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DETERMINATION OF GENUINE ARCHAEOLOGICAL FINDS BY AN IRREVERSIBLE THERMODYNAMIC APPROACH

The differences of the energy contents belonging to genuine archaeological finds of metallic nature are sharply different from counterfeits. Experimental determinations based on non-destructive and non-invasive (SEM, EDS, XRF) methods were applied to discriminate genuine archaeological finds from fakes. Differences between a genuine aureus coined by Iulius Caesar and a modern counterfeit aureus of Sextus Pompeius obtained by mean of a press-fusion procedure were evidenced on the basis of here proposed theoretical and experimental acquisitions.

The different techniques followed for the production of metallic devices are responsible for endowing metallic tools, including coins, with inner structural arrangements characterized by a high transference of energy when obtained by striking and mainly if compared with the ones obtained by techniques based on fusion, or press-fusion. These thermal processes can be widely utilized to produce counterfeits of archaeological metallic finds, and mainly of ancient coins.

Even if the macroscopic aspects of differently obtained metallic tools (genuine or counterfeits) apparently do not reveal appreciable differences, nevertheless suitable methods performed by means of appropriate physico-chemical devices, like X-Ray Fluorescence (XRF), Energy Dispersion Spectroscopy (EDS), and Scanning Electron Microscopy (SEM), are suitable to discriminate among different structural dispositions at microscopic and at sub-microscopic levels, associated to the different techniques of production.

The interesting and relevant feature of such physico-chemical methods is the possibility to ascertain the genuinity of archaeological finds in general and of coins in particular. Furthermore such methods are not destructive nor invasive and never affect the structure of metallic sample, so that the examined specimens are always left strictly unsullied and, in case of doubts, there is the possibility for physico-chemical determinations to be repeated again.

The thermodynamic principles of irreversible processes are at the basis of a correct approach to explain the irreversibility of the energy transfer, that is at the basis of all the mechanisms followed for the formation of coins: hammering, or striking, endows metals or metallic alloys, with highly compact and "ordered" structural arrangements, in agreement with a considerable amount of mechanical energy transferred to the metal, or metallic alloy, in comparison to the required energy to perform metallic tools by means of fusion, or press-fusion processes, that are the mainly used to counterfeit ancient metallic tools in a more simple and economic way.

The structural changes involved by means of a coinage, is a process that takes place on a solid metallic mass that is transformed, thanks to a mechanical energy transfer, in an another and more "ordered" solid structure, while either fusion or press-fusion processes never affect a solid structure but simply affect the final form of a liquid metal before to leave over the liquid mass to be cooled and then to solidify.

The peculiar modifications imposed by hammering to the inner structure of the metallic mass are of energetic nature: it is an energy transfer, in fact, that bestow to metallic archaeological finds in general, and to coins in particular, responsible for better technological features to the metal or metallic alloys, first of all a hardening of the specimens, in front of the ones obtained by simple fusion processes, where the energetic contribution is very low or negligible.

Counterfeits of ancient archaeological finds, including silver and gold coins, are mainly produced by fusion or press-fusion techniques, based on fusion of metals and consequently by pouring the molten mass inside appropriate smooth moulds, or in previously engraved dies, so that they should present, after solidifying, size shape and an aspect that is apparently similar to the genuine ones obtained in ancient times by hammering.

It is in fact well known that hammering is always responsible for improvements of several technological properties of metallic tools, so that it can be said that the "label maker" mechanism of hammering bestows mainly a hardening of the metallic alloys. So, for instance, it is just the hammering that bestows to blades of knives and swords better cutting properties and to spikes high penetration power, as proved since in ancient times by the famous sabres produced in Iberia and also, up to date, in Toledo (Spain).

The excellent performances of metal alloys after striking are also valid for the ballistic improvements of firearms, for instance barrel of guns sharply improve the ballistic power after cold hammering treatments.

The main ancient production of genuine coins was done by coinage, while in modern times their counterfeits is mainly done by means of fusion or press-fusion techniques.

In ancient times striking was obtained by strong shots of a sledgehammer onto a solid metallic small disk, clamped between two engraved dies. In this connection it is of fundamental importance to take into account that the intensity of the applied force to the sledgehammer shot as well as its direction was only approximately but never exactly perpendicular with the respect to the plane of the coin, so that it is virtually impossible to obtain exactly identical coins by following the coinage procedure applied in ancient time, as widely proved by careful inspections by means of the electron microscopic images respective to "hand made" coinages, carried out by means of sledgehammer shots.

These limitations are also applied to leave unaffected the surface coatings formed along centuries on the metallic surfaces of metallic archaeological finds after interactions with a lot of chemical species present in the environment and suitable to interact with metals.

This kind of investigation is valid for gold and silver coins owing their refractory nature towards many environmental agents, but the above mentioned methods cannot be applied in the study of bronze coins, being the ancient bronze coins always coated with materials formed by interactions between the different component of the various bronze alloys and all the many possible and different kinds of environmental contaminants that took place along centuries.

Owing the historical and economical values of these specimens, the removal of such coating layers is strictly forbidden.

The dissipation function

The fundamental approach takes into account the conditions associated to coinage assumed as an irreversible process that can be defined in terms of a dissipation function, responsible for energetic transferences and/or exchanges.

Striking, as well as all other processes to cast coins, are based on the action of driving forces of mechanical, thermal or thermo-mechanical nature, acting either instantaneously and totally responsible for the coins formation (hammering) or slowly and progressively (simple cooling and/or cooling and applied differences of pressure) and merely responsible for an improvement of the homogeneity in the molten mass and mainly in the surface state of the coins.

All the processes, however, affect the size, shape, images and inscriptions of the metallic mass respective and peculiar to different technologies followed to obtained coins.

The entity of the involved changes are all sharply different owing the different contribution of involved energy in the two above mentioned processes, since the energetic contributions of different entities are stored, in news stable arrangements of the solid state structure into the "body" of the coins.

Obviously in the coinage the mechanical energy is transferred instantaneously by hammering and is stored into the solid metallic structure. The entity of energy involved in this process is remarkable, while it is nearly worthless the mechanical energy associated to the difference of pressure required in the press-fusion technique.

In the coinage the metallic structure of the solid mass undergoes to a disorder → order transition that takes place from the action of a strong and immediate mechanical driving force applied to the solid metallic mass. Such a condition is also consistent with the hardening of the coin.

The transference of energy can be evaluated by means of the dissipated energy, φ , but it is, obviously, different in each coinage being function of the entity of the each single sledgehammer shot as well

as of the metallic mass and its dimension where the energy transfer takes place.
The disorder → order transitions peculiar of each structural variation involved in the irreversible process can be evaluated by the product of the generic energy flows, $\vec{J}_t$, for the respective acting driving forces, $\vec{X}_t$.
The basic principles of irreversible thermodynamics allow to have, in such a way, a correct correlation among the total flows and the respective driving forces (mechanical in the case of striking or thermo-mechanical in the case of press-fusion processes) that define the entities of the dissipated energy, that is in part transferred to the metallic disk.
So generic flows of energy, $\vec{J}_t$, can be correlated to one or more driving forces, $\vec{X}_t$, by means of fenomenological coefficients, *L* and *R*, with the dimension respectively of conductivities (or permeabilities) and resistances.
If a system is not far from equilibrium and the linearity conditions between flows and driving forces are verified, one can, therefore, write: $\vec{J}_t = -L\,\vec{X}_t$ or, inversely, $\vec{X}_t = -R\,\vec{J}_t$, being, obviously $L=1/R$.
The hardening of the metal alloys is a main feature of a far from equilibrium process associated to the dissipation of energy, φ, given by the product of an involved flow, *J*, times the respective driving force, *X*:

$$\varphi = JX = \sigma T = (dS/dt)T \qquad (1)$$

where σ is the velocity of entropy production, $[\sigma = (dS/dt)]$, and *T* is the absolute temperature.
The change of entropy of any thermodynamic system that undergoes to an irreversible transition in a given interval of time is:

$$dS = dS_e + dS_i \qquad (2)$$

where the *dS* is the total entropic transference associated to the irreversible process, dS_e, is the entropic change respective to the environment and dS_i is the entropy change involved inside the system.
The thermodynamic system here represented by the metallic disk, is defined a "closed system" since inside the coin occurs only a change of energy and no exchange of matter can take place.
However the transference of energy inside the coin, associated to the hardening of the metal structure, is consistent either with a decrease of entropy inside the "closed system" and with an entropic increase outside the system, in the environment.
Equations (1-2) are valid for thermodynamic systems also in far from equilibrium conditions and evidence how it is possible to obtain two almost identical coins as far as their mass, size, shape and images is concerned. However the energy dissipated, in both given examples, is sharply different according to the two completely different experimental conditions, respective to coinage and to press-fusion processes.
The dissipation energy involved, defined by equation (1), takes into account all the terms (flows, driving forces and velocity of entropy production) that are determinant and sharply time-dependent.
This acquisition is consistent with the high mechanical energy transferred and stored inside the coin by means of the sledgehammer shot in front of the low mechanical energetic contribution in the press-fusion, where the low applied energy is not transferred inside the thermodynamic system represented by each coin, because the coin formation takes place from a spontaneous cooling of a molten metallic mass. Furthermore the time required to realize the coins by means of two different experimental techniques are completely different ways of transferring energy.

Energy transfer involved in striking, in fusion and in press-fusion processes

Striking (or coinage)

Striking bestows on metallic tools in general, and on coins production specifically, a considerable increase of energy, as evidenced by the hardening of the metallic structure. Such an increase of energy is transferred instantaneously on a metallic tool by a mechanical driving force, $\vec{f}_t$, generated by an instantaneous sledgehammer shot:

$$\vec{f}_t = \frac{d\vec{M}}{dt} \qquad (3)$$

where $d\vec{M}$ defines the variation of the motion, at full speed, of the beating mass, namely the variation of the velocity, $\vec{v}$ of a beating mass, *m*, on a solid metallic body along an instantaneous interval of time *dt*.
The driving force, $\vec{f}_t$, is, in turn, responsible for an energy flow, $\vec{J}_t$:

$$\vec{J}_t = \Delta\vec{M}_{\Delta t} \qquad (4)$$

so that the flow of energy transferred by hammering, $\vec{J}_t$, is an "impulse of energy", defined by an equation, also known as "impulse equation" or "percussion equation":

$$\vec{J}_t = \int_{t1}^{t2} \vec{f}_t\,dt = \Delta\vec{M}_{\Delta t} = m\vec{v}_2 - m\vec{v}_1 = m\Delta\vec{v}_{\Delta t} \qquad (5)$$

The maximum value of the speed of the moving beating mass at the time t_1 is $\vec{v}_2$ and $\vec{v}_1$ is the value of the speed of the beating mass at the time t_2, that is coincident with the instant at which the percussion takes place and when the velocity, $\vec{v}_1$, vanish.
The equations (3-5) define what happened in ancient times, when a beating mass of a sledgehammer was matching a small metallic disk clamped between two engraved dies to be transformed in a coin.
The shot is therefore responsible for a sharp and sudden increase of energy density inside the small mass of the coin and here stored as an improved hardening of the metal. Such a new structural modification is consistent to a new "ordered" organization of the metallic structure, part of which "emerges" out of the plane of the coin, as evidenced by the peculiar structure of a sort of a "bring out" or "born out" from the mass of metal embossed images and letters present in

all coinages. This increase of energy is, at the same time, consistent to a consequent sharp decrease of entropy that takes place inside the coin. Consequently a dissipation of energy and an increase of entropy takes place in the environment, features that are consistent to the hardening of the metallic structure.

Such an entropic/energetic inter-exchange is defined by means of a dissipation function (see again equation (1)), which is suitable to define all the processes that take place in far from equilibrium conditions, consequent to entropic/energetic inter-exchanges.

As far as the procedure followed in ancient times to obtain coins by hammering, it must be taken into account that all the sledgehammer shot were applied in a direction only approximately, but not exactly, perpendicular to the plane of the coin.

The lack of an exactly perpendicular shot as well as of a reproducible intensity of the applied strength is a further peculiarity verified in all the genuine coinages and that is responsible for an existing difference among all the ancient specimens obtained by coinage. This is also the answer to the not written rule, but widely applied by dealers, that it is impossible the existence of two perfectly identical coins, if supposed to be obtained in ancient times by coinage. Therefore such a dealers' rule is an excellent test to prove the presence of forgery and it is in agreement to the irreversible thermodynamic approach.

Fusion

Ancient fakes are frequently obtained by means of a simple fusion process, based on a liquid-solid phase transition, occurring at room temperature along the time in which the cooling of the liquid metallic mass takes place.

The change from a liquid to a solid state of a liquid mass is a merely spontaneous phase transition, so that the molten metallic alloy does not require any further energetic supply to solidify into the engraved dies.

In the course of the spontaneous transition of a molten metallic mass from high temperatures to room temperatures, thermal energy, as heat, is dissipated in the environment.

The liquid mass poured into the dies fills out the empty space of the engraved dies to assume, after cooling, the solid and definitive embossed aspect of the images and inscriptions preformed in the engraved dies. But frequently minute cavities into the solidified metallic mass are left unfilled and in such a way optical inspections by means of simply magnifying glass are more than suitable to detect the presence of unfilled little holes.

The production of counterfeits by a simple fusion process is, therefore, a merely a spontaneous process of filling, that does not require any mechanical contribution of energy to be performed.

Press-fusion

In spite of the simple fusion process where an energetic supply is never requested, the press-fusion technique requires a transference

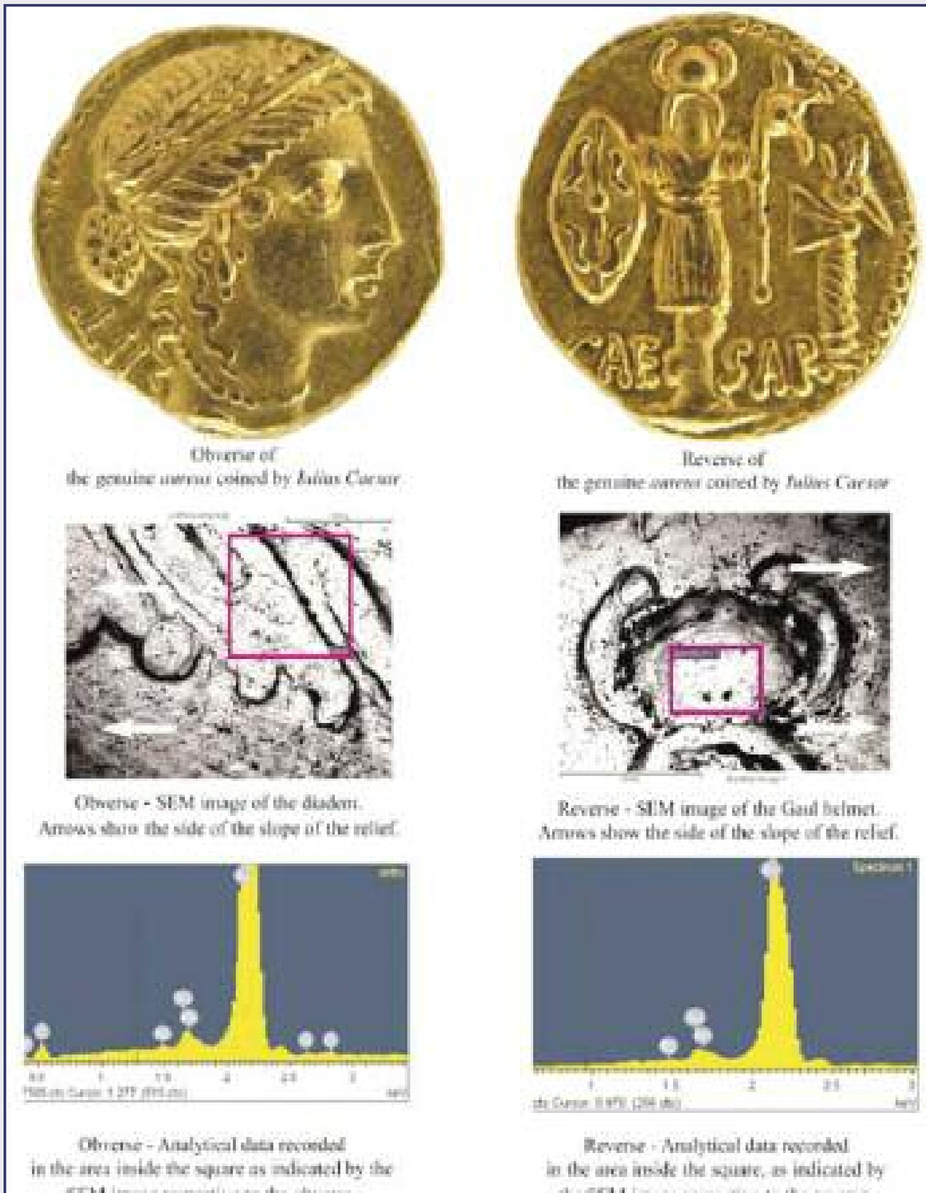

Fig. 1 - SEM imagines and EDS spectra both recorded on the obverse and reverse of this genuine *aureus* belonging to the first emission done by *Iulius* Caesar. This *aureus* was coined in Gaul by *Caesar* after the battle of Alesia (52 bC) to celebrate his victory. Reference RRC 452/1, g 8.661.
The high purity of the gold of this coin (higher than 99,9%) is a peculiarity of this coinage as well as the *not* exact perpendicular direction of the embossed imagines on the plate of the coin. The shift of the embossed imagines on the left (obverse) and on the right (reverse) sides proves that the sledgehammer shot was not performed in an exact perpendicular direction on the plate of this coin. It was, in fact, virtually impossible to bring a "hand made" sledgehammer shot in an exact perpendicular direction on the plate of a coin according to the ancient coinage procedure

of mechanical energy, as a difference of pressure that, obviously, must be supplied while the cooling of the molten metal, wrapped into dies, takes place.

The difference of pressure in the press-fusion is required merely to improve the fill out process into the small empty spaces of engraved dies, respective to images and, mainly, to inscriptions of the counterfeit coins, that is very difficult to eliminate by a simple fusion process.

The applied difference of pressure is a very moderate driving force, associated to a negligible energetic contribution, when compared to the entity of dissipated energy, as heat, that takes place during the spontaneous cooling of the molten metallic mass inside the engraved dies and much more negligible in front of the energetic amount dissipated from the heavy sledgehammer shot and responsible for the striking procedure.

The press-fusion technique is, therefore, an improvement of the simple fusion with the aim to obtain better smoothen away images and inscriptions as a consequence of a more careful filling of micro-cavities on the surface of the counterfeits and also suitable for minimizing some structural defects, easily formed and always present, even if the fill out on the edges of the coins does not always give successful results. The lacking of a perfect fill out the body of the coin, however, can be easily detected even by means of simple inspections with an electron microscope.

In this connection some details will be discussed and differences, between a press-fused fake and an ancient genuine specimen obtained by coinage, evidenced by the examples given in the following section.

The size and shape of the embossed images on the surfaces of the fused or press-fused coins show, in fact, sharp structural differences when compared to the ones of the respective images obtained by coinages.

In conclusion the basis of the forgery obtained by press-fusion can be expressed in terms of a melting process of the metal (or alloy) associated to a relatively low difference of pressure, ΔP, between two suitably engraved dies with a surface area, A, and with a slow, or stepwise, energy transfer, but on a still molten metallic mass.

Such a process is therefore defined by an energy flow, J, that does not act instantaneously, but with slowness, being the mechanical driving force a relatively moderate difference of pressure, ΔP, responsible for the flow of energy, ΔJ, while the metallic mass, still in a molten state, is not in conditions to acquire energy in terms of a more ordered structural arrangement.

The moderate energy supply to merely improve the process to fill out micro cavities is defined by equation 6:

$$\Delta J_{\Delta t} = \left[\int_{t1}^{t2} \frac{df}{dA} \right] dt \qquad (6)$$

On the basis of the equations (1-6) is self evident that all the processes utilized to cast coins, either genuine or counterfeit, are always linked to strictly irreversible processes.

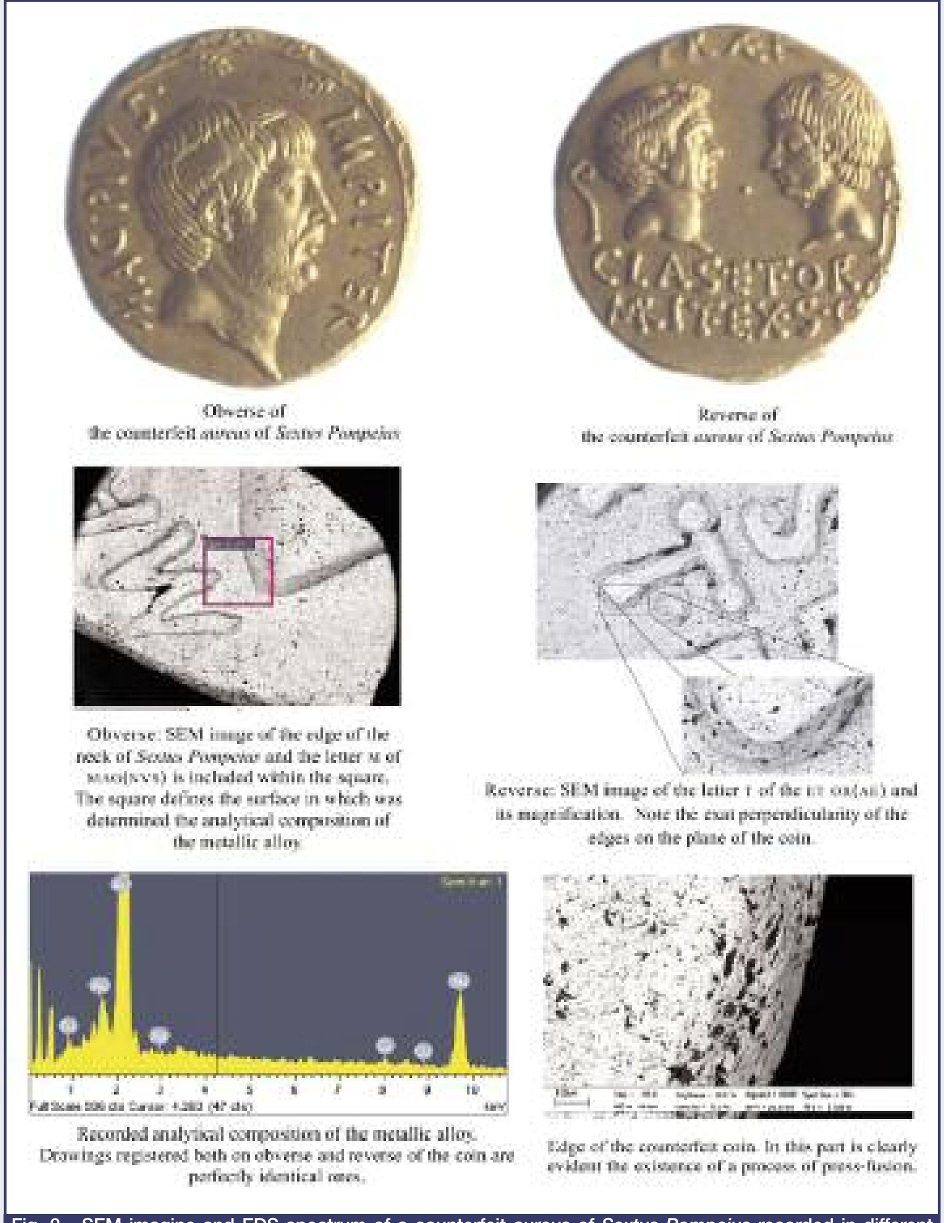

Fig. 2 - SEM imagine and EDS spectrum of a counterfeit *aureus* of *Sextus Pompeius* recorded in different zones of this coin obtained by means of a press-fusion technique. The recorded EDS spectra both on obverse and reverse are identical as well as the analytical composition. The perfect perpendicularity of all the embossed imagines and inscriptions is a peculiarity that proves that the sledgehammer shot was not utilized to cast such a coin, as well as the sponge like aspect of its edge that proves the application of a pressure difference between the two engraved dies for stamping the coin while the metallic alloy still was in its liquid state before left it to cool. Counterfeit *aureus*: g 7.850 - Au 98.0%, Ag 1.0%, Cu 1.0%. Ref. RRC 511/1

Experimental comparison of a genuine *aureus* of *Iulius Caesar* with a counterfeit *aureus* of *Sextus Pompeius*

The approach to detect significant structural differences suitable to discriminate genuine from counterfeit coins, the apparatuses used were:

1) a scanning electron microscope (SEM) LEO1450VP equipped, for micro-analytical determinations,
2) an Energy Dispersion Spectroscopy (EDS) INCA300 (EDS) and
3) a X-ray fluorescence (XRF) spectroscope Philips model PW 1404, for extensive analytical determinations.

The determinations performed by means of such apparatuses are based on non-destructive and non-invasive physico-chemical methods of investigation and each determination can be repeated again without affecting the specific features of each metallic specimen.

To discuss the sharp and specific differences between a genuine coin obtained by means of coinage and a counterfeit one obtained by means of a fusion technique, here are compared a genuine *aureus* emitted by *Iulius Caesar* certainly in Gaul, in the year 50 bC [6-7] or perhaps in the year 52 bC, immediately after the victory in the battle of *Alesia* and a counterfeit *aureus* attributed to *Sextus Pompeius*, that clearly represents a modern fake, obtained by means of a press-fusion technique [8].

In Fig. 1 and 2 are summarized the results of the determinations, respectively to the genuine *aureus* of *Iulius Caesar* (Fig. 1) and to the counterfeit one of *Sextus Pompeius* (Fig. 2).

The obtained results evidence how different structures are belonging to the surface of embossed images and inscriptions present in an ancient genuine coined *aureus* or in a modern counterfeit one obtained by means of a press-fusion technique.

Conclusions

In conclusion the equations (1-6) are at the basis of a theoretical approach to evaluate the different amounts of transferred energies to obtain either genuine or counterfeit coins, according to theoretical principles of irreversible thermodynamics and that are also consistent to the SEM images respective to the two specimens. In this connection what it seems to be relevant is that the “time” is a parameter that is never directly taken into account, in the “classical” thermodynamic while it is a parameter of paramount importance in the irreversible thermodynamics, as proved by the validity of impulses equation (5). Here the intensity of involved energy and, consequently, the velocity of entropy production, plays a critical role also in metallurgical processes where irreversible changes take place on the structural modifications of the solid metallic masses involved.

In other words the irreversible thermodynamics approach allows to take into account why the hammering, or striking, is associated to higher values of dissipation energy and responsible for an improved and more organized the metal structure of solid state as compared to other techniques applied on the liquid state of the metallic masses (fusion and press-fusion) merely suitable to modify size and shape of a metallic specimen and therefore widely employed to produce counterfeits, not only respective to coins, but also to counterfeit other metallic archaeological finds.

The high values of dissipation energies associated to coinages are consistent with the improved features of different metallic structures obtained by striking, not only applied in the ancient times to produce swords, but also, up to date, to realize equipments that require high performances in peculiar applications, like, for instance, steel equipments devoted to be safely applied at very high pressures, and/or temperatures, in many different and special purposes.

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RIASSUNTO

La discriminazione tra reperti archeologici autentici e falsi in base all’approccio previsto dalla termodinamica dei processi irreversibili

Lo scopo di questa ricerca è stato quello di evidenziare le differenze di carattere energetico rispettive a reperti archeologici ottenuti per battitura o per fusione. Sono state eseguite ricerche sperimentali su due diversi aurei romani: uno antico e autentico coniato da Giulio Cesare in Gallia dopo la battaglia di Alesia (52 a.C.) e uno moderno e falso per renderlo attribuibile a Sesto Pompeo. Le misure sperimentali eseguite su questi due esemplari sono discusse in base all’approccio teorico previsto dalla termodinamica dei processi irreversibili, relativi a trasferimenti energetici, elevati se di natura meccanica, propri della battitura e a quelli molto di entità molto minore o trascurabile se ottenuti per presso-fusione o per fusione. SEM, EDS, XRF sono i metodi sperimentali non invasivi utilizzati per l’esigenza assoluta di mantenere i reperti assolutamente intatti dopo l’esecuzione delle misurazioni sperimentali.