Alloying in the small workshop

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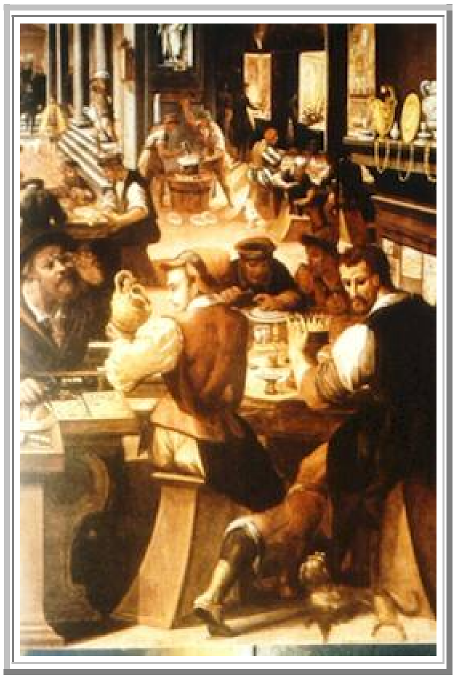
As a jewellery craftsman of 50 years standing, 30 years of which have been devoted to custom casting for the jewellery industry, I have pleasure in describing some of the pitfalls and successes I have experienced in the making of gold alloys in general with particular reference to a silicon containing master alloy for the lower carat rated yellow golds which I invented in 1964, and gave to The Worshipful Company of Goldsmiths in 1969 (Figure 1). Whether alloying gold for ingots, granulation or casting, I have found there are some basic parameters to be observed.



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Safety is the first essential

- When melting metals correct protective eyewear is necessary
- Sunglasses do not provide sufficient protection from the U.V. and infra-red rays emitted
- A full face mask is recommended
- Leather gloves may be necessary for the higher melting point metals
- Good ventilation is necessary

I also recommend solid footwear and a leather apron, as molten metal spilled or splashed on bare flesh continues to burn for a considerable time after making contact. When a bead of molten metal falls between your toes and you are holding a crucible of molten metal with one hand and a blazing torch with the other, a fairly high degree of self restraint is required if you wish to complete the task without further calamity.

Good housekeeping is the second essential

When selecting the elements for an alloy, the most important thing is metal purity. Even minute quantities of impurities such as lead, arsenic or antimony (any one of which will probably cause embrittlement) will result in a less than desirable alloy. It is preferable to start with all pure metals, e.g. pure copper and pure zinc. If brass is to be used as master alloy it is essential to know its composition, e.g. ensure it is not a leaded brass.

A particular example of bad housekeeping occurred early in my career. For granulating I used a plastic coated drum with a container on the bottom to catch the granules. I didn't empty the drum each time I granulated; in fact, sometimes I would not empty it for up to a fortnight. Eventually I began to get complaints of black spots in the castings. On close examination under the microscope, a small piece of magnetic substance was extracted from a casting. This was identified as iron. The plastic lining in the granulating drum had deteriorated allowing the water to rust the drum. The iron oxide thus formed was collected by the granulation and reconverted to iron during the subsequent melt.

Accurate weighing is the third essential

Having decided on the alloy to be made, each of the metals must be accurately weighed. Particular attention must be given to weighing. There are at least four reasons for attention to accurate weighing:

Predictable properties.

Consistent quality.

To avoid fraudulent under-carat ratings.

To avoid costly over-carat ratings.

The fourth essential is melting order

When I commenced to formulate these alloys, having failed to find published instruction, I was neither assisted nor restricted by prior knowledge. It was this freedom that allowed me to experiment with silicon.

Results were achieved purely by trial and error and observation. Initially I just melted the metals together without any order. Then observing the way the metals melted with their quite different melting points and vaporising points, I soon deduced there should be a definite order for melting the metals.

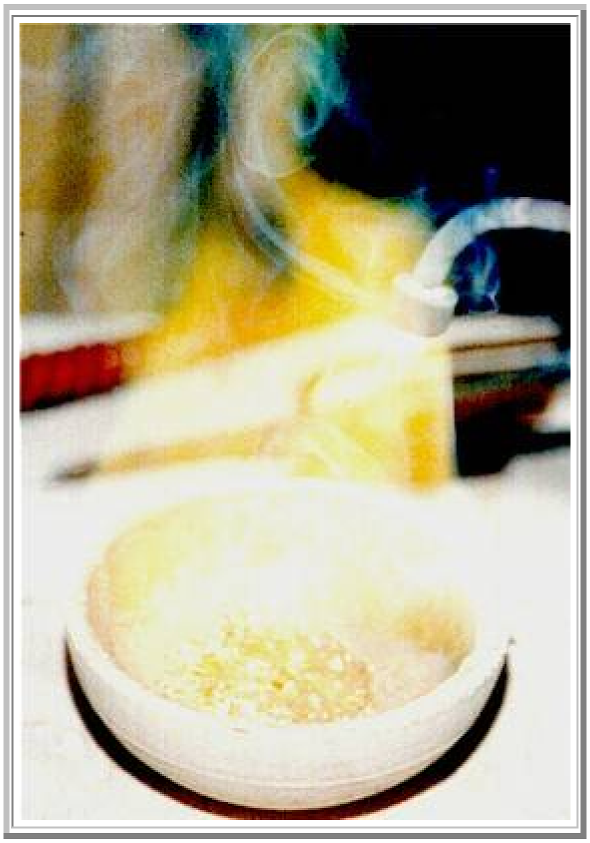
Due to the very low boiling point of zinc, melting order is particularly important for any zinc-containing alloy. The order I have established is (after preglazing a crucible with boric acid) place the zinc with a pinch of boric acid in the bottom of this preheated crucible and gently melt with a reducing flame. The copper, with the silicon copper, is now placed on top of the zinc. With each addition of metal add another pinch of boric acid. All the time maintain a reducing flame on the melting metals.

By melting in this order, the molten zinc is drawn to and begins to alloy with the copper as it is heated. The silicon copper begins to alloy with the copper, further lowering the melting point of the alloy as it is forming, bringing it closer to the volatilisation point of the zinc. At this point a small amount of zinc oxide may be formed but as the silicon begins to alloy with the other constituents, it scavenges the oxides.

The melting can continue without fear of more zinc oxide being formed, provided the temperature is not allowed to rise too high and a reducing flame is maintained. The result is an oxide-free alloy. Although zinc oxide fumes are not regarded as toxic, inhalation can cause flu-like symptoms and a temporary illness. Avoid inhaling zinc oxide fumes.

What one must bear in mind are not only the melting point of zinc, 419°C, but also the boiling point of 907°C, the boiling point being below the melting point of any of the other constituents (Figure 10). At the point of volatilisation of zinc, any oxygen present will combine with the zinc and produce white zinc oxide fumes. I found zinc oxide to be a major cause of porosity problems. If not kept to a minimum, zinc oxide remains in the metal and leaves random porosity in any part of the casting.

It is preferable that the alloy be melted without volatilising the zinc. Gas torch melting makes this a difficult, but not impossible task, depending on temperature/flame control and the order of the addition of the metals.



It is particularly important to control the formation of zinc oxide as once formed it is unlikely, under these conditions to reconvert to metallic zinc. This was proven to me quite graphically about 6 or 8 months after I had started using this system. Finding I no longer had the time to make the amount of master alloy I needed, I asked my refiner to make 50 kg's of master alloy. Immediately random porosity was evident in the castings, so I went to see how the master alloy was being made. I arrived in time to see the silicon copper in a molten state and the furnace-man throwing the zinc on top. This of course filled the furnace room with zinc oxide fumes and the resultant silicon brass with zinc oxide inclusion. I reiterated my procedure for alloying zinc-containing alloys. When this alloying procedure was adopted, I had no further problems with zinc oxide inclusion.

Deoxidising is the fifth essential.

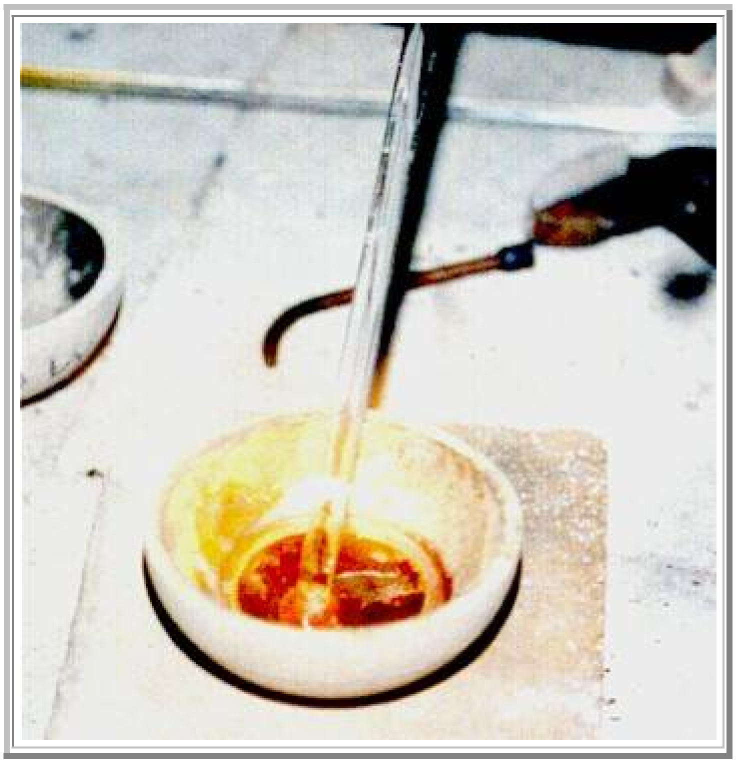
When gas torch melting, deoxidisation is accomplished by the use of scavenging elements and fluxes. Fluxes shield the surface of the metal from exposure to atmospheric oxygen. Scavenging elements dissolve the oxides in the molten metal and become a part of the finished alloy. The Oxy/gas torch must be controlled to limit the amount of oxygen used to feed the gas flame and to maintain a reducing atmosphere.

Fluxes used are usually borax (sodium tetraborate), melting point 760°C, or boric acid, melting point 870°C, and powdered or lump charcoal. Charcoal will form a carbon monoxide/dioxide gas cover to the melt. Boric acid is used as it melts easily and forms a protective layer on top of the metal. It also combines with the metallic oxides, thereby keeping the molten metal clean.

Although there are many oxygen scavenging elements available, my preference is silicon added in the form of 10% silicon copper. The addition of silicon in this form is easily controlled to minute quantities. Silicon is an efficient scavenger. Minute additions are all that are necessary; indeed in my experience all scavenging agents are only required in minute amounts.

Correct temperature control is the sixth essential

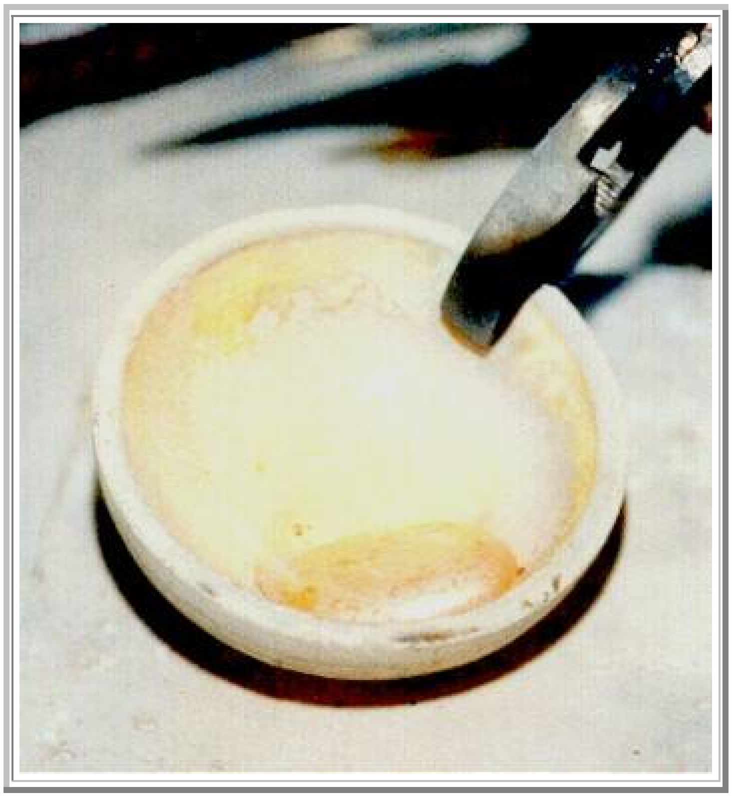
Temperature control is very important. Since time immemorial the experienced eye has been the thermocouple most used in the small workshop. The practiced eye is regarded as being very reliable. Today we are able to fast track to a practiced eye with the aid of small digital readout pyrometers. These establish accurate parameters to which we can adhere and from which the inexperienced eye can learn.



As the alloy is approaching it's pouring temperature, the metal needs stirring to be sure of a homogeneous mix. If using a stirring rod, this is best done with a soda glass, or Pyrex rod, which will also collect any excess flux.

My preference for stirring is to pick up the crucible with a pair of tongs and gently swirl the metal until the majority of flux is deposited around the sides of the crucible. This also has the benefit of making sure all components are melted, as little lumps will be observed just below the surface if the melt is not complete. The excess flux I melt and pour from the crucible at a later time. Pouring of the molten metal is done when the operator is sure all components are molten, the resultant alloy is homogeneous, and the surface is cleared of extraneous flux.

Care must be taken to ensure the metal does not overheat. The recommended pouring temperatures for precious metal alloys are usually between 75°C – 100°C above the liquidus. Ingot moulds should be preheated to approximately 150°C. Granulation water should be cold. Casting moulds usually range between 200-650°C this depends upon the pouring temperature of the metal and the physical proportions of the item to be cast.



In discussing these six essential points of care, I have used as an example the making of a master alloy to which is added fine gold and fine silver to create 9 ct, 10 ct, or 14 ct yellow gold alloys. I believe the making of master alloys to which fine precious metal is added is the best practice. This minimises the possibility of a non-homogenous alloy. Master alloy is efficient to make in larger quantities and economic to hold in stock.

The best equipment to use is that which successfully accomplishes the task and with which the craftsman feels comfortable. In my small workshop I use an Oxy/L.P. gas micro torch, 70-100 mm clay crucibles (scorifiers) always preglazed with boric acid. My melts do not exceed 300 grams. For yellow gold alloys I use a nozzle with 5 x 1.1 mm holes, this produces a soft reducing flame. When pouring yellow gold ingots, I prefer to coat the mould with carbon black (soot) as a release agent.

There are two reasons I do not use silicon as a scavenging agent in higher carat rated alloys, such as 18 ct, 22 ct, etc. The antipathy of gold to silicon means that only insignificant quantities can be used without detrimental effect; also, gold does not readily attract oxygen, consequently scavenging agents are not needed if due care is used in melting.

So far I have only spoken of yellow gold alloys. White gold alloys require other considerations. Nickel white gold alloys have been used in the past. The inherent metallurgical limitations and current understanding of allergenic problems preclude them from consideration here. I have always produced palladium white gold alloys in all carat ratings. Recently we have added platinum-palladium alloys to our range.

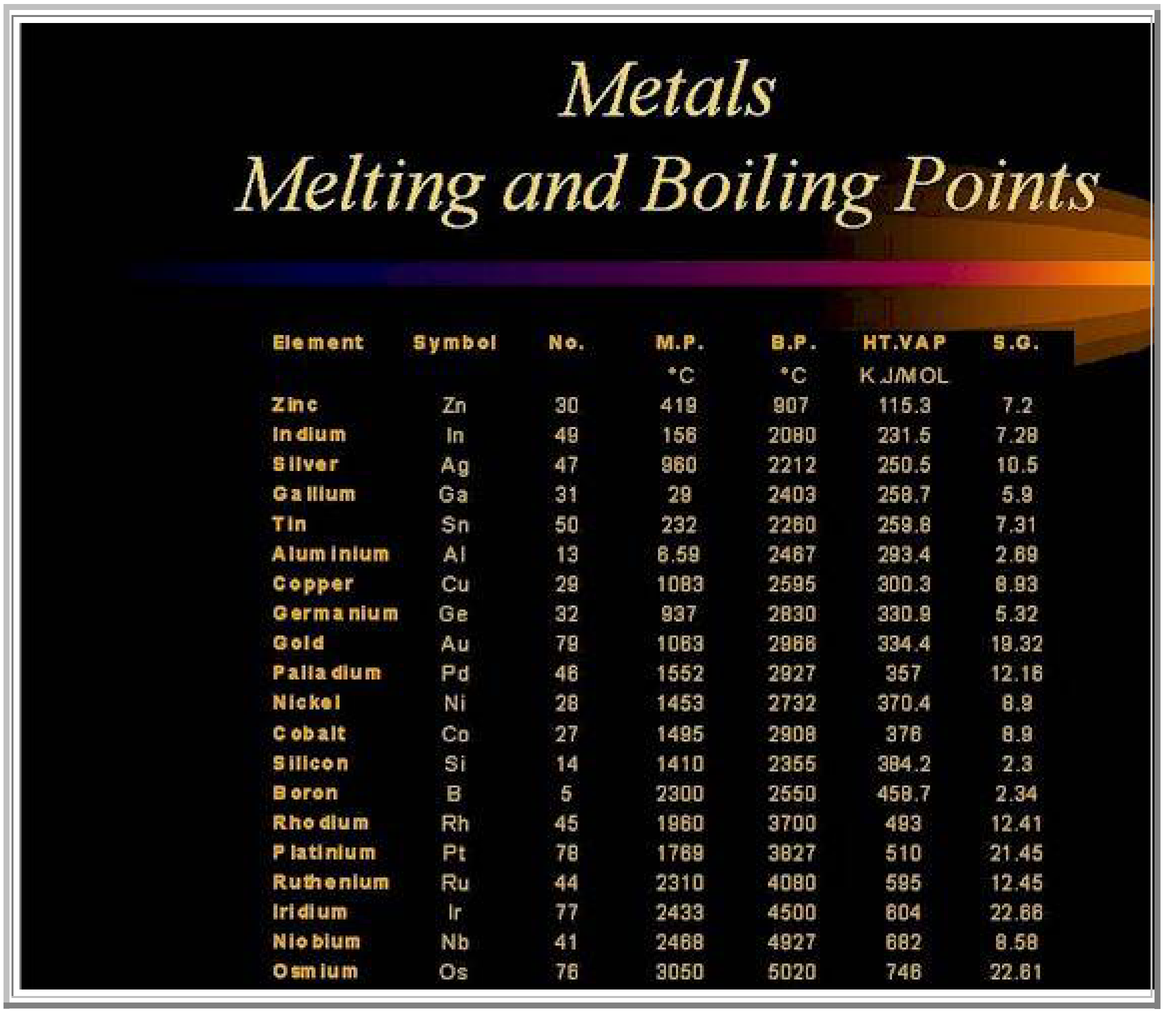
For platinum and palladium alloys, I use a single 1.5-mm orifice nozzle which will produce an oxidising flame and attain the higher temperatures required. I use the same type of clay crucible. 18 ct platinum/palladium white gold alloys should not be cast into gypsum bonded investment moulds. Due to the higher casting temperatures required, the gypsum (calcium sulphate) releases sulphur dioxide with harmful results. With platinum and palladium white gold alloys, the ingot mould should be free of carbon, as it can have harmful effects on the metal. These alloys can be produced in the small workshop using similar procedures and equipment. Due to the higher melting point of these alloys, protective glasses with appropriate gas welding filters must be worn.

A master alloy of copper and zinc is made, in similar manner as previously described. That is, place the zinc first into the crucible, add the copper, with boric acid. Using a reducing flame, apply heat to the copper and zinc. Be patient, take every care to control and minimise the formation of zinc oxide.

The palladium and platinum are each rolled to a 0.1-mm shim and alloyed with the gold. The palladium is placed first in the crucible with a little of the gold and the platinum on top. Bring the metal temperature to where the palladium begins to alloy with the platinum, add the rest of the gold, piece by piece, being careful not to allow the melt to become so cool that the platinum stops alloying with the rest of the melt. As soon as you are satisfied of a homogenous melt reduce the temperature a little, then add the previously alloyed copper and zinc.

After pouring, if you are not sure the alloy is homogeneous, *remelt!*

With subsequent melts, the use of scrap is beneficial to assist in the alloying of the platinum and palladium and is added with the shim. Indeed a little scrap added at the beginning of new melts will assist higher melting point metals to alloy.



Metals
Melting and Boiling Points

Element	Symbol	No.	M.P. °C	B.P. °C	HT.VAP KJ/MOL	S.G.
Zinc	Zn	30	419	907	115.3	7.2
Indium	In	49	156	2080	231.5	7.28
Silver	Ag	47	960	2212	250.5	10.5
Gallium	Ga	31	29	2403	258.7	5.9
Tin	Sn	50	232	2260	259.8	7.31
Aluminium	Al	13	6.59	2467	293.4	2.69
Copper	Cu	29	1083	2595	300.3	8.93
Germanium	Ge	32	937	2830	330.9	5.32
Gold	Au	79	1063	2966	334.4	19.32
Palladium	Pd	46	1552	2927	357	12.16
Nickel	Ni	28	1453	2732	370.4	8.9
Cobalt	Co	27	1495	2908	376	8.9
Silicon	Si	14	1410	2355	384.2	2.3
Boron	B	5	2300	2550	458.7	2.34
Rhodium	Rh	45	1960	3700	493	12.41
Platinium	Pt	78	1769	3827	510	21.45
Ruthenium	Ru	44	2310	4080	595	12.45
Iridium	Ir	77	2433	4500	604	22.66
Niobium	Nb	41	2468	4927	682	8.58
Osmium	Os	76	3050	5020	746	22.61

The periodic table is my main reference. This table details the eight precious metals and some alloying elements; note especially the melting points, boiling points and heat of vaporisation columns.

These have been a guide to more predictable results.

The alloys I have described were formulated and made using gas torch melting and have proven working characteristics, that is they will produce consistently good results either as cast or wrought metals, provided due care and attention to detail as described, is taken. They will remelt and recast retaining their good working properties.

My metal formulations have always started in the scorifier under gas torch. My initial trial sample is often no more than a one-gram button, which I test for colour, ductility and malleability. If it shows potential I make a larger sample for evaluation by casting and as plate and wire. Alloys formulated in theory do not always work in practice, but one must start somewhere. Formulate, alloy, trial, record, and fine-tune; my progress has followed this path. Every alloy we produce began with this process; they include all carat ratings of gold, in yellow, white, and red alloys, and a special palladium-gold alloy which retains it's spring in the as cast state and shows a marked improvement in tensile strength when heat treated.

Formulating alloys, searching for new properties to provide the characteristics my customers require, has been a challenge. The special palladium-gold spring alloy which is so useful for cast catch tongues and flat springs, the silicon-gold alloys from 1964 as well as other precious metal alloys have been rewarding achievements.

Traditionally jewellers prepared their own metals. Today we are fortunate to have precious metal suppliers who supply most of our needs. However, there are often special qualities in a metal a jeweller would like to achieve. These are not always available in stock alloys. Thus today's artisan needs the skills of his traditional predecessor. In conclusion, I quote from an ancient metallurgist, Edward F. Law, who wrote in 1909: -

"It has long been known that the temperature at which metals and their alloys are poured has an important influence on their mechanical properties, and the most suitable casting temperature for any particular alloy has been determined by practical experience. Deoxidisers should only be used to free the metal from the unavoidable oxidation, which takes place even during the most careful melting. The knowledge that oxidation can be wholly or partially cured should not hinder the strictest precautions being taken to prevent oxidation during melting. Excessive oxidation caused by too rapid melting and consequent overheating of the metal, or by overcharging the crucible, is often incompletely remedied by the addition of deoxidisers.

In the manufacture of metals on a large scale it is not always easy to produce a mixture of uniform composition even with careful stirring, and in practice it is often considered desirable, if not necessary to remelt the metal a second time. The difficulty is greatest when the metals to be alloyed have widely different melting points, and is still further increased if one of the metals is volatile. In order to reduce this difficulty to a minimum the pure metals are not melted together, but previously made alloys (master alloys) whose composition is known are used to make the final alloy."

Finally I would remind you of the essentials:

Safety, good housekeeping, accuracy in weighing, melting order, fluxes and scavenging agents, temperature control.

References

Mark F. Grimwade, "Basic Metallurgy For Goldsmiths", Gold Technology, 2, June 1990

E.F. Law "Alloys and their Industrial Applications", Charles Griffin and Company, London, 1917