



ANDREA FRISO
Legor Group S.p.A.

Andrea Friso performs at Legor Group S.p.A. as Sales Division Manager of Master Alloys. Materials engineering graduated in 2003, he starts his cooperation with Legor Group in 2004 by writing his graduation thesis about 'innovatively colored gold alloys'. He is the company business role operating between sales force, production and R&D, relying upon matured professional experience on the different product types and their positioning on different markets. He supports sales forces on commercial planning and the achievement of objectives together with their periodic control. He cooperates with the technical and R&D dept. as for development, enhancement and promotion of products.

The world of costume jewellery and fashion accessories production is a broad field, which in some respects has similarities with the jewellery sector. The aim of this work is to provide an overview on the world of brasses and bronzes, with reference to the decorative sectors only, in particular those of costume jewellery and fashion accessories. The main categories of these alloys, and their most important properties for the production process, will be identified. The technologies used, the methods of protection against wear and oxidation, and the possibilities for technological innovation in these areas will be outlined.

Alloys for Costume Jewellery and Fashion Accessories: an introduction to the field

Andrea Friso, Massimo Poliero, Andrea Basso

Legor Group S.p.A., Bressanvido (VI), Italy

INTRODUCTION

This article intends to focus its attention on particular aspects of very large areas such as the field of costume jewelry, or those identified by the term "accessory industry", or "fashion industry". The goal is to give an overview on the production processes involving metals and alloys, the metallurgy of non-ferrous alloys generally used, and technologies for surface protection of finished products.

The main reason for which this article is presented at a conference traditionally dedicated to the production of precious jewelry is the fact that, although it doesn't use precious metals in the formulations used for the production of objects, the field of costume jewelry and fashion uses technology and finishing which are in many cases similar to those of precious metal industry. Moreover, in recent years we are witnessing to an interesting dialogue that has begun between the precious and the non-precious sectors: as a matter of fact, on one hand an increase in the prices of precious metals has pushed gold jewelry producers to lower the intrinsic cost of the jewel, moving from gold to silver and from silver to bronze or brass. On the other hand, manufacturers of costume jewelry become more and more challenged to find the points of differentiation to enhance their product. In both cases there is an important role for surface protection and in particular for galvanic processes to obtain a satisfactory corrosion resistance of the product.

There are also several ideas from the fashion industry that could be exploited also in the jewelry sector, at least in terms of methodology to identify or standardize the forms of internal control over product quality.

MARKET ANALYSIS

The sectors that use copper alloys for decorative uses are actually a small niche of the market with regard to what is currently produced as copper and its alloys. According to a study published by the European Copper Institute in 2012, the world consumption of copper and its alloys has been a total of 25.5 million metric tons, out of which about 4 million tons for the European market. Of this amount, most are intended for technological uses, with a predominance of the energy sector and the conduction of electricity. According to this study the percentage of material that is directed to the production of alloys which can be compatible with the decorative sector is around 1%, then with a theoretical size of about 260,000 tons worldwide, and 40,000 tons for the European market. These numbers may not seem relevant for other industries, but they become rather conspicuous in the case of producers in the industry of fashion and jewelry, and they represent a completely different size range than that of gold jewelry alloys, which have moved in year 2011, in regard to the consumption of gold alloys as equal to a little less than 2000 tons for the world market of which only about 180 tons on the European market (source: Thomson Reuters Gold Survey).

METALLURGICAL CHARACTERISTICS

Regarding the field of costume jewelry, two of the categories of alloys mainly used are clearly brasses and bronzes, which are probably the best known among the copper-based alloys, as used since antiquity. Copper alloys are notoriously appreciated because they are harder and more resistant than pure copper and because their mechanical properties can be further enhanced by cold working or, in some specific cases, with a suitable heat treatment. Additional alloying elements may improve the characteristics of castability and it is well known the use of bronzes and brasses containing special added elements to improve the performance in investment casting.

The most commercially important copper alloys are classified as follows:

1. Brasses : Alloys of copper and zinc, which can be divided into :
 - a. Alpha Brasses containing up to 36 % zinc, which are further divided into :
 - i. Red Alpha Brasses with 5-20 % zinc;
 - ii. Yellow Alpha Brasses with 20-36 % zinc ;
 - b . Alpha + Beta Brasses containing from 36% to 45 % zinc .

2. Bronzes : Copper alloys containing up to 12% of an alloying element, obviously different from zinc, which can be divided into:

- a. Tin bronzes;
- b. Silicon bronzes;
- c. Aluminum bronzes;
- d. Phosphorus bronzes.

3. White metals: alloys of copper, nickel and zinc.

In addition to the copper-based alloys, which for economic reasons are considered higher-end products in some areas, low-melting alloys are used, such as zamak, trade name that indicates a family of zinc-based alloys, whose main other elements are aluminum, magnesium, copper, antimony.

The parameters from which the choice of a specific type of alloy is made are several: the first is the price of the alloy, followed by the type of manufacturing process that will be used, and then focusing on specific technical details.

BRASSES

Brasses are essentially alloys of copper and zinc. Some of them also contain small levels of lead, tin or aluminum as alloying elements. Slight changes in the chemical composition lead to a desired combination of color, hardness, mechanical strength. The mechanical strength and ductility grow with the addition of zinc up to a content of about 30% ; above, although the resistance continues to grow, the ductility decreases rapidly. The growing presence of the Beta solid solution, harder and more fragile than the Alpha, is more visible and thus the alloy becomes less tenacious.

Yellow and red Alpha brass

Red Alpha brasses are alloys with low zinc content (from 5% to 20%): they have a color ranging from pink to golden and are also known with the name of "fake gold". In this category there are the most widely used formulations, ranging from 5% to 15% zinc that provide progressively paler colors, and a decrease in the workability with increased zinc content. Particularly appreciated are brasses at 5% and 10% zinc for their good workability and low tendency to smoke coming from the evaporation of the zinc during the melting phase.

Alpha yellow brasses are alloys that contain between 20% and 36% zinc; they combine good mechanical strength and high ductility and are therefore particularly suitable to undergo deformation by drawing and stamping. The addition to yellow brass of 0.5% - 3% lead improves machinability, so this type of brass is used for threaded machine parts, keys, lock parts, watches. We'll see how the title of lead in the alloy undergoes limitations on use due to new regulations.

Alpha + Beta brasses

Alpha + Beta brasses contain zinc in levels between 35% and 40% and at room temperature they have a microstructure with two phases (Alpha and Beta). Due to the presence of the Beta phase, harder and more brittle, these alloys are more difficult to work; the high zinc content lowers the melting temperature.

Brasses with lead

Brasses containing lead have specific characteristics and are used for special applications, mainly for mechanical processing. Lead is an element that does not form a solid solution with the copper or with the Cu-Zn solution, but remains completely separated; being the last element to solidify (for its lower melting temperature), it is distributed to the grains boundaries of the Cu-Zn alloy. A binary Cu-Zn brass, for its high plasticity is worked with difficulty to machine tools, because long chips are formed, due to the continuity of the alloy microstructure. If a small quantity of lead (2-3%) is added to the composition, this separates to the grain boundaries and while working the machine tool breaks more easily the chip at each discontinuous layer of lead that it encounters while processing. The presence of lead also has the advantage of facilitating the operations of mechanical finishing with removal of deburring, drilling, or milling operations.

The presence of lead, together with a very low content of impurities, allows to work at increasingly higher cutting speed by limiting the wear of the tool cutting edge and therefore increasing the time between a sharpening (or exchange) and the other.

Lead brasses have a high content of zinc: the high percentage of β structure reduces the ductility of the alloy, but it improves the deformability in hot forging. Being used primarily in processes of machining tool, the low deformability of the semifinished product is no impediment to their use; as a matter of fact, lead brasses represent a material of great consumption in several different sectors.

In brasses having Alpha structure one must keep low lead content, as this may deteriorate the workability at all temperatures. Lead brasses with higher zinc content, in which Beta phase is present at processing temperatures, are hot

formable: the solubility of lead in the Beta phase avoids the presence of a liquid phase at the grain boundary. Lead brasses with high % of Beta phase are therefore suitable for the hot working; they are generally supplied in the form of bars in different size.

The lead brass rods, especially those in large sections, exhibit considerable internal stresses unevenly distributed in the section for the different degree of deformation, particularly in areas near to the cold finishing extruder; such tensions can lead to breakage or to stress corrosion, a phenomenon favored by the high percentage of Beta phase present; bars must therefore be subject to stress relief treatment.

Lead brasses are also very sensitive to the phenomena of "dezincification", a phenomenon of selective corrosion that attacks mainly the Beta phase microstructure, rich in zinc. The dezincification of the Beta phase can not be inhibited by addition of arsenic, antimony, phosphorus: these elements are effective only in the Alpha phase.

Examples of this type of composition are alloys with zinc content between 37% and 39%, and lead between 1% and 4%; they are suitable for the production of fine mechanics such as watch balance arms and watch cases, parts for watches and clocks, gears, gearboxes, bolts, screws, pins, eyelets, hooks, household items, small metal parts, locks.

Workability index measurement

For brasses designed for machining with chip removal, as well as for other metallic materials, it is extremely important to have a method that allows to quantify the ability of an alloy to be worked with machine tools. In regards to the suitability for drilling a test is used which consists in drilling a sample at known thickness acting with constant rotation speed and feed force on the tool. The degree of workability is given by the time it takes for the tip to perform a predetermined advancement stroke. Another test is to measure the heating that undergoes a particular tool during machining of the test sample .

The subdivision of brass with respect to machinability involves three groups of alloys:

Group 1: alloys with high workability (free-cutting alloys), in which an appreciable quantity of lead, sulfur or tellurium are added to improve the processing characteristics of the tool;

Group 2: low machinability alloys, mainly binary lead-free brass, containing copper between 60 and 85%;

Group 3: hard to machine alloys, such as brass with low zinc content.

The alloy CuZn36Pb3 (free-cutting brass) belongs to the group 1 and is used as a reference for the chip removal working, with an index of 100. All the alloys of group 1 have small and brittle chippings. Since this type of chip easily separates leaving the tool or the machine free, they are very suitable for fast processing to machine tools with chip removal.

Typical shavings in the processing of alloys of group 2 are slightly open with spiral or helix shape (which resembles a spiral staircase). These chips are relatively fragile and a small additional distortion will break them into separate fragments.

A typical chip of an alloy of group 3 is long and continuous and is often curved. Because it is strong and tough, this chip will bear considerable distortion without breaking down.

BRONZES

The term bronze, which designated initially only the copper-tin alloys, is now generally attributed to any alloy of copper not containing zinc and containing an element instead among the following: tin, aluminum, silicon, beryllium.

Tin bronzes

Tin bronzes (with levels between 1% and 12%) are among the most common and are characterized by the presence of small amounts of phosphorus as a bath deoxidizer. Tin increases the hardness and wear resistance of the copper more effectively than zinc. Alloys up to 8% tin, easily cold machinable, are used for production of semi-finished products for the production of sheets, coined products, gaskets, springs. Elements characterized by greater resistance to wear can be produced with titles in tin comprised between 8% and 12%. Tin can reach up to very high values (20-25%), characterized by extreme hardness and with compositions similar to those of galvanic baths for finishing as the so-called "white bronze", as tin at this level is sufficient to whiten the alloy. Zinc is sometimes added as a partial replacement for tin. The result of the addition of zinc is an improvement of the properties of castability and toughness of the casting, similarly to what happens in some goldsmithy alloys where zinc has the effect of lowering the melting temperature and to widen the melting range.

Beryllium bronzes

These alloys have superior characteristics compared to those tin bronzes, and are used in areas that need to combine good performance in casting to a marked effect of age-hardenability, excellent properties of elasticity, good tool response. An example is the use in the eyewear industry. They are particularly popular in other technology areas, such as electrical engineering, especially in the manufacture of springs and fatigue contacts, or high-strength bolts that have to withstand corrosion. These alloys may meet problems from the point of view of pricing (originated by the relative difficulty of supply of beryllium metal). Of particular interest are alloys containing beryllium comprised between 1.3% and 3 % in which the effect of the age-hardening is remarkable. The hardness of a commercial alloy with 2% Beryllium subjected to age-hardening at 350 ° C for 90' in fact sees an increase from 125 HV as cast state to 220HV of age-hardened state.

White metals

White non-precious metals belong to the group of ternary copper-nickel-zinc alloys called "Alpaca" in Italy and abroad under different names (Neusilber, Nickel silver, white copper, German Silver, Argentane). The addition of nickel to copper-zinc binary alloys affects :

- The color of the alloy, where nickel content increasing up to 10-20% changes from yellow to shades closer to silvery white;
- The mechanical properties that improve compared to brass.

In some cases silver is added to enhance the color of the alloy without having an excessive hardening effect.

For reasons of color, alpacas are used for ornamental articles usually, almost always finished with galvanic processes of silvering or gilding.

In respect of compliance with the UNI EN 1811:2011, it must be said that the normal alpacas are not able to exceed the requirements of the legislation, as the title in nickel and the absence of precious elements in the alloy leads to values of non-compliant nickel release. In fact, the standard UNI EN 1811 was created with the intention of limiting the problems related allergenicity of the nickel contained in a metal alloy in contact with the skin. Since the first version the investigation studied a broad category of artifacts that goes under the name of "jewelry", a term that may mean in English both the precious jewelry (including the one in white gold) and the non-precious jewelry, which is also referred to as "costume jewelry" or "faux bijoux", which has a much lower resistance to nickel release due to the absence of precious elements.

Zamak

The term "Zamak" refers to a family of low-melting alloys based on zinc, aluminum, magnesium, copper (hence the name, which is an acronym from the German for "Zink, Aluminum, Magnesium, Kupfer"). These alloys have melting temperatures below 400°C, very low elongation at rupture; they are rather inexpensive; thanks to these features have been chosen in areas characterized by the need to use a cheap production process, such as the centrifugal casting with the use of silicone molds, not having specific demands of high mechanical strength. It is in fact alloys with very low elongation at break, lower than 7%. They are used for the production of zippers, handles, locks, objects.

IMPURITIES AND INTERNATIONAL STANDARDS

At international level, both in Europe, and in the U.S., a growing emphasis on the possible problems to the health of the user that is in prolonged contact with articles of jewelry is present, in case of alloys which contain substances that have a documented toxicological significance.

In the extensive list of metallic elements that may be relevant from this point of view, the best known and most used traditionally for technical reasons are cadmium, lead, nickel. These three elements are for different reasons cited by toxicological studies as potentially dangerous elements, and the direction taken by the regulatory authorities is therefore to minimize exposure to alloys containing these metals, with particular attention to children who are physiologically more vulnerable to the absorption of harmful substances.

The legislation which identifies the limitations on the use of hazardous substances in the field of European legislation is the REACH (Registration, Evaluation, Authorization of Chemicals), which through a single piece of legislation enacted by Parliament and which came into force on June 1st, 2007, replaces much of the previous legislation relating to chemical substances and preparations and provides specific guidance relating to restrictions on the presence of certain heavy metals in the composition of metal alloys.

Similarly, in the U.S. some laws were enacted (in California, the Health and Safety Code section 25214.1-25214.4.2, about cadmium and lead), and along with these, directions by the Consumer Product Safety Commission, the leading federal American agency ruling the lead content in items for the consumer market. The California law speaks of maximum 600 ppm of lead in the formulation of the alloy, in order to be marketed on the market as an object of jewelry. To the best of our knowledge, a clear position in the U.S. market in respect of nickel and its problems of allergenicity is lacking. European legislation is in this case more stringent and protective of final consumers than the American ones, although we can say that in this respect there are some gaps from the practical point of view with regard to the tests carried out using the method EN 1811 2011.

Focusing on a European level , within the REACH Regulation (1907/2006 CE), some points of Annex XVII of the Regulations are of particular interest, of which we give the details .

Nr 1907/2006, paragraph 27, limitations concerning nickel: it can not be used in quantities greater than 0.05% (500 ppm):

a) in all post assemblies which are inserted into pierced ears and other pierced parts of the human body unless the rate of nickel release from such objects is less than 0.2 $\mu\text{g}/\text{cm}^2/\text{week}$ (migration limit);

b) in articles intended to come into direct and prolonged contact with the skin such as

- a. earrings,
- b. necklaces, bracelets and chains, anklets,
- c. rings ,
- d. wrist watch cases , watch straps and tighteners,
- e. buttons, tighteners , rivets, zippers and metal marks, when these are used in garments,
- f. if the rate of nickel release from the parts of these articles coming into direct and prolonged contact with the skin is greater than 0,5 $\mu\text{g}/\text{cm}^2/\text{week}$;

c) in articles such as those listed in letter b), if they have a nickel coating unless such coating is sufficient to ensure that the rate of nickel release from the parts of these articles coming into direct and prolonged contact with skin does not exceed 0.5 $\mu\text{g}/\text{cm}^2/\text{week}$ for a period of at least two years of normal use of the article.

The UNI EN 1811:2011 is the reference for the execution of the release test, and entered into force April 1st, 2013.

Nr 494/2011 EC: Cadmium content in alloy is limited to 100 ppm, if used for the production of jewelry or in the production of alloys for brazing. The use of cadmium in jewelry, plastics and brazing sticks is banned in the EU since 10 December 2011.

Nr 836/2012 EC, adding the item 63: Lead and its compounds are not to be placed on the market or use in individual pieces of jewelry if the concentration of lead (expressed as metal) in that portion is equal to or greater than 0,05 % by weight. With "articles of jewelry" reference is to articles of jewelry, costume jewelry and hair accessories (bracelets, necklaces and rings , piercing jewelry, watches and bracelets for men). This limitation does not apply to the internal components of watches, inaccessible to consumers, glass crystals, semi-precious and precious stones and synthetic or reconstructed are also in derogation, except those treated with lead or its compounds or mixtures containing such substances. The rule clearly states that the limitation is found only in areas relating to jewelry; currently other industrial sectors are excluded. The standard has been operational since October 9th, 2012.

Toxicological effects of lead

The toxic effects of lead have been known for a long time, especially in its acute manifestations (saturnine colic). But recently, as has happened to many other pollutants, the threshold level has been significantly lowered. Absorbed mainly through respiration and nutrition, lead is not metabolized, but mostly expelled, while the rest (about 20%) is distributed into tissues. Lead is capable of damaging virtually all tissues, especially the kidneys and the immune system. The most deceptive and dangerous effect of lead poisoning is towards the nervous system. Lead neuropathy affects mostly in the development age, with behavioral disturbances and cognitive impairments. Epidemiological studies have shown a strong correlation between the level of lead in the blood and bones and poor performance in aptitude tests (IQ or psychometric tests), and a similar correlation was also found in behavioral studies on animals exposed to lead shortly after birth. The learning process takes place through the formation and remodeling of synapses and the toxic effect of lead on this process suggests that this metal damages specifically synaptic function. The particular vulnerability of children to lead poisoning is one of the reasons for which the metal is affected by restrictions on the use, due to the risk of accidental ingestion or prolonged contact with mucous walls.

Toxicological effects of cadmium

Cadmium derives its toxicological properties of its chemical similarity to zinc, an essential micronutrient for plants, animals and humans. Cadmium is biopersistent and, once absorbed by an organism, remains resident for many years (in the order of decades for humans) before being ejected.

In humans, the long-term exposure is associated with renal dysfunction. High exposure can lead to obstructive lung disease and is linked to lung cancer, even if the data relating to the latter are difficult to interpret because of other factors. Cadmium can also cause problems with bones (osteomalacia, osteoporosis) in humans and in animals.

Toxicological effects of beryllium

It is a metal that can be very harmful if breathed in, because it can damage the lungs and cause pneumonia. The effect of the most commonly known of beryllium is called berylliosis, a dangerous and persistent disorder of the lungs that can also damage other organs such as the heart. Inhalation of beryllium in the workplace is the main cause of berylliosis. Beryllium can also cause allergic reactions in people who are hypersensitive to this chemical. These reactions can be very heavy and can even cause a person to fall ill, a condition known as chronic beryllium disease (CBD). Apart from berylliosis and CBD, beryllium can also increase the chances of developing cancer and DNA damage.

Toxicological effects of nickel

Nickel is a metal widely used in various fields, mainly for the production of steels and ferrous alloys. We have seen how it is used also for the production of copper-based alloys of white color. Nickel has been listed as a substance of concern for human health. In addition to a possible risk of carcinogenicity due to the inhalation of dust or fumes, among the main reasons for which the REACH legislation intends to limit the nickel in artifacts ranging in contact with the skin, is the fact of being the cause of problems allergenicity, which can lead to contact dermatitis. This standard considers as previously mentioned not just the bare formulation as the discriminating factor, but rather the value of nickel released on the skin. The use of the sole formulation would make it unusable very common alloys such as austenitic stainless steels widely used for example in the field of watchmaking. In practice, for the fashion sector, the introduction of REACH regulation excludes the possibility of using alpacas for the production of manufactures in white metal, when they are not properly protected superficially.

The regulation on nickel release also implies limitations in the field of plating: it is not possible anymore to use the nickel-plating baths, which have long been the most practical and economical way to get a hard, white, covering pre-layer to then proceed to final colors. Thickness nickel plating baths, very used also by the silversmiths, have showed to be not compliant to the requirements of UNI EN 1811:2011. Operators must therefore employ different galvanic deposition, such as white bronzes or other non-precious baths, when the object type does not justify the use of plating baths based on precious elements, such as baths based on palladium or palladium-iron systems.

On the one hand the new regulations, on the other hand more and more demands, especially from large distribution groups and brands in the world of fashion, make it necessary to be able to control with absolute certainty the nature of the alloy and of the superficial deposits that are used in the production a fashion accessory. For a manufacturer it becomes necessary to be able to ask its provider to certify the level of harmful impurities in the composition of an alloy intended for the consumer market within the parameters prescribed by the regulations or even more stringent. It's the case of some fashion brands towards the use of brass, for which the internal specifications clearly speak of allowed lead quantities in the alloy to be up to 10 times lower than what is required by law. In any case, these requests are justified by

the need to give some added value to the end user with a product that might otherwise be perceived as poor or worse, risky use.

Active legislation in a country or in a community of countries that are particularly restrictive in respect of a matter can become a form of control from commercial point of view, as it may limit the number of suppliers able to offer certain types of product. It is however necessary to be able to rely on suppliers that are able to respond properly to these requests.

SEMI-FINISHED ITEMS AND RAW MATERIALS

There are various types of semi-finished items available, functional to specific production processes. The semi-finished bar or plate type are best used for companies that work with CNC machining centers or milling / laser cutting systems. The size of the bar or sheet are dependent on the size of the work center, but sizes are relatively large (very commonly 500 mm x 500 mm plates are used on the CNC machine).

In these cases, the manufacturer of the component for the fashion industry prefers to buy the semi-finished externally, in order to start with tolerances, surface finish and composition that are always controlled. The main difference with the gold sector in this case lies in the relatively low cost of raw materials and products in large quantities, which makes it much more advantageous to purchase a semi-finished product ready for use rather than to produce it at home as it is done in case of gold or silver alloys at title, in which any melting operation may represent a very significant cost factor. The same type of consideration applies to those who produce chains of brass or bronze; also in this case the supply of a wire already in diameter and controlled metallurgical structure is more practical and inexpensive and therefore advantageous.

In addition, the manufacturing process of sheet and wire brasses and bronzes, other than just for economic considerations, requires some technical skill in the continuous casting, which make it relatively complex to produce them in small batch quantities. For example, the tin title should be quite limited in bronze, as this might otherwise tear the blank or have problems of excessive adherence to internal chain of graphite. In the case of brass, zinc title may be difficult to control because of its tendency to smoke and to oxidize, and then to generate variations in color or surface defects. However, to optimize the success of a continuous casting of bronzes or brass, it is appropriate to include small quantities of alloy deoxidizers (phosphorus, lithium, boron) to prevent the effects of oxidation of the copper in the liquid phase, and which are useful in improving drawing from the die during solidification.

Regarding the casting materials, the size of the material to be melted ranges from drops of 2-6 mm diameter to ingots of various sizes, which may have weights ranging from 100-200 g up to about 25 kg, suitably cut where necessary to facilitate the insertion of the crucible. The alloys in drops have the advantage of being much easier to dose, to be faster to melt in the crucible, to have a form factor that allows to better exploit the space in the crucible. Moreover, in many cases, the formulations of the products supplied in ingots are preferably designed for heavy foundry processes, on which is not guaranteed or controlled the content of impurities, or worse, they may be produced using waste materials from other casting processes with natural deterioration of casting performance. This can lead to an advantage from the point of view of a lower price, but certainly not from the safety of the product quality, both in terms of technical performance (color, reusability, deoxidization), and in terms of compliance with regulations.

PRODUCTION PROCESSES

The sectors of fashion and accessories use materials that, at least with regard to the copper-based alloys, are perfectly compatible from the technological point of view with the processes goldsmiths and silversmiths adopt, given that there are several parameters that appear to be similar. The process temperatures are compatible, as hardnesses required are close enough. Very similar requirements are present also from the point of view of the finish, given that in these areas aspects such as gloss, oxidation resistance of the article, and the control of roughness are fundamental.

The main difference is given by the production quantities of industrial items using non-precious materials, which are far more substantial. For this reason, producers in the industry of fashion and costume jewelry may also use production systems of high cost, relying on a low-cost raw materials and large quantities of production.

Hot forming: Plates of lead brass can easily be hot-processed, working with single or multiple steps of molding for forming or stamping. This type of process is by far the most widely used, consisting of more than 50% of the production for the fashion industry.

CNC sheet working, laser cutting: it starts from a sheet of brass with a composition capable of responding properly to the tool. For this reason, for the production of sheet formulations containing lead are widespread where possible, as this element makes it easier to break the chip during cutting, facilitating the machining process and subsequent finishing.

Production of wire, chains: very commonly CuZn15, or CuSn6 alloys are used, as they ensure good deformability and optimum hardness for the forming. The semifinished products of this type are welded in laser machine, or are welded

with the use of powders based on zinc, containing relevant titles of phosphorus in order to facilitate the welding of the joint.

Casting: necessary for objects of complex shapes, with undercuts, the process is mainly used in the case of small number of objects, or for processes that involve embedding of large quantities of stones. Given the need to ensure a good level of deoxidization to the casting, for brass formulations with silicon titles averagely quite high (3-4 %) are much appreciated, given that in this case the silicon in the copper-matrix does not meet to problems of miscibility as instead happens in alloys containing gold or silver, and therefore does not generate low-melting phases or obvious brittleness problems. The high silicon title also ensures a good reusability of casting scraps (sprues, trees) and also has a role in the improvement of hardness properties of these alloys.

PROTECTION FROM OXIDATION

It's necessary to remember that non-precious alloys such as brass, bronze, or other copper alloys do not possess the characteristic of being able to obtain protection from oxidation directly in the alloy. This is because the electrochemical potential of the copper and of its non-precious alloys is too low compared to the surrounding environment in which they are introduced in order to avoid problems of surface chemical reaction which results in tarnishing in very short times, of the order of a few days. For decorative sectors it should be emphasized that the problem is the generation of a thin patina also surface oxidation, which affect the aesthetic value of the article.

For this reason in the fashion industry the procedure involves the use of standard finishing processes and types of surface depositions to overcome this intrinsic problem of the base alloy.

The processes of electro-deposition are among the most widely used, because they allow to overcome several limitations given by the use of non-precious materials, and to obtain a high quality product.

Among the advantages of the galvanic finishing we mention:

- Obtaining of a good surface quality: the presence of small porosities, or surface defects can be corrected or at least reduced thanks to the use of thickness plating baths which generate a layer of sufficient thickness to overcome certain types of surface defect.
- Color selection: similarly to what happens in the gold sector, the surface color is a matter of primary importance for the artifact, and is identified by the most superficial layer of electro-deposition.
- Increased wear resistance: Depending on the number of layers, their hardness and thickness deposited, an artifact increases its resistance to wear in order to ensure compliance with at least the specifications agreed within the company.
- Increased resistance to tarnishing and corrosion: it is another aspect of primary importance with regard to the quality perception of the article. The use of a layer of valuable material generates a surface barrier to corrosion; if price considerations or others make it impracticable to choose a classical precious galvanic deposition, the fashion world offers, much more and much better than other areas, a wide range of solutions from the point of view of depositions via alternative methods such as painting.

A classic electroplating process for the fashion industry has different procedure steps, each with a specific purpose. The plating baths used in this sector are often very significant in size, which can range from 50 to 1000 liters of bath. Systems of this size require control procedures and maintenance, as well as technical support services that are particularly efficient in order to avoid shutdowns or unsatisfactory results from the point of view of quality.

The key steps of a galvanic process for the fashion industry are generally as follows:

Alkaline copper plating bath: this is the first activating layer, which is mandatory on alloys with high content of zinc, such as zamak or brass at high content of zinc. It's a great leveling bath, able to cover a certain degree of surface defects of the product, but it is not shiny and is cyanide-based.

Acid copper plating bath: is the classic shiny deposit, the thickness of which is summed to the alkaline copper plating, and which is an excellent preparation layer for the subsequent deposition of precious metals. The sum total of the two layers is on average 20 microns.

White bronze: The recent revision of the legislation on nickel resulted in the need to find an alternative to nickel in the galvanic coating. Nickel, in fact, deposited by electroplating produces surfaces that are extremely bright and pleasing to the eye and, for that reason, it was widely used. This impediment has created difficulties for the companies as there is no pure metal, as nickel, which is able to produce deposits of great brilliance and remarkable capacity leveling at a low price. A solution was found thanks to a quaternary alloy of copper-zinc-tin-lead whose deposits can produce both yellow-gold and bright white colors, with a white that is similar to palladium.

This particular type of alloy is called, in fact, white bronze and is deposited obtaining compact surfaces with a hardness of 500 HV. The main advantage of the white bronze layer is to prevent phenomena of diffusion between the underlying

copper and gold on the surface, which may lead to noticeable oxidation of the surface layer. Furthermore, it is an economical alternative to palladium, with which it has much color similarity.

Palladium: intermediate noble plating layer able to guarantee an excellent electrochemical resistance, good covering, interesting white color. Some plating systems, based on palladium-iron have excellent leveling and give a good shine to increase the performance of the final decorative layers. Deposited layers are lower than 3 µm.

Rhodium or gold plating: These precious plating baths are characterized by high surface quality and wide variety of colors from which to choose. They represent the baths of the highest standard for setting color of a product, consistent with the cost due to the presence of precious elements. Similarly to what happens in the gold sector, there are different gold baths compositions from which to choose. Generally the operation involves the deposition of a thick gold pre-layer, followed by a passage of gold flash for the final color. For white metals, a deposition that provides a pre-layer performed with a bath of palladium to a thickness of less than 3 micron, is completed with rhodium plating of a thickness lower than 0.25 micron, and is able to ensure excellent resistance to corrosion and wear due to the high hardness of the surface layer of rhodium (700-800 HV). This is well bonded to the intermediate layer of palladium, which has a hardness that is intermediate (about 400 HV), minimizes the risk of cracking or failure to adhere to the lower layers.

QUALITY AND PRODUCT WARRANTY

On the base of the above considerations, relating to large quantities and variety, for size and competitiveness, the fashion industry has long since developed careful procedures to control the quality of the product that make it much more similar in many respects to a technological industry than to that of a fancy object, as it is perceived to be the jewel in the precious metal sector.

The type of controls that are performed varies based on the expectations of the product, in terms of perceived quality, maximum cost per part, to the intrinsic characteristics and certifications to be provided to the end customer. The various checks are summarized with a term often little known to the gold sector namely that of "technical specifications". A company that produces for the fashion industry is obliged to carry out a series of tests that are considered significant in various capacities for the final performance of the object. There are no specific regulations regarding the preparation of technical specifications; every company shall make its own choice regarding the number, the characteristics and the quantity of tests to run, with the aim of qualifying the manufacturing process and each batch of their product to their end customers. This is based on choices by the quality office of a company or on the basis of requests from a client. At the regulatory level there are many standardized test procedures, but a company may decide at its discretion to develop internal procedures that it considers most relevant. The most used are tests that can certify characteristics such as wear resistance, corrosion resistance or the adhesion of the galvanic layer to the substrate.

	Test	Standard	Duration
1	Thioacetamide test	ISO 4538	48 h
2	Salt spray	ISO 9227 NSS	96 h
3	Artificial sweat	NFS 80772	24 h
4	Humid heat	ISO 4611	96 h
5	Adhesion	ISO 4524/5	-
6	Wear	UNI EN 12472:2009	5 h
7	Climate chambre	DIN 9022-2	120 h
8	Tension test	EN ISO 105 E03	-

Tab.1: List of test requested on an object (extract from a technical specification of a company of fashion industry)

This means that a component of a product must demonstrate that it will pass all these tests in order to be accepted by the customer. On each batch produced, sample tests will be carried out to certify compliance with the technical specifications. As onerous, this procedure is the best guarantee in front of the customer, who receives the results of the analyzes requested by a third party such as a laboratory for analysis, which essentially certifies independently the quality of the production process.

For the jewelry sector, the presence of technical specifications is less frequent, and it becomes necessary in large companies that have to do with sub-contractors, or who have clear policies regarding the quality of the product. A technical specification is a means of protection for the manufacturer, and is particularly useful in the case of galvanic deposition, as it may be used for example to certify the thickness of deposited precious just to check the work of the contractor.

MARKET PLACEMENT

As for the companies in the fashion industry, it is clear from the above that the client, usually a big brand in the industry, is the centerpiece of both the technical requirements (which are devolved to the manufacturing company), and of the commercial push on the end user of the accessory, thanks to the strength of its name.

For a company of costume jewelry, in many cases the fact of having to work on large amounts to obtain acceptable revenue, often in a competition with companies that make their productive capacity their own strength, leads more strongly to wonder how to differentiate one's own product. In this sense, and although the current period is characterized by high prices for precious raw materials, the costume jewelry market is already seeing lucky examples of differentiation, for example through the introduction of quantities of precious elements in the alloy formulation. The inclusion of a certain quantity of a precious element in the formulation conveys an added value, at a fraction of the price for a jewel made with a standard precious alloy. The price of such alloy must, however, be appropriate in relationship to the target clients who wish to be reached, as this is expected to be higher than that of the standard costume jewel; it is forbidden to hallmark jewelry alloys that contain lower quantities of precious elements than what is required by the precious metals legislation. Moreover, for these alloys the need to proceed to a surface protection remains, as the percentage of precious metals in the formulation is not sufficient to provide a barrier against oxidation.

For a project of this kind, it is therefore necessary that the jewelry has one or more unique characteristics, such as those which can make it patentable, or to allow it to be protected by a collective trademark. In addition, the operator of this project must be able to convey it in innovative ways, by using different sales channels than the usual ones, or by forcing an exclusive distribution partnership. The objective is to become recognizable, and to make sure that one can find a new niche market. The success of an operation like this, that could be considered only commercial, however, requires also key technical aspects, such as outlining correct plating specifications for the finishing of the product. These specifications must be delivered to the companies operating in the field so that the type and quality of the protection is satisfactory, as it is a characteristic of primary importance in the moment in which there may be different manufacturing companies that operate with this alloy. They could be anywhere in the world, but the product must ensure standardized quality standards: this aspect, borrowed from the world of fashion is also important food for thought for all the gold sector.

CONCLUSIONS

The sectors of fashion and of costume jewelry are united by the use of technologies and materials in most cases compatible. They also share similar regulations on the type of materials restricted. What in the fashion industry has perhaps already become the norm is the idea of continuous control and adjustment of quality on the final product. Not that this should be translated directly in the gold sector, where in many cases experimental control procedures are missing or are not correctly calibrated, but it is very interesting to open a debate on whether and which may be the correct quality certification of product, also in our industry, identifying a minimum quantity of significant tests to be carried out to demonstrate in front of customers the superiority of one's product. In this sense, the tests to be performed on plated surface layers can be a beginning of the path, both because they are already ripe with regard to other areas, and because they focus on the important aspects of perceived quality of a jewel, such as gloss, resistance to wear, resistance to corrosion, that are the most obvious point of contact between the different sectors studied in this article.

Bibliography

1. *Manuale dei materiali per l'Ingegneria*, a cura di AIMAT (McGraw-Hill, 1996)
2. *Manuale degli ottoni*, V. Loconsolo, L. Nobili (Ed. Consedit)
3. *Corrosione e protezione dei metalli*, G. Bianchi, F. Mazza, (Ed AIM)
4. *Gold Survey 2011* (Thomson-Reuters)
5. *Consumer Product Safety Improvement Act (CPSIA) on Lead* (Sito web)
6. *Istituto Italiano del Rame*, (sito web www.copperalliance.eu)
7. *Progetto PhyLeS* (sito web www.phyles.ge.cnr.it)