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Thanks to many years of experience of UnoAErre, in this presentation we will discuss the problems related to silver processing when the alloy contains a high oxygen level, due to the raw material or to incorrect melting/casting technique. Practical recommendations will be given on how to avoid these problems.

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The Difficulty of Working with Silver Alloys with a High Oxygen Content

Abstract

Oxygen content is a critical parameter for success in the production of silver and silver alloy semifinished or finished products.

When "not certified" raw materials are used or melting is not carried out with sufficient care, quite frequently poor quality castings are obtained and consequently a high reject rate is observed in the finished product. Thanks to many years of experience of UnoAErre, we can illustrate these problems and give an explanation to some defects caused by a high oxygen content.

Moreover we will give a short description of melt degassing techniques and molten metal protection during pouring for some silver alloys.

Foreword

It is surely wrong to consider Uno-A-Erre as a company producing only gold jewellery. Since several years it is present also in the trade of silver products, mainly with the production and marketing of semifinished products, such as plate, wire and tube or findings (beads, clamps, etc.).

About 50 tons of silver semifinished products have been sold in the year 2000 only. In the Uno-A-Erre factory of S. Zeno (Italy) the production of silver can be subdivided into two parts:

- 90% production from continuous casting (wire and plate)
- 10% cast ingots.

Continuous casting is strongly preferred in comparison with ingot casting because of two simple reasons: higher productivity and better quality of the product.

Year after year product quality has been steadily improved, thanks to accurate control of raw materials, careful control of cast product quality and some technical improvements in the casting shop.

Control of raw materials

The ASTM Standard B-413-64T gives the following upper limits for the foreign impurities content in the different grades of fine silver.

Table 1 -Silver purity levels - ASTM Standard B-413-64T

| Element | Composition, % by weight | | |
|-------------------------------|--------------------------|-------------|-------------|
| | Grade 99.90 | Grade 99.95 | Grade 99.99 |
| Silver min (Ag) | 99.90 | 99.95 | 99.99 |
| Silver and copper min (Ag+Cu) | 99.95 | - | - |
| Bismuth max (Bi) | 0.001 | 0.001 | 0.0005 |
| Copper max (Cu) | 0.080 | 0.040 | 0.010 |
| Iron max (Fe) | 0.002 | 0.002 | 0.001 |
| Lead max (Pb) | 0.025 | 0.015 | 0.001 |
| Palladium max (Pd) | - | - | 0.001 |
| Selenium max (Se) | - | - | 0.0005 |
| Tellurium max (Te) | - | - | 0.0005 |

In a note to the above table we can read: "In this specification it is to be noted that, while oxygen is neither specified nor determined analytically, it is known to be present in the refined silver. When calculating the purity of refined silver by difference, **oxygen will be considered as silver**".

This statement is clearly questionable, and the comments will be given later.

Table 2 shows the results of the analyses carried out with an ICP spectrometer on some lots of pure silver grain used by UnoAERre.

**Table 2 - Concentration of impurities in fine silver grain samples
(parts per million = ppm)**

| Sample | Cu | Pb | Te | Fe | Pd | Se | Bi | Total Impurities |
|--------|-----|----|----|----|----|----|----|------------------|
| Ag1 | 28 | 9 | 14 | 0 | 11 | 0 | 0 | 62 |
| Ag2 | 29 | 17 | 30 | 2 | 19 | 0 | 0 | 100 |
| Ag3 | 35 | 12 | 40 | 2 | 14 | 0 | 0 | 103 |
| Ag4 | 309 | 29 | 0 | 1 | 24 | 4 | 0 | 367 |
| Ag5 | 286 | 7 | 17 | 0 | 33 | 2 | 2 | 347 |
| Ag6 | 244 | 20 | 24 | 1 | 13 | 1 | 0 | 303 |

If we compare table 1 and table 2, we can see immediately that the first three samples belong to the highest purity grade (99.99%), while the last three belong to the intermediate grade (99.95%), that is more commonly marketed.

We have very frequently found a concentration higher than the upper acceptable limit for some most undesirable impurity elements (Pb, Bi, Te, Se). Sometimes appreciable concentration levels have also been found for other elements, like gold (Au), platinum (Pt), tin (Sn), zinc (Zn) and antimony (Sb).

The quality certification of silver grain bags (when present) guarantees only the fineness of silver but not the level of impurity elements.

Nevertheless many goldsmiths, silversmiths and producers of master alloys surely know that the presence and concentration of some impurity elements in the silver grain can be very important. Some more pollution problems in silver alloys can be ascribed to the purity of the metals used for alloying. Copper is the most important,

because of its higher concentration. To be on the safe side, we should use only high quality certified copper (OFHC). Raw materials like electrolytic copper, recovered copper and phosphorous copper will not enable to obtain high quality products. The same statement holds true for other metals commonly added to silver (indium, tin, zinc, brass): *high purity (certified) = high quality of the end product*.

Table 3 shows the oxygen (the *non-existing* impurity) content of the above listed silver lots.

Table 3 - Correlation between copper and oxygen concentration in fine silver grain

| Sample | Cu ppm | Oxygen ppm |
|--------|--------|------------|
| Ag1 | 28 | 188 |
| Ag2 | 29 | 156 |
| Ag3 | 35 | 173 |
| Ag4 | 309 | 250 |
| Ag5 | 286 | 267 |
| Ag6 | 244 | 268 |

We can easily see that oxygen content is not negligible. If we examine the oxygen analyses recorded in the archives of UnoAERre, (since more than ten years these analyses are carried out routinely with an oxygen analyser) we see that oxygen concentration ranges from 50 to 400 ppm max.

How is oxygen bound to silver? Why oxygen level is so high? Can such high oxygen level in the "pure" starting material have deleterious consequences?

Since long time it is known that oxygen is highly soluble in molten silver and that oxygen solubility is favoured by a high temperature of the melt. At the moment of solidification, the largest part of dissolved oxygen is released as oxygen gas. If oxygen is released too vigorously, we have the phenomenon of "spit". This phenomenon is partially reduced when oxide forming alloying metals like copper are present, that reduce oxygen evolution.

The same phenomenon is well known as "sprouting" in connection with silver analyses. At the end of silver cupellation, the silver bead will "sprout" if cooled too fast and it will take a cauliflower like shape, Figure 1.

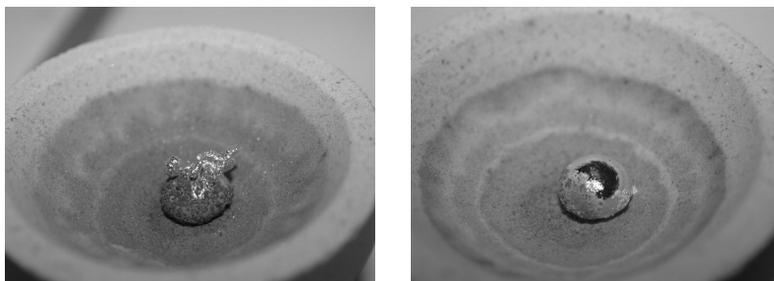


Figure 1- "Sprouting" of pure silver

Figure 2 shows the plot of oxygen evolution from a sample of 99.99% pure silver grain analysed with an oxygen analyser.

We have examined the rate of oxygen evolution with increasing temperature, to evaluate the content of dissolved oxygen gas and the nature of combined oxygen. The first two peaks (the first one is much higher) are observed before melting of the sample and are related to dissolved oxygen. With increasing temperature (third step) the sample is molten. At this point we find a peak that is probably related to combined oxygen.

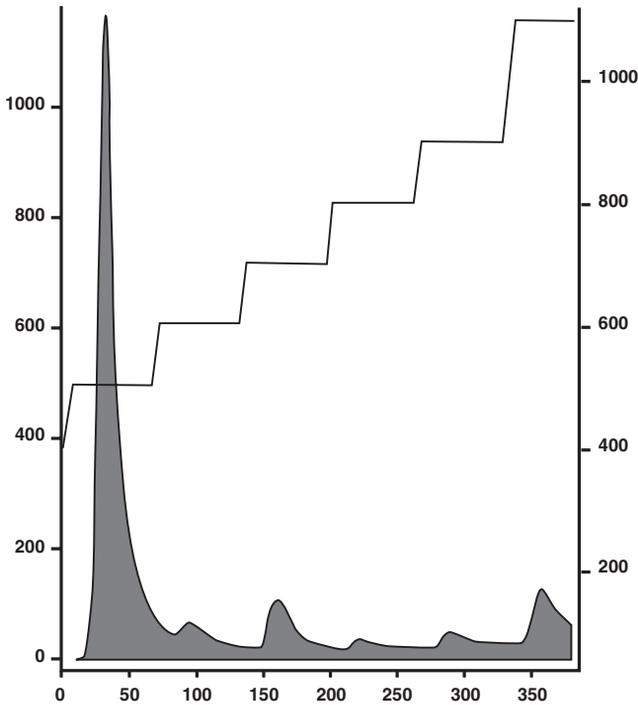


Figure 2 - Oxygen evolution from 99.99% fine silver grain
x-axis: time (seconds)
y-axis, left: gas release rate (arbitrary scale)
y-axis, right: heating power (arbitrary scale)

Therefore the ratio free oxygen/combined oxygen is strongly shifted towards free oxygen. This observation is confirmed by Figure 3, showing the result of the analysis of 99.95% pure silver grain, having higher content of copper and other polluting elements.

As in the preceding case, we observe the first two peaks of dissolved oxygen before melting, while after melting there are two more well defined peaks, ascribable to chemically bonded oxygen (metal oxides).

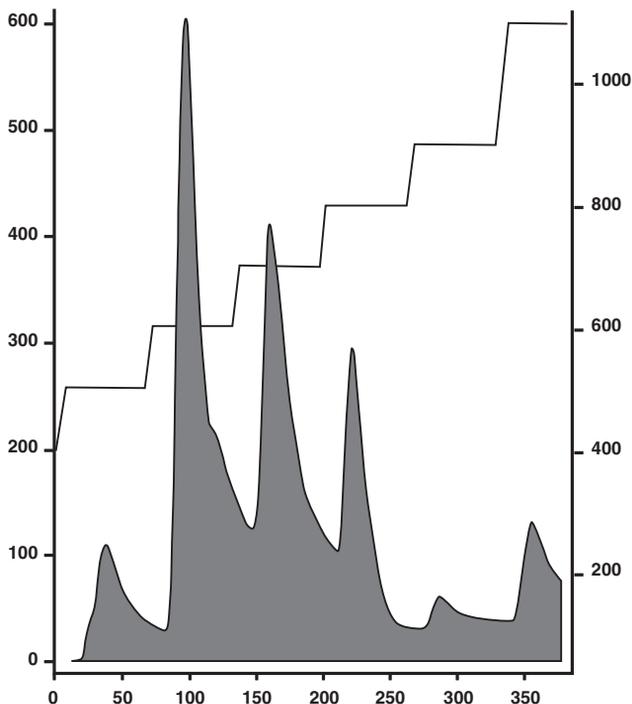


Figure 3 - Oxygen evolution from 99.95% fine silver grain
x-axis: time (seconds)
y-axis, left: gas release rate (arbitrary scale)
y-axis, right: heating power (arbitrary scale)

Our oxygen analyser does not allow an accurate identification of the different peaks of oxygen evolution, but we tried to identify the peaks of bonded oxygen by comparing them with the peaks obtained from some pure metal oxides. From these analyses it appeared evident that copper oxides (both Cu_2O and CuO) were present. Some doubt remains about the presence of Ag_2O .

The analyses showed also that there is an effect related to the shape of the sample. The wider is the surface of the sample, the higher will be the oxygen content. Therefore, under the same working conditions, fine silver grain will contain more oxygen.

We can now answer the two questions we asked before:

- There are both dissolved oxygen and oxygen combined as copper and/or silver oxide.
- If impurity metals concentration is negligible, oxygen will mainly be in solution.
- If impurity metals (mainly copper) concentration is not negligible, oxygen will still be mainly in solution, but there will also be an appreciable fraction of combined oxygen.
- Oxygen pollution is always present, irrespective of silver grain purity.
- The quantity of absorbed oxygen is directly proportional to surface area of silver grain.

Therefore shouldn't it be more correct to include oxygen too in the ASTM Standard, as it has been done for other raw materials, like OFHC copper or palladium sponge?

Quality control of the cast metal

We have used the 6 fine silver grain lots we have studied for making 6 plates with 930 fineness, by alloying silver with OFHC copper.

Melting and casting have been carried out with the usual melt protection methods, that are well known to all casters. We will describe them later.

The oxygen content of the 6 alloys is shown in table 4.

Table 4 - Oxygen content of the 93% Ag - 7% Cu alloys

| Sample | Oxygen ppm |
|---------------|-------------------|
| Lega Ag1 | 4.0 |
| Lega Ag2 | 6.2 |
| Lega Ag3 | 6.6 |
| Lega Ag4 | 4.0 |
| Lega Ag5 | 5.3 |
| Lega Ag6 | 6.2 |

The oxygen content can be considered negligible, as it is always less than 7 ppm. This means that, even if we start with silver grain with high oxygen content, the final product is not polluted, if degassing and melt protection are performed correctly. The same is true if we melt fine silver grain alone instead of an alloy, to produce pure silver castings.

After different rolling stages, with intermediate annealing in deoxidising conditions, the plates do not show defects attributable to the oxygen present in fine silver grain.

What does occur when degassing and melt protection are not performed correctly?
In an oxidizing atmosphere, at about 600°C, copper oxidizes rapidly and oxygen readily diffuses into the bulk of the material, with formation of copper oxides ("firestain" or "fire"). The penetration depth of such oxidation depends on temperature and treatment time. This kind of oxidation can be remedied only by removing a considerable amount of metal, with chemical or mechanical means. With deep oxidation this operation can be very difficult. If the oxidized material is not removed, the manufactured items will show slightly reddish and dull areas.

Now we will describe other evident effects of too high oxidation of the material.

1. Worsening of mechanical characteristics

Hardness, ultimate tensile strength and percentage elongation to fracture for different silver and silver alloy samples are shown in Table 5. The results show that there is a slight worsening of ductility, independently from purity of fine silver or silver alloy. This worsening is higher with stronger oxidation.

Table 5 - Mechanical characteristics

| | Silver 1000‰ | | Silver 930‰ | |
|--------------------------|-----------------|---------------------|-----------------|---------------------|
| | <i>oxidized</i> | <i>not oxidized</i> | <i>oxidized</i> | <i>not oxidized</i> |
| HV _{5Kg} (*) | 95 | 86 | 145 | 132 |
| UTS (N/mm ²) | 180.3 | 168.6 | 310.1 | 298.1 |
| Elongation % | 26 | 30 | 30 | 35 |

(*) with 70% cold reduction

2. Embrittlement of the alloy

When oxygen concentration in the cast alloy is about 500 ppm, Figure 4, the result is easily predictable: after a 30% cold reduction of section the cracks are very evident, Figure 5.



Figure 4 - Cast silver alloy rod

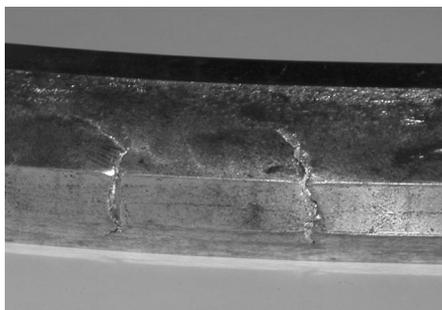


Figure 5 - The same of figure 3 after 30% rolling reduction

Cracks of the same type form after stronger cold reduction (50-70%), when oxygen concentration is lower (200-300 ppm).

3. Poor weldability

Poor weldability can be observed in the production process even with relatively low oxygen concentration (20-50 ppm). Figures 6 and 7 show the macrograph of a microplasma welded joint on pure silver strip containing about 60 ppm of oxygen. The high porosity of the welded joint is easily visible. Consequently the 2.5 mm outer diameter and 0.25 mm thick tube will show longitudinal cracks in the welded joint, after the first few drawing steps, Figure 8.

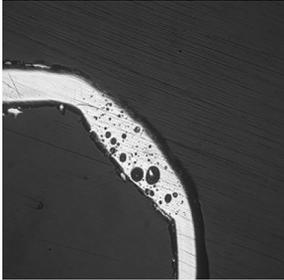


Figure 6
Oxidation of a welded joint, 5x

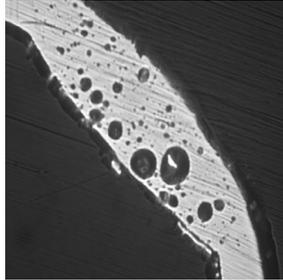


Figure 7
The same welded joint of figure 6, 10x

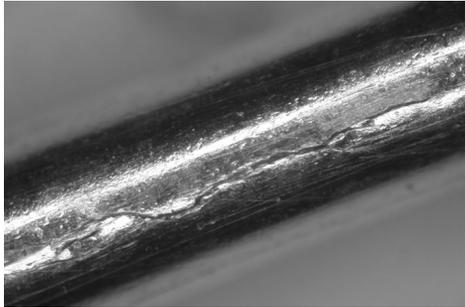


Figure 8 - Longitudinal cracks in the welded joint after drawing

Similar problems are met also with laser welding.

Figure 9 is a cross section of a part, laser welded without addition of filler metal, that showed brittleness in the zone of the weld. The scanning electron microscope image of the fracture surface, Figure 10, showed porosity in some areas.

The high porosity can be confirmed at higher magnification, Figure 11. The embrittlement is a logical consequence. The chemical analysis showed a high oxygen concentration in the wire used for making the chain link to be welded to the tube.

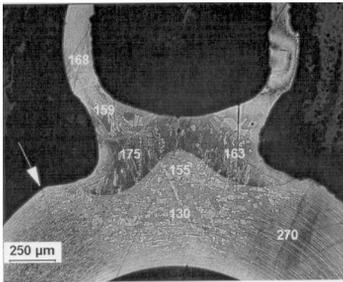


Figure 9
Laser welded part

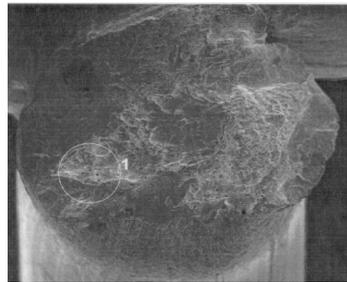


Figure 10
Fracture surface of the welded joint

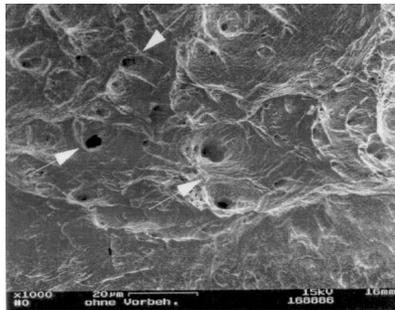


Figure 11 - Porosity on the fracture surface (see Figure 10)

Methods for melt degassing and protection

When we melt fine silver or silver alloys, it is very important to keep a low oxygen concentration in the melt before pouring. There are several ways to protect the melt from a detrimental oxidation.

- Addition of deoxidisers

The most frequently used deoxidisers are: lithium, sodium and phosphorus. A correct dosage represents the biggest difficulty for using these additions. We must add the correct amount, not more nor less. For example, in the case of phosphorus, if we add an amount larger than strictly required in copper rich alloys (Ag 800%), unwanted intermetallic components can form, that segregate at grain boundaries and will embrittle the alloy during annealing. In the same alloy a too low amount of phosphorus could favour the formation of firestain. The addition of phosphorus is frequently made as copper-phosphorus alloy.

Lithium shows the same drawbacks of phosphorus and is usually added only a short time before pouring.

- Addition of other alloying elements

Some other elements act as deoxidisers and in addition improve alloy fluidity: the

most frequently used are zinc, indium, tin and gallium. Cadmium is no more used because of its toxicity.

Each of these elements brings both advantages and disadvantages, therefore we will choose the most convenient one according to the requirements of the alloy and of the melting equipment.

Tin increases alloy fluidity, and is very useful for continuous casting, but it oxidizes very easily and forms a polluting residue that remains in the crucible. To reduce oxidation, tin is added only a short time before pouring and is not used for ingot casting.

Zinc improves alloy fluidity less than tin, but zinc oxide forms white flocks, that are easily removed from the crucible and do not pollute the melt. Zinc is favoured also by its lower cost. Zinc can be added as brass to reduce oxidation loss.

Indium is surely the alloying element showing the best combination of advantages and in addition substantially improves the workability of silver alloys.

Because of these favourable characteristics, in recent years indium is the most frequently used addition for silver alloys, in spite of its high price: the price of indium is not far from the price of silver.

Gallium is not frequently used, but improves alloy fluidity better than zinc. Even in this case the cost could be a limiting factor (the price of gallium is slightly higher than the price of indium), but its use is limited mainly by the fact that, when present in the alloy, gallium is easily oxidized during the usual annealing operations.

- Graphite cover

If we cover the melt with a layer of graphite powder, we form a barrier against oxidation. In continuous casting, this method gives the advantage that, when the crucible is emptied at the end of the casting operation, the graphite residues do not adhere to the crucible wall and can easily be sucked out. If new molten metal is added, the graphite powder will float and will continue protecting the melt without polluting it. However this method should be used in combination with a reducing flame, because graphite powder alone is not sufficient to give the required protection.

- Reducing flame

Burning the oxygen contained in the air is surely a way to protect the melt from contact with oxygen. Usually natural gas or propane are used for making a reducing flame. This method can also be used for ingot casting. The flame protects the melt while pouring in the cast iron mould. The design of the nozzles for distributing the gas is very important to protect both the crucible and the mould.

- Poling

This technique has been borrowed from copper smelting. A green pine log is introduced in molten copper to reduce oxygen concentration. The pine wood burns and gives off water vapour and reducing gases. This operation is named poling and enables to remove oxygen from the bulk of the melt. In the case of silver, some wooden sticks are used instead of the pine log, but the result is the same.

- Blowing in

This practice is widely used for steelmaking but finds little use by the goldsmith. A graphite tube with a ceramic end is used. This tube is introduced in the melt and inert gas, like nitrogen or argon, is blown in the molten metal to remove dissolved oxygen. There is high probability of projection of hot liquid metal squirts and, if we compare the equipment for melting precious metal to a steelmaking plant, it can be easily understood why this technique finds little use.

Conclusions

The main objective of this paper was to give practical recommendations for obtaining silver products free from defects caused by oxidation. We have discussed the main variables of the process - raw materials and processing techniques - and different examples of defects. Therefore we can recommend the following "golden rules" for producing high quality silver castings:

- Use fine silver with impurity content within the limits given by the ASTM standards and not too high oxygen concentration (lower than 200 ppm).
- Use OFHC certified copper (do not rely on other types of copper).
- Use pure, certified metals for alloying (In, Sn, Zn, etc.).
- Protect the melt before and after pouring.
- Perform a degassing step before pouring.

It should be advisable to have an oxygen analyser, at least in the casting shops producing large quantities of silver products. A prompt evaluation of the quality of the cast material enables to avoid further work or at least to shift the material to a more suitable use, if too high oxygen concentration is detected.

After years of careful study, UnoAERre has formulated factory acceptance specifications for silver semifinished products (plate, wire). Oxygen content is one of the more attentively considered parameters, mainly when further processing includes welding.

The average oxygen content required for acceptance is ≤ 10 ppm.