Fineness homogeneity in gold alloy castings

1. Introduction

1.1 Melting and casting involve different chemical and physical phenomena that, in the case of alloys, can show very complex aspects. Also the temperature gradient can affect the composition distribution in the solidified material. As an example we can consider the solidification of a binary alloy. The solid forming in different moments of the solidification process has different composition and the liquid becomes gradually poorer in the element with higher melting point. This rule holds true not only for the binary alloys, but also for all types of alloys, where usually the phenomena become considerably more complex. Therefore it is obvious that the different parts of all objects produced through melting and casting processes could show a different composition, when subjected to a close scrutiny. These composition differences can even be very remarkable, if the material has not been correctly processed.
Presently master alloys to be alloyed with the precious metal are currently used for jewelry production. The master alloy, if correctly prepared, can guarantee composition homogeneity for all the base metal components of the alloy. When we consider the segregation phenomena taking place during the solidification of an alloy, we can easily understand that the difference in composition homogeneity obtained by adding a previously formed master alloy to a pure metal, rather than using pure metals, is very significant and favors the use of base metal master alloys.
Melting the base metal master alloy with the precious metal without a previous melting and casting operation is a common practice. In this case fineness homogeneity is not guaranteed. Even if the master alloy is supplied as small size pieces, it is difficult to mix it homogeneously with the pieces of solid precious metal and this affects also the subsequently melted metal.
A better result can be obtained by using induction heated melting/casting machines, because the induction generated magnetic field contributes to molten metal stirring. Also mechanical stirring can improve the homogeneity of the molten metal. But in our opinion the most effective way to obtain adequate mixing of the material is to carry out a preliminary melting and casting operation of the precious metal with the master alloy.
However presently specific experimental data were not available, to verify the suggestions obtained through our experience.
Therefore the aim of our work is to evaluate the homogeneity of the castings for different melting/casting practices. Also the influence of the type of alloy has been taken into account.
So white and yellow gold alloys with different caratage, namely 9, 14 and 18 ct, have been experimented. We also investigated if grain refined alloys could give improved homogeneity and alloys with or without additions of grain refiners have been compared. After choosing the composition of the different alloys, these have been used for different casting experiments. Investment casting and ingot casting have been experimented, both with or without pre-melting. In this way we aimed to substantiate with experimental data the impressions obtained from everyday practice.
Therefore about 100 casting operations and more than 1000 fire assays have been carried out for the whole set of experiments. So this work will confirm with higher confidence and accuracy the information that up to now has been obtained with the equipment, the time and resources of the producers, who have problems in making the great number of experiments necessary to understand these phenomena.

2. Preliminary analysis

2.1 The preliminary tests aimed to analyze the alloy homogeneity level that can be obtained with two most commonly used production methods, i.e. investment casting (or lost wax casting) and ingot casting. For this purpose samples have been taken from different points of the various cast piec-

es, to verify alloy fineness in the different points by means of the fire assay. Different alloy types have been studied (white gold and yellow gold) with different caratage. Also different production practices have been tested (with or without pre-melting), to evaluate the different conditions that can be met in jewelry production as thoroughly as possible. Duplicate samples have been analyzed for each set of parameters. Also duplicate fire assays have been carried out for each sample (even quadruplicate fire assays have been made for the first sets of parameters, to test the reliability of laboratory results).
Standard size specimens have been used for the investment casting tests, i.e. 30 rings with 16 mm inside diameter and 32 mm outside diameter that have been assembled on a tree with 5 layers of 6 rings each. The final casting operation has been carried out in an induction heated vacuum casting machine. All trees have been cast with a casting temperature 100°C higher than the liquidus temperature. All flasks have been water quenched 600 seconds after pouring.

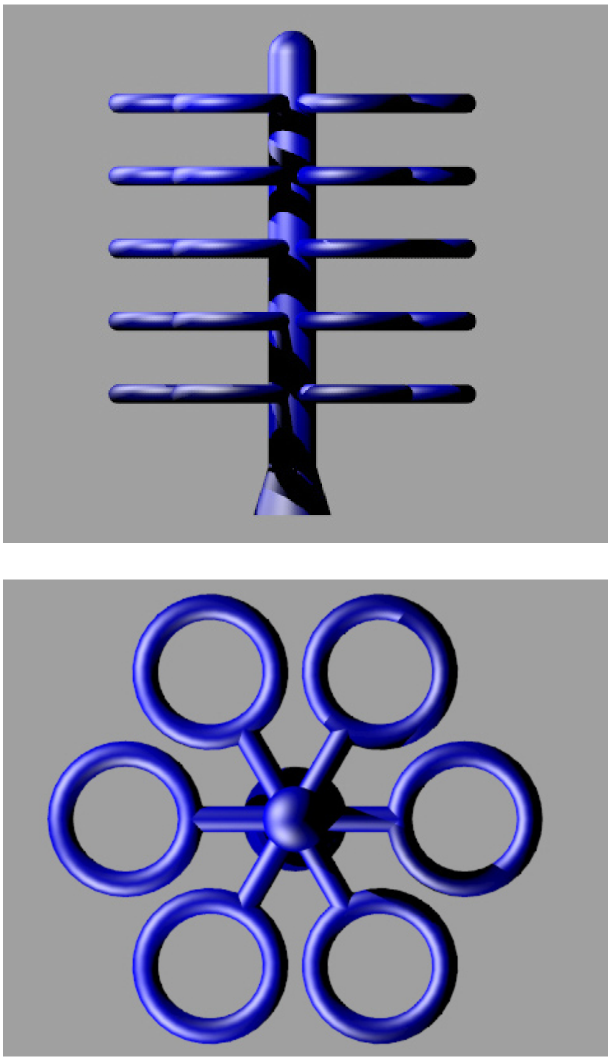

Figure 1 - Geometry of the tree for the investment casting tests

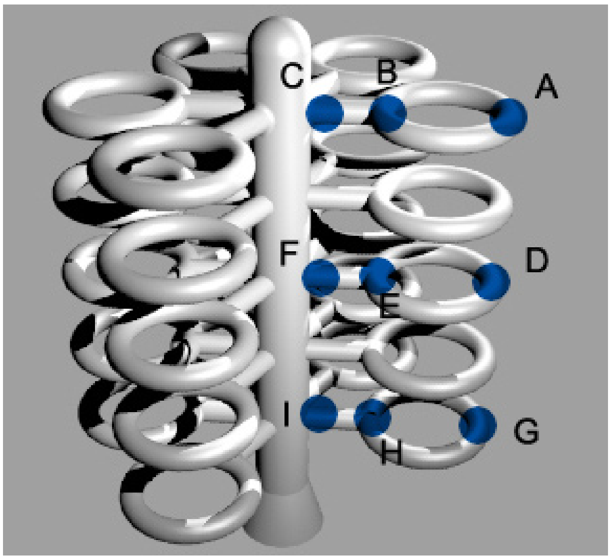

Figure 2 - Sampling points from the investment cast trees

A 40 x 8 mm size vertical mold has been used for ingot casting. The sizes of the tree and of the mold for the ingots have been selected in order to melt a sufficient amount of metal (400 g) for each test, to obtain results representing the actual production practice.

3. Preparation of the specimens

3.1 The first part of the study focused on investment casting. Firstly we decided to verify whether a refined grain structure could improve fineness homogeneity. These control experiments have been carried out only with 14 ct alloys, to find if it was possible to neglect grain size in further experiments. The names of the alloys used for this study are listed in Table 1.

Caratage	White		Yellow	
	Grain refined alloy	Alloy without grain refiner	Grain refined alloy	Alloy without grain refiner
14ct	14CTB2	14CTB1	14CTG2	14CTG1
9ct		9CTB1		9CTG1
18ct		18CTB1		18CTG1

Table 1 – Names of the alloys used for the investment casting tests

The composition of the alloys listed in Table 1 is shown in Table 2.

Lega	Au	Ag	Zn	Ni	Cu
9CTB1	375	-	125	75	Bal.
9CTG1	375	93.7	93.7	-	Bal.
14CTB1	585	-	75	83	Bal.
14CTB2	585	-	75	83	Bal.
14CTG1	585	83	62	-	Bal.
14CTG2	585	83	62	-	Bal.
18CTB1	750	-	45	50	Bal.
18CTG1	750	117	10	-	Bal.

Table 2 – Composition of the alloys used for the investment casting tests (wt. ‰)

The alloys most commonly used for jewelry production have been selected for the tests.

The effect of grain refiners on the variation of fineness can be seen in the Figures 3 and 4. It should be noted than only the average of duplicate analyses has been shown, for the sake of simplicity.

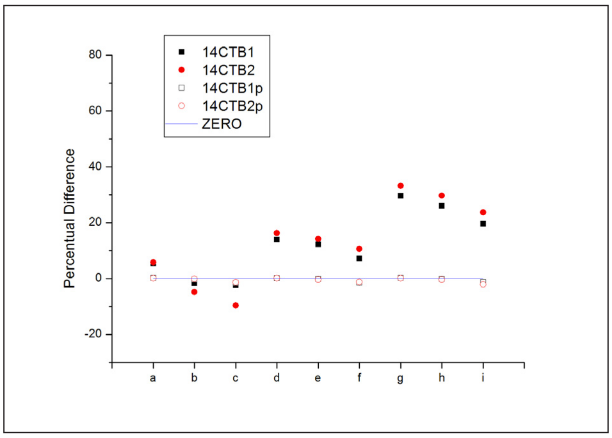

Figure 3 – Effect of a refined grain structure in a white alloy

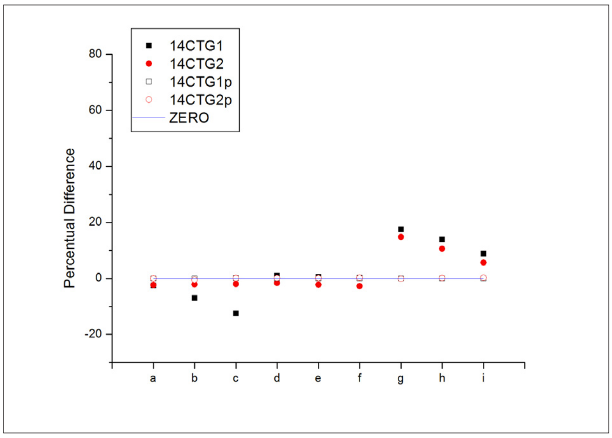

Figure 4 – Effect of a refined grain structure in a yellow alloy

The name of the alloy followed by a small p denotes the specimens produced with pre-melting. The position of the sample taken from the tree is given on the x axis, while on the y axis the percentage difference from nominal fineness is shown.

We can see that the difference between the grain refined and not grain refined material is practically negligible, for both white and yellow gold alloys. These tests suggest that a fine grain structure does not guarantee a higher fineness homogeneity. Therefore only alloys suitable for the specific production technique have been used in the following experiments, i.e. silicon containing alloys for investment casting and grain refined alloys for ingot casting.

In addition to the effect of grain size, we verified whether there were differences in the homogeneity of the castings caused by different pre-melting methods. We used 14 ct alloys for this investigation and compared the two most commonly used methods for pre-melting:

- Pre-melting followed by ingot casting, ingot rolling and cutting the rolled product into small pieces.
- Pre-melting and graining by pouring the melt into water.

The results are shown in Figures 5 and 6. The black squares correspond to samples from ingot cast pre-melted material, while red circles represent water grained material.

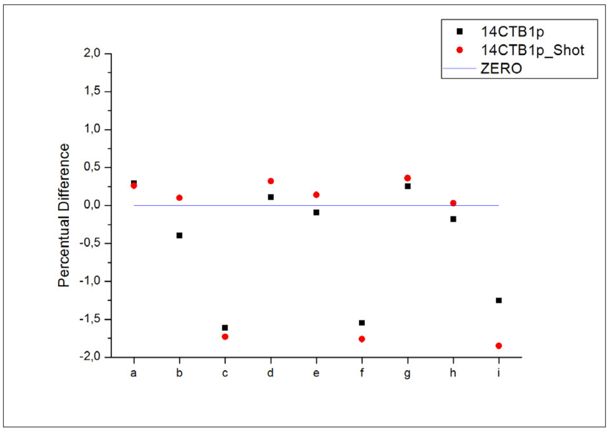

Figure 5 – Comparison of different pre-melting methods. White alloys

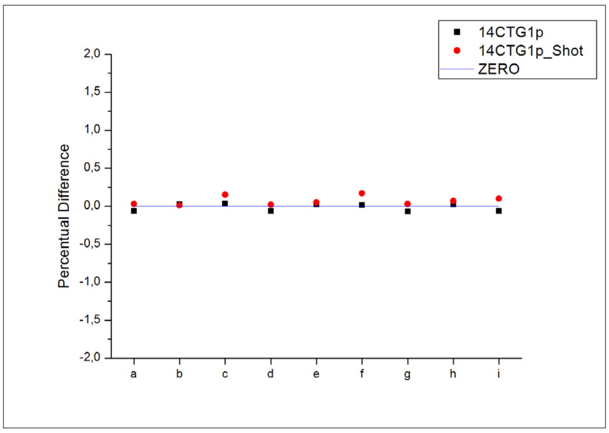

Figure 6 - Comparison of different pre-melting methods. Yellow alloys

It can be seen that homogeneity differences in the final cast pieces are similar for both pre-melting methods. Both the absolute values and the trends are similar, within the limits of experimental uncertainty. Therefore both methods have been considered valid and for convenience in the rest of the work pre-melting has been carried out by ingot casting.

The second phase of the work concerned ingot casting, with the use of the alloys listed in Table 3.

Caratura	Bianco	Giallo
9ct	9CTBS	9CTGS
14ct	14CTBS	14CTGS
18ct	18CTBS	18CTGS

Table 3 – Alloys used for ingot casting

More specifically, the composition of the alloys is shown in Table 4.

Lega	Au	Ag	Zn	Ni	Cu
9CTBS	375	-	93,7	93,7	Bal.
14CTBS	585	-	75	83	Bal.
18CTBS	750	-	30	50	Bal.
9CTGS	375	93,7	93,7	-	Bal.
14CTGS	585	83	62	-	Bal.
18CTGS	750	117	5	-	Bal.

Table 4 – Composition of the alloys used for ingot casting (wt ‰)

As already said, two different ways have been followed for producing the investment cast material:

- without pre-melting,
- with pre-melting.

Pre-melting has been carried out in an induction heated melting machine. The molten metal has been mixed with a graphite stirrer and then it has been manually poured in a mold, with a pouring temperature 100°C higher than the liquidus temperature. The cast ingot has then been rolled and the rolled material has been cut into pieces for further processing. The final investment casting operation has been carried out under vacuum in an induction heated casting machine. The casting temperature was 100°C higher than the liquidus temperature. The flask temperature and the time before water quenching were kept constant for all flasks (600°C and 15 mm respectively).

Also the mold cast plates (Figure 7) have been produced with and without pre-melting. In this case all melting operations (pre-melting included) were carried out under vacuum in an induction heated casting machine, to avoid the human factor that could affect manual casting. The samples have been taken from a total of 6 points situated at 3 different levels of the plates, Figure 24.

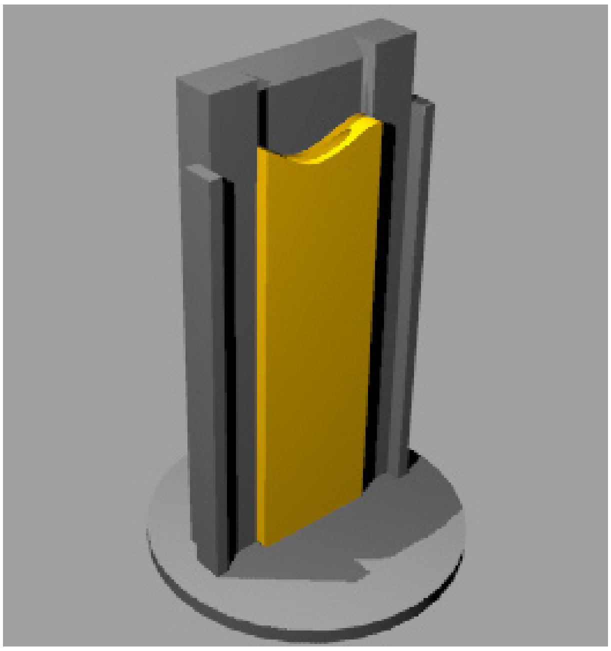

Figure 7 – Cast plate

4. Data analisys - Investment Casting

4.1 The results of investment casting experiments have been discussed first. The first objective was to consider the effect of the composition separately. The results are shown in Figures 8 and 9.

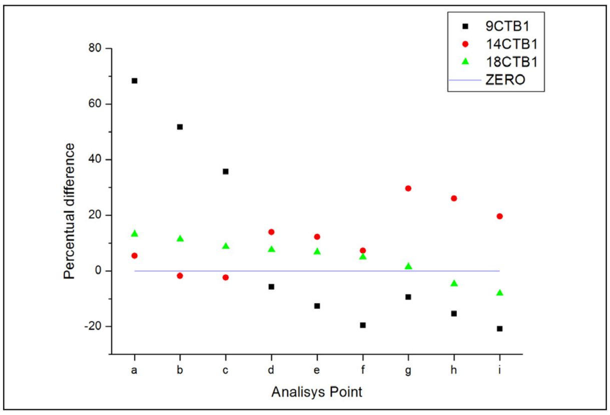

Figure 8 – Fineness variance for white gold without pre-melting

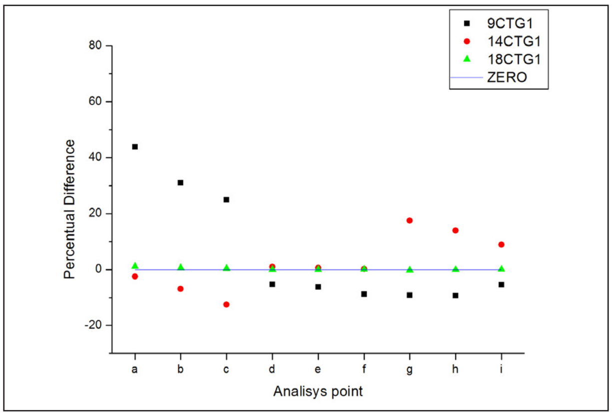

Figure 9 – Fineness variance for yellow gold without pre-melting

Figures 8 and 9 have been plotted with the same scale, so it can be easily appreciated that for all considered caratages the spread of fineness values is wider for the white gold than for the yellow gold alloys.

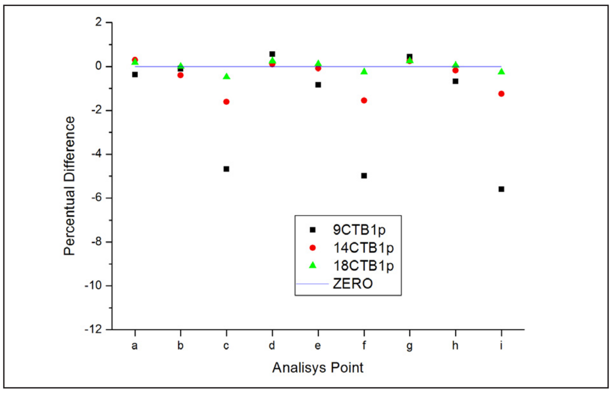

Figure 10 – Fineness variance for white gold with pre-melting

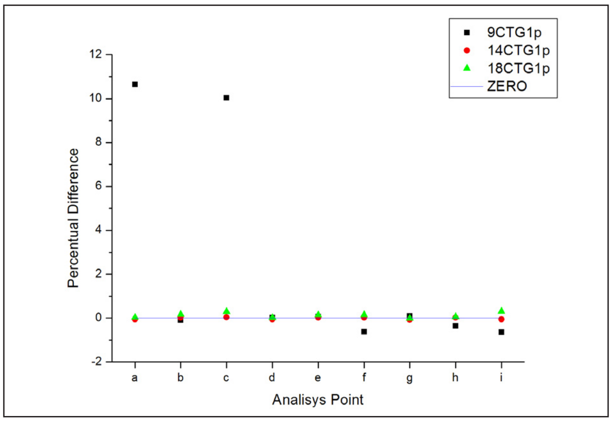

Figure 11 – Fineness variance for yellow gold with pre-melting

The same considerations can be made for the castings obtained from pre-melted material (Figures 10 and 11). In this case too we can say that fineness inhomogeneity decreases when we go from Ni-containing to Ag-containing alloys. Therefore we could conclude that Ni-white gold alloys are much more affected by the segregation phenomena taking place during solidification (Segregation is a natural phenomenon in an alloy during solidification).

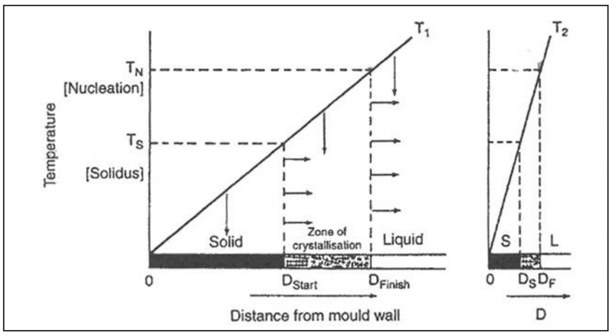

Figure 12 – Effect of temperature gradient and alloy composition on the size of the "pasty zone"

We should first remember that solidification is controlled by the so-called "pasty zone", Figure 12. When we do not deal with pure metals, solidification does not take place at a constant temperature but in a temperature range between the liquidus and solidus temperatures. Therefore on the solidification front there is a zone that is not fully solid nor fully liquid, where the growing solid dendrites are mixed with interdendritic liquid metal. Therefore critical conditions can occur during solidification of metal alloys, because of the segregation of some components in the liquid surrounding the growing dendrite grains, Figure 13. The composition of the pasty zone will then change with the progress of solidification and the composition of the last portion of liquid metal to solidify will be substantially different from the nominal average composition of the alloy. We could then have composition variations caused by macrosegregation phenomena.

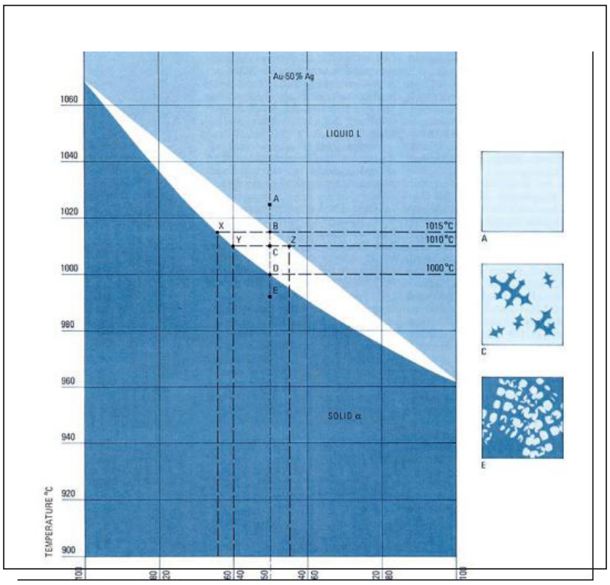

Figure 13 – Phase diagram of a binary alloy

This phenomenon can be more or less critical, depending on alloy components and their concentration in the alloy. Segregation is also affected by

solidification rate. Segregation is more important when the material solidifies relatively slowly. Fast solidification reduces macro-segregation.
When we have a substantial inhomogeneity in the solid charge of the furnace, there will be composition differences in the different points of the melt. Consequently solidification temperatures and mechanism will change from point to point and the risk of inhomogeneity in the cast material will increase.
Casting obtained from pre-melted metal show fineness values nearer to the nominal value because during pre-melting the material is mechanically and chemically mixed. Therefore the solidifying liquid metal has nearly constant composition in the whole mass. This behavior can be highlighted by averaging the results of the assays carried out on the same level (row) of the tree (Figures 14 to 17).

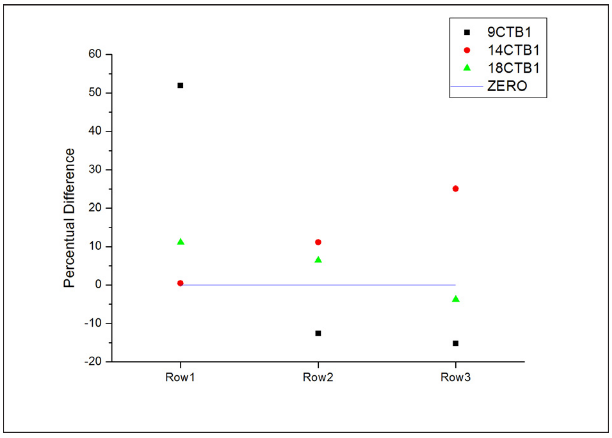

Figure 14 – Fineness variance among the different rows for white gold without pre-melting

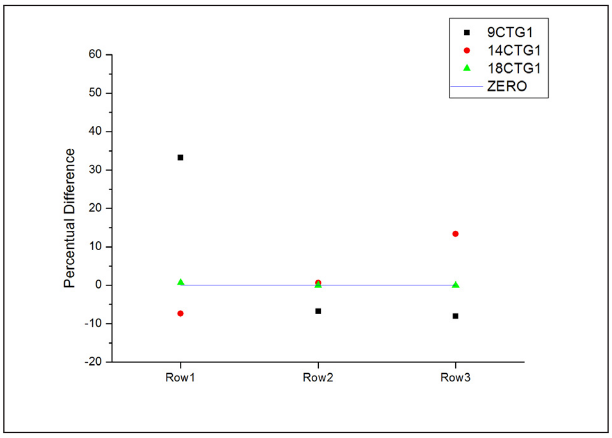

Figure 15 – Fineness variance among the different rows for yellow gold without pre-melting

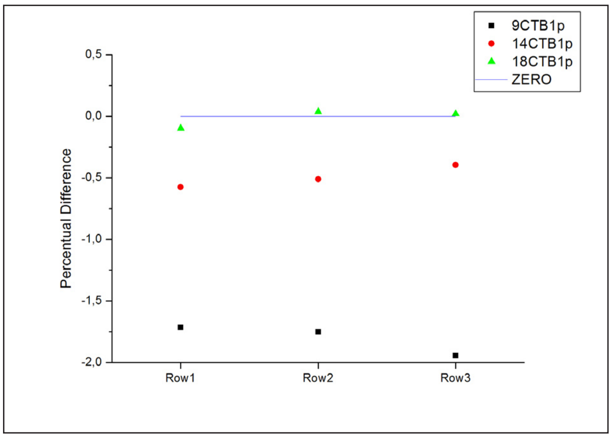

Figure 16 – Fineness variance among the different rows for white gold with pre-melting

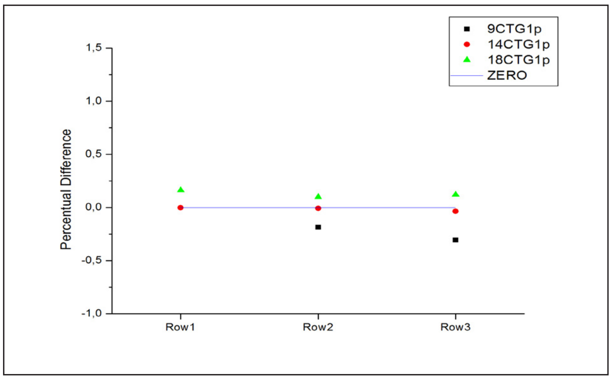

Figure 17 – Fineness variance among the different rows for yellow gold with pre-melting

In this case too the difference between Ni-containing and Ag-containing alloys is rather obvious. Probably this different behavior can be ascribed to the fact that Ni favors segregation phenomena by increasing the composition difference between liquidus and solidus lines in the phase diagram. Figures 14 to 17 give also further information: the homogeneity difference decreases with increasing caratage. This behavior is not surprising, because when we increase the concentration of a component (in this case Au) we come closer to the solidification conditions of a pure metal, and the segregation phenomena become gradually less important, with the related benefits for fineness homogeneity. We emphasize the case of the yellow alloy 18CTG1, where, even without pre-melting, fineness figures are noticeably near to the nominal value. The same statement does not hold true for the 18 ct white alloy.

We can also consider the diagrams of Figures 18, 19 and 20, where alloys with the same caratage but with different color and processing method (with or without pre-melting) are compared.

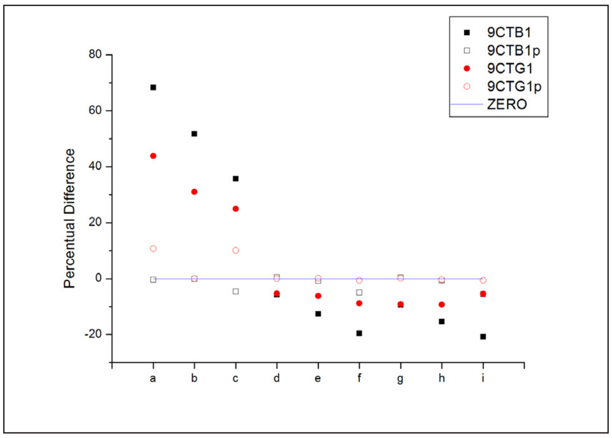

Figure 18 – Fineness variance for 9 ct gold alloys

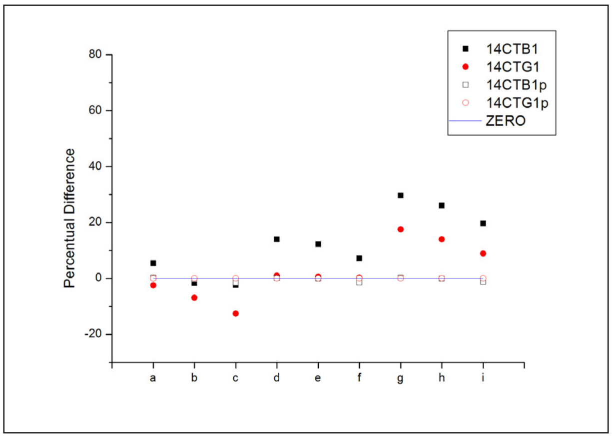

Figure 19 – Fineness variance for 14 ct gold alloys

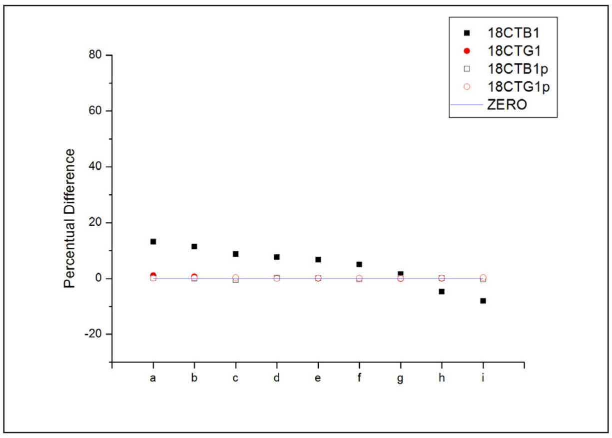

Figure 20 – Fineness variance for 18 ct gold alloys

In this case too yellow alloys and higher caratage alloys show a better homogeneity than white alloys and lower caratage alloys. Moreover another detail could be obtained by considering the above data. When we consider the points on the same layer of the tree (i.e. the points ABC, DEF and GHI respectively) we see that usually the points lying farther from the main sprue (A, D, G) show a fineness level higher than the average fineness of the layer. This aspect is highlighted in Figures 21, 22 and 23. More specifically, only the data obtained without pre-melting have been considered, because with pre-melting the fineness figures showed so small differences that it was difficult to see a definite trend. The outer, intermediate and inner points of each layer are represented on the x axis, while the percent deviation from the average fineness of each layer of rings is shown on the y axis. Each set of data represents a layer with the name of the alloy followed by the indication of the layer (e.g.: 9CTB1R1 = 9 carat white gold, ABC layer).

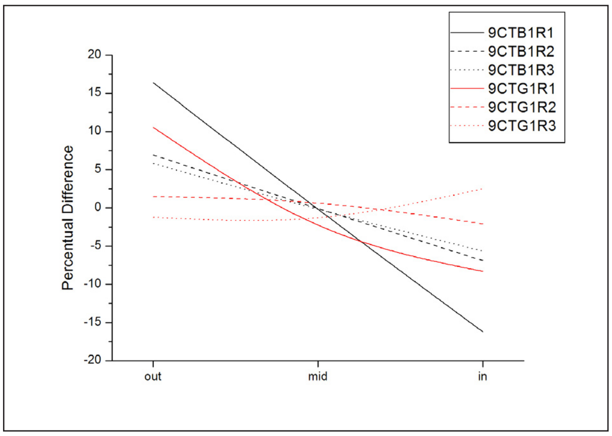

Figure 21 – Fineness variation as a function of the distance from the main sprue – 9 ct gold

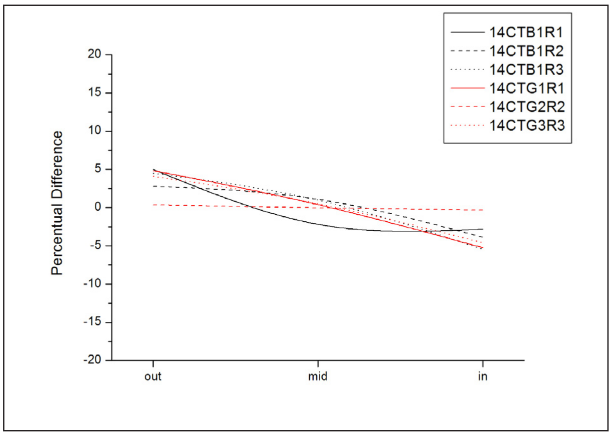

Figure 22 – Fineness variation as a function of the distance from the main sprue – 14 ct gold

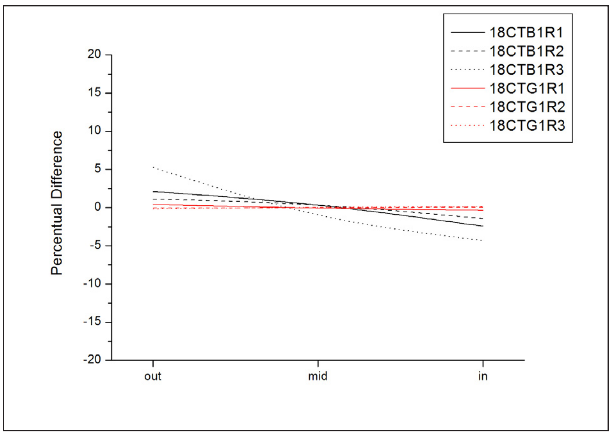

Figure 23 – Fineness variation as a function of the distance from the main sprue – 18 ct gold

The fineness difference between the inner and the outer points of the tree could be ascribed to different cooling rates. As above said, the solidification is driven by the pasty zone, that can be originated by supercooling. There are two types of supercooling: thermal supercooling and constitutional supercooling. Constitutional supercooling is caused by the variation of the solidus and liquidus temperatures originated by composition variations, and we discussed this point above. In this case the composition difference should probably be ascribed to segregation phenomena caused by thermal supercooling.
The cooling rates in the inner and in the outer part of the tree are quite different, because of the heat content of the main sprue and of the inner part of the tree.
When we evaluate the data from the investment casting process on the whole, we can state that casting with or without a pre-melting operation gives a remarkable difference in fineness homogeneity. This difference is more noticeable with low caratage and/or Ni-containing alloys.

5. Discussion of the results - ingot casting

5.1 In the case of ingot casting, two samples have been taken from each of three different levels (rows) of the plate, Figure 24.

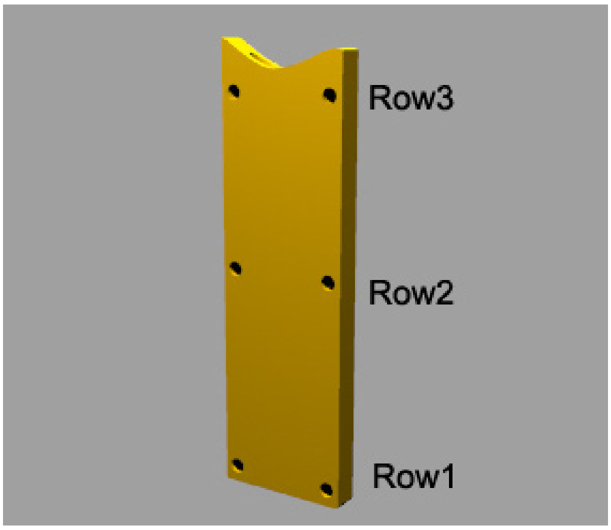

Figure 24 – Sampling points for the experiments of ingot casting

In this case too duplicate fire assays have been carried out. In all the following plots the average values of the fineness of the samples taken from each row are shown, because no significant differences have been found between them. As already done in the case of investment casting, the percent variation with respect to the nominal fineness has been given in the plots. The code name of the alloy followed by a small p denotes the samples that have been submitted to pre-melting.

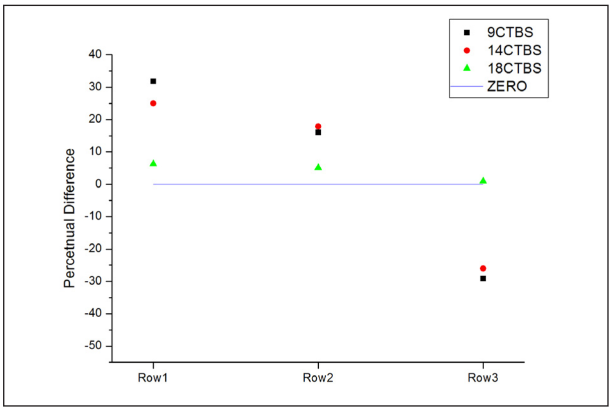

Figure 25 – Fineness variance for white gold plates cast without pre-melting

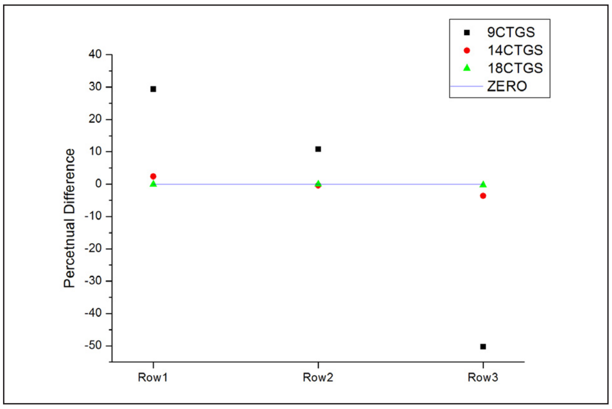

Figure 26 – Fineness variance for yellow gold plates cast without pre-melting

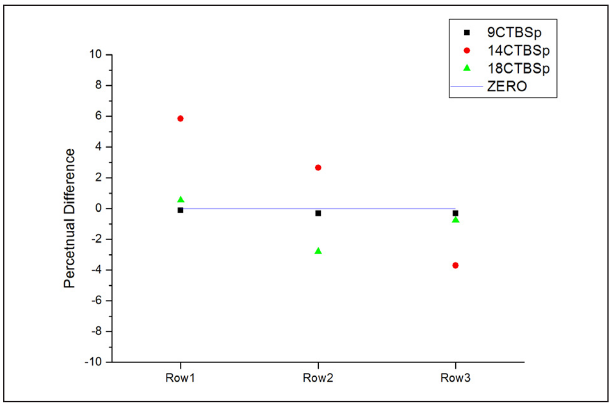

Figure 27 – Fineness variance for white gold plates cast with pre-melting

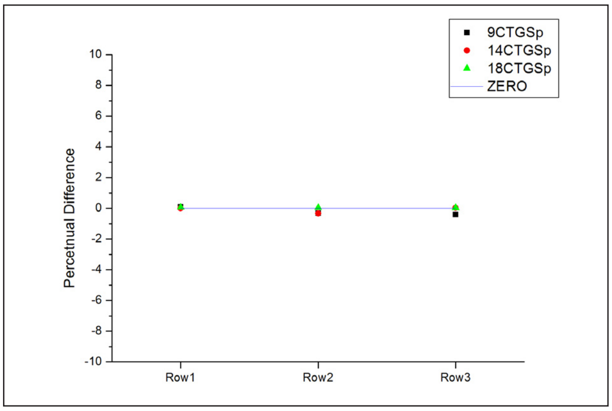

Figure 28 – Fineness variance for yellow gold plates cast with pre-melting

The results of the experiments of ingot casting are in substantial agreement with the results of investment casting. However it should be noted that the difference between yellow gold and white gold alloys is less evident than in investment casting.
Heat exchange geometry during cooling is much simpler and easier to understand in the ingot mold than in the flask. Also solidification is slower. Therefore, in our opinion, in the case of ingot casting, thermal super-cooling rather constitutional super-cooling is the main driving factor for solidification. As a consequence the effect of material type is less evident and fineness variation are similar for both Ni-containing and Ag-containing alloys of the same caratage.
However the difference between lower caratage and higher caratage alloys (more and less inhomogeneous, respectively) seems to be retained as well as the noticeable difference between pre-melted and not pre-melted material.

6. Conclusions

6.1 The results of this study show that, if we want be sure that homogeneity, and consequently fineness, of the alloy will comply with given limits, it is necessary to carry out at least one pre-melting operation. Moreover in the case of more “difficult” alloys a single pre-melting operation seems not to be sufficient.

The indications obtained from this work tend to classify low caratage alloys and Ni-based white golds as “difficult”. For these two types of alloys the same behavior has been observed, for both investment casting and ingot casting. With this kind of material, melting a charge with average fineness higher than legal fineness could not always avoid the risk of having objects that do not comply with the limits set by the law. Figures 14, 15, 16 and 17 show that low fineness values have been found even after a pre-melting operation.
As an extension of the present work it could be interesting to study the effect of the elements used for obtaining the desired color (Ag and Zn for the yellow alloys, Ni and Zn for the white alloys) on alloy homogeneity. A first example is shown in Figures 29 to 32. As usual, the percent difference from the nominal fineness is shown on the y axis. The ratio between the concentration of the “coloring element” (Ag for the yellow alloys and Ni for the white alloys) and the concentration of gold is given on the x axis.

A set of values has been considered for each level (row) of the tree.

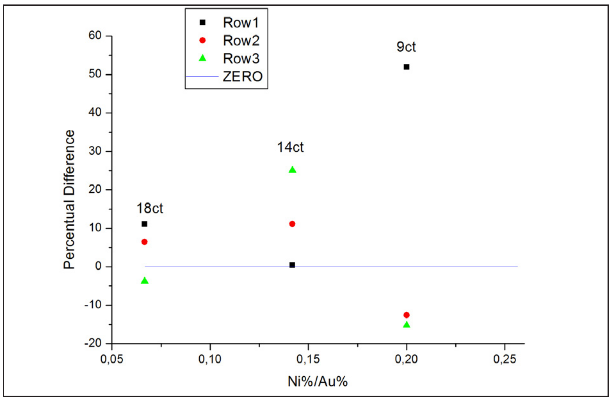

Figure 29 – Fineness variation as a function of Ni and Au concentration in investment casting

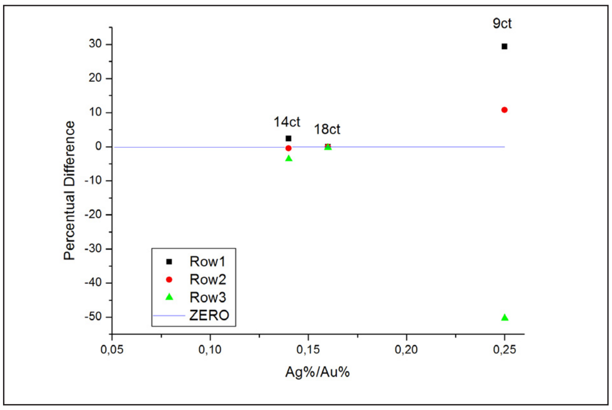

Figure 30 – Fineness variation as a function of Ag and Au concentration in investment casting

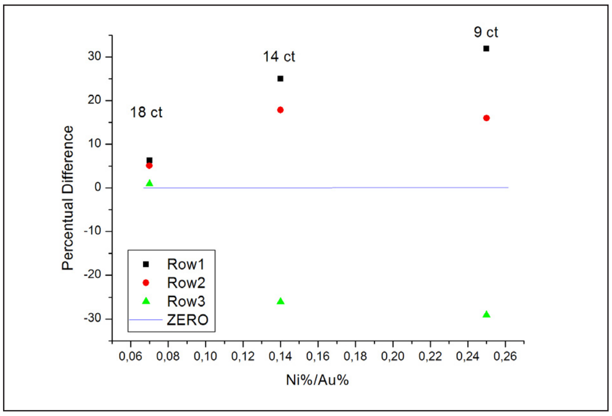

Figure 31 – Fineness variation as a function of Ni and Au concentration in ingot casting

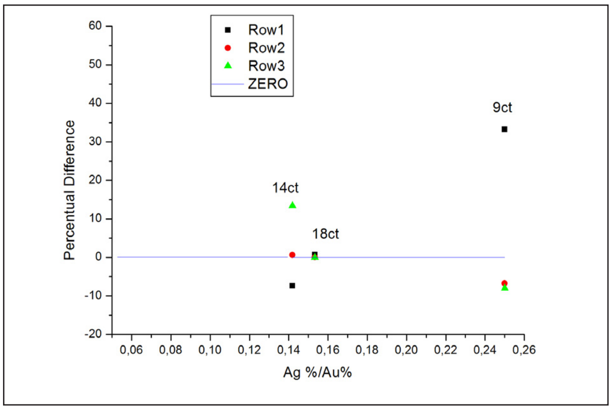

Figure 32 – Fineness variation as a function of Ag and Au concentration in ingot casting

In this study we focused mainly on the effect of caratage on composition homogeneity in standard alloys. We did not consider the differences arising from the use of master alloys with different color shades in alloys of the same caratage.
It could be interesting to evaluate if there could be a homogeneity difference between 2N and 3N 18 ct gold alloys. In this way the effect of silver could be separated.
Continuous casting should be another process to investigate.
In this process melting, casting and cooling are substantially different from the methods investigated up to now. The material dwells for longer time at high temperature. On this basis it is believed that a different behavior will be observed in comparison with the present cases.