1. Introduction

The term hard spots usually indicates the imperfections displayed on the piece surface after polishing. Basically they are high and hard relief spots which the mechanical finishing cannot eliminate, but usually stresses even with more force. In fact by insisting on polishing the hard spot zone, the material around the defect is removed, since it is tender. The result is to have hard spots that can be visible to the naked eye. The problem is that these defects, mostly, can be individuated only after polishing, therefore together with the damage due to the piece removal there is also all the time taken to produce and finish the piece.

The causes on the rampage which usually give birth to this defect are several. In this work the most common origins of hard spots growth have been analyzed and reported.

One of the main causes surely is the presence of impurities in the raw materials used. When gold items are produced everyone (producers and final users) pays very close attention to the gold content, especially that the gold composition corresponds to the mark printed, while on the other hand, no one pays attention to impurities, i.e. to what is no gold and it is not purposely added, neither the pure gold ingot nor the master alloy. Such impurities can have very serious consequences on the quality of the items produced, like for example the hard spots growth.

An impurity is a compound or an element of the same nature of the alloy, which presence in the material is not provided or wanted. Mainly the causes of this problem are of two types:

- Raw material impurities
- Contamination of the production process

Above all it is harder to prevent against the impurities due to raw materials. Therefore it is necessary to chose reliable and certified suppliers. Especially it is advisable to pay very close attention to the pureness of gold, which is generally stated at 99.99%.

The gold refining available on the market is usually carried out by chemical treatment. As per this method, it is hard to separate completely gold from the other elements of the platinoid group (Ru, Rh, Pd, Os, Ir, Pt), called PGM.

The refining mechanism is based on the solution of elements in a solvent (aqua regia). The solute is left then to settle to allow gold precipitation, but even the other elements of the alloy to refine (Platinoids) do have the same behaviour. In order to separate them the chemical differences are exploited like for example the different density which drive to the stratification of the elements. It is therefore possible to intervene, physically, by removing the undesired layers. In any case it is a very delicate process.

Anyways, gold refining methods which guarantee more purity do exist. These sort of technologies are based on electrolytic systems which consists in the application of a potential difference to a galvanic cell, where inside gold is melt. That way the gold separation is facilitated from the other elements through the semi-reaction of reduction here following:

\[
\begin{align*}
\text{Au}^+ + e^- & \rightarrow \text{Au (solid)} \\
\text{Au}^{3+} + 3e^- & \rightarrow \text{Au (solid)}
\end{align*}
\]

Such processes allow reaching extreme grades of pureness but they are too expensive and not applicable to the industrial reality.

It has to be taken into consideration that even the production process displays a spring of potential contaminations of different nature, which contain undesired residuals. A typical example is to use contaminated crucibles with traces of grain refiner or deoxidizing elements to produce alloys which do not require their presence, or when the same crucible is used for different colours. It must be noted also that the same crucibles (even when not contaminated) can be a spring of corruption by releasing noxious elements to the alloy.
Further on we will mention this sort of hard spots generated by the causes above mentioned as hard spots generated by impurities.

Another cause may derive from a wrong use of master alloys. In fact master alloys are generally used in the goldsmith field, they are made by different kinds of elements, which are worked together with gold during casting and are made on purpose to confer the precious alloy specific characteristics, both mechanical and aesthetical. By taking for granted that such master alloys are produced only with raw materials of great pureness and quality, it must be said from the beginning, that the master alloy is generally planned to display good results only when alloyed with specific finenesses. This is because some elements must be present in the alloy in very reduced quantities (for example grain refiners and deoxidizing elements), and they work properly only when they are in well determined quantities. This means that by alloying to different finenesses that those mentioned, may produce important effects on the concentration of such elements and then also on the efficiency of their action. At the same time the simultaneous use of two different master alloys (for example one with grain refiner and one with Silicon) favours the growth of hard spots.

Another cause for hard spots can be the use of the same material for more than a casting. It might happen that alloys with grain refiner (Iridium, Ruthenium and Rhenium) drive to the presence, on the surface, of spots with entirely different composition and usually of higher hardness, due to the fact that casting by casting they accumulate and aggregate among each others. Even Silicon may display such a problem, in fact especially in white alloys, it tends to react with Nickel and to form compounds which the more the number of castings increases the more they grow and create hard spots. A very important consideration to be done is that for all the elements added in small quantity (parts per million, as refiners and Silicon) it is fundamental to have a good homogenization in the alloy, since when they are concentrated in some areas, they can combine and create very hard aggregates as described above. Here following we will call the just described as agglomeration hard spots.

2. Practical cases

Here are reported the practical cases found during three years of work by ProGold. They are divided in hard spots observed as hard spots by impurities or agglomeration. Together with any practical example some advices are given to avoid such defect to happen again in the future.

Hard spots due to impurities.

Impurities are present in the raw material (gold) and can work as nucleants and favour the refiners aggregation in some areas of the metal. It might happen also that such impurities correspond to the elements working as refiners; in this case there is a saturation of the refiner which draws to the growth of small spots (in fact the compositions are calibrated, a higher presence of such an element draws to create this problem).

The impurities can also accumulate casting by casting; it is of common practice to reuse the scraps of old castings and take the material to refine only after a certain amount of refining cycles, with the aim to reduce the production costs. Anyways, during the production cycles the material keeps collecting impurities from the most different origins: therefore an excessive use of the scraps can charge the metal, step by step, with corrupting elements.

This damaging effect is even more amplified when the scraps are not correctly cleaned, especially when they derive from castings made of different alloys from the one under use. The corrupting elements usually have higher melting temperatures if compared to the alloy one, so they are present in the cast under solid particles. Due to the low solubility of the impurities, caused by the scarce capacity of the crystal lattice of the base alloy to contain extraneous elements, aggregates of solid particles, with a non-homogeneous distribution, can form. These generate surfacing defects as hard spots (picture 1) which extremely worsen the aspect of the piece.

![Picture 1 - impurities hard spots](image1.png)

The aesthetical impact is even worsened, because if you polish a piece with hard spots, you obtain the so-called comet effect. The polisher in fact, cannot remove the aggregate, since this one is characterized by high hardening, and the material below this forms a relief which appears to be visibly as a comet (picture 2).
Iron worked as a nucleant and favoured Iridium coalescence. To avoid such problem, scraps with corrupting elements should be avoided. For sure those coming from workings with the removal of the crucible, display a very high chance to contain polluting elements, therefore it will be better to eliminate them beforehand. A very similar case is displayed in Picture 4, it is a defect observed on an 18ct red alloy (5N colour).

Also here they are Iron-Iridium aggregates, obtained this time by continuous casting. The iron probably comes from the attachment bar of the continuous casting. Therefore we advise to pay the closest attention in continuous casting, particularly do not take out the solidified gold on the bar, by putting this last one inside the pre-melting bath to liquefy the precious metal. Another important shrewdness is to use different crucibles in function to the kind of alloy to be cast. It should be better to avoid the use of the same crucible for alloys with Silicon and for alloys with refiner, but anyways, it will be enough to avoid sharing the same crucible among coloured gold and white gold. With regards to the crucible, we advise to pay particular attention to their quality and to the material they are made of. Some problems can come from the use of crucibles made of Silicon carbide. This last one, during casting processes, can release Silicon which, mixing with molten metal, pollutes the alloy favouring the growth of hard spots as in picture 5:
In Picture 6 Osmium and Iridium hard spots are reproduced. Further on it is reported an example of hard spot formed by Osmium and Tungsten, picture 7.

Such hard spots were observed in an 18 ct white gold alloy and are composed by Nickel silicides. Its growth has to be attributed to Silicon release by the crucible which saturated the quantity of Silicon bearable by the alloy drawing to the growth of agglomerates. It is advisable, therefore, to use crucibles which corresponds to the specific requisites, like low chemical reactivity with molten metal and high resistance to thermal shocks.

The most frequent types of hard spots observed derive from impurities present in the raw material, particularly in raw gold. A very common case is the one of Osmium presence in gold. Unfortunately even by buying 99.99% pure gold you cannot be sure about this defect not to display as we have already explained.

Osmium works as nucleant and draws to the growth of aggregates with refiner. Osmium hard spots normally display an well characterized, squared and with sharp edges. Furthermore various examples of such defects can be observed.
We relate also to the pictures of Osmium and Ruthenium hard spots (Picture 8). As you can see in picture 6 the morphology does not change so much.

![Picture 8 – Osmium and Ruthenium hard spots](image)

The Osmium hard spots are bigger if compared to those analyzed so far. To avoid such problem it has to be bought, exclusively, gold coming from electrolytic refining. If chemically refined gold is used, there is always the chance for Osmium to be present and to be a polluter. Once the defect is observed, the whole material must be send to refine and begin again with brand new material.

We are going to take into consideration a problem we faced mainly with 14 ct red gold. To be able to refine a 14 ct red gold it is necessary to introduce a huge amount of Iridium, since this element is soluble in Copper and therefore a big part of it works to produce the refining effect (gold displays red colour because there is a big quantity of Copper in the alloy, it’s Copper which confers the colour).

We learnt that various producers, after having sent the scraps to refine, for a couple or three times, started to have big problems of hard spots, with the typical morphology of Iridium hard spots but very big and evident like if their cause was the over-saturation of Iridium in the system. An example is displayed in Picture 9.

![Picture 9 – Hard spots by Iridium saturation](image)

The cause of this problem has been found out to be that, after refining, gold is obtained with Iridium. Iridium belongs to the platinoids group and as before explained, it turns out to be very difficult to separate from gold. Therefore when you alloy gold with a master alloy there is a higher quantity of Iridium than the one tolerated by the system, which provokes the growth of hard spots. Its proof is that if the pure gold itself is alloyed with a master alloy without refiner you can obtain a microstructure which is refined anyways, because the refiner is introduced together with gold. To avoid such problem we recommend, during the refining phase, to pay particular attention. In fact when Iridium is present, some small grey/ black particles, which remain in gold after the refining step, should be recognizable.

**Hard spots generated by agglomeration**

If you do not have a wide experience in the master alloy production, it might happen very often, that you cannot grant an homogenous distribution in the alloy of those elements added in small percentages (like for example refiners and deoxidizing elements), which, as explained above, if introduced in a non proper way, can provoke the growth of hard spots. In Picture 10 there is an example of such hard spots observed on 18 ct yellow gold pieces:
In this case, the inconvenient is the result of small quantities of pure Iridium added, which the producer used to add to the metal during the casting step. The use of a master alloy, already with Iridium in its composition, was enough to eliminate and solve the problem. By any case, Iridium must never be added as a pure element but through a master alloy to guarantee better homogeneity. Another example can be observed in Picture 11.

In these two pictures you can see an hard spot in a 14 ct white alloy. Such spot is made by a “cloud” of very close spots of Ni silicates. The most probable cause, this time, is due to an excessive reuse of the scraps, incrementing the little spots coalescence, which after the polishing phase, are even more evident due to the comet effect. To solve the problem it was enough to start with fresh metal from the very beginning. The same problem, related to an excessive scraps reuse, was noticed in 14 ct red alloys. In this case iridium hard spots were noticed, which morphology turns out to be identical to the one in Picture 10. The problem can be solved as displayed above.

In picture 12 it can be noticed a completely different case:

In these two pictures is displayed an example of hard spots observed on items produced by continuous casting. The morphology turns out to be the exact same of picture 10. Such spots are mainly made of Iridium (like in picture 10). The only difference is the production process used. In this case the spots grew due to a microsegregation in the liquid phase, caused by the elongated stay in the molten state, that the metal undergoes when it is used in continuous casting. According to this the grain refiner segregation is improved for the gravitational effect, this is because Iridium shows a higher density than all the other elements (22.5 g/cm3) and therefore tends to deposit on the low
part of the crucible (over the solidification front). The problem solution was to execute a pre-melting in an aside crucible and moreover to keep the metal stirred mechanically (using a graphite stick) during the continuous casting in order to limit the segregation. Furthermore, it is suggested to set the casting speed the higher the possible (according to the quality of the product obtained) in order to reduce the time of permanence at the liquid state of the metal and, consequently, the entity of hard spots growth. This kind of problem can also appear in investment casting processes, when the pre-melting is not carried out, in fact there could be many differences of finenesses in pieces set in different parts of the tree. There have also been many cases of hard spots growth even by using entirely fresh metal. In this case, the problem can depend on the casting temperature.

The explanation is that a grain refiner grants a good result only when homogeneously melt in liquid before the solidification to start: the temperature of the cast should be fairly high and there has to be time for the dissolution. Therefore, in such cases, it is advisable to rise a lot the casting temperature during the pre-melting. To our opinion it is always helpful to do a pre-melting, because it favours a higher homogeneity of the alloy, eliminating the possible causes which inhibits the refiner action, which could in case not be distributed homogeneously (for example if it concentrates in some areas, like in the previous case, and so there is not enough to cover all the material). This problem is normally more evident with white gold. In picture 13 a big grain structure can be observed, obtained after the first casting of a 14ct white gold.

3. Conclusions

In conclusion to our practical analysis we advise to work, if possible, with pure gold 99.99%. The best will be if in the details of purchase there were together with the fineness also the chance to have an analysis of the dangerous impurities. When the ingots are sent to refine, it will be advisable to ask for a 99.99% refining with a procedure which eliminates the PGM (metals of Platinum family); in fact the impurities are dangerous and turn out to be Os, Ir, Ru, Rh (so-called PGM), while the presence of Ag and Cu it is not dangerous because they are elements usually added to gold. It is advised also to work the more possible with clean and good quality material. This means that you must pay attention both to the cleanliness of the scraps more than to all the components which get in touch with the liquid metal. Therefore the scraps must be cleaned before use, and if possible also clean the crucibles and the various sticks. You have to be very careful also about the number of times the scraps are reused, and better it will be to register after how many times the defects appear in order to prevent them, by sending the metal to refinery before the defects appear (for example if I take a close look to my production and see there is the presence of hard spots only after reusing the scraps for 10 times, to avoid the defect I will send them to refinery after 8 castings, so that I can prevent myself and do not have any problem anymore).

4. Bibliography

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