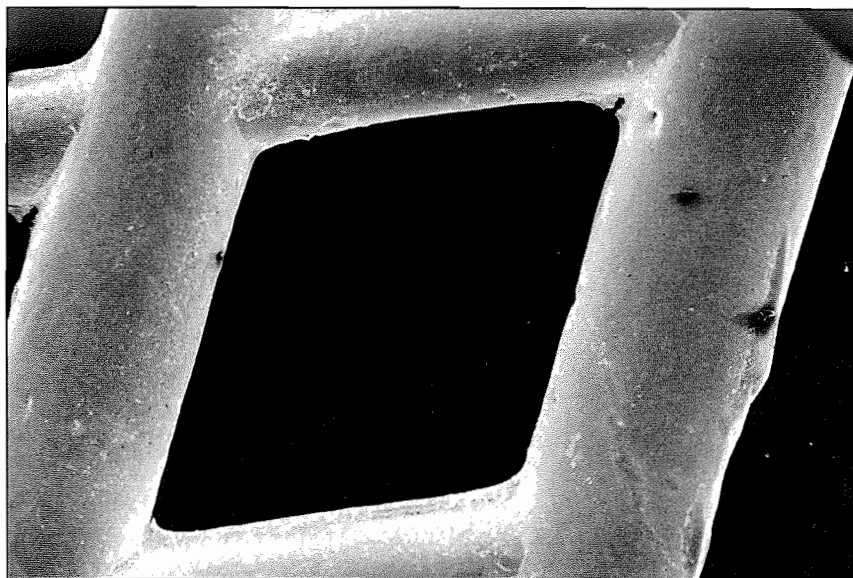


Figure 18: SEM of Pt-Co-Cu grid showing no lines

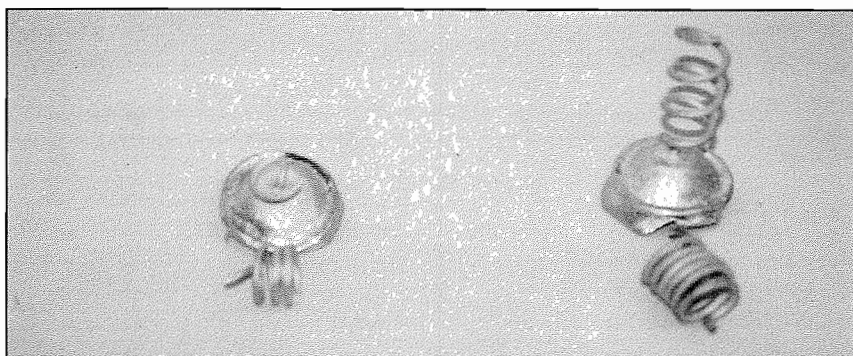


Figure 19: Cast coils showing fill

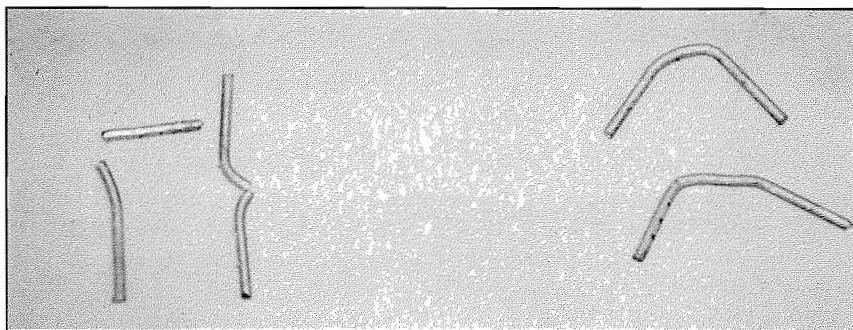


Figure 20: Bend tests (rods)

Surface Quality

Both plates filled well. The Pt-Co-Cu alloy showed a very slightly rougher surface than the Pt-Ru.

This was the case with all samples cast, regardless of size and shape. The slightly rougher surface was probably due to oxide formation.

Ductility

All rods filled completely. Both rod sizes were placed in a vise and bent 90° and back with pliers. The Pt-Ru alloy broke after only two or three bends while the Pt-Co-Cu alloy survived up to 10 bends before breaking. The new alloy showed much more ductility near the fracture area (fig. 20). The test was repeated several times, since any slight porosity in the rod would greatly influence the results. Repeating the tests produced the same results. Qualitatively, we can say that the Pt-Co-Cu is more ductile than the Pt-Ru.

Porosity

Our .25-inch-diameter cast rods were ground down halfway along their length in an effort to measure the degree of porosity throughout the piece. The Pt-Co-Cu showed porosity around the sprue junction, while the Pt-Ru alloy showed a more random distribution throughout the piece (fig. 21).

Color

To determine any color difference, rings were cast from the two alloys and polished. Placed side-by-side the two alloys were virtually indistinguishable from each other (fig. 22). Polishers reported that polishing of the Pt-Co-Cu rings took less effort. The tests were done without identifying which set of rings was a different alloy to try to keep the tests objective.

Joining

The rings were cut and then welded together by traditional torch methods. Rings were also laser-welded. The results of the welding are as follows: Pt-Ru

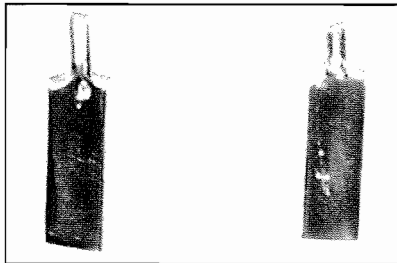


Figure 21: Rods showing porosity



Figure 23: SEM of weld joint of Pt-Ru ring



Figure 24: SEM of weld joint of Pt-Co-Cu ring

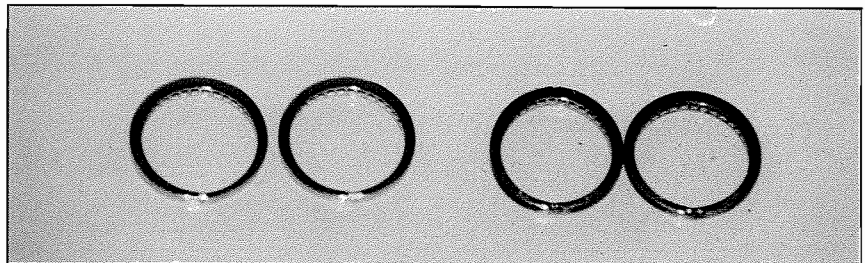


Figure 22: Polished rings

rings soldered without any oxidation (fig. 23). The Pt-Co-Cu rings actually started to melt before the weld filler material started to flow completely. The filler material was a thin sheet of platinum placed in the joint. The rings also showed a slight discoloration. After running one hour in a magnetic tumbler, there was still a slight stain evident that had to be hand polished off (fig. 24). Laser welding produced no noticeable surface oxidation with either alloy.

Conclusions

After casting about 50 items of various shapes and sizes from rod to plate to cylinders, the general conclusion seems to be that the Pt-Co-Cu alloy would be eas-

ier to cast and process into jewelry. The only serious drawback with this alloy is its tendency to form a surface oxide during welding or soldering operations. If an efficient means of preventing or removing this oxide was made available, then one could conclude that this alloy would be an improvement over the Pt-Ru alloy currently in widespread use.

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