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Gold parting with nitric acid in gold-silver alloys

IACOPO CIABATTI

R&D Manager, TCA|Precious Metals Refining, Zona Industriale Castelluccio 11, Capolona, Arezzo

E-mail: i.ciabatti@tcaspa.com

Abstract. This article is an overview of gold parting with nitric acid on a both industrial and laboratory scale, supported by more recently reported experimental and theoretical studies on the gold dealloying process for the fabrication of nanoporous gold material.

Keywords. Parting, assay, gold refining, dealloying, nanoporosity.

INTRODUCTION

Metals have played a fundamental role in human history and were the basis for the development of ancient societies. Precious metals and gold in particular have always been considered status symbols and a measure of power. In all likelihood gold was one of the first known metals due to its presence in native form as grains or nuggets [1]. As soon as gold was discovered, men recognized its extraordinary properties, such as malleability and incorruptibility, which differentiates it from all other metals.

The earliest gold artefacts known to us were found in a pre-historic settlement in southern Bulgaria and date back to 4500-4600 B.C. [2]. However, the metallurgical expertise required to purify gold did not develop until the second millennium B.C. Most gold in its natural state is a gold-silver alloy (*electrum*) containing other base metals as impurities [3]. In the latter case, purification was historically achieved via cupellation, although this metallurgical treatment was originally conceived as an extractive process of the silver contained in lead ores, and only later it also became a refining and assay process of alloy gold metals [4]. However, the separation of gold and silver, generally referred to as gold parting, cannot be done via cupellation. The oldest gold parting process involved salt cementation and the first evidence of this dates back to the 6th century BC in Sardis, Lidia [5]. In this process, silver metal was converted into its chloride salt by alternating thin sheets of gold alloy with layers of a mixture of sodium chloride, brick-dust, vitriol, alum, and other materials which were then heated together in a sealed pot. The main drawback of the cementation process is a tangible loss of material, though a high-grade gold purity can be

achieved. With the discovery of the nitric acid synthesis, cementation soon became obsolete. Alchemists were pioneers of this approach as they recognized that this new product was ideal for the purification of gold in silver- and copper-gold alloys. Nitric acid could be made by distilling saltpeter with a specific sulfate salt, the choice of which historically fostered the dissemination of a variety of terms [6]. For example, the term *spiritus nitri* was used when nitric acid was made from saltpeter and alum, while it was called *aqua fortis* when made from saltpeter and vitriol (such as iron sulfate, known as green vitriol) according to the follow reaction:



The first mention of nitric acid is in the writings of Pseudo-Geber, who described its obtaining from calcining a mixture of saltpeter, alum and blue vitriol (copper sulfate) [7]. However, nitric acid preparation was no simple matter and it is likely that only small amounts of this compound were originally available, thus allowing for only limited-scale treatment. Nitric acid concentration and purity were the main challenges throughout the Middle Ages and the Renaissance. Indeed, hydrochloric acid was often present because saltpeter contamination with potassium chloride and this made nitric acid unsuitable for gold parting. Prior to gold parting, small quantities of pure silver were added to the acid solution as a sacrificial reagent to precipitate chlorides. After Geber, more detailed descriptions of gold parting with nitric acid appear in the writings of Vannoccio Biringuccio [8], Georgius Agricola [9] and Lazarus Ercker [10].

In the nineteenth century, the large-scale nitric acid production using the Birkeland–Eyde, and thereafter the Ostwald process, via nitrogen and ammonia oxidation respectively, allowed extensive use in gold refining on a commercial scale. In the modern period, gold parting with nitric acid has been largely replaced by other treatments such as chlorination using the Miller process [11]. Nonetheless, nitric acid is still used today in the parting stage on the laboratory scale after cupellation assay.

PARTING WITH NITRIC ACID IN GOLD ASSAY AND REFINING

Gold parting consists of a selective corrosion process, also known as leaching or dealloying, which is based on the “incorruptibility” of gold to nitric acid. As a result, in the case of silver-gold alloys with a suitable composition, silver is oxidized and transfers into the solution as silver nitrate. If an alloy contains also other

metals, these elements can either be solubilized like silver (e.g. copper) or behave in the same way as gold (e.g. iridium). In addition to these two borderline cases, other metals can be partially dissolved (e.g. palladium) or lead to the formation of insoluble compounds (e.g. tin).

On a laboratory scale parting occurs after cupellation, which consists in an oxidative fusion in which samples are melted with lead in a cupel at 1050°C [12, 13]. Atmospheric oxygen reacts with lead to form litharge (lead oxide), which catalyzes the oxidation of the other base metals present in the sample as alloys. Magnesite cupel absorbs the metal oxides, leaving only precious metals in the cupel as small doré bead made up of noble metals, generally silver and gold and PGMs (Platinum Group Metals). This alloy usually contains insufficient quantities of silver to be oxidized by nitric acid. When parting is used as assay, selective dissolution of silver is quantitative and the residual gold compacts enough to be weighed after annealing without powdering on handling. For this purpose, the first operation is designed to make suitable Au-Ag alloys, which consist in three parts of silver and one of gold, hence the term “inquartation process”. At this point, the common procedure is to melt bead with pure silver to generate a suitable alloy. After the inquartation process (Figure 1a) and prior to the parting process, bead is hammered (figure 1b), annealed, rolled to a thin strip (Figure 1c), annealed for a second time (Figure 1d) and rolled up to a shape like ionic order column volute (Figure 2). The hammering and rolling stages serve to increase the surface area for the subsequent silver dissolution with nitric acid, while annealing is designed to relieve residual stress. Moreover, a second rolling stage must be carried out to allow the wettability of the whole surface, thus avoiding the occlusion of impurities as oxides obtained from the previous cupellation process. In this regard, the ionic volute is probably better than the cornet shape (Figure 2), as Battaini *et al.* pointed out [14], on the basis of the greater distance between the internal metal walls. The parting process takes place in two stages by keeping the sample in boiling nitric acid inside a Kjeldahl flask, which has a long neck. The first treatment makes use of a 5.6 M nitric acid aqueous solution (22°Bè) and the second one of a 9.4 M nitric acid aqueous solution (32°Bè).

The stoichiometry of pure silver and copper reactions with nitric acid have been the subject of a great deal of enquiries and, in particular for the latter metal, the attribution of the correct reaction coefficient sets is discussed in several articles reported in the literature [15]. The oxidation of silver by nitric acid takes place mainly according with the following parallel reactions [16]:

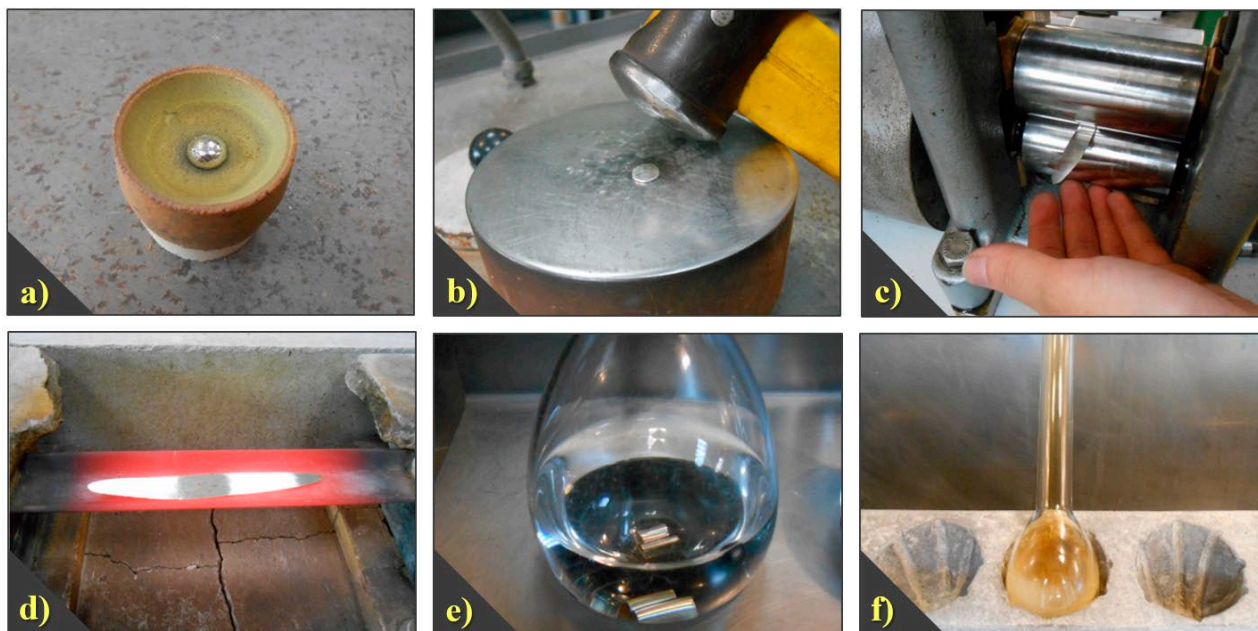
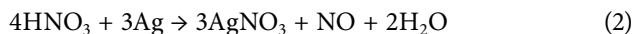


Figure 1. Characteristic gold parting steps on a laboratory scale. After the inquartation stage (a), the precious metal bead is hammered (b), rolled (c) and annealed (d). The parting process occurs inside a Kjeldahl flask (e), keeping the rolled specimen in a boiling acid solution (f).



As reported by Martinez *et al.* [17], it is possible to determine the contribution of each reaction by titration of the unreacted nitric acid moles in relation to the moles of silver dissolved. In the case of high concentrated acid (5.3 M) the reaction (3) dominates, on the contrary when the concentration is low (2.5 M), nitric oxide is the main nitrogen product, according to the reaction (2). Similar behavior has been also observed for Au-Ag alloys, suggesting that, during parting stage, reaction (3) represents the main contribute for silver oxidation.

In the case of large-scale refining, a correct balance between a suitable separation gold-silver alloy and the rate of dissolution should be considered. Indeed, gold parting is not necessarily quantitative. In all likelihood, this compromise is the main reason for the different silver content values recommended by scholars which ranges from 60 to 80% [12, 18, 19].

In the case of the laboratory scales discussed above, beads obtained after fire assay are rolled in order to increase the surface area. The same strategy can be used on an industrial scale. The operations involved are similar: first of all, the material is heated to a dull red and chilled in cold water to anneal it. Then it is rolled and the thin foils thus formed are twisted into what



Figure 2. Cornet (top) and volute shapes (bottom) in the same rolled cupellation bead.

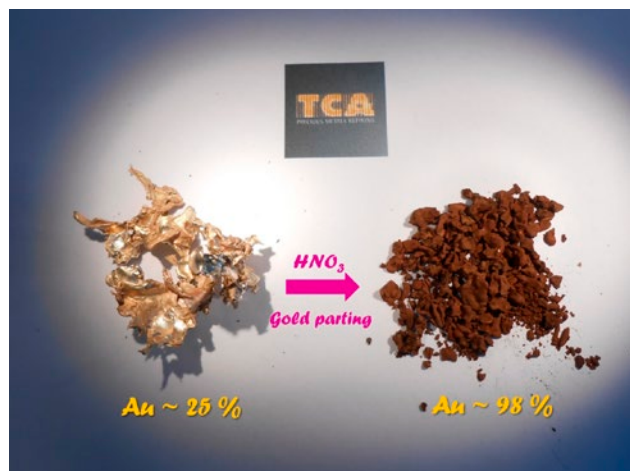


Figure 3. Effect of the silver dissolution by nitric acid on the gold-silver alloy grains.

are called cornets to prevent them from lying flat in the reactor. The second and more common approach is granulation. After melting, the molten alloy is poured into cold water with a thin stream moving the crucible in a circular motion or bobbling air in the water. The grains are small shell shaped (Figure 3).

The parting process takes place in two stages involving nitric acid solutions with different concentration. The solution is often heated only at the beginning because silver dissolution is exothermic. Generally, the nitric acid concentration is lower in the first process than in the second, but this is not a rule and the formulation changes from company to company [19]. A small amount of silver is removed by the second nitric acid treatment and this solution may be used once again in a subsequent parting treatment. When the reaction is finished or the acid is exhausted, hot water is added to have more solution for the decantation of residual gold, avoiding the precipitation of silver nitrate.

In contrast with the laboratory scale, the firmness of the residual gold is not necessary even if it involves different types of reactors and filters. This is due to the fact that gold content varies from a minimum of 1%¹ to a maximum of 35%, close to the value used in assay.

Concerning the reactor, parting is normally carried out in steel vessels including roto-barrels (tumbler machines) or tanks, which are equipped with a rotating basket. The right choice between the two model plants is dictated by the physical form of the final gold prod-

uct. Indeed, when the gold content in the bullion is low and/or there is a quantitative presence of other base and precious metals, the formation of impure and gluey gold powder requires the use of a rotating basket which is suspended in the tank. This arrangement enables the powder to be continuously separated from the grain and avoids the passivation of the latter. Particle size is related to gold concentration in the alloy, the presence of other metals and reaction conditions. If gold content is less than 1% the dealloying process can lead to the formation of undesirable gold colloids which are difficult to separate². Generally, gold powder is separated using a filter press.

By contrast, when parting is carried out after an inquartation process, the bullion conserves some of its firmness and a roto-barrel can be used for the reaction (Figure 3). This reactor consists of a cylinder tilted to about 20-30 degrees which rotates by means of a motor. In such cases, solid-liquid separation is simpler and industrial Büchner funnels are commonly used. Parting pure Au-Ag alloy alone is rare and the quantitative presence of other metals is common, however only traces of base metals such as tin³ and antimony should be present for a satisfactory refining [19].

After filtration, parted gold is washed with hot water and finally melted, obtaining bullion ranging from 994 to 999 fine. Moreover, silver is recovered from the spent nitric acid solution as insoluble chloride salt or by means of cementation with a more electropositive metal (*e.g.* iron).

Alternatively, gold parting can be carried out with sulfuric acid. On a laboratory scale this is suitable when the specimen is a silver-rich alloy. From an industrial point of view, sulfuric acid is a cheaper reagent than nitric acid, which incidentally it also has the drawback of generating toxic pollutants such as nitric oxide (NO) and nitrogen dioxide (NO₂) according to reactions (2) and (3).

Nitric oxide reacts instantly⁴ and almost quantitatively with atmospheric oxygen to produce nitrogen dioxide [20]. Conversely, the kinetics of the nitrogen dioxide adsorption are relatively slow and large scrubbers are required to provide minimum residence times for complete removal. The scrubbing of nitrogen dioxide with water results in the production of nitric acid and nitric oxide as the following reaction shows:

² This problem can be overcome by treating the sol with activated carbon.

³ Tin is oxidized by nitric acid to gluey insoluble Sn(IV) oxide which passives the grains, hindering their further dissolution.

⁴ In the gas phase, this oxidative reaction is second-order in NO because a transient dimer (NO₂) is produced which subsequently collides with oxygen molecules. Because the reaction is second-order, the concentration of NO seriously influences the rate of oxidation. In this case, the high concentration of NO ensures fast oxidation.

¹ Note that in this case the separation of the two metals using electrorefining should be taken into account. This approach is cheaper and the final product is pure metal silver (99.95% or more). The impure gold is recovered as sludge and after melting it can be parted with nitric acid.

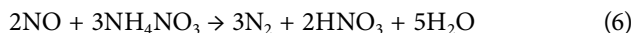


The reaction is exothermic and thus the liquid circulated over the scrubbing equipment may be cooled to increase absorption efficiency. The nitric oxide generated undergoes oxidation by atmospheric oxygen to produce new nitrogen dioxide. As a consequence of this tandem reaction, where the product of one process generates the starting material for another, large scrubbers are required to provide minimum residence times for the NO_x removal in order to fit into legal emission limits. Significant residual NO_x content in the exit gas stream is typically abated by absorption into an alkaline solution in a second tower. Moreover, from an industrial point of view, dilute nitric acid has little or no value and, in practical terms, represents a waste treatment problem⁵.

To reduce the volume of the towers, either air or oxygen may be introduced into the gas or liquid phases to improve nitric oxide oxidation rates. Formally, the generation of NO_x by metal dissolution with nitric acid may be overcome by moving the oxidation of nitrogen oxide from the gas phase to the reaction solution. This goal can be achieved using hydrogen peroxide, according to the follow overall reaction [20, 21]:



Another approach is the reduction of NO_x with soluble ammonium nitrate [22]. In this case, the *incipient* formation of NO_x in solution reacts with the ammonium nitrate release of nitrogen gas according to the follow reactions:



GOLD PARTING: A MICROSCOPIC ENQUIRY

Gold parting with nitric acid in gold-silver alloy has been the subject of several studies supported by theoretical and experimental data. Martinez *et al.* [17] systematically studied the effect of silver-gold alloy composition on silver dissolution using a 6.56 M nitric acid solution at 80°C for 48 hours. Their experiments showed that such alloys become completely resistant to nitric acid oxidation when the gold content is greater than 40% by weight. This value is the so-called *part limit* above which the dealloying process is quantitative. The various

thresholds reported in the literature are due to different reaction conditions such as lower temperatures or lower nitric acid concentration. However, from a practical point of view, the relationship between the dissolution rate and the composition of the alloy should be taken into account. In particular, in the case of the inquartation process, when the gold content is 25% by weight, the dealloying process is slow as compared to that of other silver-rich alloys [17, 23].

During the dealloying process, in the first instance, a static model in which silver ions may exit the alloy lattice only through the holes previously generated by the dissolution of more superficial silver atoms without invoking any type of atomic rearrangement might be assumed. On the basis of this consideration, after the first selective dissolution of silver on the surface, the progress of the reaction depends on composition and alloy metal lattice. The exclusive presence of face centered cubic lattices for any metal Au-Ag composition alloys, partly due to almost identical radii, makes the model easier to describe and analyze. Each atoms in the lattice displays a coordination number of 12 and the probability that a gold displays n homometallic contacts can be calculated using statistic equations [17].

Trends in these probabilities against silver-gold alloy composition are reported in Figure 4. In particular, for $\text{Au}_{25\%}$ -Ag alloys, gold atoms come principally into con-

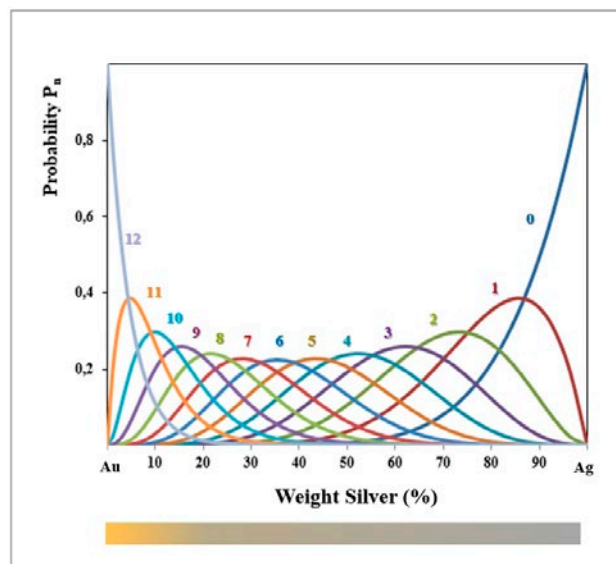


Figure 4. Probability (P_n) for a gold atom to display n homometallic contacts against the percentage of weight silver in gold-silver alloys. P_n functions are calculated using the same statistic expression used by Martinez *et al.* [17]. Note: the absence of a mirror image across 50% of the silver is due to the different weights of the two precious metals.

⁵ The dilute nitric acid recovered by this process may be returned to the process. Basically, it is used as “water dose” for the other parting treatments.

tact with one or two other gold atoms, although the presence of gold with three and zero Au-Au contact is not negligible. Thus, with this composition, the random alloy lattice excludes the presence of suitable preformed gold networks as required by a static model in order to justify the lack of powdering. Moreover, without any type of atom surface diffusion, it might be expected that dissolution would stop after about 4-5 metal monolayers have been dissolved, making the separation of the two metals non-quantitative. This is in contrast to experimental values [17] which show quantitative dealloying characterized by a faster dissolution rate than those observed in the case of pure silver (99%).

Thus, a simple static process in which silver is removed by means of nitric acid, which leaves only gold atoms inside the bulk alloy, is not sufficient to describe exactly what happens. From a macroscopic point of view this is corroborated by volume contraction and an unexpected product color obtained after the dealloying process. Indeed, after the parting and subsequent annealing stages, the $\text{Au}_{25\%}\text{-Ag}$ alloy shows characteristic shrinkage, with memory of form, that is particularly visible in the case of laboratory scale assays. Moreover, after the dealloying stage, including when parting is quantitative, gold color is not the characteristic bulk phase yellow but generally brown.

In order to give a qualitative idea of this phenomenon, parting and annealing stages starting from an $\text{Au}_{25\%}\text{-Ag}$ alloy specimen with a TCA logo shape are shown in Figure 5. Dealloying occurred in two stages using 22° and 32° Bè boiling nitric acid for 30 minutes respectively. After parting, these fragile specimens were slowly dried in the oven at 105°C (Figure 5b) and finally put into a furnace at 1050°C (Figure 5c).

Battaini *et al.* [14] described the changes in shape and color during the parting stage with an extensive study by means of scanning electron microscopy, which revealed the nanoporosity architecture obtained after the parting stage. The nanoevolution of porosity during dealloying is well known, and over the last two decades it has received great attention from the scientific community [24-27]. Indeed, the porous gold materials obtained by selective dissolution of silver present numerous potential applications as functional materials on the basis of their chemical stability and unique surface chemistry⁶. As a result, fabrication of newly performed

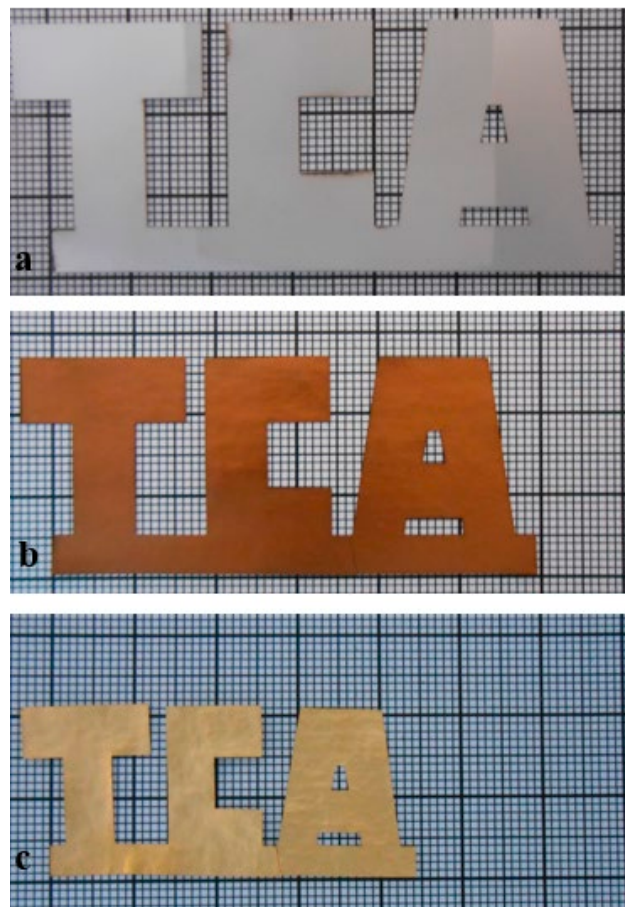


Figure 5. Effect of gold parting (b) and annealing treatments (c) on an $\text{Au}_{25\%}\text{-Ag}$ alloy specimen (a) with TCA logo shape.

tailor-made porous gold materials, and their related characterizations, have favored an understanding which moves in the direction of a clearer vision of what happens in gold parting.

However, whilst the first detailed look by Forty at the porosity formed by dealloying processes using electron microscopy dates back to 1979 [28], the mechanisms involved in the gold nanoreorganization were studied only two decades later. According to Erlebacher's studies [29-32], during silver dissolution, gold is freed to move along the surface, reorganizing into a three-dimensional network, which generates nanoporosity. The dissolution of silver primarily involves atoms from surface defects, *e.g.* terraces or steps, which are more reactive [30]. This leads to the creation of terrace vacancies that then grow sideways into vacancy clusters as lateral near neighbors are subsequently dissolved. As a consequence of silver oxidation, unsaturated gold atoms, which are thermodynamically unstable, move from low- to high-concentration areas leading to the formation of two-dimensional

⁶ Whilst several other methods have been developed to fabricate porous gold materials such as sintering, templating and additive manufacturing, the dealloying approach has attracted remarkable interest on the basis of its simplicity and reproducibility [25]. In addition to chemical gold-silver dealloying, the subject of this work, the selective oxidation of silver may be carried out by electrochemical and liquid metal dealloying.

gold clusters. As dealloying proceeds, new gold-silver layers are exposed to nitric acid solution around the base of the gold islands previously formed in the top layers after dissolution and surface reorganization. The three-dimensional development of such gold islands results in gold covered hills with base perimeters that grow in diameter as dealloying proceeds. This increased surface area requires more gold atoms compared to the gold adatom generated, leading to undercutting and bifurcation of ligaments. The result of this process is a continuous porous structure with gold-rich surface ligaments. The large surface area to volume ratio of these ligaments leads to metastable nanoporous structures. Thus, the length scale of porosity tends to increase over time and, as the atoms move from smaller to larger ligaments, residual silver atoms are exposed and dissolved.

Thus, from a kinetic point of view, the dealloying process can be viewed as a competition between three processes: (i) silver dissolution; (ii) surface diffusion of gold and (iii) mass transport of the dissolved silver ions and the nitric acid through the cavity between the gold nanomounds. The rate-limiting step of nanoporosity evolution is the dissolution of silver from surface defects which is nearly ten orders of magnitude slower than the two other processes. As a result, the dealloying front advances at a constant rate, as shown for a first time by Martinez *et al.* [17] who employed electron microscopy for kinetics studies of an Au_{25%}-Ag alloy. Recently, similar conclusions were reached by Chen-Wiegart *et al.* [33], who studied the dealloying front in an Au_{30%}-Ag alloy by means of transmission X-ray microscopy.

After dealloying, the final gold nanosponge is isotropic and characterized by ligament spacing in the order of 10 nm and surface areas greater than 8 m²/g [34]. It has been found that the length scale of the porosity inversely increases with the dealloying front velocity. Thus, factors that can be related to the dealloying rate such as acid concentration [23], alloy composition [35] and temperature [36] affect the evolution of nanoporosity. The dealloying process is controlled by the diffusion of gold atoms on the alloy surface, which is strongly dependent on the reaction temperatures [37]. Low dealloying temperatures significantly reduce the interfacial diffusivity of gold atoms and the overall result is an ultrafine nanoporous structure. Obviously, the presence of other metals in the alloy, in addition to silver and gold, may play an active role during the gold nanoevolution but no systematic studies have been reported.

Gold evolution during the dealloying process at nanometric scale justifies the preserving memory of larger size structures such as specimen form (Figure 5a-b). Moreover, the nanoporous structure explains the brown

color on the basis of the interaction between light and gold by surface plasmon resonance [38-39]. As previously observed, the high surface area makes the gold sponge thermally unstable. In the annealing stage, higher temperatures increase the surface diffusion of gold atoms leading to thermal coarsening. This process is exothermic in accordance with reduction in the energy of the system moving from high to lower surface material. With the annealing process the nanoporous structures disappear, resulting in a typically yellow gold bulk color. Generally, at 500°C the nanoporous structure is almost completely destroyed [14], although in the case of assays specimens are heated to 1050°C for practical reasons.

CONCLUSIONS

Gold parting with nitric acid substantially contributed to historical knowledge acquisition relating to the development of building furnaces, chemical glassware and synthesis of inorganic acids. With the development of large-scale industrial production of nitric acid, the use of the latter in the parting stage grew, with a peak in the first half of the 20th century. However, more recently, the high cost of nitric acid and the requirement for large NO_x scrubbers have vetoed its extensive use in large-scale industrial refining. As a result, other treatments are now used to refine low-grade gold bullion, such as the Miller process due to its technological development. However, nitric acid is still used at the parting stage on the laboratory scale after cupellation assay. Over the last two decades, the experimental and theoretical studies reported in the literature of dealloying process have allowed the mechanism involved in the formation of nanoporous gold material to be understood.

In conclusion, from a historical point of view, gold parting development occurred as the result of human experience without real scientific understanding of the treatment taking place. Recent academic research on the dealloying process represents a bridge to the understanding of the same phenomenon that occurs during the parting stage in the case of gold refining.

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