

Abstract

The daily routine of the goldsmith is plagued with unexpected problems such as random casting defects, which are very difficult to diagnose properly. This often causes a big waste of time and useless attempts to find the right solution. From our archive of defect analyses, collected over a ten-year period, we selected cases involving hard spots commonly occurring and difficult to diagnose correctly with the resources normally available in a goldsmith's laboratory. It can be stated that the usual definition of hard spot actually identifies defects which, even when displaying the same appearance (under the naked eye or at low magnification), are a consequence of different causes. Basing our assumptions on such considerations, we sketched a detailed classification of various classes of hard spots, providing a series of causes and possible solutions.

Introduction

In the last four years, thanks to the help of information systems, we have been able to carry out a simpler analysis of the data obtained from the technical assistance to our customers. Our statistics showed that about 38% of the problems were generically outlined as a problem of inclusions with a possible "comet tail effect" (Graph 1).



Graph 1 - Distribution of the defect types noticed by the customers between 2004 and 2007

However the perception of the human eye or the instruments of general practice in a goldsmith laboratory rarely allows defining the problem properly. Defects of different nature are very often confused as if they were the same defect, or they show almost the same features. This is the reason why defects due to oxidation are frequently confused with porosity or how a "comet tail" could be ascribed to two different defect categories (Graph 2).



Graph 2 - Real distribution of "inclusion" defects noticed between 2004 and 2007

The comet tail defect hides, in fact, a whole series of causes even extremely different from each other. The definition of comet tail usually describes a final effect which is displayed, at the naked eye or at low magnification, always in the same way, i.e., a part of the surface stands in relief and some scratches start from that point. This is due to the impossibility of removing the part of metal lying behind the "hard spot" during the polishing process, causing a noticeable aesthetical damage to the piece, whose surface cannot be finished properly (Figure 1).



Figure 1 - Illustration of the "hard spot" problem

The comet tail defect could be originated by a large number of different causes, such as problems faced during the polishing process, various kinds of inclusions, problems connected with the raw materials, external pollution, scrap recycling, etc. Of course, a complete knowledge of the whole production cycle can provide fundamental elements to understand the problem correctly and, as a consequence, to find a solution. However at present in most cases the instruments required to find the causes of the problem are not available in a goldsmith's laboratory.

For an exhaustive and definitive analysis, it is always essential to use instruments allowing both the visual observation and the chemical analysis at high magnification. The SEM (scanning electron microscope) equipped with an EDAX microanalysis system can best satisfy these needs. This equipment enables us to observe the morphology of the defect and to carry out the localized chemical analysis of the defect area, so it provides fundamental information for a precise diagnosis. The experience we gathered with the use of such technique provided the idea for this paper: to clear the ground from all those ambiguities around this topic, by trying to provide an exhaustive and clarifying analysis of each problem sub-class. Moreover, we thought about supplying a practical device (a sort of atlas of the hard spots), which could contribute to finding the correct solution for the problem in the most immediate and simple way.

The first classification may be done by distinguishing between hard spots and "inclusions" (Graph 2).

A hard spot is a particle of metallic or intermetallic origin, while a particle of ceramic or nonmetallic origin is defined as an inclusion.

A further distinction can be made on the basis of the nature of the elements composing the particles (Graph 3).

The hard spots can be therefore divided into:

- Hard spots due to impurities
- Hard spots due to segregation phenomenon
- Hard spots due to agglomeration phenomenon



Graph 3 - Distribution of hard spots based on their nature

Hard spots due to segregation and agglomeration can be traced back to elements present in the raw materials, while the hard spots due to impurities can be traced back to unwanted polluting elements. It is very interesting to note that about half of the hard spots derive from pollution phenomenon.

Inclusions can be divided into (Graph 4):

- abrasive inclusions
- graphite inclusions
- oxide inclusions
- investment inclusions



Graph 4 - Distribution of the inclusions based on their nature

Investment inclusions involve the cases where particles of investment are detected on the items' surface. Graphite inclusions come from graphite particles released by crucibles, dies or mixers.

Oxide inclusions can be due to oxides present in the alloy during the casting step. Abrasive inclusions are due to problems caused by an improper matching between the material and the abrasive in the polishing process. Abrasive inclusion in particular are very often confused with the socalled hard spots.

These preliminary distinctions provide a draft regarding the way in which the problem can be faced and, therefore, it will be necessary to examine each category separately. Before continuing, it is necessary to clarify a concept that will be used very often, i.e., the definition of an intermetallic compound.

The aim of this paper is not to strictly discuss the theory and formation of intermetallic compounds, but only to give an idea of the main causes

The definition of intermetallic compound is particularly important since most of the hard spots are made of intermetallic compounds and understanding what they really are and why they form can help the full understanding of the hard spots phenomenon.

From a theoretical point of view, the words "intermetallic compound" refer to a particular set of chemical compounds which do not follow the classic valence rules or the multiple proportions law (the so-called Dalton's law). This is the reason why they are also identified as electronic compounds or non daltonic compounds.

The formation of intermetallic compounds is explained by a statistic law written by the British chemist and metallurgist William Hume-Rothery and the "Hume-Rothery rule" was defined in his honor. In other words, intermetallic compounds are compounds with a specific chemical composition (for example, Ir4Si5, Ir3Si4, OsSi2, etc.).

The reason for the existence of the intermetallic compounds derives from quantum chemistry laws, which demonstrated that to such structures show low potential energy and therefore maximum probability when compared to other theoretically predictable atomic structures.

Therefore, intermetallic compounds have very high probability to form. As a consequence, as soon as the chemical-physical condition makes the formation of such compounds possible, it is almost sure they will form. The base theory of quantum chemistry may be too long and difficult and might not support the discussion at all, but it may be helpful to use an analogy to better explain this concept. Let us consider, for example, the solidification process. It is ruled by precise thermodynamic laws which involve also a parameter called free-energy. Free-energy is a function of the state of the matter, or better it is able to define the state of a system in function of two variables only, in this case pressure and temperature. Considering that most of working operations take place under atmospheric pressure, we may also reduce the variable to one only, taking the pressure as constant and equal to 1 atm. Therefore, the free-energy represents the value of available energy present in the matter at a given temperature. The energy is a function both of the material and of its state. For example, gold has different free energy functions, one referring to the solid state and one referring to the liquid state. In both cases they are state function, so they will be a function of temperature only. It is therefore possible to outline a graph of the free-energy vs. temperature for solid gold and for liquid gold (Graph 5).



Graph 5 - Trend of the free-energy in function of the temperature

Each element present in nature tends to minimize its own free-energy. This concept is valid starting from the atoms to end up with any physic state of the matter. It must be therefore applied also to our case. Gold will tend to have the minimum possible free energy. This is the law ruling not only phase changes, but also all chemical and physical transformations.

At a temperature less than Tf, gold in the liquid state will have a free-energy higher than the energy at the solid state. Thus, at a temperature T<Tf, gold, having more opportunities to be in a state with less energy, will usually be found in the solid state. Shifting the concept of energies and probabilities to the intermetallic compounds is a short step. We are no longer talking about the possibility of finding a compound in the solid or the liquid state, but about the probability it will organize in different ways in the solid state. The difference of free energy between an intermetallic compound and a homogeneous solution is so wide to be nearly sure that the compound is going to form in certain circumstances.

Here following we will proceed to distinguish all those risky situations and to identify the related consequences.

Hard spots caused by impurities

Introduction

We can define as an impurity a compound or an element whose presence in the material is unde-

sired or not required. There can be two different sources causing the material's contamination:

- pollution from the raw materials
- pollution from the production process.

Impurities from the raw material are the pollution source most difficult to avoid because it concerns the external suppliers. Therefore it is strongly recommended to select reliable and certified suppliers. In the case of precious alloys, it is advisable to pay particular attention to the purity of the main components (Au or Ag in our case), without failing to consider the base metals, both when using master alloys or the pure elements.

Processes of gold refining

Introduction

Gold is an element belonging to the Group IB of the periodic table (like Ag and Cu) and it presents an electronic configuration very similar to the next groups (Figure 2). This is one of the reasons why this elements has a chemical-physical similarity to all the elements of the PGM family. All these elements are normally used for various purposes in the precious metals alloys and consequently they will be found in the gold to be refined. Some of these elements are also found in ores typically associated to the extraction of gold such as Pyrite (FeS2), Chalcopyrite (CuFeS2), Galena (PbS), Sphalerite ((Zn,Fe)S), Arsenopyrite (FeAsS).

26	2,3	AB	27	2,3	AB	28	2,3	Bw	29	1,2	Bw
7,86	iron	3000	8,9	Cobai	2900	8,9	NICKe	2730	8,96		2595
1536	Fе	55,847	1495	Co	8,9332	1453	NI	58,70	1083	CU	63,546
1,26	7,43	1,8	1,25	7,88	1,8	1,25	7,67	1,8	1,28	7,72	1,9
44	2,3,4,6,8	B Aw	45	2,3,4	AB	46	2,4	Bw	47	1	AB
ru 12.2	itheniu	um 4900	12.4	hodiu	m 4500	12.0	alladiı	um 3980	10.5	silver	2210
,.	Ru		,.	Rh		,.	Pd		,.	Ag	
1966		101.07	1966	10	2,9055	1552		106.4	960.8	1	07 868
						1002		100,1	000,0		07,000
1,34	7,28	2,2	1,34	7,46	2,2	1,37	8,33	2,2	1,44	7,57	1,9
1,34 76	7,28 2,3,4,6,	2,2 B Aw	1,34 77	7,46 2,3,4,6	2,2 Bw	1,37	8,33 2,4	2,2 Bw	1,44 79	7,57	1,9 AB
1,34 76 22,6	7,28 2,3,4,6,i osmiun	2,2 8 Aw n 5500	1,34 77 22,5	7,46 2,3,4,6 iridiun	2,2 Bw 5000	1,37 78 21,4	8,33 2,4 platinu	2,2 Bw m 4530	1,44 79 19,3	7,57 1,3 gold	1,9 AB 2970
1,34 76 22,6	7,28 2,3,4,6,i osmiun OS	2,2 8 Aw 0 5500	1,34 77 22,5	7,46 2,3,4,6 iridiun	2,2 Bw 5000	1,37 78 21,4	8,33 2,4 olatinu Pt	2,2 Bw 4530	1,44 79 19,3	7,57 1,3 gold Au	1,9 AB 2970
1,34 76 22,6 3000	7,28 2,3,4,6,i osmiun OS	2,2 B Aw 5500 190,2	1,34 77 22,5 2454	7,46 2,3,4,6 iridiun	2,2 Bw 5000 192,22	1,37 78 21,4 1769	8,33 2,4 elatinu Pt	2,2 Bw 4530 195,09	1,44 79 19,3 1063	7,57 1,3 gold Au 19	1,9 AB 2970 6,9665

Figure 2 - Abstract of the periodic table

The five most used processes for refining gold alloys are:

- Inquartation
- Aqua Regia Process
- Miller process
- Electrolysis
- Fizzer cell

We will proceed now with a short description of these processes to understand their potential and

limits.

Inquartation

This method implies a first phase when gold scrap is melted and cast together with copper and/or Silver. This step is necessary to obtain an alloy with a maximum gold content of 25% (from here the word inquartation). The obtained alloy will be soluble in nitric acid (HNO3). A layer of insoluble precipitate, formed basically by gold (even if not necessarily pure), will deposit on the bottom of the container used for the dissolution. Then a further refining will be needed. Therefore, the inquartation process turns out to be a preliminary step for the refining process which will be completed later with the use of aqua regia.

Process using Aqua Regia

The aqua regia process can potentially produce gold up to 99.99% fineness. It is based on the use of aqua regia (a mixture of hydrochloric acid and nitric acid in a ratio 4,5:1) to transform gold into water soluble gold chloride. An important limitation of this method is that the starting material should contain less than 10% silver to avoid stopping gold dissolution. This is the reason why this phase comes after inquartation. The inquartation process produces a gold grit with a low silver content. This grit is dissolved with a series of aqua regia additions. This solution should always have a little excess acid, without leaving residual undissolved gold. A yellow-green solution will be obtained, with undissolved silver chloride, nonmetal materials and PGMs. This phase is quite critical, because it is not always possible to separate gold from the PGMs completely. The method is also very much in uenced by the ability, experience and skill of the operator.

The process goes on with filtering the solution to separate the liquid (containing Au) from the undissolved residue. At this point, gold will be precipitated from the solution using a selective chemical reduction with proper reactants, such as ferrous sulphate, oxalic acid, hydrazine, formaldehyde etc. Gold will then begin to precipitate from the solution and it will be necessary to wait until the reaction is complete, before being able to filter the pure gold precipitate.

Miller process

The Miller process is an old method dating back to 1867. It is simple but dangerous and allows to obtain only fair results; it is possible to reach a maximum fineness of 99.5%.

The method consists of injecting gaseous chlorine in an molten alloy bath. In this way base metals and silver are eliminated in the form of chlorides, but it is not possible to separate gold from the PGMs.

Electrolytic process

This method too is very old (it was developed in 1863), but it represents also the best solution from the point of view of final quality. In fact, it is the only way guarantying the complete separation between Au and PGM. It involves the electrolytic dissolution of gold through the application of a potential difference to a galvanic cell. It favors the separation of gold from the other elements thanks to the semi-reactions reported below:

 $\begin{array}{rcl} \mathrm{Au}++\mathrm{e}-&\rightarrow&\mathrm{Au}\ (\mathrm{solid})\\ \mathrm{Au}3++3\mathrm{e}-&\rightarrow&\mathrm{Au}\ (\mathrm{solid}) \end{array}$

The reaction will dissolve an anode composed of impure gold in an electrolyte containing hydrochloric acid. Gold with 99.99% fineness will be deposited on the cathode.

Silver and the PGM separate as anode sludge, while non-precious metals remain in solution. This method is widely used only for refining primary gold, i.e., gold extracted from the ores. It is rarely used to refine small gold quantities, especially for economic reasons.

Firstly, the immobilization of gold in the electrolyte and in the electrodes represents an unfavorable economic factor. Secondly, in case you have to refine normal scrap, before using this method it is necessary to carry out a preliminary refining enabling to produce gold alloy anodes.

Process with Fizzer cell

This method is a variant to the electrolytic process. The electrolytic cell is divided by a semi-permeable membrane separates the anode zone from the cathode zone. In this way gold chloride remains in the anodic electrolyte and cannot reach the cathode to deposit.

This method uses impure gold anodes containing about 10% silver. A solution of gold and nonprecious metals is obtained, while silver chloride (insoluble) and insoluble metals (PGMs) will fall to the base of the cell. The solution is filtered and pure gold is precipitated with the same reactants used in the aqua regia process.

Gold refining - Considerations

As mentioned before, the electrolytic process is not widely used, basically due to financial reasons. This represents a considerable weakness. It has been already said that, from a theoretical point of view, it is possible to refine gold up to 99.99% fineness with chemical processes. However, these processes involve a wider set of variables than the electrolytic process. Too many of these variables are left to experience, ability, awareness of the operator. The result of the process of chemical refining may therefore go from excellence to poor-quality in what ma be an uncontrolled way. Another problem is the assay accuracy of the raw material and its consequent quality mark.

As is well known, it is possible to buy fine gold of different purity, as defined by the ASTM Standard B562 - 95 (2005):

- Grade 99.5 Minimum fineness 995 ‰
- Grade 99.95 Minimum fineness 999.5 ‰
- Grade 99.99 Minimum fineness 999.9 ‰
- Grade 99.995 Minimum fineness 999.95 ‰

This is an international standard, but it does not bind the producer, since he can choose whether or not supply pure gold following this standard. In fact, there are also intermediate fineness grades, such as for example 996, 997, etc.

Going deeper into the standard, it specifies that to define gold fineness it is also necessary to grant that several foreign elements are under the limits shown in Table 1

Element	Concentration,%						
-	Grade 99.5	Grade 99.95	Grade 99.99	Grade 99.995			
Au, min	99.5	/	/	/			
Au, min (difference)	/	99.95	99.99	99.995			
Ag+Cu, max	1	0.04	/	/			
Ag, max	/	0.035	0.009	0.001			
Cu, max	/	0.02	0.005	0.001			
Pd, max	/	0.02	0.005	0.001			
Fe, max	/	0.05	0.002	0.001			
Pb, max	/	0.05	0.002	0.001			
Si, max	/	/	0.005	0.001			
Mg, max	/	/	0.003	0.001			
As, max	/	/	0.003	/			
Bi, max	/	/	0.002	0.001			
Sn, max	/	/	0.001	0.001			
Cr, max	/	/	0.0003	0.0003			
Ni, max	/	/	0.0003	/			
Mn, max	/	/	0.0003	0.0003			

Table 1 - Chemical r	requirements	specified	by	ASTM	B
562 - 95 (2005)					

It can be very easily noticed that to quality mark gold as 99.5 it is necessary to guarantee only the gold percentage and the remaining 0.5% can be of whatever element. The remaining three grades have restrictions for other elements, but platinum group elements (PGMs) such as Os, Ir, Ru, and other heavy metals (Re) that are extremely dangerous for the formation of hard spots are not considered. Even if a producer may follow this norm, it is not granted that the material is free

from PGMs.

The analysis method is left up to the producer. A first solution is to carry out an assay to test gold fineness. But Au and PGMs cannot be distinguished with a fire assay. The obtained fineness value must be corrected. Therefore the gold sample from the fire assay should be dissolved with aqua regia. The undissolved residue is composed by PGMs. By weighing then this residue it is possible to define the real fineness and to calculate the percentage of PGMs in the alloy. It is a non trusted method because the ability and experience of the operator play a fundamental role, together with the fact that we can do only a semi-quantitative analysis. The second option is to rely on extremely precise analysis methods, like ICP-OES, to detect small traces of impurities. The analysis is done only on the impurities and the fineness of gold is calculated by difference. In this case more reliable results can be obtained, although the cost is high.

There is also a legislative problem as well, because there isn't anything to guarantee that fine gold is PGM-free.

These are the reasons to choose reliable suppliers. The best suppliers complete the ASTM standard with internal methods and widen the number of checked elements with the use of advanced analysis methods.

Quality of other raw materials

Obviously the attention for the quality of raw materials may not rest only at the main component of the alloys (Au in this case), but also the addition elements must be considered. In this case, too, it is recommended to choose the supplier with great care. This aspect is less critical from a theoretical point of view because the base metals (Cu, Ni, Zn) do not display the same problems as gold in the refining process. These elements are widely used in the industry and are readily available in high purity, electrolytically refined, grades.

It should be underlined also that the concentration of polluting elements could be diluted in the alloying process. Nevertheless, it is always important to deal with reliable suppliers, because even minimum traces of polluting elements can drastically compromise the result. A reliable supplier is a company that carries out accurate quality controls both on the raw material and on the outgoing product, using analysis techniques that are able to detect even minimum traces of polluting elements.

We can conclude that for a goldsmith laboratory it could be undesirable to buy all the elements required for the production of its own alloys. Very often the goldsmith is not properly equipped (neither it is financially advantageous to do it) with all the instruments required for a careful quality control on the incoming materials. During the production process this involves the risk to face problems hard to trace, especially considering the high number of alloying elements to be used.

After the quality of raw materials has been checked, further attention must be paid to the production process that is an additional potential source of pollution. Many may be the causes of pollution i.e.:

- Use of the same crucibles, mixers, or other instruments for different alloys
- Inadequate chemical inertia of the materials in contact with the molten metal
- Indiscriminate recycling of potentially polluted scrap

We will now analyze each case more deeply.

Hard spots from polluted raw materials

100% of the hard spots due to raw material pollution that we analyzed so far can be attributed to impurities present in the main component of the alloy, i.e. gold, because it is difficult to separate gold from the elements close to it in the periodic table.

The main factors common to all types of hard spots caused by pollution of the raw materials are two:

- The problem occurs also when casting fresh metal
- The problem occurs with different kinds of alloys.

These hard spots can be distinguished in function of their chemical composition.

Hard spots caused by osmium

Osmium is a typical polluting element of gold: in nearly all the cases where a problem of pollution from the raw material was seen, osmium was present. The morphology of the hard spots deriving from osmium pollution is typical. They are particles:

- With regular and quadrangular shape
- Usually isolated one from the other
- With relatively large size (typically about 50 μ m)
- Mostly intermetallic or composed by osmium and other PGMs or elements close in the periodic table

All the above features occur every time osmium is present. Even though the chemical composition of the defect involves other elements (Re, Fe, or others), differences were not noticed in the morphology or position of the hard spot. Being more precise, we could refer to a Os-Ir-Ru ternary system, because in the case of pollution of the raw material, these three elements are usually detected together. So, it seems that this ternary system plays a predominant role in the formation of the particles, with various combinations with other non-PGM elements. This result is evident from the following case studies.

"Case" #1

In this example, hard spots were found in an investment cast 10K yellow gold alloy. The master alloy contained Ag, Cu, Zn and Si.

Observation of the cast piece showed the presence of large inclusions randomly placed all over the surface. These inclusions displayed a quadrangular shape, as seen in Figure 3.



Figure 3 - SEM image of the defect

A microanalysis evidenced that these particles were made of Os, Fe, Ir, Ru (Figure 4). None of these elements was present in the master alloy, and the elements responsible for the problem were typical of pollution from the precious metal. So the attention was focused on gold quality. Further investigation confirmed that gold fineness was 99.95%.



Figure 4 - Microanalysis of the defect

This case proves that it is important to buy gold with 99.99% fineness. Even a 0.05% of impurities can be fatal to the final result. 0.05% may seem to be an almost meaningless percentage, but even much lower concentrations of these elements can cause such problems. When the polluting elements are present in considerable percentages, the problem can be easily observed also with the naked eye, as in the following example.

"Case" #2

In this case the problem was related to a 18K white gold alloy used for investment casting without stones in place. The used master alloy contained Cu, Ni, Zn, Si. All the pieces of the ask displayed evident nodules, visible to the naked eye (Figure 5).



Figure 5 - Appearance of the piece after polishing

Also in this case the SEM analysis detected hard spots (Figures 7 - 10) formed by unwanted elements such as Os, Ru, Ir (Figure 6). The analysis of the master alloy showed that it was not the cause of the pollution. Since the problem was observed also when using fresh material, gold was the only suspected remaining.



Figure 6 - Microanalysis of the defects



Figure 7 - Image at low magnifications of the piece



Figure ${\bf 8}$ - Magnification of a hard spot found on the piece



Figure 9 - Magnification on one "hard spot" found on the piece



Figure 10 - Magnification on one "hard spot" found on the piece

As it can be seen from Figure 7 - 10, size, shape and position of the defects are similar to Case #1, even if the elements found in the hard spots are not identical (in this case Fe is absent). We suggest this points to the predominant role of the system Os-Ir-Ru. The presence of Fe in the previous case did not in uence size and shape of the particles appreciably.

The pollution deriving from the raw material may also be worsened by further pollution from the working process, as it can be seen in the next example.

"Case" #3

This case regards hard spots observed on 14K yellow gold watch cases (Figure 11).



Figure 11 - Appearance of the examined piece

The watch cases were produced with the following production process: ingot casting, rolling, blocking, machining. The master alloy contained Ag, Cu, Zn, Ir. The problem occurred more predominantly when recycled scrap was used for casting. SEM analyses showed that the particles present on the surface of the pieces were made not only of Os-Ir-Ru, but also of W and Fe (Figure 12 and Figure 13).



Figure 12 - Microanalysis of the defect



Figure 13 - Microanalysis of the defect

In this case too, the particles (Figure 14 - 16) were quadrangular, with large size, and once again showed the typical shape of the Os-Ir-Ru system, in spite of the presence of Fe and W.



Figure 14 - Magnification of one hard spot found in the piece



Figure 15 - Magnification of hard spots observed in the piece



Figure 16 - Magnification of one hard spot found in the piece

In this case the presence of W and Fe may be caused by scrap recycling. The scrap from machining is polluted by small particles of highspeed steel detached from the tool. Recycling of this scrap involves the risk of contamination of the molten bath with small quantities of elements such as Fe or W. The presence of these elements can increase the chances for hard spots formation, especially when associated with the pollution of gold. As mentioned before, in the case of pollution of the raw material, the hard spots can occur in different production cycles, as shown by the following example.

"Case" #4

In this case the same problems were found, in the same period of time, both with a 14K white and a 14K yellow alloy (Figure 17 and Figure 18).



Figure 17 - Appearance of the 14K white alloy piece



Figure 18 - Appearance of the 14K yellow alloy piece

SEM observations (Figures 21 - 23) and SEM microanalyses confirmed the presence of unwanted PGMs (Figures 19 and 20).



Figure 19 - Microanalysis made on the white gold piece







Figure 21 - Magnification of a hard spot found in the white gold piece



Figure 22 - Magnification of a hard spot found in the yellow gold piece $% \left({{{\mathbf{F}}_{{\mathbf{F}}}}^{T}} \right)$



Figure 23 - Magnification of a hard spot found in the yellow gold piece

Hard spots caused by other elements

There were also a few cases where it was supposed that the main alloy components (Au or Ag) were polluted by elements different from Os-Ir-Ru, as for example Fe or Re. However, in these cases there might have also been the concomitance with other pollution sources, and it has never been possible to make sure that the cause of the problem was the raw material alone. These were hybrid cases and we preferred not to report them, because they did not contribute to a precise and distinctive classification. The solution of these doubtful cases could require direct actions during the production phase to eliminate some possible pollution sources.

Hard spots caused by pollution during the production process

Hard spots caused by pollution during the production process differ basically from the cases examined so far, since they never involve the same elements. There are some noticeable differences in morphology and in chemical composition.

Pollution caused by the production process may be distinguished into:

- Pollution caused by tools
- Pollution caused by crucibles, stoppers, dies and mixers
- Pollution caused by contamination with other alloys
- Deliberate pollution.

Hard spots caused by tools

The pollution caused by tools is typical of production processes involving continuous casting or machining. In both cases, the most common polluting elements, namely Fe, V, Cr, W, come from tool steels.

The characteristics of the hard spots caused by tools are:

- Reduced size (usually under 10 µm)
- They generally form clusters
- Present only when using scrap metal

A typical case of such pollution has already been described in Case #3, where, together with the pollution caused by the raw materials, characteristic pollution caused by tool steel components was observed. Therefore, Case #3 represents a hybrid situation where two concomitant causes contributed to form the hard spots. In any case, it is difficult to distinguish whether one of the two played a protagonist role.

The following example represents an unambiguous situation.

"Case" #5

Problems were found when polishing 14K white gold pieces produced by continuous casting. The problem occurred only when using scrap coming from previous castings. This observation, together with SEM examination of the pieces (Figures 24 and 25), showed the possibility of pollution caused by the tools used in the production process.



Figure 24 - Magnification of a hard spot found in the piece



Figure 25 - Magnification of one hard spot found in the piece

SEM microanalysis of the defect (Figure 26) detected the presence of Fe, and restricted the investigation field to items made of steel.



Figure 26 - Microanalysis of the defect

The problem was probably due to using the first part of the continuously cast bar. This portion of material, being attached to the pulling bar (usually made of steel), undergoes a high pollution by the components of steel that display a higher tendency to diffusion. Therefore, the first part of the bar tends to be rich in elements such as iron, and when reused as scrap, may cause problems. Even worse, the pulling bar is often dipped into the crucible with the gold alloy to recover the precious metal by melting, giving place to the above described pollution effects.

"Case" #6

In this example, hard spots were found on the surface of investment cast rings (Figure 27) after polishing.



Figure 27 - Item affected by the problem

SEM observation showed particles of irregular and edgy shape, embedded in the pieces and surfaced during the polishing process (Figures 28 and 29). The problem occurred only after scrap recycling.



Figure 28 - Magnification of one hard spot found in the piece



Figure 29 - Magnification of one hard spot found in the piece

In this case SEM microanalysis gave a surprising result (Figure 30), because only Al and O were found.



Figure 30 - Microanalysis made on the defect

Usually such particles are found only when mistakes are made in the polishing process, as better illustrated later on. But in this case the morphology did not match perfectly, since the particles were included instead of being stuck into the surface. We can conclude that the presence of alumina was due to the contamination of the cast material with scrap coming from the finishing department. Alumina is insoluble and can remain included into the metal to surface later during the polishing phase.

Hard spots caused by pollution from crucibles, stoppers, dies and mixers

Such problems occur when the surfaces in contact with the molten metal show inadequate chemical inertia at high temperature. For example, graphite provides high guarantees for this. But we cannot say the same of materials such as silicon carbide. Our experience on the matter seems to suggest that a crucible made of silicon carbide has a high probability of releasing Si in the molten metal. In this way an extraneous element is added to the melt, or, if already present, its concentration is changed in a significant way.

Nickel white gold alloys are particularly subject to this kind of problem. Nickel is an element that may easily form intermetallic compounds with silicon. The presence of uncontrolled quantities of silicon represents a condition of extreme risk for the formation of nickel silicide hard spots. Silicon may coexist with Ni in the alloy, but it has to be set in precise percentages. As soon as the right concentration ratio is overcome, intermetallic compounds are precipitated. This phenomenon will be discussed further later on, but here we will analyze one aspect. Hard spots due to pollution from crucibles, stoppers, dies or mixers generally present the following characteristics:

- Rounded shape
- Usually form clusters
- Size depends on the amount of pollution (up to circa 50 $\mu m)$
- White gold alloys are more frequently affected
- Present also in castings produced with fresh metal

"Case" #7

This case refers to hard spots in an 18K white gold investment cast without stones in place (Figure 31).



Figure 31 - Item affected by the problem

The master alloy was made of Ni, Zn, Cu, Si. An observation of the defect under the SEM revealed the presence of large rounded particles (about 80 μ m) (Figure 33).



Figure 32 - Magnified image of a hard spot found in the piece

The microanalysis of the hard spots revealed that these were made of Ni and Si (Figure 33).



Figure 33 - Microanalysis made on the defect

Silicon carbide crucibles were used for casting, so we hypothesized that the problem was not due to the master alloy, but that Si release from the crucible was altering the equilibrium of the percentages of Ni and Si in the master alloy. Casting in graphite crucibles solved the problem.

Hard spots caused by contamination with other alloys

This kind of hard spot occurs when different alloys are more or less consciously mixed together. A classic case is to mix two alloys of the same color and same fineness, but designed for different use; for example, one is designed for casting and the other for plastic deformation. Generally, they will contain Si and grain refiners (elements belonging to the PGM family). In this case we are dealing with major mistakes, but also the use of the same crucibles, stoppers, dies etc. for different alloys may involve this kind of pollution. The main characteristics of the defects are:

- Rounded shape
- Usually form clusters
- Size depends on the amount of pollution (up to about 50 $\mu m)$
- Present also in castings produced with fresh metal

"Case" #8

In the following example the problems occurred during the finishing process of an 18K yellow gold alloy investment cast without stones in place (Figure 34).



Figure 34 - Item affected by the problem

Large bulging particles, easily visible to the naked eye, were spread on the whole surface of the pieces. The SEM observation detected the presence of many rounded bulges (Figures 35 - 37).



Figure 35 - Magnification of one hard spot found in the piece



Figure 36 - Magnification of one hard spot found in the piece



Figure 37 - Magnified image of some hard spots found in the piece

The morphology appears to be similar to the hard spots presented in "Case" #7.

The chemical analysis evidenced the presence of Ni and Si, together with traces of cobalt (Figure 38).



Figure 38 - Microanalysis made on the defect

Ni and Co were not among the components of the master alloy and deeper analysis revealed that separate crucibles were not used for white gold and yellow gold alloys. The presence of Ni and Co was therefore due to a white gold alloy polluting another product line.

Hard spots caused by deliberate pollution

Another pollution type deriving from the production process may be seen in what we call deliberate pollution. This is when some elements are purposely added to the alloy to improve some characteristics of the material. An example of deliberate pollution is related to the use of cobalt. Co is a grain refiner (efficient only in specific conditions) and an element able to increase the hardness of the material (when added in consistent quantity). Very often cobalt is used to improve the performance of the material, but when it is added by the final user of the alloy, the risk to worsen the situation is rather high, as you can see in the next example.

"Case" #9

In this case we observed hard spots in the production of 14K gold rings by investment casting. A master alloy containing Cu, Zn, Si and 15% silver was used. After polishing (Figure 39), bulges and a comet tail effect were noticed on the pieces.



Figure 39 - Item affected by the problem

Magnifying these bulges under the SEM, large clusters of small particles were seen (Figures 40 and 41).



Figure 40 - Magnification of a hard spot found on the piece



Figure 41 - Magnification of one hard spot found in the piece

The microanalysis evidenced the presence of Co and Si (Figure 42).



Figure 42 - Microanalysis made on the defect

Further investigations made on the piece revealed a deliberate pollution problem. In this case the pieces did not reach the required hardness. Because it was not possible to carry out a hardening heat treatment, an attempt has been made to increase the hardness of the material by adding cobalt. However, this trial was made without taking into consideration that there may have been elements that could react with Co. The result was the formation of hard spots.

Hard spots caused by pollution – Mechanisms of formation

To get a better understanding of the mechanisms of hard spots formation when caused by pollution, we must recall the concept of intermetallic compound. As soon as there are the conditions for an intermetallic compound to form, it has high probability to form. The whole family of the PGMs, with the elements around it in the periodic table (Figure 2), can form different types of intermetallic compounds (Ir-Si, Ni-Si, Co-Si, etc.). It should also be added that the PGMs tend to form mutual solid solutions. Moreover, PGMs have very high melting points and at the casting temperatures, show an evident trend for nucleation and coalescence.

We should also emphasize that an excess concentration of even very few parts per million of these elements may allow the formation of intermetallic compounds. This process, once started, may involve not only the polluting elements, but also other deliberately added components. These last components would not present a problem in the absence of impurities. In this case we are making reference to elements such as Si, Ni, or PGMs commonly used as grain refiners. This phenomenon may become clearer if we look at Figures 43 - 45.



Figure 43 - Magnification on a Ni/Si-Ru agglomerate



Figure 44 - Magnification on a Ni/Si-Ru agglomerate



Figure 45 - Magnified image of a Ni/Si-Ru agglomerate

These images display a type of hard spot found on 14K white gold pieces. These pieces were affected by pollution caused by Ru. It seems that Ru did not limit the formation of precipitated particles, but that these particle acted as nuclei for the precipitation of other elements present in the alloy (Ni and Si). This can be supported by the different areas visible to the naked eye as a hard spot. The clearer areas are made only of Ru (Figure 46).



Figure 46 - Microanalysis of the clearer areas

The darker areas, that include the Ru particles, are made mainly of Ni and Si with some Ru (Figure 47). This suggests a formation of the hard spot in two steps, i.e., formation of Ru nuclei, which caused the precipitation of Ni and Si.



Figure 47 - Microanalysis of the darker areas

However, it is difficult to define the mechanism of formation with certainty and precision. Referring to the Ni and Si-containing particles, it can be seen that they can show both a rounded shape or an acicular or lamellar shape (see some Cases presented later on). The rounded shape might be explained in two different ways.

The first explanation refers once again to the previous images. The shape of the Ru-based areas seems to be typical of solidification. If we consider the shape of the dark areas, we could suppose that the Ru solid particles actually coordinated atoms of Ni and Si still at the liquid state as if Ni and Si were able to form an immiscible liquid in the remaining molten metal under particular conditions. These drops may solidify later on in aggregates of a rounded shape.

The second hypothesis was made on the base of an analogy with the morphology of cast iron. Cast iron is an alloy made of Fe and C. A metallographic analysis of such material will display a matrix of metallic nature dotted by graphite inclusions. These inclusions can have different shapes: spherical, acicular, lamellar, vermiform, but their composition is always the same: carbon (graphite) or iron carbide. During the solidification of cast iron, carbon tends to segregate forming these particles. Their final shape depends on the cooling and segregation process and depends also on small percentages of addition elements.

Back to the gold alloys containing Ni and Si, it can be understood how the aggregates formed by these two elements may have different shapes in function of the chemical composition and of the cooling process of the alloy. This second theory can explain both types of morphology we observed.

Generally speaking, an explanation such as this last one, may be suitable also for all other types of hard spots. In the case of Os-Ru-Ir particles, a particular in uence of polluting elements or of micro-alloying has not been observed. However it should be underlined that these are only hypotheses based on simple investigations using the microscope, not supported by direct analysis. To create the basis for a supported theory, it may be necessary to do specific studies on the topic itself.

Hard spots caused by agglomeration

Introduction

In the case of hard spots caused by agglomeration, the formation of aggregates is caused by the presence of an element with concentration higher than required, due to a phenomenon different from pollution. These problems are caused by mistakes in the production process, especially when too much scrap metal is used.

These hard spots involve elements normally present in the alloy and used as grain refiners or deoxidizers (Si).

These defects show the following characteristics:

- Regular and rounded shape
- They form clusters
- Reduced size (up to 10 $\mu m)$
- Mainly intermetallic compounds formed by some alloy components
- They form only when using scrap metal.

A too high percentage of scrap metal or when it is reused too many times is a factor that favors the agglomeration of hard spots that were not detectable before. In any case it is preferable to discuss the possible mechanisms of formation after taking some examples into consideration.

"Case" #10

In this case the presence of hard spots was noticed in rings without stones in place, produced by investment casting with a 14K red gold alloy. This alloy contained Cu, Ir, Si, Zn, Ag.

Agglomerates of even noticeable size were observed on the surface of the pieces. A deeper examination by SEM showed that they were clusters of many small, hard spots with rounded shape (Figures 48 and 49).



Figure 48 - Magnification of one hard spot in the piece



Figure 49 - Magnification of a hard spot found in the piece

The microanalysis of the defect showed the presence of Ir and Si (Figure 50).



Figure 50 - Microanalysis made on the defect

Further investigation showed that the problem occurred only when scrap metal was used and also when it was common practice to refine the material only every two months.

These elements suggested that the defect was due to agglomeration processes triggered by repeated scrap recycling. In these conditions, Ir particles began to grow and to react with Si, leading to the formation of bulges, as above.

There aren't only alloys containing grain refiners which display such behavior. White alloys for investment casting are also prone to this kind of problem, as can be seen in the next example.

"Case" #11

The presence of hard spots was detected on the surface of investment cast pieces (Figure 51) made of a 18K white gold containing Ni, Cu, Zn, Si.



Figure 51 - Item affected by the problem

SEM observations revealed that these bulges were clusters of small size particles (Figures 52 and 53).



Figure 52 - Magnification of one hard spot found in the piece



Figure 53 - Magnification of a hard spot in the piece

The microanalysis showed that these particles were formed of Ni and Si (Figure 54).



Figure 54 - Microanalysis made on the defect

In this case, too, the defective pieces were made of an alloy that had been recycled about twenty times. Therefore the defect was due to agglomeration problems, enhanced with the increasing number of recycling operations, until a critical level was reached which led to the formation of clusters and to the comet tail effect during the polishing phase.

Hard spots caused by agglomeration – Mechanisms of formation

An element should have two fundamental characteristics to work as a grain refiner in investment casting:

• High tendency to form crystallization nuclei

• High melting point

All PGMs act as grain refiners for gold alloys and some of them are commonly added to improve alloy microstructure. If concentration and distribution of these elements remain within well-established ranges, there are not noticeable problems. As soon as these conditions are missing, the solid particles suspended in the melt begin to grow and to attract each other to form agglomerates which tend gradually to grow in size.

Elements such as grain refiners or Si are added in small percentages, almost always less than 0.2%. When the alloy undergoes a melting and casting process, some small variations of composition can be detected that are due to some metal loss because of oxidation (for example, Cu). After a single casting operation these variations are usually unimportant, but the same cannot be said when the material has been recycled many times, or when a casting is made with more than 50%scrap metal. Moreover, prolonged permanence at high temperature favors coalescence and growth of the precipitated particles, because increased particle size (and corresponding reduction of particles number) means reduced total surface extension and reduced free energy. When recycling scrap metal many times, the above described phenomenon can gradually lead to the formation of clusters and consequently of hard spots.

An example of the above described phenomenon is given below.

Experiments of repeated casting were carried out and the surface of the pieces was examined under the SEM, to test the evolution of the phenomenon. After the first casting operation the surface of the pieces was free from defects, but as soon as scrap metal was used, the first precipitation phenomenon was noticed with the SEM.



Figure 55 - Acicular intermetallic compounds

As seen in Figure 55, some intermetallic compounds of extremely reduced size and acicular shape were formed inside the Au-Cu-Ni alloy. These very fine and thin acicular particles were spread all over the surface but were not visible to the naked eye. Therefore, surface finishing was not affected (Figures 56 - 58).



Figure 56 - Acicular intermetallic compound



Figure 57 - Acicular intermetallic compound



Figure 58 - Acicular intermetallic compound

Such compounds were made of Ni and Si. The thickness of the particles was not measured directly, but it can be stated that it was very small (lower than 1 μ m), because of an appreciable transparency effect during the SEM observation. The electron beam went easily through the intermetallic layer and was affected also by the under-

lying matrix.

Going along with recycling the same metal, the particles grow but retain the same acicular shape. In this case too, there were no problems in the finishing process.



Figure 59 - Acicular intermetallic compounds

Polishing problems occurred when the shape of the particles changed from acicular to rounded. It is presumed that this phenomenon takes place when a critical point is reached in the composition of the alloy, with regard to the balance among the various components. Probably major changes of alloy composition are not necessary, even if we suspect that a fundamental role could be played by the presence of oxides. Up to now we did not find data on this subject in the scientific and technical literature, so it is not possible to be more precise on this matter.

Presently, the only conclusion we can draw is that with the reuse of the same material for an excessive number of times, the system degenerates, creating the formation of clusters of rounded particles, always containing Ni and Si (Figure 60).



Figure 60 - Rounded intermetallic compounds

The reasoning followed for the Ni-Si intermetallic compounds may be easily extended to other intermetallic compounds, typical of jewelry alloys containing silicon and grain refiners (see, for example, Case #10). Shape and distribution of the compounds may change, but the mechanism will probably be similar.

Hard spots caused by segregation phenomenon

Introduction

Hard spots caused by segregation refer to cases where the formation of precipitated particles is favored by composition differences also at short range. Alloys that display higher homogeneity problems, such as low fineness alloys and nickel white golds, are potentially affected by such kind of phenomenon. Even in this case, the elements playing a key role in the process are part of the nominal composition of the alloy and are used either as grain refiners or deoxidizers (Si). This class of defects shows chemical-physical features similar to the previous case:

- Regular and rounded shape
- They form clusters
- Reduced size (up to 10 µm)
- Mainly intermetallic compounds formed by some alloy components.

The difference is that they can form also in castings produced with fresh metal.

The cause is represented by a lack of homogeneity. Manufacturing processes including continuous casting are particularly subjected to this kind of problem.

The phenomenon can be subdivided into two different categories:

- hard spots caused by macro-inhomogeneity
- hard spots caused by micro-inhomogeneity.

Hard spots caused by macro-inhomogeneity

This category includes all the cases where a difference in the macroscopic composition is found, i.e., when carrying out an assay on different points of the piece we find different compositions. Typicaly, pre-melting has not been carried out on alloys that required it. An example may be:

"Case" #12

This case refers to the presence of hard spots on rings obtained by continuous casting with a 14K white gold alloy containing Ni, Cu, Zn, Ru (Figure 61). The material was charged into the crucible without any pre-melting.



Figure 61 - Item affected by the defect

The bulges detected by SEM were rounded and clustered (Figure 62).



Figure 62 - Magnification of a hard spot found in the piece

The microanalysis evidenced that such clusters were composed mainly of Ru (Figure 63).



Figure 63 - Microanalysis of the defect

It is well known that nickel white gold alloys present problems of composition homogeneity, particularly in the case of low fineness alloys. In this case the production was made by continuous casting. Such technology, when not correctly used, presents problems of homogeneity. Without mechanical mixing it is difficult to mix the various components of the alloy correctly. Moreover, the metal is kept in the liquid state for a long time and stratification phenomena of elements of different density can take place.

Therefore, it can be assumed that in this case the material entered into a critical window for the formation of hard spots. This could be ascribed to even minimal composition differences among the different points of the cast bar. To confirm this thesis, when casting the same material in the same conditions but after a pre-melting operation, the problem disappeared.

Hard spots caused by micro-inhomogeneity

By micro-inhomogeneity, we mean cases where true segregation occurred during solidification. This cannot be detected by carrying out assays on different points of the cast material, but by microanalysis of specific areas. Also, in this case, low fineness white golds, which are more susceptible to segregation, are the most affected alloys. As mentioned before, the process of continuous casting is particularly unfavorable from this point of view. This case is represented in part by Case #12 and #13.

Case #13

In this case problems were found on 18K yellow gold watch cases produced by continuous casting. When polishing, clusters of particles were noticed on the surface of the pieces (Figure 64).



Figure 64 - Item affected by the defect

SEM observation detected the presence of clusters of small, rounded hard spots (Figures 65 - 67).



Figure 65 - Magnification of a hard spot found in the piece



Figure 66 – Magnification of one "hard spot" found in the piece examined



Figure 67 - Magnification of a hard spot found in the piece

The microanalysis showed that these bulges were mainly formed by Ir (Figure 68).



Figure 68 – Microanalysis of the defect

However, in this case the problem also appeared when using only fresh metal and after pre-melting. The explanation of the problem has been found in the conditions of continuous casting. The continuous casting parameters were optimized to obtain a good-quality bar easily, but these parameters involved keeping the alloy at high temperature for too long time.

The problem was solved by modifying the casting parameters, in particular with an increase of casting and pre-melting temperatures, and a shortening of the cooling time.

Hard spots caused by segregation – Mechanisms of formation

In our opinion the formation mechanism of this defect is similar to the formation of hard spots by pollution. This defect could be favored by the above mentioned working conditions, i.e., lack of homogeneity (absence of pre-melting) and conditions close to the equilibrium at high temperature, typical of the continuous casting process.

We would also like to draw the attention to the pictures of Case #13. Near the Ir particles rounded porosity cavities were also found, similar to gas porosity. It should be noted that this is not unusual, because the same phenomenon has been observed in many cases, but the interpretation is still unclear.

Inclusion of abrasives

Introduction

As already mentioned, abrasive inclusions very

often show the same symptoms of the other hard spots, i.e., scratches of the surface and comet tail effect. Therefore, it is important to examine this topic in deeper detail.

This problem is mainly related to mistakes in the finishing operations and is distinguished by the hard spots by the following characteristics:

- irregular and sharpened shape
- random placement but most of all concentrated on at surfaces
- occur independently from the recycling of the alloy
- occur mainly on relatively soft alloys.

A practical example of problems during surface polishing may be provided by the following.

Case #14

This case refers to hard spots on the surface of a 925 silver alloy. This kind of problem occurred only during the polishing operation. SEM examination detected sharpened particles on the surface of the pieces (Figure 69).



Figure 69 - Particle stuck onto the surface of the piece

The microanalysis of the particle detected the presence of Al and O only, evidencing the defect as a problem related to abrasive particles (Figure 70).

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0.30	0.60	0.90	1.20 1.	50 1.8	0 2.10	2.40	2.70	3.00	3.30
EDAX ZAF Element M SEC Table	Quantif Normaliz e : Defa Wt %	ication red ault At %	(Standar	dless) Z	A	F			
O K AlK Total	41.70 58.30 100.00	54.68 45.32 100.00	0.1407 0.3974	1.0393 0.9711	0.3244 0.7020	1.0010 1.0000			

Figure 70 – Microanalysis of the defect

The defect occurred on a silver piece, so it can be assumed that the problem was due to the use of abrasives with a hardness that is too high to polish such soft metal.

Case #15

In this case hard spots were found on the surface of 3N 18K yellow gold pieces (Figure 71).



Figure 71 - Item affected by the problem

In this case, too, the observation at high magnification detected irregular and sharp particles on the surface of the pieces (Figures 72 and 73).



Figure 72 - Particles stuck onto the surface of the piece



Figure 73 - Particles stuck onto the surface of the piece

The hypothesis that they were particles of abrasive stuck into the surface was supported by the microanalysis (Figure 74), which detected the presence of Al and O only.



Figure 74 - Microanalysis of the defect

If we consider that the hardness of the alloy in

the annealed state was about 150 HV, it is difficult to think that the defect was due to the use of an inappropriate abrasive, but of a low quality one instead.

A further example of this kind of defect follows.

Case # 16

In this case, too, a comet tail effect was observed when polishing 18K red gold pieces (Figure 75).



Figure 75 - Item affected by the problem

SEM observations detected inclusions with evident pulling marks (Figures 76 and 77).



Figure 76 - Particles stuck in the surface of the piece



Figure 77 - Particles stuck in the surface of the piece

SEM microanalysis evidenced the presence of Si, Cr, Fe (Figure 78).



Figure 78 - Microanalysis of the defect

Oxides of these elements are used as abrasives; consequently the defect is presumably due to the use of low-quality or worn-our abrasives.

Hard spots caused by abrasives – Mechanisms of formation

The shape of the inclusions of this kind depends on the material used as abrasive, mainly aluminum, silicon or iron oxides. Their position and their occurrence mainly on items with low hardness derives from the mechanism of dragging and the inclusion of these particles (Figures 79 - 81).



Figure 79 - Ring before polishing



Figure 80 - Ring during the polishing step



Figure 81 - Ring with abrasive stuck in the surface

Surface polishing takes place following the same mechanism of machining (Figure 82).



Figure 82 - Stresses during machining

The part of the material in front of the abrasive particle undergoes a plastic deformation with formation of a burr.

When low-quality abrasives or unsuitable abrasives are used, or when abrasive particles are easily detached from the tools, these particles will tend to dig into the surface instead of taking out the material, as in the following figures (Figure 83 - 87).



Figure 83 - Drawing of the sticking phenomenon



Figure 84 - Drawing of the sticking phenomenon



Figure 85 - Drawing of the sticking phenomenon



Figure 86 - Drawing of the sticking phenomenon



Figure 87 - Drawing of the sticking phenomenon

An abrasive is considered unsuitable to a given material when its hardness is too high compared to the hardness of the piece. Therefore, the pieces with a hardness lower than 70-80 HV are particularly troublesome. This is the case of 925 silver items. There is also the effect of the shape of the pieces to be polished, which may in uence the chance of abrasive particles digging into the surfaces. The use of brushes on wide, at surfaces implies a contact length of an abrasive particle that is much higher than the contact length in the case of convex surfaces, where the particles can more easily be ejected from the system (Figure 88 and Figure 89).



Figure 88 – Distance covered by an abrasive particle on a flat surface



Figure 89 - Distance covered by an abrasive particle on a curved surface

Also finishing with rotary barrels can cause such defects, especially when the right products and process parameters are not used. In this case, however, it will be less probable that a comet tail will be present on the piece.

Conclusions

It is not possible to give a single and unequivocal definition of hard spot, which could provide information on the real nature of the problem. These defects can occur in quite different cases.

The phenomenon involving inclusions or formation of clusters of particles hide a whole series of complex cases, whose full comprehension requires knowledge and instruments presently not available in the goldsmiths' shops. In this paper we underlined the practical aspects of the problem, and we tried to present the more ideal cases, i.e. cases that are traceable to only one specific problem. Very often, in the daily experience, we have to deal with hybrid cases where different causes concur in creating the same problem, with consequent complications for making a correct diagnosis and finding a solution.

Having access to well-researched information on defects, along with images that can be used for identification and suggestions for possible solutions, should be a great aid to production managers, quality managers or the artisan. A deeper understanding of the mechanisms involved in the formation of defects, together with experience and complete information regarding the production cycle, could probably narrow the field of possible solutions, enabling focused corrections to solving the problem. The consequence should be the saving of energy, time and resources. Using these elements together should be sufficient to solve many defect problems without specialized analysis instruments that are too expensive and difficult to master to be suitable for a jewelry production department.

However, on the basis of the analysis made on this topic, rules to be followed can be outlined to reduce the impact of this phenomenon.

A large number of hard spots is caused by the materials in contact with the melt, especially raw materials, crucibles and various tools. Therefore, the need to rely on trustworthy suppliers for the purchase of such materials is clear. From a theoretical point of view, the best alternative could be to buy the ready alloy, since in this way there is only one supplier to refer to. If such a solution turns out to be economically unsuitable, it is not advisable to purchase each element of the alloy separately, because of the strong increase of the process variables. If it is not possible to carry out a quality control on all the incoming raw materials, a hard spot problem could be more difficult to solve. In addition, the use of pure metals for the production of alloys also involves a wide series of technological problems, which require a specific experience in the field.

Problems such as proper concentration of the elements, homogeneity grade and consistent product quality can easily be solved by trusting professional people. Here is the intermediate solution, i.e., to purchase fine gold and master alloys. This represents a good compromise from an economic and practical point of view.

All over the world there are producers of master alloys which are able to supply materials with high quality and purity standards. These suppliers can also support the production by providing technical service to the customers, to help them find the correct solution to their problems, even when the formation of hard spots is ascribed to improper production practices. This leads to a faster and more painless solution to get the customer back into production as soon as possible.

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