THE EVOLUTION OF AN ALLOY

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ABSTRACT

Definition of
Reason for
Approach to
ALLOYING PRECIOUS METALS

With examples of

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1. 9ct to 14ct silicon bearing gold master alloy.

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2. 18ct Palladium White Gold

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3. Carat Gold / Palladium spring master alloys.

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4. Fire-scale free, tarnish resistant, Sterling Silver

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KEYWORDS

Alloy, Carat Gold, Casting, Colour,
Copper, Design, Element, Fashion,
Fire-scale, Formula, Gold, Germanium,
Investment Casting, Master Alloy, Nickel,
Palladium, Platinum, Porosity, Precious Metals
Silicon, Silver, Spring Alloy, Sterling, Tarnish,
Tensile Strength, White Gold, Zinc

A Little History;

Historically, the earliest alloys created by man were brass, a simple alloy of copper and zinc, from the late Neolithic period and bronze, an alloy of copper and tin known to be in use from as early as 3000 BC.

Although gold and silver were known and used at this time, they were used more or less, in the form they were found, for decorative purposes, as bronze fulfilled all practical needs.

King Croesus of Lydia during the years 560-546 BC desired and developed the first official government coinage system using a naturally occurring alloy of gold and silver, known as Electrum.

In historical terms the alloying of gold for jewellery purposes is a comparatively modern development.

What is an Alloy?

According to the Hamlyn World Encyclopaedic Dictionary the definition of the word "ALLOY" is a substance composed of two or more metals, or sometimes a metal and a non metal, which have been intimately mixed by fusion, electrolytic deposition, or the like.

We as jewellers, understand alloying as the melting together of any two or more of the following -- gold, silver, the platinum group, copper, zinc or other elements, some metallic and some non-metallic such as Boron and Silicon.

Our interest is in the eight noble metals, or more specifically of, gold, silver, platinum and palladium.

Why Alloy?

There are several reasons why the precious metals need to be alloyed.

1. Strength;

Of the precious metals, gold and silver are too soft for practical use. Because they are so soft, malleable and ductile in their elemental form, it is necessary to improve the characteristics of the metals by increasing their modulus of elasticity and to obtain greater rigidity and wear resistance by rendering them hardenable.

To enable precious metals to be worked into shape by hand fabricating, casting, pressing, spinning, etc., they need the influences the alloying agents impart.

Each manufacturing method has it's own requirements for degree of ductility and hardness; each may require an adjustment of the alloy formula.

2. Economy;

The cost of pure precious metals is restrictive in marketing terms.
By alloying precious metals with less costly components a more affordable metal is produced.
Alloying enables people to own precious metals who would not otherwise be able to do so.

3. Fashion and Design

That which fashion dictates, designers attempt to produce.
The modern art of alloying for colour variation or physical property is driven by the designer's request.
Gold the only naturally occurring metal so-coloured, can impart its strong, unique golden hue even when alloyed to 50%.
Gold has been the most popular and fashionable metal since woman understood it's allure and man gave it a value.
Platinum is appreciated for it's durable lustre as well as its strong alloying attributes.

4. Status;

Although governments of the world no longer back their currency with gold, it remains the universal currency recognised across all borders.
To own gold, be it as nugget, ingot, or worn as jewellery, in most cultures is a tangible symbol of status.
For 5000 years people have fought and died for the possession of gold; to demonstrate one's status with gold has always been a desirable goal.

The Inspiration for an Alloy;

When a requirement is identified for a metal with particular attributes, a decision may be made to create a new alloy, market research having established that this is not available from the many commercial alloys already offered.
It's easy to take a few components and melt them together in a crucible and see what comes out, but to achieve a desired result, a little judicious planning is required.

For instance, is the ultimate alloy to be hard, or soft? Will it work harden quickly? What colour is it to be? What other special qualities are needed for the particular application?

Ideally the alloy will be able to be worked using normal jewellery fabrication techniques and polish easily and well to present a lustrous surface.

Ultimately the major qualities must fit within the set parameters of precious metal standards established by tradition and maintained by legislation in most parts of the world.

The known and proven qualities of metals and elements previously used for alloys should be studied.

Even with these parameters in mind one still has a very broad selection of elements from which to draw, to achieve the required properties.

Evolution;

An alloy evolves through:

1. The need – either to attain a design or fashion attribute or for practical reasons or physical qualities.
2. Market research establishes the economic potential for the proposal.
3. Survey reveals that existing alloys do not provide the qualities needed.
4. The parameters sought are listed in order of importance.
5. Existing knowledge is studied.
6. A trial formula is selected on the assumption of how certain elements, when added to a selected metal **should** behave. I stress should, as my experience has been that what should and what actually does happen may be rather different.

Alloy Development;

The development of the optimum alloy can be a lengthy and time consuming task. In formulating a new alloy it is important to keep in mind the needs and the skills of the bench trained jeweller.

The majority of craftsman jewellers in the world are small workshop operators. My research is initially carried out and tested in and for these conditions.

The steps we take to develop a new alloy are;
1. First the theoretical formulae are composed.
2. Weighing and recording is very carefully addressed.
3. Melting of the components must be carefully controlled.
4. Prospective alloys selected to evaluate their potential.
5. Then the resultant alloy assessed.

The assessment involves testing for any particular aspects of jewellery fabrication, hand working, casting and any methods of machine working by which the new alloy is to be processed.

Once proven it then goes into trials in one of Australia's largest custom casting and fabricating factories, ultimately going into production with several large scale precious metal suppliers throughout the world.

As an example of the evolution of an alloy, I use here the master alloy for our lower carat rated yellow gold alloys. This master alloy is used for gold alloys with carat ratings up to and including 14 ct.[1]

In 1964 I began my business and needed to make casting alloys. I asked around my trade associates for a formula with which to start and was given a formula for a 9ct yellow gold alloy.

Realising it needed a little modification, I adjusted the silver, copper and zinc until it looked fairly evenly balanced.

I had a place to start. The 9ct alloy which I made, although possibly a good metal for wrought product, gave me problems with porosity when cast.

A friend who was neither jeweller nor metallurgist suggested the use of silicon to 'aid the fluidity', as he had observed the use of silicon in brazing rods.

Not being hampered with the knowledge that silicon and gold are not readily compatible, I set out on a course of discovery which has led me to seek further improvements in precious metal alloys.

The first silicon-containing alloy I made included 5% silicon in the form of a 10% Si / Cu alloy, which was added to a master alloy of Cu, Ag and Zn. This appeared to have some beneficial results in that the castings were bright, smooth and cleaner looking, and did not bear the oxide coating which the non-silicon bearing alloys had always produced.

The problem was that the castings virtually crumbled in my hand. Nonetheless I was satisfied that silicon was a beneficial additive, certainly worthy of further research.

It only remained to establish the optimum quantity.

As a result I lowered the silicon content 50% and found this showed a marked improvement. I continued to halve the amount of silicon addition and eventually established 0·32% silicon content as a workable alloy. The metal no longer cracked and now produced bright porosity free castings.

Further research proved, due to the de-oxidising properties of silicon, zinc oxide is not able to form, surface tension is increased and the resultant alloy when cast is free of the porosity previously caused by inclusions of zinc oxide.

Our customers, happy to be rid of the problems of porosity they had previously endured, embraced the new alloy with enthusiasm.

Over a period of 2 months, further trials established a lower parameter for silicon. There were some slight modifications to the formula in the following 3-4 years, but the current formula has been in use for 25 years[1].

I was so pleased with the discovery of the effect of silicon on gold alloys I immediately tried it in 18ct yellow gold. The initial result was that the rings fell off the tree, and crumbled in my hand. I tried lesser and lesser amounts of silicon until I was convinced the amount of silicon 18ct gold could tolerate was so insignificant as to be of little, if any, benefit. Although others have found some benefit with silicon in the higher carat rated alloys, my opinion has not changed.

When I espoused the use of silicon in gold alloys to the Worshipful Company of Goldsmiths in 1968, it was received with astonishment.

I gave them an alloy formula, which was trialed in the trade by the two largest precious metal suppliers in that country at the time. By the time of my next visit three years later, silicon containing gold alloys, especially in lower carat ratings, had become a commercial reality.

I'm pleased to say silicon is now a standard alloying constituent in the lower carat rated gold alloys and accepted worldwide.

White Gold;

During my thirty-three year search for the optimum precious metal alloys suitable for investment casting, white gold alloys have gone through quite an evolution of their own.

My attempts to make an 18ct white gold have lead me through the nickel / palladium alloys and many combinations.

Nickel containing white gold 18ct alloys gave me no end of problems. Although I made and cast a lot of this metal, my success rate was not as profitable as desired, so I concentrated on palladium as the whitening agent for white gold alloys.

Casters found the nickel alloys easy to cast due to the lower melting/casting temperatures, that is in the 950-1050°C range for nickel alloys versus 1200°C+ for Pd alloys, but the ensuing cast quality of nickel gold alloys has not provided the most desirable consistency.

Gold / nickel alloys, although cheaper and whiter than the palladium alloys, were more problematic both in casting and handling at the bench. Where, if not treated carefully at all stages of manufacture, castings would present problems to the jeweller and the setter, with claws and beads that would not bend without breaking, but worse, shanks breaking after sale.

I ultimately settled for a 12% palladium alloy which, while not producing a very white alloy, at least was cost efficient when marketed against the nickel alloys. This alloy's main attribute is in being a very stable alloy at all stages of manufacture. Furthermore, I found 12% Pd would give a colour that was acceptable.Albeit I was often told, to my chagrin, "Anyway it'll be plated, so who'll see it".

With the use of Pd alloys, setting is much easier, the claws and beads stay on, and shanks do not break.

After some time I was able to convince some customers to pay a little more to take a 15% Pd 18ct white gold which has a much better colour, although still toward grey rather than white. This 18ct Pd alloy is the one we still use largely, unless I can convince someone to take a Pd / Pt alloy [2]. The addition of 5% Pt gives a superior white colour.

Due to the higher melting point of these alloys and the mould temperatures required it is recommended that phosphate-bonded investment be used to achieve smooth castings.

Rather than by means of electroplating, I consider that by means of alloying, the inherent colours of the metals can be used to obtain the colours required.

Cast Gold Springs;

The next problem I was set was to provide a harder 9ct yellow gold for an earing clip post that would not bend when being opened and closed. The design was such that when the clip was opened there was the likelihood of the post bending due to the nature of the design, which was soldered on two small points, and the softening of the component taking place during soldering.

I had observed whilst formulating 18ct palladium master alloy that the resultant metal was quite tough, so I used this to try a tough alloy for the post.

It achieved the desired result regarding the toughness but unfortunately the colour was deficient as it had a distinctly pale colour due to the palladium content.

Further work on this by the addition of copper only brought about a slight softening, not enough to preclude it from doing it's job, but with a brownish colour.

I could not get the colour for the job required so didn't do any more with it for some time.

Until a customer needed some necklet clasps cast, so I tried this alloy for the tongues with success, as the tongues can be cast and retain their tensile strength after casting, only needing their sprues removed and to be polished.

This alloy has proved to be very useful for this purpose. The main drawback with it is it's limited colour range as the palladium necessarily keeps it pale.

Starting with the master alloy I then used for 18ct Pd white gold consisting of copper, silver and zinc I added 12% Pd and 37.5% Au.

We then replaced the Zn with additional copper to try to improve the colour for use with yellow gold. Then reduced the Pd to 5%.

We now use a master alloy Pd 8.1, Cu 43.7, Ag 48.2. to which we add gold to make the appropriate carat rating required.

We use this master alloy for 14ct and 18ct which, due to the increase in gold content, gives a much better yellow colour. The lower carat ratings are still not yellow but perform the task of retaining their tensile strength as cast.

This series of alloys, which has evolved over a period of 20 years, can be wrought using normal jewellery fabrication methods.

We make flat springs for Albert clips or draw wire to make springs for Cartier type clips. The fact that it will work harden means it will also lose some of its tension if being heated near red heat but it will still retain sufficient of it's tensile strength to maintain some of its spring advantage to be of benefit under certain situations.

The main advantage of these alloys is their ability to retain an increased tensile strength when cast. Consequently cast jewellery components requiring spring tension action can be marked carat rated completely as the article contains all carat rated alloys.

Bright Sterling Silver;

For many years people have been striving to produce a fire-stain free silver, but it is only in the last 5-6 years that a breakthrough has been made with a real improvement to the qualities of standard sterling silver. Until recently there was only one standard alloy of sterling silver in major use, being 92·5% silver and 7·5% copper, the qualities and characteristics of which are well known. A beautiful, white, lustrous, decorative metal, easy to fabricate and cast, but difficult to work without developing fire-scale, using normal soldering and annealing techniques. When polished, it in time develops a nasty shade of black if not paid sufficient attention.

Now we have formulations that improve the hardness and minimise finishing time by virtue of the anti fire-scale properties and with improved tarnish resistance.

Due to complaints of fire-scale in sterling silver in the early 80's I tried an alloy containing silicon and zinc but found it too soft and didn't continue with it.

A little later whilst attending a Santa Fe Symposium I was offered a formula for a fire-scale free, sterling silver. It certainly proved to be fire-stain free, but for most practical jewellery purposes, it too was soft, and did not harden appreciably.

The challenge was to give it some degree of hardness to make it a more useful alloy.
So with the judicious use of Germanium, I began a series of test alloys to increase the hardness.
Within a very short time I had proved that the hardness could be increased.

To achieve the optimum alloy with improved characteristics, yet retaining similar working properties as standard sterling silver, has been an ongoing search, with improvements occurring at regular intervals over the past 5 years.
The original master alloy contained seven elements and to balance all of these to obtain the qualities required for a particular purpose entailed a lot of trial and error in formulating.
As even less than 0·1% of any given constituent could change the result.
By the addition of a careful formulation of mainly germanium, zinc, silicon and trace elements we have been able to develop a range of sterling silver alloys.
The broad range of parameters within our patent specifications allows for silver alloys from 830/1000 through 925/1000 (sterling silver), to 950/1000.
The scope is there to create an alloy for a particular purpose i.e. one that will work harden quickly or slowly or will cast a little harder than standard sterling, with the attributes of being fire-stain free and with increased tarnish resistance.

Handling the New Alloy;
Every new alloy has it's own idiosyncrasies and these have to be learnt and allowances made for differences in processing, possibly with slight variations to that used for a supposedly similar alloy.
For instance standard sterling silver is an alloy that has working characteristics familiar to all jewellers and silversmiths.
A new alloy is bound to perform at least a little differently in some aspects.

In the instance of the Bright or Ge / Si silver alloys, due to the lack of oxidation when annealing, the usual visual temperature indicators are not evident and it is easy to raise the temperature passed its solidus without being aware. A jeweller must therefore adapt his/her technique: in this instance being alert to the red heat rather than the black oxidation.
One must be adaptable to change and willing to make an effort to learn the idiosyncrasies of a new alloy with improved qualities.

The Future;
There are always improvements to be made with the alloys we are using, for instance the Pd spring alloys need to be able to be produced to be a better match for yellow gold alloys.
White gold alloys can and should be developed further to give better colour with economic benefits.
Personally I always advocate using solid carat rated precious metals, meaning no plating. When a white colour is required using 18ct or higher yellow gold alloys, I believe platinum should be used if economically possible. Failing this a carat rated metal as white as can be obtained should be used.
Current research to develop a near to 24ct gold, capable of being wearable as jewellery, is a challenging and exciting prospect.
The resultant alloy will need to be able to be hand wrought as well as cast, as precious metal alloys that cannot be worked by traditional working methods have not had a successful history.
Since the founding of Apecs Investment Castings in 1963 we have always formulated the alloys we use for casting.
All are quite practical for wrought product.
These include red, pink, white, and green, 9, 10, 14, 18, and 22ct gold carat rated alloys.
But with regard to the colour of metals, there is no colour as beautiful as 24 carat, pure, fine……………….GOLD.

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HARD GOLD SPRING ALLOYS

	AU	PD	AG	CU
9CT	**37.8**	**5.0**	**27.2**	**30.0**
10CT	**42.0**	**4.66**	**25.36**	**27.98**
14CT	**58.7**	**3.32**	**18.06**	**19.92**
18CT	**75.2**	**1.99**	**10.85**	**11.96**

References

Santa Fe Symposium on Jewellery Manufacturing Technology
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'The Effect of Various Additives on the Performance of an 18 Karat Yellow Gold Investment Casting Alloy'. Greg Normandeau

'Alloying in the Small Workshop' A. P. Eccles
[1] 9 to 14ct. Yellow Gold Master alloy.

[2] 18ct Pt / PD White Gold Master Alloy

My thanks also to Aldo Reti for assistance with metallurgical terminology.

PROPERTIES OF THE EIGHT NOBLE METALS

ELEMENT	Symbol	NO	M.P. °C	B.P. °C	S.G
SILVER	AG	47	960	2212	10·5
GOLD	AU	79	1063	2966	I9·32
PALLADIUM	PD	46	1552	2927	12·16
PLATINUM	PT	78	1769	3827	21·45
RHODIUM	RH	45	1960	3700	12·41
RUTHENIUM	RU	44	2310	4080	12·45
IRIDIUM	IR	77	2433	4500	22·66
OSMIUM	OS	76	3050	5020	22·61

AND SOME

ALLOYING ELEMENTS

ELEMENT	Symbol	NO	M.P. °C	B.P. °C	S.G
GALLIUM	GA	31	29	2403	5·9
INDIUM	IN	49	156	2080	7·28
LITHIUM	LI	3	179	1377	·534
TIN	SN	50	232	2260	7·31
BISMUTH	BI	83	271.3	1560	9·75
ZINC	ZN	30	419	907	7·2
MAGNESIUM	MG	12	650	1105	1·74
ALUMINIUM	AL	13	659	2467	2·69
GERMANIUM	GE	32	937	2830	5·32
COPPER	CU	29	1083	2595	8·9
MANGANESE	MN	25	1244	2097	7·2
SILICON	SI	14	1410	2355	2·3
NICKEL	NI	28	1453	2732	8·9
COBALT	CO	27	1495	2908	8·9
BORON	B	5	2300	2550	2·34