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In studying the ancient objects made of noble metal alloys, such as gold with copper or silver, the phenomenon of surface enrichment is often encountered [1]. This phenomenon is regarding the composition changes of the surfaces, changes that happen because objects had been buried for a long time. In fact, this alteration of surfaces is not due to their enrichment, that is, to an addition of gold, but it is due to a depletion process, during which the less chemically stable elements leach out slowly, causing the surface composition to change. It is the same for gilding; we can have an enrichment of the surface when gold is added to it, or a depletion of the surface when other elements of the alloy are removed and the local percentage of gold is increased as a consequence. Therefore, an ancient object can have a surface rich of gold because of time or because of an ancient depletion gilding treatment. This depletion gilding was used by pre-Columbian populations for the tumbaga, a gold and copper alloy, to give it the luster of gold.

The term "gilding" covers several techniques for applying a gold leaf or a gold powder to solid surfaces to have a thin coating of this precious metal. The methods of gilding include hand application, chemical gilding, and electroplating, which are additive methods. They act depositing gold onto the surface of an object, which usually does not contain it. As previously told, there is a method which is a subtractive process, the depletion gilding. In this process, some material is removed to increase the purity of the gold that is already present on the surface of an object. For this reason, this gilding procedure can be applied only to objects composed by gold alloys, usually gold with copper and/or silver, and works removing the metals which are not gold. These metals are etched away from the surface by means of the use of acids or salts, often combined with the action of heat. Of course, there is no gold addition, because the object already contains gold.

Depletion gilding is based on the property of gold of being resistant to oxidation or corrosion by most chemicals, whereas many other metals, such as copper and silver, are not so. Both copper and silver react with a variety of chemicals. Then the object, cast for instance by one of these alloys, is immersed in a suitable acid or packed in a salt, which attacks the copper and silver in the object's surface, transforming them to some copper/silver compounds that can be removed from the object's surface by washing or heating, or by using a brick dust [2,3]. The result is a thin layer of nearly pure gold on the surface of the object. Sometimes it is necessary to repeat this procedure several times, making the resulting surface soft and spongy with a dull appearance. For this reason, most depletion gilded objects are burnished to make their surfaces more durable and attractive.

Depletion gilding is not used in modern times, but it was widely used in antiquity. It requires some skill to execute it properly, however the process is technologically simple, needing materials that were available to most ancient civilizations, those able to make alloys. An alloy is a mixture or a metallic solid solution composed of two or more elements, which usually features different properties from those of the component elements. The alloys of gold and copper were used especially in the copper-rich compositions in South America. These alloys were known as "tumbaga" and used widely both for castings and for hammered metal works. The phase diagram in the Figure 1 shows that copper and gold are completely soluble in each other with eutectic melting point, occurring at a composition of 80.1% gold at 911 °C. The rounded shapes at the bottom of the diagram show the regions where ordered phases exist. According to [4], these ordered phases are usually harder than the disordered alloy of the same composition, and they may make the process of working to shape more difficult. Moreover, the quenched alloys between about 85% gold and 50% gold are softer than the alloys that are allowed to cool slowly in air (quenching is the rapid cooling of a work piece). This is the opposite of what happens in alloys such as iron and carbon, where the material is hardened by quenching because of the formation of martensitic phase. For the gold-copper alloys, the softening by quenching process is due to the fact that it is suppressing the formation of the ordered phases which need some time to form. South American Indians used water quenching after annealing in order to make their alloys easier to work to shape and to avoid embrittlement. Annealing in metallurgy is a heat treatment, usually applied to soften the material to allow further deformation.

The alloys of gold with copper or silver were produced by the pre-Columbian people to create statues and ornaments, such as those in Figures 2 and 3. In the Figure 3 it is shown the Muisca Raft, created by the Muisca culture in a region which currently corresponds to the center of Colombia. This votive object is exhibited at the Gold Museum in Bogota. It is a lost-wax casting in gold with a small amount of copper. This Raft refers to the ceremony of the El Dorado, during which the Muisca chief, after covering his body with gold powder, dove into the Guatavita Lake. Most of beautiful objects such as these shown in the images were plundered by the Spaniards and melted into bars for transport across the Atlantic. Hernan Cortes and his men for instance improvised a manufacture of such metallic bars. Because all the metals that reached Europe were melted back into their constituent metals in Spain, there is only an example of such a load, a group of over 200 silver, copper and gold ingots, defined as tumbaga bars, discovered in the remains of an unidentified shipwreck (around 1528), off Grand Bahama Island. This shipwreck was found in 1993 [5].

The word tumbaga is not native to any language of the area and it is not a Spanish word, it is coming from Malay and means copper [6]. The historical documentation of tumbaga alloy begins with Columbus, who reported that the word "guanin" was employed to express this alloy. In a 1546 communication to his king, the explored Juan Perez de Tolosa reported on a population of the Northwestern Venezuela that, in addition to possessing gold and other precious metals the Indians wore ornaments of a copper-gold alloy called carcuri. Similar reports appear in the writing of Pedro de Cieza de Leon, who explored the Cuca Valley of Northern Colombia during 1532-1550. In Ref.6, it is told that the first modern report about tumbaga was that by G. Créqui-Montfort and P. Rivet, published in 1919 [7], who describe the tumbaga in Colombia. The documentation of a similar pre-Columbian alloy with depletion gilding to produce a golden surface is given in the Ref.8. In a report of 1949, W. Root is comparing the physical properties of tumbaga with those of unalloyed gold and copper. In this review [9], Root tells that tumbaga seems to have originated in Colombia or Venezuela before AD 1000 and spread to Ecuador and Peru. About the gilding, Heather Lechtman made some relevant points, remarking that two gilding processes, the depletion gilding and an electrochemical replacement plating, were first developed by the Moche culture of Peru, about AD 100-800. Moreover, the depletion methods of gilding used in Peru, from this center of origin, spread north into Ecuador, Columbia, Venezuela, Panama till Mexico [10].

The features of the layer of gold obtained by depletion gilding are discussed by Stuart J. Fleming in Ref.11. This gold-enriched layer is prone to hairline cracking, in particular in the regions where there is more stress, for instance the sharp edges produced by hammering or folding. Once the gold layer is broached, the copper in the underlying tumbaga becomes oxidized, that is, it becomes the reddish brown cuprite. Because the cuprite has a lower density than the surrounding alloy it swells outward (Figure 4). As a consequence, the depletion layer fractures and is forced away from the surface. But, according to Fleming, the tumbaga has a "self-healing" property. The cuprite is created only if the corrosion is tunneling into the tumbaga. However, when there is a sufficient proportion of gold in the alloy, the gold atoms that have been set free by the corrosion, can migrate and seal the minute channels due to the corrosive attack. Therefore, the objects made of a relatively gold-rich tumbaga can retain for a long time their original luster, the luster of gold.

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References

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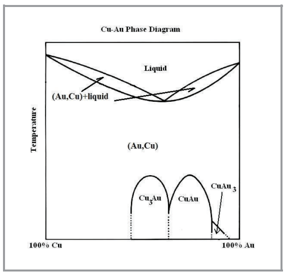

Figure 1: Phase diagram of the alloy of gold and copper.

Figure 2: Pre-Columbian male and female zoomorphic figures (known as dragonera) of tumbaga cast by the Tairona using the lost wax process and polished to obtain a 23 carat gold surface. Image courtesy of E. Lee Spence.

Figure 3: Muisca raft, a representation of the legend of El Dorado. It was found in a cave in Pasca, Colombia in 1856, together with many other gold objects. The cacique in the center is surrounded by attendants and oarsmen. Image courtesy of Andrew Bertram.

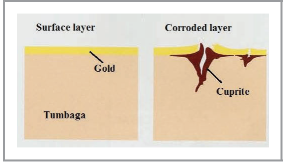

Figure 4: The gold-enriched layer is prone to cracking in the regions where there is more stress. Once the gold layer is broached, the copper in the underlying tumbaga becomes the reddish brown cuprite. Because the cuprite has a lower density than the surrounding alloy it swells outward and the depletion layer fractures and is forced away from the surface.

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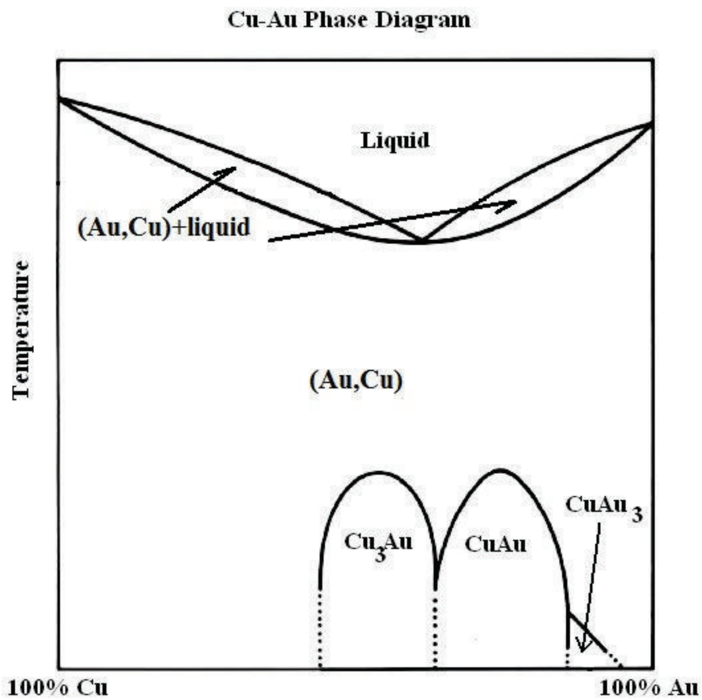

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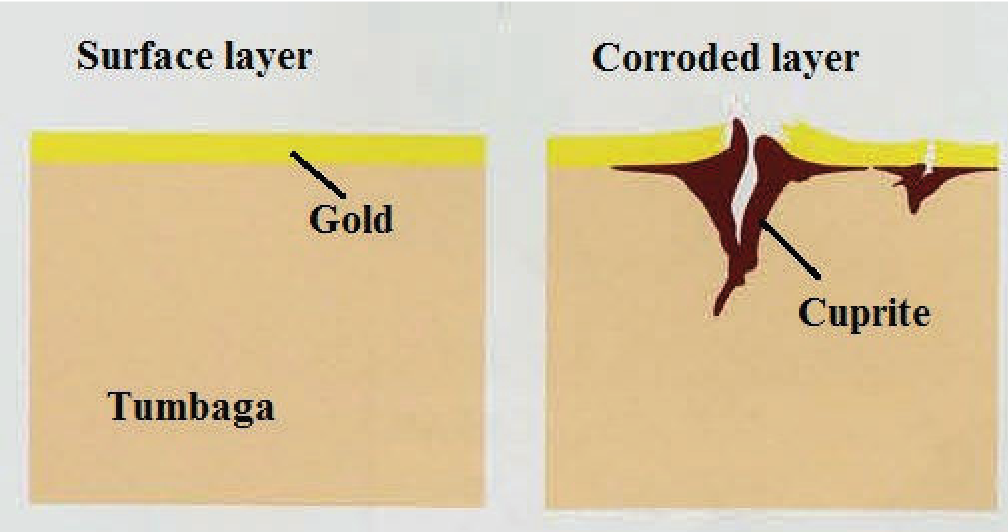

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