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The improvement of the characteristics of yellow gold alloys for jewellery production is a topic gaining increasing interest from the jewellery industry, most notably for hollow jewellery products.

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Hardening of Gold Alloys: Mechanisms and Possibilities of Improving their Performance

Summary

The improvement of the properties of yellow gold alloys for jewellery production is gaining increasing interest by the goldsmiths, specially for the production of hollow carat gold jewellery.

The purpose of this presentation is to highlight the metallurgical processes more suitable for hardening gold alloys and to present the results we obtained for some gold alloys.

Key words:

Hardening of gold alloys, cobalt, precipitation, order-disorder, solid solution.

Introduction

The production of thin walled, hollow jewellery occupies a prominent position in the Italian jewellery production: we can say that it approximately corresponds to about 70% of the whole production in the Arezzo district and 50% in the Vicenza district, that are two of the most important Italian districts for jewellery production¹.

The importance of this sector of jewellery production depends on the characteristics of this production, that requires high technology and excellent professional ability. The adoption of ever more sophisticated production techniques increases the cost of manpower, that is hardly comparable with the cost in foreign countries. However the high quality standard achieved in our country represents a distinction and an advantage in the competition.

The production of this type of jewellery is obtained by means of mechanical working, with three fundamental types of process: TIG welded hollow tube, “aggraffato” and “stampato”.

Availability of very thin materials and high hardness of the finished product are fundamental for this type of production. A suitable alloy should satisfy the following requirements:

- very good formability. It should tolerate a high reduction of section with a minimum number of intermediate annealing treatments.
- It should have high structural purity. The ability to reach very low thickness ($< 70 \mu\text{m}$) is adversely affected by undissolved or foreign particles and embrittling elements.

- Core dissolution with acid (HNO_3 or HCl) is an important step in the production of hollow tube. Therefore the alloy should be highly resistant to chemical attack.
- The alloy should be easy to weld or solder. That means that joints free from cracks can be consistently obtained, that are sufficiently strong and wear resistant.
- It should be possible to harden the alloy by heat treatment to a relatively high hardness level (usually higher than 200 HV). The heat treatment should be easy to carry out and should require limited time and reduced cost. Moreover the heat treatment must not generate cracks or internal stress.
- Surface quality should be very good, to enable finishing with conventional techniques. A fine crystal grain is a fundamental requirement for this purpose.
- The scrap should be reusable without problems.

Increasing the hardness of the finished product is a very important aspect also for investment casting, with special reference to yellow gold alloys. Investment cast objects produced with alloys having improved hardness can be more easily finished with conventional techniques and can acquire higher resistance to wear and corrosion².

This work aims to give a survey of the present knowledge on hardenable gold alloys, with special reference to metallurgical properties, hardening mechanism, possible use and limitations. We will discuss more deeply yellow gold alloys, where hardenable materials are more commonly needed.

The metallurgy of hardening: mechanism and examples

It could be appropriate to recall some basic metallurgical concepts before describing the mechanisms for strengthening the metals.^{3, 4, 5, 6, 7, 8}

In solid metals the atoms are geometrically ordered in a regular lattice, the crystal lattice. There are several different types of crystal lattice: each of them is characterized by specific dimensions and level of compactness, that largely determine the properties of the elements. In the most commonly used metals the most important types of crystal lattice are: cubic (e.g. face centred cubic - f.c.c. - for gold and copper or body centred cubic - b.c.c.- for chromium) and hexagonal (e.g. zinc). These types of crystal lattice are shown in Figures 1 and 2. Usually, metals with f.c.c. lattice are ductile and malleable, while metals with exagonal lattice are difficult to work. Metals with b.c.c. lattice have intermediate properties.

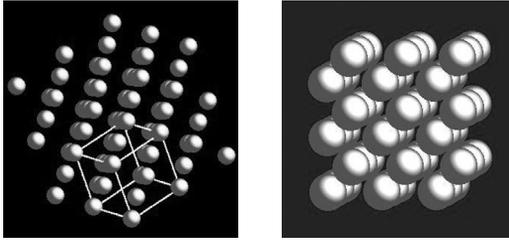


Figure 1 - Schematic representation of the face centred cubic lattice of gold (a) and of the body centred cubic lattice of chromium (b)

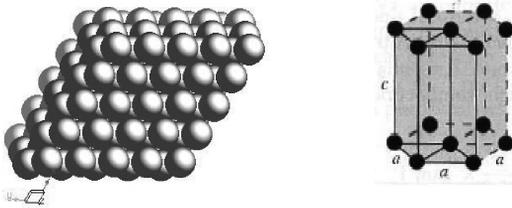


Figure 2 - Schematic representation of the hexagonal lattice of zinc

An alloy is a metallic material containing two or more elements and can be formed by a single phase or by many phases, depending on the type and concentration of the constituent elements. Usually an alloy results from the introduction of an element in the crystal lattice of another element, therefore it has properties different from the properties of the pure elements.

The elements forming an alloy can give rise to different structures: solid solutions and intermetallic compounds.

In a solid solution we name “solvent” the metal retaining its own crystal lattice, while the other component is the “solute”. When the solute atoms replace the atoms of the solvent in the lattice, we have a “substitutional solid solution” (e.g. gold - copper) than usually retains the ductility of the solvent metal.

When solute atoms are much smaller than the atoms of the solvent, they are accommodated in the spaces between the atoms of the solvent and generate an “interstitial solid solution” (e.g. carbon in iron) that usually shows reduced workability.

Lastly, intermetallic compounds form separate phases with a well defined range of chemical composition and a structure different from the structure of the pure components.

Information on the behaviour of the different metal systems can be found in the “phase diagrams” or “equilibrium diagrams”, where the effect of the temperature and composition on the structure of the alloys formed by mixing two or more elements is graphically represented.

The interaction between the atoms of different elements that are present in a crystal lattice can cause significant changes of the mechanical characteristics with respect

to the pure metals. This is the case of some gold alloys, which can be hardened with a heat treatment. This characteristic, if properly used, can give considerable benefits in jewellery production and give new possibilities for production technology and product diversification.

Then we can ask: when can an alloy be considered hardenable by heat treatment? The hardness level required by the goldsmith in the finished product depends on different factors, like the shape, the weight, the thickness and the use planned for each object. In the specific case of yellow gold alloys, where the need for high final hardness is particularly widespread, we can aim to reach a final hardness level ranging from 180 to more than 210 HV (Vickers Hardness), that corresponds to an increment of about 50% with respect to the starting hardness level. On the basis of this statement, Legor has created his own standard, stating that an alloy can be considered as hardenable when its hardness can be increased of at least 50% with a suitable heat treatment.

Now we will briefly describe the main metallurgical mechanisms that make hardening (or strengthening) possible: solid solution hardening, hardening by ordering and precipitation hardening.

Solid solution hardening

Alloys are usually stronger than the pure metals. This is due to the fact that a solute atom, when introduced into the lattice of the solvent metal, originates a field of elastic distortion immediately around.

This disturbance hinders the plastic deformation produced by an external load, and increases strength and hardness of the material.

The strengthening effect increases with increasing solute concentration and is more marked when the size difference between solute and solvent atoms is larger.

When we look to an alloy with 75% wt gold (18 ct), if the remaining 25% is formed by silver, we have a 36 HV hardness in the annealed alloy, slightly higher than the hardness of annealed 24 ct gold (20HV). If the alloy contains 25% copper in the place of silver, the hardness of the annealed alloy reaches 115 HV. This is because silver atoms are slightly larger than gold atoms, while copper atoms are much smaller than gold atoms. In both cases the solute originates a field of elastic distortion in the lattice. There will be a tensile stress for smaller atoms and a compressive stress for larger atoms.

The effectiveness of this disturbance for strengthening the alloy does not depend on the presence of larger or smaller solute atoms, but on the absolute value of the size difference between solvent and solute atoms.

The mechanism of solid solution hardening has little effect in high caratage alloys, because in these alloys the solute represents only a limited fraction of the material.^{9, 10, 11, 12}

Strengthening by disorder to order transformation^{3, 4, 5, 6, 7, 8}

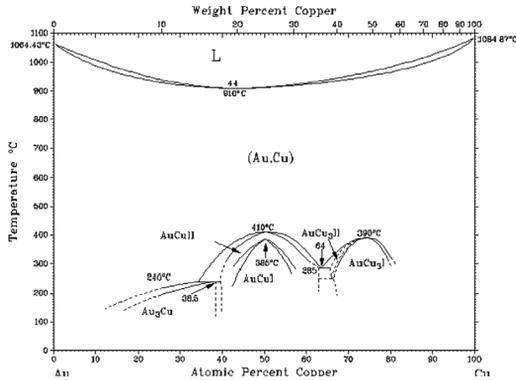


Figure 3 - Gold-copper phase diagram showing the stability zones of the different phases

When we consider the gold-copper phase diagram, we see that, for an alloy formed by 50% gold atoms and 50% copper atoms, above 410°C we have a solid solution with a random distribution of gold and copper atoms. When we slowly cool the alloy below the 410°C critical temperature, the atoms will occupy new positions in the lattice, with an ordered distribution, through a diffusion process.

In the new structure there is an apparent superposition of a lattice of copper atoms on a lattice of gold atoms, that distorts the original lattice and hardens the alloy.

It is very important to underline the importance of the cooling rate on this phenomenon. In the case of a 18 ct gold-copper alloy, fast cooling (water quenching) from the annealing temperature gives about 185 HV hardness, while slow cooling (air cooling) gives an alloy with hardness higher than 240 HV. Rapid cooling leaves no time enough to the atoms to rearrange themselves, but the ordering process can take place if we hold the quenched alloy at 150-300°C for a suitable time.

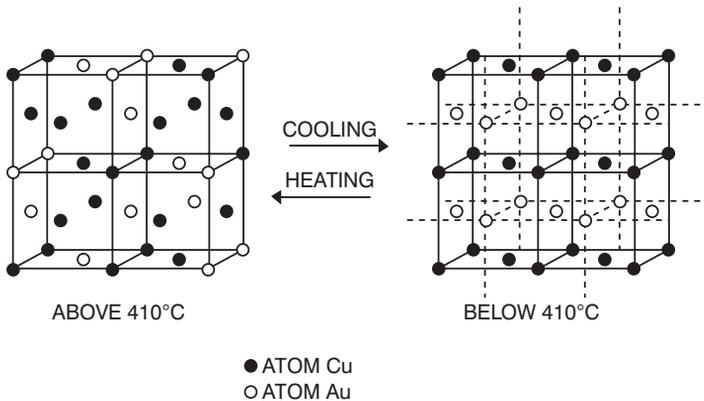


Figure 4 - Disorder to order transformation in gold-copper alloys

The fact that the ordered alloy is considerably harder and less ductile than the disordered alloy creates problems for investment casting with stones. When cooling the tree, we should avoid the disorder to order transformation with a fast cooling, but there is a risk of thermal shock for the stones.

The importance of composition can be exemplified in the case of the master alloy A (Ag5%, Cu93%, Zn2%), when it is used for making gold alloys with different caratage. When the same master alloy is used for making gold alloys with different caratage, the gold/copper ratio changes, and so changes the response of the alloy to heat treatment. When heat treated at about 250°C, the homogenised and quenched 18 ct alloy hardens up to 320 HV, but it can give brittleness problems if it is slowly cooled after annealing at 550-650°C. When used for investment casting with stones, this alloy can give problems, while it is very good for making wire and tube. If we use the same master alloy for producing a 14 ct alloy, we obtain an alloy that is not hardenable. That is, the same master alloy can give gold alloys with different response to heat treatment.

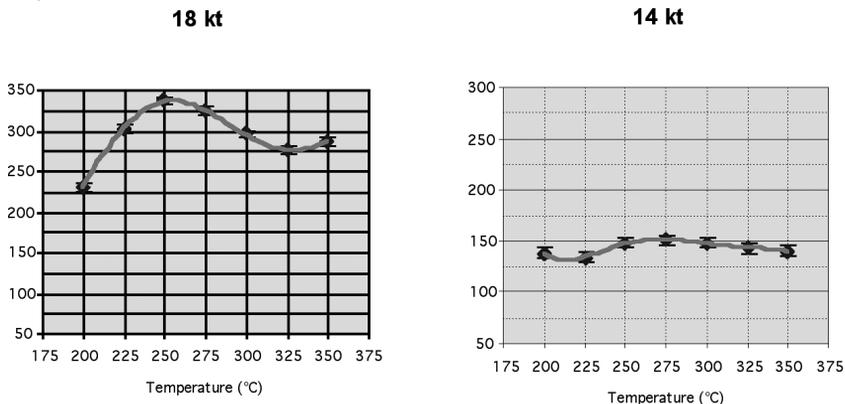


Figure 5 - Hardening of 18 ct (left) and 14 ct (right) gold alloys obtained with the master alloy A. We can see that the result of the heat treatment changes with the caratage

Precipitation hardening^{3, 4, 5, 6, 7, 8}

The systems must satisfy two requirements to make precipitation hardening possible:

- sufficient mutual solubility
- a solubility limit rapidly decreasing with decreasing temperature

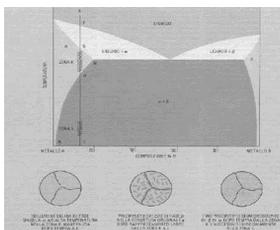


Figure 6 - Hypothetical binary equilibrium diagram illustrating the principle of precipitation hardening

Let us denote with α the A rich partial solid solution and with β the B rich solution. Let us now refer to the vertical line drawn in Figure 6: if we rapidly cool the alloy from the single phase field, there is no time for precipitation of the β phase in the α phase matrix, that will remain homogeneous. With a slow cooling coarse precipitates of β will form in the α phase. However the best microstructure to obtain good characteristics in the alloy should be formed by a uniform dispersion of submicroscopic particles of β in the α matrix. Such microstructure can be obtained by age hardening and represents the best solution for hardening, because the very small particles of precipitated β phase offer the maximum resistance to plastic deformation. Such structure can be obtained in the following way: the alloy should be homogenized (solution annealed) by heating at a temperature slightly lower than the solidus temperature, to dissolve all β particles in the α matrix. Then a fast cooling (water quenching) gives no time enough for the expected precipitation of the β phase to occur and the single phase structure is retained as a metastable super-saturated solid solution at room temperature. On reheating the quenched alloy to a relatively low temperature for a suitable period of time, the β phase precipitates out of the α grains in such a way that a very large number of extremely small submicroscopic particles are obtained. The reheating treatment is known as ageing and it results in a considerable increase in the strength and the hardness of the alloy.

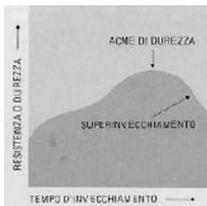


Figure 7 - A typical age hardening curve, showing the effect of the ageing time on the properties of the material

As shown in Figure 7, the length of ageing time is very important. If it is too long (usually, longer than 60-90 min.) there are not further benefits, but strength and hardness begin to fall again. This is known as overageing and is due to the continuing growth and coalescence of the β phase particles. This reduces strength and hardness considerably.

The equilibrium diagram of the silver-copper system, Figure 8, is very similar to the A-B hypothetical binary equilibrium diagram shown in Figure 6, and this indicates the possibility of obtaining precipitation hardening in silver-copper alloys (e.g. sterling silver).

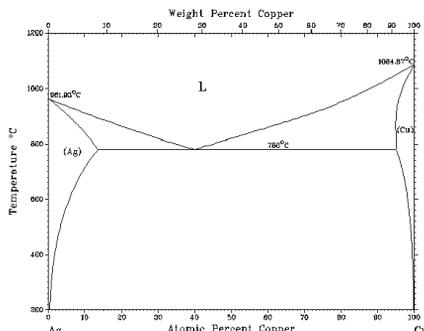


Figure 8 - Silver-copper equilibrium diagram, showing the possibility of precipitation hardening

A research on silver alloys (13), carried out on Ag 925 homogenized at 750°C and hardened at 300°C/1 hour, showed the potential of this mechanism. An increase of hardness from 50 HV in the standard sterling silver to 120 HV in the hardened alloy has been obtained.

We can find in the technical literature some information and patents on the use of calcium and rare earths elements (cerium, lanthanum, yttrium, gadolinium etc.) for developing gold alloys that can be precipitation hardened. However these alloys can give problems for casting, cold working and recycling of scrap.

In nickel white golds slow cooling from the annealing temperature can cause the formation of unwanted precipitates, and this shows the importance of the cooling rate for the alloys of this type. In fact the selection of a suitable rate of cooling is fundamental for these alloys. It should not originate dangerous internal stresses, but, at the same time, it should prevent precipitation, to avoid embrittlement and undesired colour changes^{14, 15, 16}.

A practical example of the hardness levels that can be attained in a nickel white gold alloy is given by the master alloy B (Cu 71%, Ni 15%, Zn 14%) that is used for producing high quality white gold alloys for cold working, Figure 9. In this case too the different effects obtained with different gold fineness shows the importance of alloy composition on metallurgical behaviour.

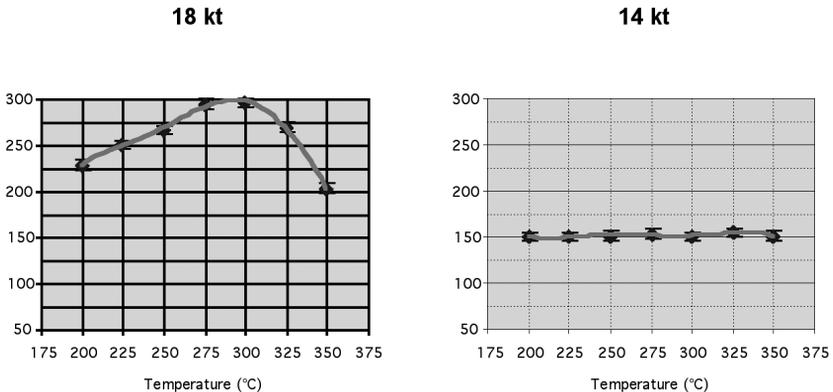


Figure 9 - Hardening of 18 ct (left) and 14 ct (right) white gold alloys obtained with the master alloy B. The effect of composition on the properties is evident

What we have said up to now makes clear that some alloys in the ternary gold-silver-copper system, i.e. the coloured carat golds, can be hardened by heat treatment, to induce both disorder to order transformation and precipitation hardening. A thorough characterisation work has given interesting results on the effect of silver concentration on hardening of gold alloys of different fineness.

Figure 10 shows the curves obtained for 9 ct gold alloys. When the percentage of silver in the master alloy increases, a progressive increasing of hardness is observed in the gold alloy. In 9 ct alloys gold and copper are far from the stoichiometric ratio

that could make the disorder to order transformation possible. Therefore precipitation hardening is the only hardening mechanism we could consider. Precipitation hardening is influenced by the silver/copper ratio, and this explains the slope of the curves.

The behaviour of the hardened alloy is similar to the as cast alloy, but the curve is shifted upwards, thanks to the beneficial effect of heat treatment.

Durezza leghe auree 9 kt

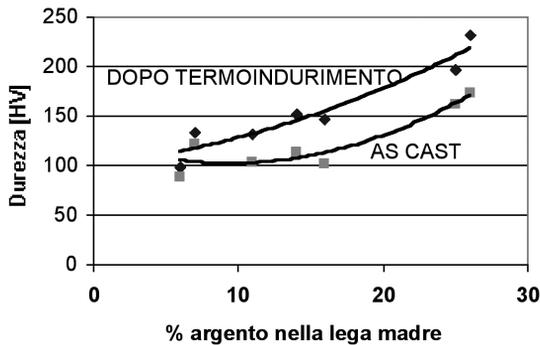


Figure 10 - Hardness of as cast and hardened 9 kt alloys with different silver content

Let us consider now the age hardening curves of two 9 ct alloys for cold working having different silver content, that have been produced with two different master alloys, low silver alloy C (Zn 22%, Ag 6%, Cu 72%) and high silver alloy D (Zn 14%, Ag 25%, Cu 61%), Figure 11. We see that the low silver alloy does not show hardness increase after heat treatment, while the high silver alloy shows an increase of about 40 HV compared to the starting level (150 HV). The above given results show that 9 ct gold alloys with low silver content cannot be hardened by heat treatment.

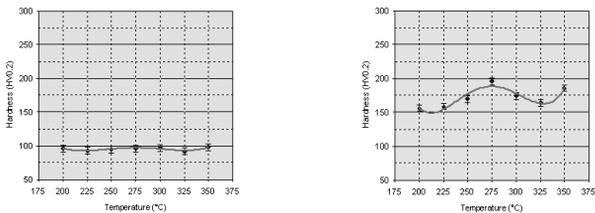


Figure 11 - Comparison between the age hardening curves of two 9 ct gold alloys with different silver content. The low silver alloy (left) shows no hardening, while the high silver alloy (right) can be appreciably hardened

The behaviour of 14 ct alloys is quite similar, with slightly higher hardness levels, thanks to the increased copper content, Figure 12.

Also in this case, in the as cast alloys hardness increases with silver content. This can

be ascribed to the rate of cooling after casting. Cooling is not instantaneous and could consent some degree of precipitation hardening.

Durezza leghe auree 14 kt

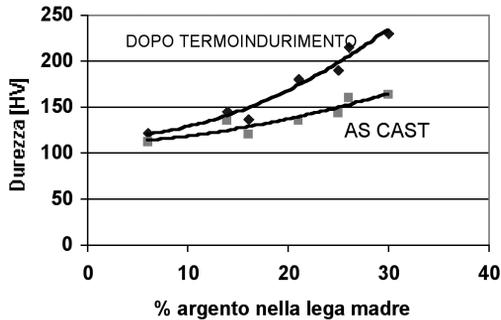


Figure 12 - Hardness of as cast and hardened 14 ct alloys with different silver content

In this case too the examination of age hardening curves can help to understand some metallurgical aspects: if we compare the 14 ct gold alloy obtained with the master alloy E (Zn 21%, Ag 6%, Cu /73%) with the 14 ct alloy obtained with the master alloy F (Zn 11%, Ag 30%, Cu 59%), Figure 13, we see that the second alloy shows hardness values higher than the first one and can also be further hardened by ageing. The use of the master alloy F is recommended for producing gold alloys with high strength and low formability, while the use of the master alloy E is recommended when good ductility and formability are required.

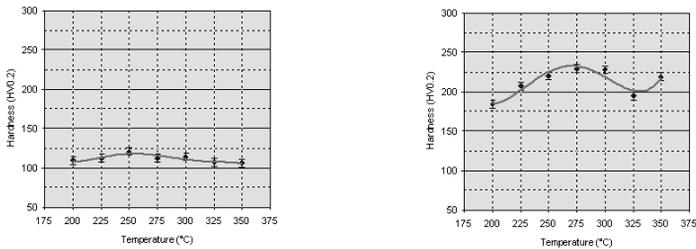


Figure 13 - Comparison between the age hardening curves of two 14 ct gold alloys with different silver content, obtained with the master alloys E (left) and F (right) respectively. The effect of silver content on hardenability is evident

The trend is inverted for 18 ct alloys, Figure 14. Copper concentration is sufficient for the disorder to order transformation to occur, and it becomes the prevailing hardening mechanism with lower silver content. When silver content increases, precipitation hardening becomes more important. The hardness values obtained from the as cast material agree with the mechanism of precipitation hardening. In 18 ct alloys the different behaviour of silver and copper is more important, so higher silver content corresponds to lower hardness.

Durezza leghe auree 18 kt

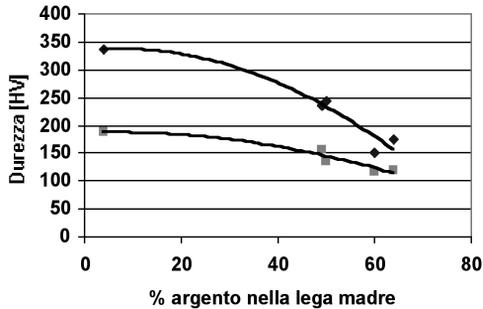


Figure 14 - Hardness of as cast and hardened 18 ct gold alloys with different silver content

The age hardening curves of the 18 ct gold alloys obtained with the master alloys G (Zn 2%, Ag 4%, Cu 94%) and H (Zn 2%, Ag 64%, Cu 34%) respectively are shown in Figure 15. Both alloys can be appreciably hardened by heat treatment, but hardening is more effective in the gold alloys prepared with master alloy G. Therefore for 18 ct alloys with this copper and silver content the disorder to order transformation, regarding gold and copper, is a hardening mechanism more effective than precipitation hardening, regarding the silver-copper system.

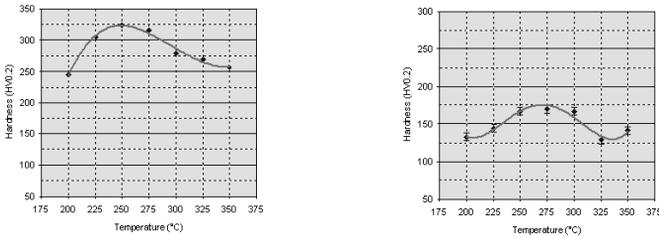


Figure 15 - Comparison between the age hardening curves of two 18 ct gold alloys with different silver content, obtained with the low silver master alloy G (left) and the high silver master alloy H (right) respectively

Strengthening by disorder to order transformation or precipitation hardening are the main mechanism for increasing the hardness of gold alloys by heat treatment. These mechanism can be favoured by secondary strengthening processes that are not sufficient to increase the strength of the alloys significantly^{17, 18}. Some elements able to increase hardness through different types of mechanism are cobalt, antimony, nickel and silicon.

Solubility of cobalt in gold is low at low temperature and it makes cobalt suitable for age hardening. Cobalt acts through precipitation hardening and grain refining. However some other factors make the use of cobalt questionable: e.g. the high melting point and the affinity for oxygen at high temperature. It should also be mentioned that the cobalt concentration in the gold alloys should be accurately determined: the composition of the alloy and the planned annealing temperature should be taken into account.

The remarkable hardening effect of cobalt in high caratage alloys should be underlined, because hardness levels higher than 200 HV can be obtained in the finished product¹⁹. A 22 ct yellow gold alloy has been obtained by us, that can reach 231 HV after hardening heat treatment.

Another example of hardening by heat treatment is given by titanium, that has been used in the 990 Gold alloy²⁰. This alloy contains 1% titanium and reaches about 200 HV after suitable heat treatment. However working with 990 Gold is not easy, because it requires an argon atmosphere for melting, casting and homogenizing treatment.

Conclusions

Our purpose is to review the most important mechanisms for hardening gold alloys. We can see that wanted or even unwanted hardening of gold alloys by heat treatment are very important for jewellery production.

The hardening processes are influenced by three fundamental parameters: composition (and, for a given master alloy, caratage), temperature and time. A deep knowledge of the different factors is required to anticipate the effect of heat treatment on the hardness of the different alloys. An accurate control of the various parameters is required, to get the best result from heat treatment. Temperature control is fundamental and should be performed with reliable and accurately calibrated instruments.

The hardening curves we have shown, evidence the possibility of obtaining substantially different results for relatively small temperature differences (for a given treatment time). Moreover it has also been shown that the structure homogenisation treatment is very important and sometimes fundamental, specially when second phase precipitation is the principal hardening mechanism. This subject is particularly delicate when heat treatment should be performed in a narrow range of temperature.

When we consider the principal hardening mechanisms for gold alloys (disorder to order transformation and precipitation hardening) we see that a satisfactory increase of hardness cannot be obtained for all alloy compositions. Usually the problem of poor hardenability occurs particularly with low silver, low caratage alloys.

In this case it will be necessary to resort to alternative alloying elements, that should be able to give a hardening effect.

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