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**Ilaria Forno** ha conseguito il titolo di Ingegnere dei Materiali al Politecnico di Torino. Sta ora svolgendo un Dottorato di Ricerca in Sistemi di Produzione e Design Industriale, sviluppando una tesi sponsorizzata dal Consorzio Prometeo, riguardante la microfusione dei metalli preziosi con una analisi di materiali e metodi

*La produzione di gioielli e di componenti di oreficeria fa tradizionalmente ricorso ad un ampio spettro di metodi di produzione dalle tecniche tipicamente artigianali a sofisticate tecniche di produzione industriale.*

*Recentemente, anche a supporto delle tecniche di metallurgia tradizionale, sono state utilizzate sempre più spesso tecniche di metallurgia delle polveri (PM). In particolare il settore orafa in senso lato, ha fatto ricorso alle tecniche PM per ovviare a problematiche di design e di controllo dimensionale che insorgono, ad esempio, con le tradizionali tecniche di microfusione. In quest'ottica grande interesse è stato rivolto alle tecnologie di Metal Injection Moulding e alle tecniche di Additive Manufacturing metallico (Selective Laser Sintering, Selective Laser Melting, Stampaggio 3D).*

*La Metallurgia delle Polveri si presenta tuttavia come un campo di studio molto vasto, che permette avanzamenti non solo in termini di design ma, ed è questa la sua tradizionale funzione, in termini di ottimizzazione di consumo di materiale e energia e, soprattutto, in termini metallurgici.*

*Considerando questi fattori, risultano essere estremamente interessanti le tecniche che vengono classificate sotto l'acronimo FAST (field-assisted sintering techniques), ovvero quelle tecniche di sinterizzazione assistita da campo che permettono quindi un processo di consolidamento delle polveri, come suggerisce l'acronimo stesso, rapido.*

*Il presente lavoro illustra una specifica tecnica FAST, Electro-Sinter-Forging (ESF), mostrando, attraverso esempi pratici, i vantaggi ottenibili in termini di rapidità di processo e di ottenimento di componenti dalle avanzate proprietà meccaniche grazie alla possibilità di ottenere condizioni microstrutturali e composizionali non ottenibili con l'applicazione di tecniche tradizionali.*

# Electro Sinter Forging: a Superhero of Powder Metallurgy

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## INTRODUCTION

In the last decades high quality jewelry industry, traditionally based on handcraft abilities, has been facing a rising interest towards new technologies and innovative materials. This renovation, mainly driven by the specific global scenario, is concerning several aspects of the industrial field, such as the introduction of new technologies [1-3] and materials [4-5], the exploitation of new design features [6] and the opening towards new markets. When considering product innovation, two different aspects have to be taken into account: in addition to the introduction of new materials, traditionally not applied into jewelry production, such as Titanium alloys, stainless steel and ceramics, a great effort has been done in enhancing traditional material properties, both via compositional optimization and via optimized processing conditions. In this fragmented and sparkling scenario, a great interest rose towards innovative production processes. The intensive work to demonstrate the applicability of rapid prototyping, machining and powder metallurgy to precious metals is clearly showing this trend [7-9]. Coming to the specific case of powder metallurgy (P/M), the technique, well exploited in other industrial fields, has been driven both from metallurgical considerations (great opportunities in terms of properties and compositions) and on production accounts (dimensional tolerances, shape complexity, ..).

An effective way to classify and select the more suitable technique might then be to consider the achievable shape complexity: Following this approach, PM techniques may be roughly classified as:

- Pressing
- Injection
- Freeforming

Press and sintering is a largely used technology, mainly to medium to simple, axial-symmetric components. Even if the shape limitation of these techniques may hinder their application on precious metals, some specific pressing techniques offer undeniable benefits in terms of properties and processing conditions.

An example of enhanced sintering techniques are the so-called FAST (Field Assisted Sintering Techniques). These techniques are based on the application of an electro-magnetic field at relatively low frequencies (<500 Hz) whilst compacting the powder. Using an electric current to heat and sinter or aid a sintering process is not really a novelty. Nevertheless, the electric current assisted technologies that have found direct industrial application, however, are few: Hot Pressing (HP) and, in a more limited way, Spark Plasma Sintering (SPS). Both these very similar methods employ graphite dies and plungers placed inside a controlled atmosphere and heated through a current flow, retrofitted in temperature either through a thermocouple or a pyrometer. Besides several differences between the two methods in terms of approach and control parameters, the results are quite similar, with typical cycles lasting for 10 to 25 minutes and similar final properties of the sintered parts.

Additional properties may be achieved by ball milling of metal powders [10]. Ball milling is a well exploited method to get comminution, mechanical alloying and structural modification of metallic and non-metallic powder. In particular, high energy ball milling (HEBM) is an advantageous technique to produce nanocrystalline materials, due to its ability to produce bulk quantities of materials in the solid state, in relatively simple to achieve conditions (room temperature and simple equipment), causing a progressive reduction of grain size up to the formation of a dislocation-free nanocrystalline grains.

The consolidation of mechanical milled powders is the key point in order to produce bulk components [11,12].

As a consequence, the use advanced sintering processes is even amplifying the opportunities offered by P/M, both in terms of the final components properties and of manufacturing conditions.

## ELECTRO SINTER FORGING – THE METHOD

In the last years, particular interest has been devoted to Field Assisted Sintering Techniques (FAST) due to their ability to reach high densities in very short processing times.

Among the different FAST, Electro-Discharge-Sintering (EDS) and its particular case Electron Sinter Forging (ESF), showed an interesting behavior for what concerns the sintering time (milliseconds in ESF compared to minutes of Spark Plasma Sintering -SPS) and in automation required, being able to produce finer and harder materials as the result of the highly metastable process. In fact, despite the extremely quick process, timing is not the main benefit deriving from ESF: the actual possibility of retain nanosized or amorphous structures and metastable compounds is highly widening the range of producible materials [13]

Instead of heating a graphite die, as for SPS and HP, these alternative methods use direct heating of the powders to consolidate them directly and to sensibly reduce the processing time. These other ways of using currents constricts the electron flow exclusively through the powders and deliver a high amount of energy in fractions of a second.

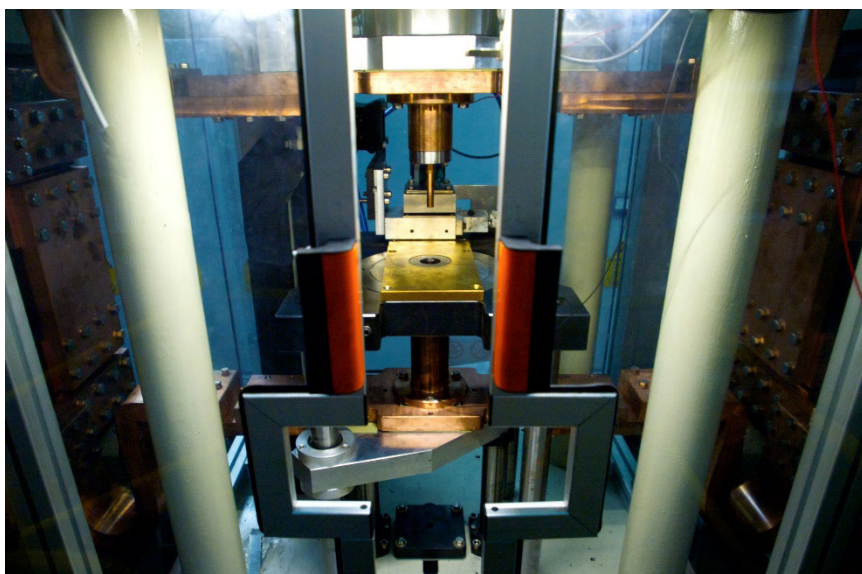


Figure 1 - Electro-Sinter-Forging machine

ESF equipment appears very similar to a conventional powder press but with a twist: two pulses, one mechanical and one electrical, are superimposed in a die previously loaded with the powders. The electrical pulse is synchronized as to begin energy transfer when a predetermined level of pressure has been reached ( $P_{start}$ ) so that a homogeneous flow of current is guaranteed. While the energy source is transferring electro-magnetic energy, the mechanical system acts to compensate, at high speed, the powder shrinkage and to increase pressure ( $P_{end}$ ) in the time frame of the electro-magnetic pulse that lasts from 30 to 100 ms ( $t^*$ ). Pressure is held from a few milliseconds to, usually 1 to 3 seconds, before the upper plunger is automatically drawn out of the die and the lower plunger is moved to the upper part of the die in order to extract the sintered piece from the die assembly. The typical cycle is shown in Figure 2. The electro-magnetic discharge is usually generated with a high voltage capacitor bank connected to step down transformers for the conversion of high voltage low current on the primary circuit to low voltage high current on the secondary sintering circuit. The voltages on the sintering die are below 50 V so the procedure is quite safe. The process seems visually identical to a conventional powder pressing system with a double action, but the result, instead of a compacted green is a sintered part.

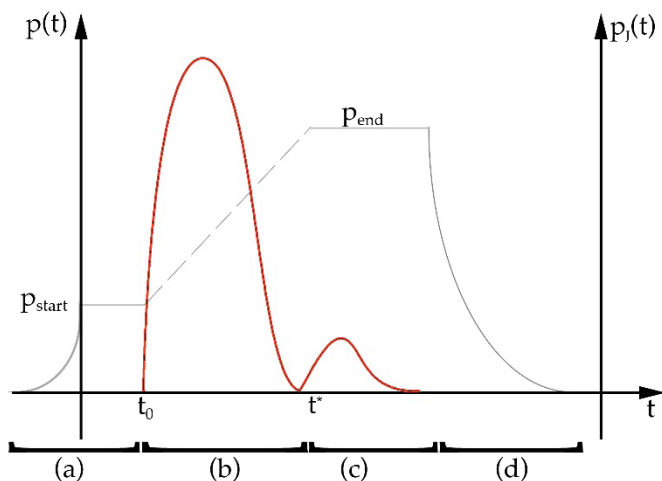


Figure 2 - ESF cycle: (a) pre pressing, (b) superimposed pulses, (c) holding in pressure / cooling and (d) release of pressure and extraction from die. Mechanical pressure in light grey,  $p(t)$ , and electric power  $p_J(t)$  in thick red. Mechanical pressure during (b) can oscillate or have different from monotonous behavior due to how the consolidation occurs.

The values of pressures employed usually range between 10-50 MPa for  $P_{start}$  and 40 to 400 MPa for  $P_{end}$ . Currents are intense: typical current densities range between 0.1 to over 1 kA/mm<sup>2</sup>. The parameter, used to have a good feeling of how much energy has been discharged on the part during the process, is called specific energy input, or SEI:

$$SEI = \frac{1}{w} \cdot E_J = \frac{1}{w} \int_0^{+\infty} v(t) \cdot i(t) dt \approx \frac{1}{w} \int_0^{t^*} v(t) \cdot i(t) dt$$

where  $w$  is the weight of powders inserted in the die (which is usually nearly coincident with the weight of the extracted part),  $E_J$  is the energy dissipated on the system by Joule effect,  $v(t)$  and  $i(t)$  and respectively the curve of voltage and current, measured during the process, while  $t^*$  is the characteristic time of the process.

The usual parameters that are set on the machine are: the axes positions (handled by a numerical control) before and after the discharge, the amount of energy [%] loaded on the capacitor banks, the amount of time that the pressure is held after  $t^*$ . The powders can be of any size, in function of the final application: from submicron (0.7  $\mu$ m Co powders used for cutting tools) to coarse 0.5 mm. Powders must be used completely dry. Any trace of lubricant or polymeric agent used in conventional PM, is detrimental to the characteristics of ESFed objects. This is a consequence of the process being so fast: there's no time for evacuation of the binder.

## ESF – MATERIALS AND APPLICATIONS

A wide range of materials can be consolidated with ESF. Metals [14,15] operating in synchrony with the electromagnetic pulse. Through an analysis of covariance (ANCOVA, metal matrix composites (MMCs) [16,17] and intermetallic [18] materials have been sintered in air up to theoretical density. Several non-precious systems have been explored, such as iron and alloys [14] of pre-alloyed powders of AISI M2, T2, H13, 316L and 410; pure nickel and pre-alloyed Inconel; pure cobalt and pre-alloyed stellite; copper and various types of pre-alloyed bronzes; titanium and pre-alloyed grade 5 powders; molybdenum; tantalum; cemented carbides [16], carbonitrides and nitrides; diamond reinforced metals for stone cutting [17]; pre-alloyed nitinol [18]; Y-titanium; Nd-Fe-B flakes; bismuth tellurides, magnesium silicides and skutterudites for thermoelectric applications.

Electro-Sinter-Forged diamond metal matrix composites for circular blades (called bits) used in stone cutting have been extensively developed and produced [17] and intensively tested on a number of granites and marbles with professional mills on the field of industrial cutting.

Considering precious metals, silver systems as been partially explored (pure silver, pure silver/pure copper blends, pre-alloyed 925 sterling silver powder) as well as gold alloys. [15]

Densities of sintered parts can be adjusted from very low (60-70%) to very high (99.9+%). The tolerances on inner and outer electro sinter forged steel rings reach a standard deviation ( $\sigma$ ) of 0,006 mm (6  $\mu$ m) on both the inner diameter (of 13 mm) and outer diameter (of 16 mm).

### A “PRECIOUS” EXAMPLE: ESF OF GOLD BASED POWDERS

Precious metals are widely used for a variety of applications, among which luxury goods, biomedical devices and electronic components. Requiring precise components, those sectors are usually looking into lost-wax casting, machining and, more recently, metal injection moulding. Material or (thermal) energy consuming and demanding, the aforementioned processes are mainly suitable for stable crystalline structures.

Switching to FAST methods, and particularly to the “super-fast” ESF, characterized by extremely rapid processing times is enabling the realization of metastable phases, in addition to the quick production of precise and fully dense components with tailored microstructures. Different powders with different features (as atomized, ball milled and admixed with nano-diamonds) were taken into account, fast sintered and the resulting samples were analyzed in terms of final density, microstructure and hardness.

Produced samples were tested in order to evaluate the main properties and check the fulfillment of jewelry industry requirements. Densities and microstructures have been evaluated, in order to estimate the accomplish of polishing requirements. As pointed out in several different studies [19-21], hardness is often used in the jewelry industry, as it is a parameter that can be easily and quickly measured. Generally speaking, the harder the metal, the easier to polish and the more wear- and scratch –resistant it will be. Many efforts have therefore been devoted to the increase of hardness of precious metals, particularly of gold alloys, both from a compositional point of view [22,23] and via process optimization [24]. Hardness of the different systems studied have been measured in terms of Vickers scale.

### MATERIALS AND METHODS

In this experimental work different high caratage gold powders have been evaluated. The following table 1 reports the alloys compositions and the main powder characteristics of the systems taken into account for the research.

Alloy	Au	Co	Cu	Ag	Powder modification
A	99,8	0,2			/
B	75		12,5	12,5	/
C	75		12,5	12,5	Ball milled
D	75		12,5	12,5	+ 15%vol. nanodiamonds

Table 1 Composition of the studied systems.

Metal powders have been produced via gas atomizing, resulting in an highly packable spherical shaped powder .

System A is pre-alloyed high caratage gold alloy powder ; alloying with 0.2% Co was finalized at grain refining.

System B, C, D use the same starting alloy based on a standard 18 kt. 3N gold composition. Fig.3 reports the 18 kt. 3N gold powder used in systems B, C and D.

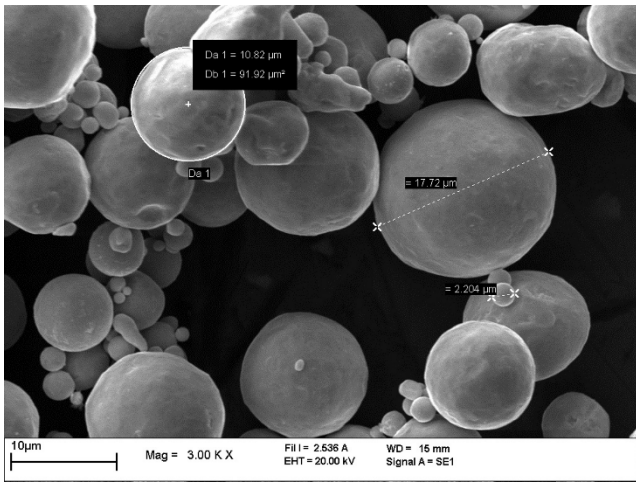


Figure 3 - 18 kt. 3N yellow gold alloys powder particles.

System C has been obtained carrying out a ball-milling process onto system B. Powder B was ground in a high energy planetary mill apparatus Retsch PM-100 with a 50 ml WC jar and WC balls. Milling was carried out with a ball-to-powder weight ratio of 10:1 and a 3 ml addition of ethanol as wetting agent at 300 rpm. Powder D was obtained by means of mixing system B with 15 % vol. of nano-diamonds (sub 250 μm.).

Powders have then been pressed and sintered with a ESF process. Samples have been sintered in an high strength graphite mould with a central circular sintering cavity with a diameter of 10 mm. The plungers also act as electrodes and are made of copper alloys (typically Cu-1,5%Co-0,5%Be). Different sintering trials were carried out with different applied pressure (40 to 210 MPa) with a final clearance of 4,6 mm.

## RESULTS AND DISCUSSION

Metallographic inspection has been carried out via light optical microscopy both on polished and etched samples. Chemical micro-etching has been carried out with a HCl/HNO<sub>3</sub> etchant accordingly to ASTM standard E407 – 99. Moreover Scansion Electron Microscopy (SEM) morphological analysis has been carried out on polished sample in order to further deepen the understanding of sintering conditions. Density was tested with Archimedes' principle on as-sintered samples, on an equipped 5 digit - Sartorius CPA225D balance in controlled conditions.

The AuCo alloy (99.8 % Au – 0.2 % Co) showed a relative sintered density of 98,7%. Sintered etched microstructure revealed spherical porosity, evenly distributed along grain boundaries, with mean dimension lower than 5 μm. Cobalt aggregates are homogeneously distributed at grain boundaries, maintaining grain dimension lower than 30 μm. Figure 5 shows the SEM image of the system A, highlighting the distribution of Co along grain boundaries. The microstructure of sintered AuCo 24kt. gold alloy is reported in following Fig.4 and Fig.5.

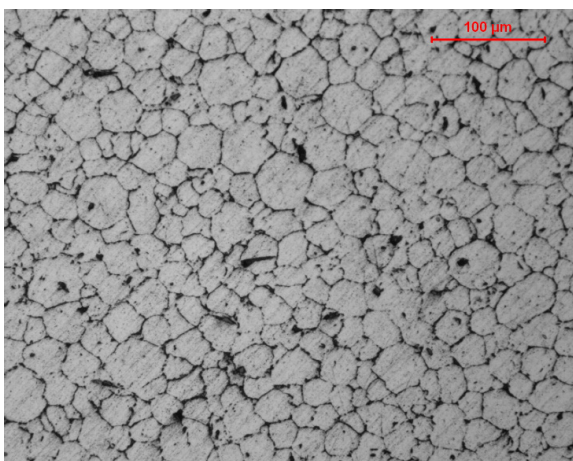


Figure 4 - LOM analysis of 24 kt. microalloyed gold (200x).

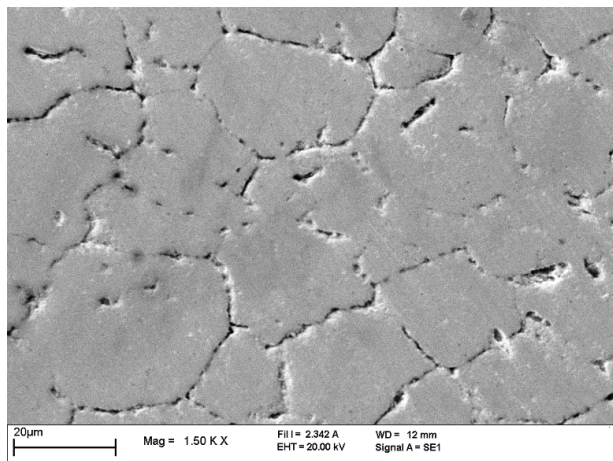


Figure 5 - SEM analysis of 24 kt. microalloyed gold.

The metallurgical analysis of system B, an 18 kt. 3N yellow Gold alloy, shows easily detectable powder particles, with evidence of inner dendritic structures (Fig.6). SEM analysis reported in Fig.7, reveals the presence of a copper-rich phase distributed along grain boundaries

In the observed structure, sintering of particles, at least at its early stages, is clearly noticeable; give the short sintering time and, most of all the overall low T of the process, no diffusion effects may occur. System B showed a relative sintered density of 98,5%.

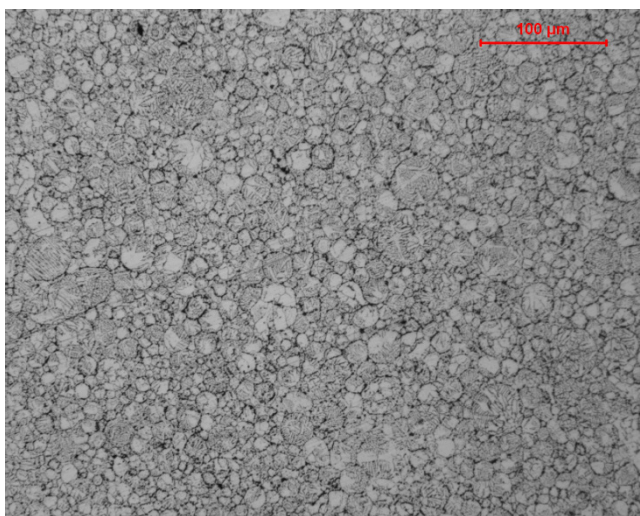


Figure 6- LOM analysis of 18 kt. 3N gold alloy(200x).

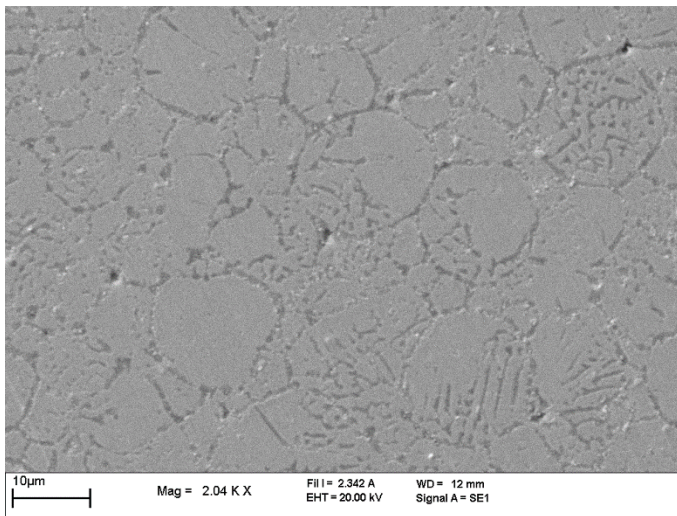


Figure 7 - SEM analysis of 18 kt. 3N gold.

As for System C (18 kt. 3N yellow Gold alloy) the 128 h. ball milling resulted in a nanostructured powder partially amorphous. The sintering of this powder resulted to be extremely enhanced. No microstructure or grain boundaries are therefore detectable by SEM analysis, whilst at high magnification (Fig.9), it is possible to identify sub-micron precipitates in nano-crystalline gold . A relative sintered density of 98,9% was obtained on system C.

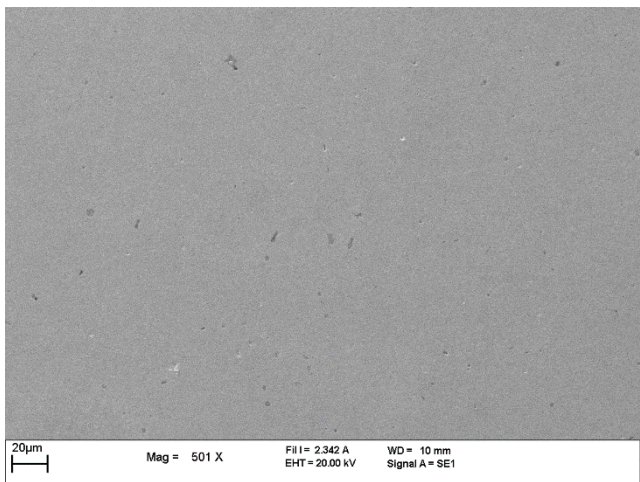


Figure 8 -SEM analysis of ball-milled 18 kt. 3N gold.

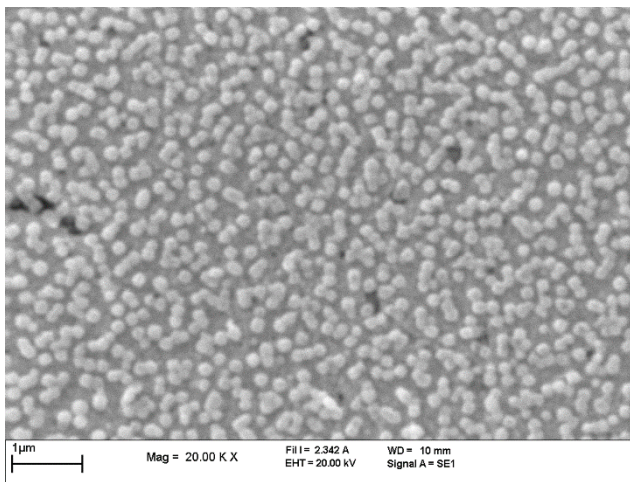


Figure 9 - SEM analysis of ball-milled 18 kt. 3N gold.

Sintering of system D, resulted in the successful creation of a composite material where reinforcing agents (nano-diamond) are dispersed in the metal matrix. The homogeneity of the dispersion of the second phase is depending on the mixing process prior the sintering and on the relative powder dimension. Figure 11 is showing the homogeneous dispersion of nanodiamonds into the matrix at a local level. Diamond powder is clearly visible and detectable testifying the absence of deteriorating phenomena at the interface.

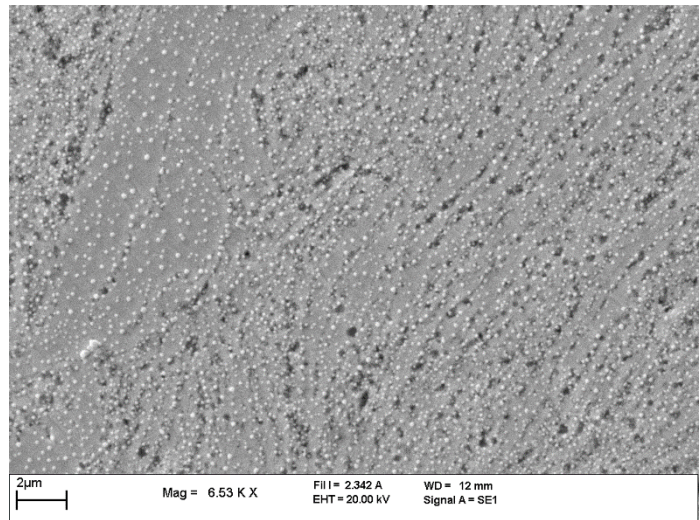
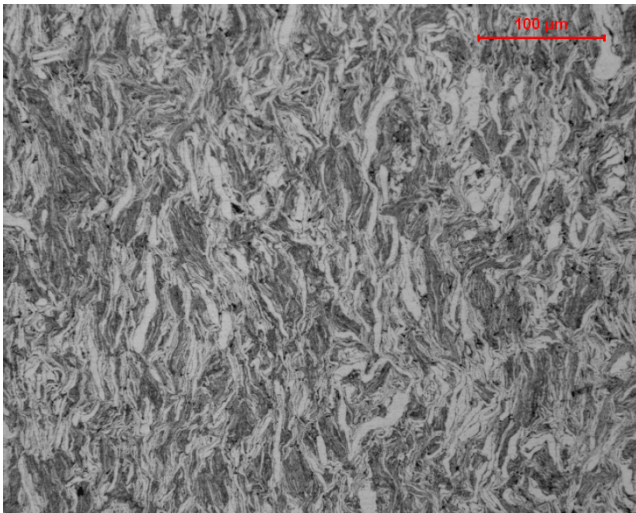


Figure 10 - LOM analysis of of 18 kt. 3N gold. + nano diamonds (200X) Figure 11 - SEM analysis of 18 kt. 3N gold. + nano diamonds

Micro-hardness results have been compared with average values for the corresponding composition. Considering 24 kt. gold, it has Vickers hardness of about 20-30 HV (in the as-cast or soft-annealed form) reaching to 60 HV for cast microalloyed gold [28]. The application of FAST sintering is improving this result, reaching 80 HV, mainly due to the effective dispersion of the alloying element and to the grain fineness.

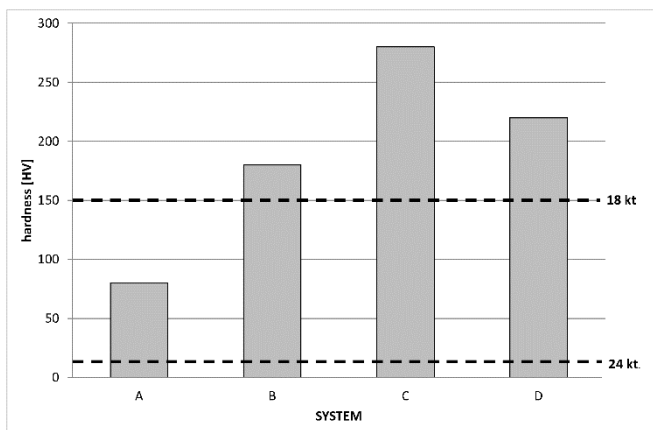


Figure 12 - Hardness value of sintered samples

A much more significant effect is observed in the considered 18kt. alloys. 3N gold has, in the soft-annealed state an hardness of 150HV [30,31]. The application of ESF allowed to reach an hardness of 180 HV for the simple 18kt. system. Considering system D, the addition of an hard second phase, increased hardness value to 220 HV. The possibility of introduce and, most of all, retain a nanostructured systems allowed to reach 280 HV on system C.



## CONCLUSIONS

When the main goal is to achieve outstanding mechanical properties, extremely fine microstructure and unbeatable processing time, FAST are offering the possibility of getting simple components to be eventually machined into complex shapes. The applicability of ESF processing technique to gold powders has herewith been demonstrated. The use of this approach allows to reach in a single-step process increased hardness values, compared to traditional casting techniques. The application of ESF is also enabling the production of metastable structures in a reliable and controlled way, thus widening the possibilities in terms of precious (and non precious) alloys with enhanced properties.

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