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Gold alloys, used in the production of gold chains, affect the optical and mechanical properties of various gold products. In fact, the corrosion resistance and the workability of the chains depends on these properties. It is important that gold alloys with high corrosion resistance do not degrade during the production process. The microstructure of the alloys strongly influences the mechanical properties, which have a key role in both the machinability and quality of the plates. In the present work, different compositions of gold alloys and different annealing steps in the deformation processes were analyzed and optimized. In particular, the choice of the suited grain refiner is very important to avoid particular unwanted behaviors of the gold alloys. The changing of the production parameters and the compositions of the alloys leads to the formation of different levels of residual stresses within the material, which can generate a variation in the behavior of gold sheets. The microstructures were analyzed by OM and SEM observation, whereas the variation of mechanical properties by micro-hardness test. The residual stresses were evaluated using XRD analysis and the corrosion resistance by potentiodynamic polarization tests. The results showed that a high homogeneity of the microstructure and a suitable recrystallization process, with an increase of the quality of semi-finished products, were obtained.

"Study of the microstructure, residual stresses, mechanical and corrosion properties of different gold alloys used in industrial processes"

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INTRODUCTION

Nowadays, with the aim to improve product quality in jewelry world, mass production methods are commonly employed and modern equipment and machines are used in jewelry factories, increasing the productivity and decreasing production costs [1]. The production of gold-based jewelry items starts with the melting process: the products can be ingots or, through a continuous casting, gold alloys wires or sheets. Gold material is alternately deformed and recrystallized, before the final finishing steps. The progressive mechanical deformations cause the decrease of workability of the material, inversely, to the work hardening. It is possible to restore the original malleability of gold alloy with suitable annealing treatments under a controlled atmosphere. During the recrystallization phase different phenomena can occur, both beneficial and negative as, for example, an excessive grain growth or undesired phases precipitations [2]. Therefore, the annealing parameters are critical variables for the results of the process, in order to avoid the embrittlement of the material. The goal of this research is the study of the gold alloy sheets used to create the structure for the final production of hollow chains.

All the whole process of deformation was done with the use of an iron core. This is necessary to support the semi-finished product and is removed by chemical dissolution in acids after the welding process. A welding alloy wire is inserted into the product, during the production cycle, to guarantee the sealing of the ring in the chain produced [3].

In the present work the parameters of the annealing treatment, used by the goldsmith company, were modified. The results were correlated to the microstructure and to the mechanical properties of the material. Two different 10 Kt alloys were investigated to improve the machinability and to optimize the final properties of the products.

Moreover, also the welding alloy compositions were investigated with the aim to improve the wettability and to study the modification which occur in the production process.

EXPERIMENTAL PROCEDURE

We have study 2 compositions of 10 Kt gold alloys. The alloy a contained Co as grain refiner and have higher amount of Ag, whereas the alloy b contained Ru as grain refiner with lower amount of Ag. It was possible to study and perform an optimization of the production processes with the alloy a. The variation on the structure and the mechanical properties of the alloys, generated by different process parameters, were analyzed by microstructural analysis and hardness tests. A mapping of the temperature over time during the annealing process was also performed. With the aim to optimize the recrystallization process, the parameters of the annealing steps were modified.

The new optimized process, performed with the alloy a, was also applied to the alloy b with a following comparison of the results obtained. A LEITZ microdurometer with a Vickers penetrator set with a 25 g load and with 30 s of loading time was used for the hardnesse tests, while a LEICA DMRE microscope was used for the optical observation. The samples were prepared with the standard metallographic technique of polishing and the electrolytic etching was performed using a low concentration HCl solution. A Cambridge Stereoscan 440 scanning electron microscope, equipped with a Philips PV9800 EDS was used to study the microstructures. The residual stresses were evaluated using a Siemens D500 X-ray diffractometer using CuK α-radiation. Potentiodynamic polarization tests in a solution of 10% HCl was used to evaluate the corrosion resistance of alloy a and b. The solution simulates the environment of the emptying process, which the company used to eliminate the iron core. Anodic polarization tests were performed with an AMEL 2549 Potentiostat, using a saturated calomel electrode as the reference electrode (SCE) and a platinum electrode as the counter electrode, with a scan rate of 8×10^{-4} Vs^{-1}.

RESULTS AND DISCUSSION

The production cycle of hollow chains products, starts with the continuous casting process, follow different deformation and annealing steps, until arrive at the plating process. In the conventional cycle the annealing treatment was performed at T between 620-680°C.

With the aim to control the influence of the annealing process parameters on the material's susceptibility to rupture, the temperatures of the annealing treatments were modified and micro-hardness and residual tests were performed. In particular, the best results were obtained with an increase in annealing temperature of 20-40°C. With these parameters, an increase of the grain dimensions was observed, index of improve in quality of the annealed product, as shown in Fig. 1.
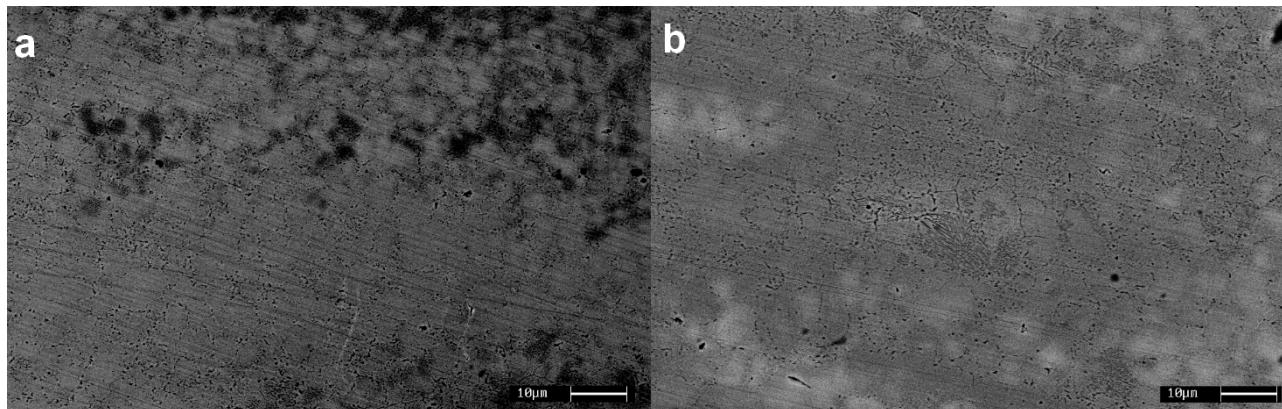

Fig. 1 - SEM observation. Microstructure of the gold alloy sheet produced by the conventional process (a) and the optimized process (b)

The correlation between the crack tendency of the gold sheets produced, during deformation, and the residual stresses generated from the specific process is showed in Tab. 1. With the optimized process, the hardness of the gold sheet decrease, with an improvement of the machinability of the material. The modification of the process parameters changed the material structure and its behavior.

Tab. 1 Hardness and residual stresses values obtained with the standard production process and the optimized production path for the 10 Kt yellow gold alloy (alloy a)

PROCESS	HARDNESS TESTS (STANDARD PROCESS) [HV]	HARDNESS TESTS (OPTIMIZED PROCESS) [HV]	RESIDUAL STRESSES − σ (STANDARD PROCESS) [MPA]	RESIDUAL STRESSES − σ (OPTIMIZED PROCESS) [MPA]
AS-CAST	160 ± 10	160 ± 5	- 55 ± 5	- 63 ± 10
1° ROLLING STEP	270 ± 5	250 ± 5	58 ± 10	30 ± 2
ANNEALING	170 ± 5	160 ± 5	- 28 ± 3	- 69 ± 7
2° ROLLING STEP	265 ± 10	215 ± 10	95 ± 8	70 ± 7
ANNEALING	170 ± 5	165 ± 5	- 48 ± 6	- 62 ± 13
3° ROLLING STEP	255 ± 5	240 ± 5	83 ± 5	30 ± 5
ANNEALING	170 ± 5	160 ± 5	57 ± 12	- 55 ± 8
PLATING	170 ± 5	160 ± 5	-29 ± 9	- 32 ± 8
ANNEALING	165 ± 5	150 ± 5	-51 ± 8	- 81 ± 7

X-ray diffraction technique was used to evaluate the residual stresses within the material [4], and in Tab.1 are showed the results. It can be observed that, passing from the rolling steps to the annealing process, the nature of the stresses, on the surface of the material, changes. Moreover, the results, after the optimized process, showed a decrease of the value of the surface tensile stresses whereas the compressive stresses increased. The change in the microstructure of the gold sheets, produced with the optimized process, allowed improving the homogeneity of the material and its properties. The ruptures under rolling train were avoided, with a reduction of the metal wastes produced.

The 10 Kt yellow gold alloy, named alloy b, was developed in order to avoid an undesired magnetic behavior presented by the final gold chains, with a particular attention to the workability of the sheets. As previously described, a different grain refiner was used and the percentage of Ag was reduced.

In Tab. 2 are showed the results obtained from the hardness and XRD tests performed on this alloy, with the previous optimized process.

Tab. 2 Hardness and residual stresses values obtained with the optimized production process for the new 10 Kt yellow gold alloy (alloy b)

PROCESS	HARDNESS TESTS (OPTIMIZED PROCESS) [HV]	RESIDUAL STRESSES – σ (OPTIMIZED PROCESS) [MPA]
AS-CAST	130 ± 5	- 54 ± 10
1° ROLLING STEP	235 ± 10	29 ± 3
ANNEALING	150 ± 5	- 83 ± 8
2° ROLLING STEP	210 ± 5	43 ± 4
RICOTTURA	140 ± 5	- 48 ± 7
1° ROLLING STEP	205 ± 5	14 ± 3
PLATING	140 ± 5	- 48 ± 10
ANNEALING	140 ± 5	- 90 ± 9

The content of silver influences the precipitation phenomena during annealing treatment. In fact, from the results of the tests performed, a decrease in hardness was obtained, with improvement in workability of the gold sheets. The greater machinability allows avoiding the final annealing before the plating process, resulting in a faster production process. After deformation process, passing from the old composition with Co to the new with Ru, a decrease in surface tensile stress has been noted. The change in the alloy composition influenced not only the first part of the production process but, also, the creation of the double-layer sheet welded during the plating process.

Modifying the grain refiner, the quality and the constancy of the material properties changed, because the two elements possess a different magnetic behavior. In fact, observing the welding lines on the iron sheet surface, it is possible to observe an higher uniformity and symmetry in the product obtained with the gold alloy b (Fig. 2a) in comparison with the other produced with the gold alloy a (Fig. 2b).
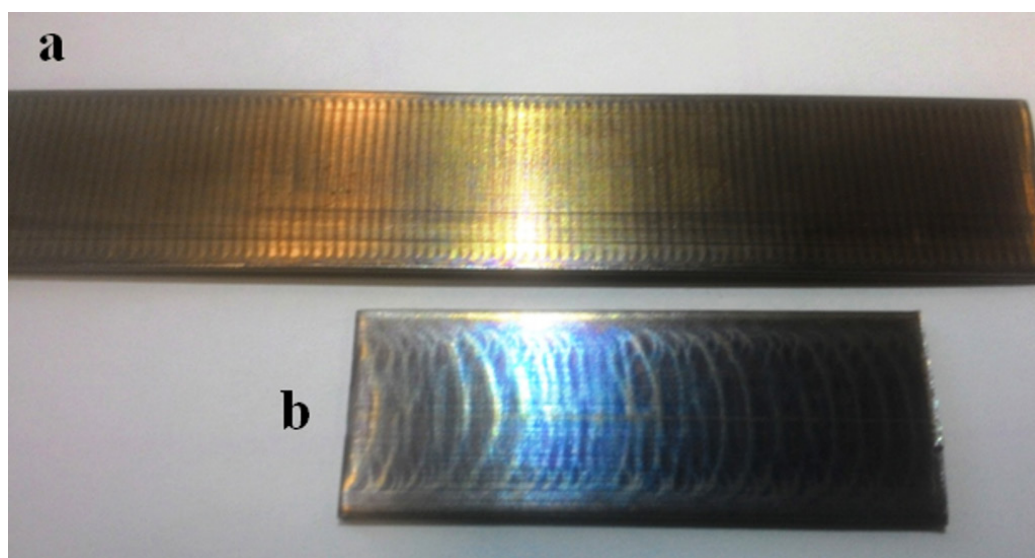

Fig. 2 – Particular of the iron sheet surface. Welding lines generated by the plating process using the gold alloy containing Ru (a), in comparison with the other containing Co (b), obtained both with the optimized process.

The microstructures of the two gold alloys are showed in Fig.4. The gold alloy b (Fig. 3a) shows an higher homogeneity in the distribution and grain size in comparison to the gold alloy a (Fig.3b). This is the cause of the different behavior during the plating process.
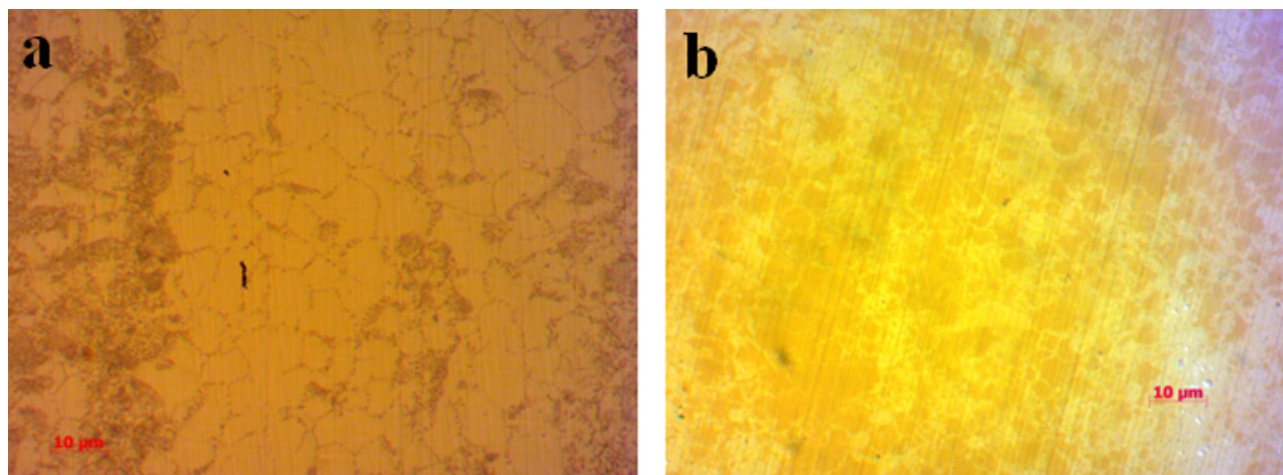

Fig. 3 – OM observation. Microstructure of the gold alloy sheet, produced using the optimized process, for the gold alloy b (a) and the gold alloy a (b)

Moreover, another part of the work was focused on the evaluation of the corrosion resistance of the gold alloys studied. A solution that simulates the environment of the industrial emptying process was used, a 10% HCl solution.
Graphic 1 compares the samples produced with the two different process performed, using the alloy a containing Co as grain refiner. The corrosion properties do not change, the different parameters used in the production cycle didn't affect the corrosion behavior of the material. The difference in the residual stresses, resulted from the two processes, was too low to generate not negligible effect on the corrosion resistance [5].
The change in the grain refiner, passing from gold alloy a to gold alloy b, ensures maintaining the same corrosion behavior and quality of the semi-finished product welded. Graphic 2 reports the polarization curves obtained for the two alloys produced with the optimized process after plating process.
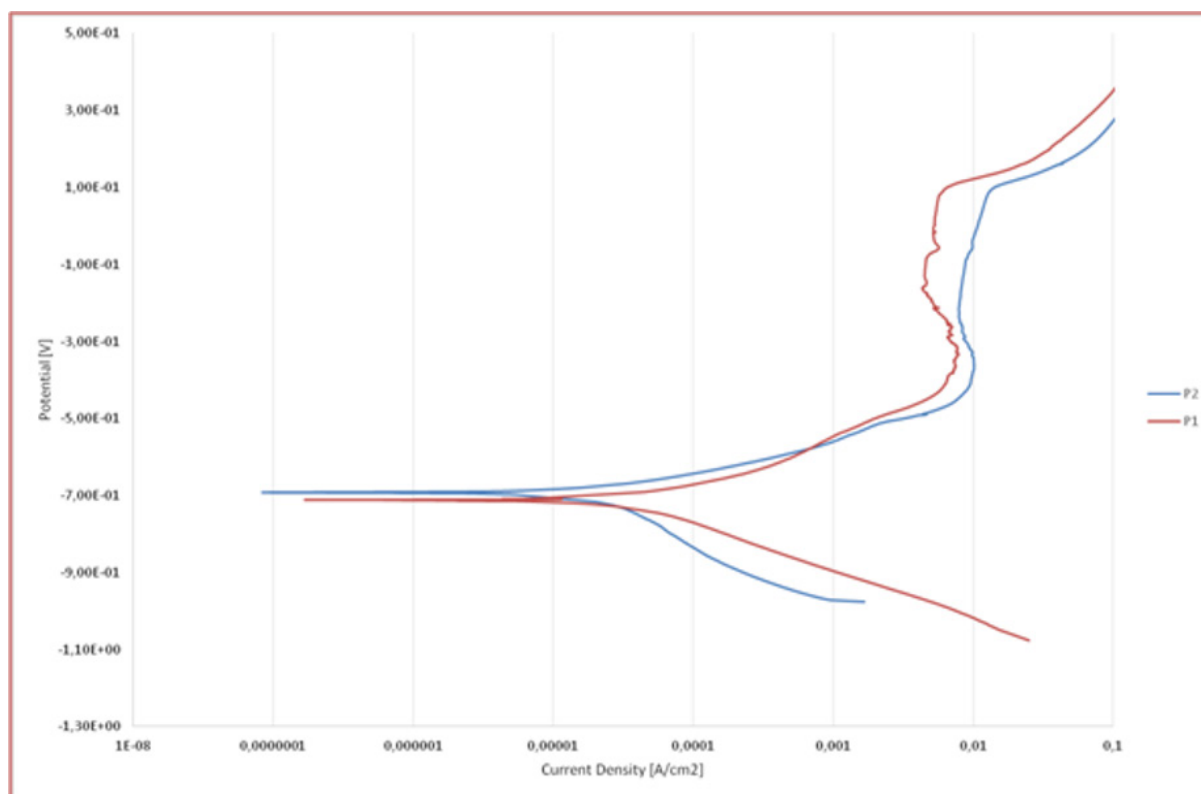
Graphic 1 – Results of the corrosion tests performed on the final annealed sheet after plating process, obtained with the two different production path. The gold alloy containing Co was investigated.
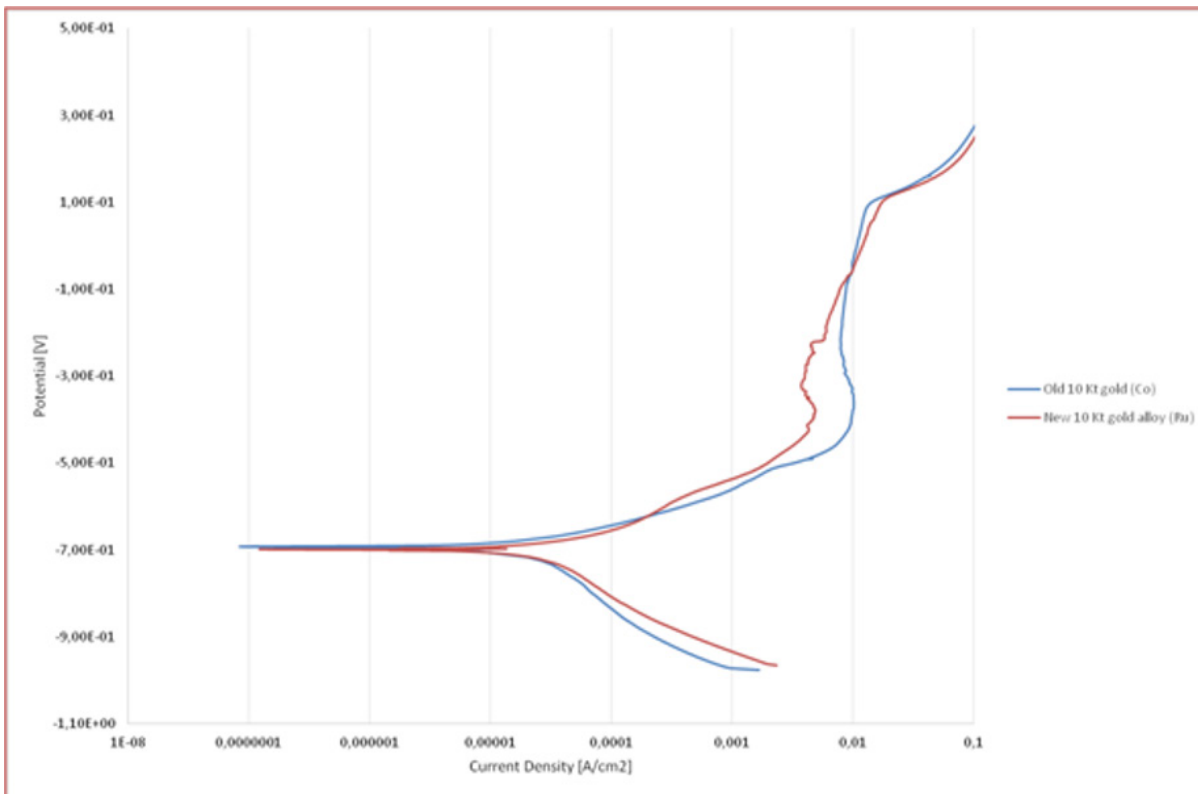
Graphic 2 - Potentiodynamic polarization tests on the final annealed sheet after plating process. The two different gold alloy compositions, obtained with the new optimized production process, are tested

CONCLUSIONS

The change in the production parameters, with the optimization of the annealing process, allowed to improve the quality and the efficiency of the industrial production cycle. This had influence on the hardness, on the ductility, on the machinability and on the microstructural homogeneity of the gold alloys.

The optimization of the process, allowed to reduce the residual stresses generated on the surface of the material, and increase the grain size, index of suitable annealing treatments. This increase the workability of the gold sheet, avoiding cracks during the deformation process.

The corrosion properties remain substantially the same. The use of a different grain refiner in the alloy, resulted in a better homogeneity of the microstructure and a greater uniformity of the properties during the production cycle, especially in the plating process. Furthermore, it allowed to avoid the undesired magnetic behavior of the final chain products. Also in this case, the corrosion properties hadn't change. Modifying the grain refiner, it was possible to maintain the same quality of the semi-finished product after the emptying process.

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