A LEAP INTO THE BEGINNING OF THE METAL AGE: RECRYSTALLIZATION AND CARBURIZING

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KEYWORDS: history of metallurgy, copper age, iron age, heat treatment, recrystallization, carburizing

INTRODUCTION

Although the great importance covered by the heat treatment and the thermo-mechanical process in the evolution of the history of metallurgy, the role of these processes has not been correctly considered even by some famous and recognized archeo-metallurgists. Moreover, it is difficult to agree with the prevalent opinion that the beginning of the metallurgical activity corresponds with the birth of the extractive processes which permit to obtain the metals starting from their ores. The most reliable hypothesis supposes that the first metallurgical activity is to be found the plastic working and heat treatment of the metals found in nature under their reduced form and this statement seems to be strongly confirmed by the fact that the first objects are constituted by gold, silver and copper, which are the metals which can be frequently found in the reduced form.

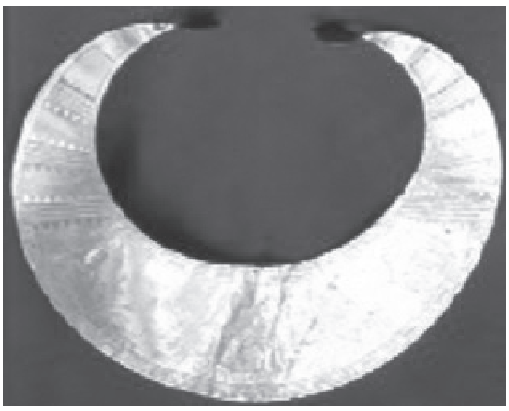

Fig. 1 ***Gold foils were often used in Prehistoric jewellery. In this example necklace found in Margerton (1800-1500 b.C.).***
Fogli in oro utilizzati spesso nell'arte orafa preistorica.

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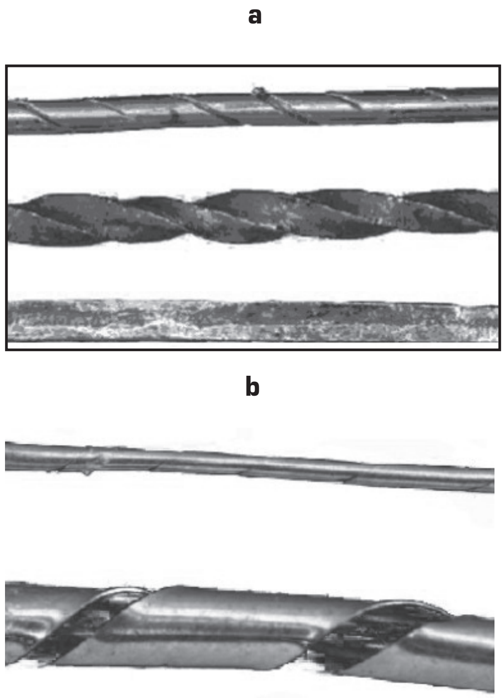

Fig. 2 ***Thread production: from bars (a); from plate (b).***
Produzione di fili: (a) da barre, (b) da laminette piatte.

At the beginning the first metallurgical artisans have probably try to work the new class of materials and that were surprisingly astonished by the favourable ductility and formability of the metals, which put them in the conditions for realizing nice and amusing objects like jewellery pieces (Fig. 1, Fig. 2)[1,2,3].
On the other hand, the deep deformations to be applied through hammering implied also the application of heating treatments aimed at restoring the formability properties by the annealing promoting what nowadays we define as static recrystallization. The good formability properties of the metallic materials made them immediately suitable for he realization of also architectural and ornamental parts on which a metal coating was often applied

Fig. 3 **Tutankamon gold throne back (XIV b.C.). It was found in 1922.**
Schienale del trono di Tutankamon (XIV a.C.), ritrovato nel 1922.

for design and aesthetic reason as well as for protection against the atmospheric and environmental phenomena (Fig. 3, Fig. 4) [4,5,6].
On the other hand, the origin and the start-up of a systematic metallurgical activity seems to be stated in the in the Iron Age, the period after the Bronze Age during which the heat treatments seems to become progressively more sophisticated.
The birth place of the Iron Age seems to be located in the central Anatolian zone at the middle of II millennium b.C., but several centuries should be spent before the technique would have been optimized allowing the extraction of metal from the iron ores and the shaping of the reduced metal.
On the basis of the famous letter dated at 1250 b.C. written by the Hittitian King Hattusili III and sent to the Assyrian King the difficulties met in the implementation of the iron reduction process, which did not permit a significant carburizing of the reduced pieces as it seems to be confirmed by the archeological findings [7]. On such ancient objects only small traces of carbon enrichment has been detected. A real technological leap took place when the ancient artisans understood the method to harden the steel by the enrichment of carbon which will open the possibility to harden the material also through the quenching treatment. Thus, the one of the first most important technological improvement in the metallurgical field is certainly to be associated with the thermal treatment. But even more interesting is the fact that in the Mediterranean area the diffusion of the carburizing technique allows also to produce interesting composite objects, in which steel featured by low carbon content and by high carbon content are joined together (Fig. 5 and Fig. 6).
Thus, it is possible to summarize in three significant step the birth and the evolution of the thermal treatment [8,9,10]:
- hardening and annealing;
- carburizing;
- realization of composite objects.

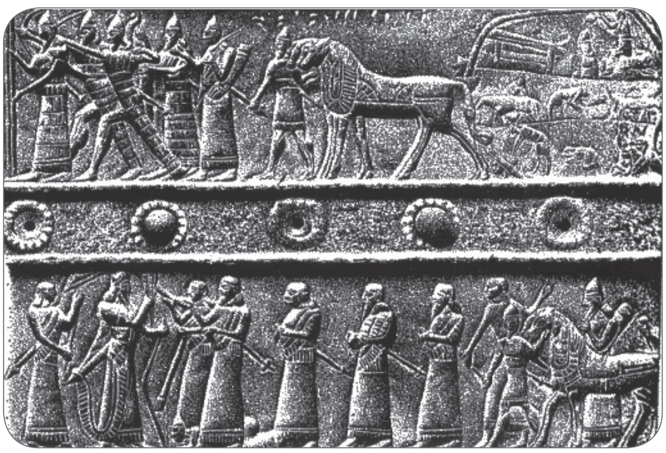

Fig. 4 **Detail of a Shalmaneser III door (850 b.C). This door is covered with a bronze foil.**
Dettaglio della Porta di Shalmaneser (850 a.C). Questa porta è stata ricoperta con foglia di bronzo.

HARDENING AND RECRYSTALLIZATION

One of the first aspect to clarified to perform a correct and satisfactory characterization of the ancient metal pieces is to understand if a plastic deformation process was applied. Actually, this processing operation was applied also to the metal found under the reduced form in the native state, i.e. gold, silver, copper (Fig. 7).
The exploiting of the metal material needs the change of their shapes in order to reach the desired functionality. But the change of shaping implies a thickening and an induction of brittleness which have to be annealed in order to prevent fracture. From a microstructural point of view the annealing is associated with the

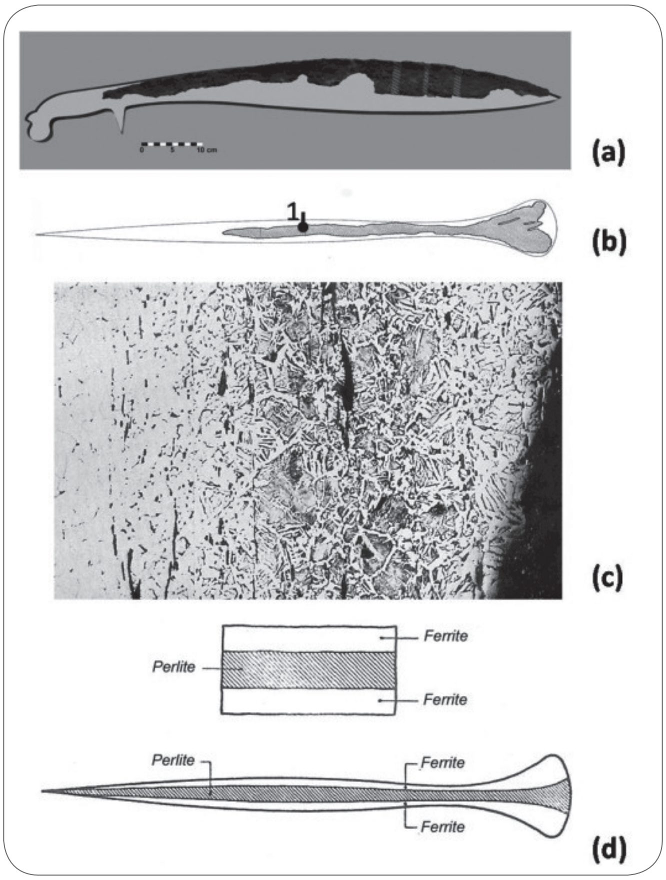

Fig. 5 **Vetulonia sword (VII a.C.) and its typical composite structure: (a), (b) shape and section reconstruction; (c) section "1" microstructure and (d) hypothetic realization process.**
Spada di Vetulonia (VII a.C.) e la sua tipica struttura composita. (a), (b) Forma e sezione ipotizzate; (c) microstruttura della sezione "1" e ipotesi sul processo di realizzazione.

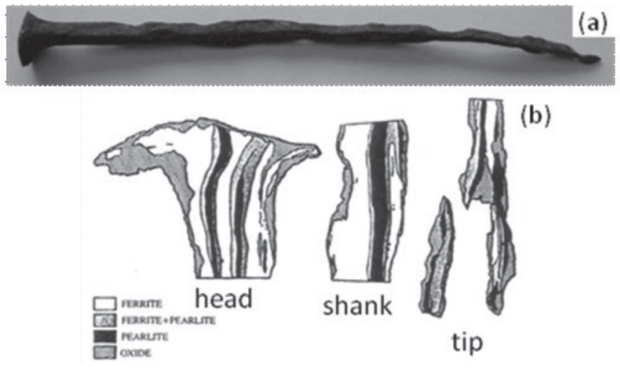

Fig. 6
Ancient nail (a) from the roman legionary at Inchtuthil (Wales, 83 a.C.) and its particular composite structure (b).
Esempio di antico chiodo romano proveniente da Inchtuthil (83 a.C.).

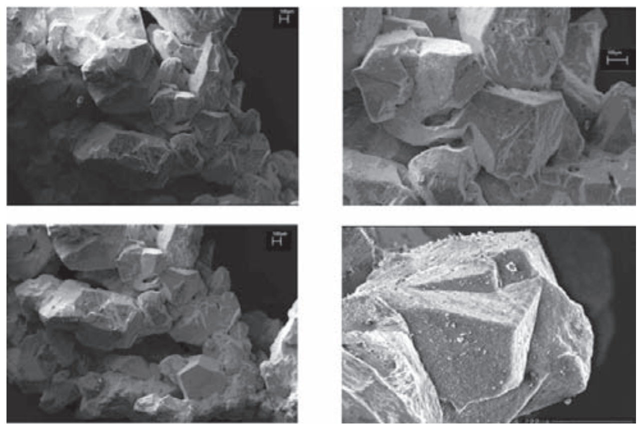

Fig. 7
VCopper in the native state (SEM micrographs).
Aspetto del rame nativo osservato mediante SEM.

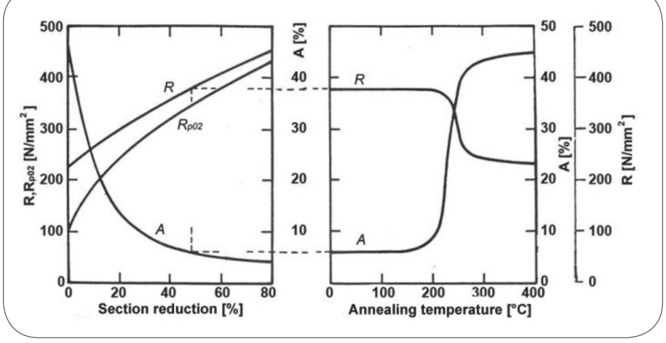

Fig. 8
Influence of annealing on work hardened copper. The pure copper recrystallization temperature is about 220°C.
Influenza del processo di ricottura sulle proprietà di resistenza e duttilità del rame precedentemente incrudito.

recrystallization, whose energy of activation can be overcome by the temperature field which can be reached during the Neolythic Age (Fig. 8). The recrystallization is a phenomenon of nucleation and growth of new grains which consume the previous deformed one, recreating soft unstrained crystallites.
The plastic deformation and the related phenomena and processes are at the basis of the working operation which follows under the name of sphyrèlaton (σφυρηλατον-worked by hammer), a technique typically applied in the first statuary art, but also for coating buildings and ships. This technique consists in the coating of a wood or marble core by a thin metal layer applied by hammering and fixed by rivets (Fig. 9) [11].
Although the recrystallization takes place, the microstructure formed after the annealing goes on to be featured by the traces of the induced plastic deformation. Actually, even if the hardening due to sliding and twinning deformation is nearly eliminated, the orientation of the new generated grains are affected by rotations undergone by the deformed crystallites (Fig.10) [12,13,14].
The crystallite rotate in the space and displace themselves following peculiar orientation; this issue appears as particularly clear in

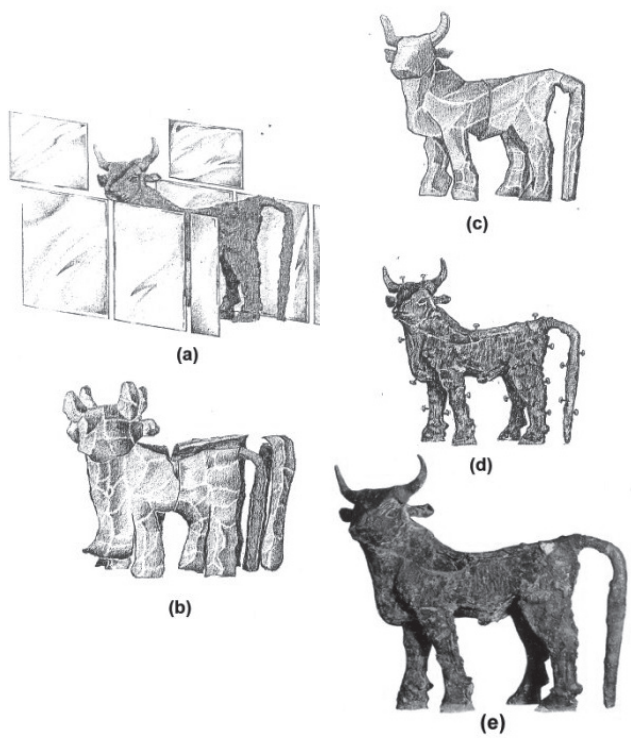

Fig. 9
Example of sphyrèlaton. Separate foils are applied on the mold (a), then they are hammer (b), until the mold are completely covered (c) foils are fixed by rivet (d); bull found in Tell el Obeid (III millennio b.C.) realized by sphyrèlaton.
Stadi del processo di realizzazione di uno sphyrèlaton (σφυρηλατον-lavorato al martello). (a) Fogli separati vengono preparati per essere avvolti su un'anima in legno o in pietra (b) e successivamente vengono fatti aderire attraverso martellatura. (c) Le lamine di copertura vengono ribattute sino a che l'anima viene completamente rivestita (d) e successivamente vengono fissate attraverso l'applicazione dei rivetti.

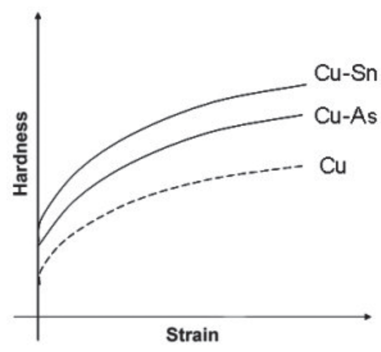

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Fig. 10
Copper alloy (Cu-As, Cu-Sn) qualitative behaviour in relation to work hardening process.
Andamento qualitativo dell'incrudimento del rame in funzione degli alliganti utilizzati.

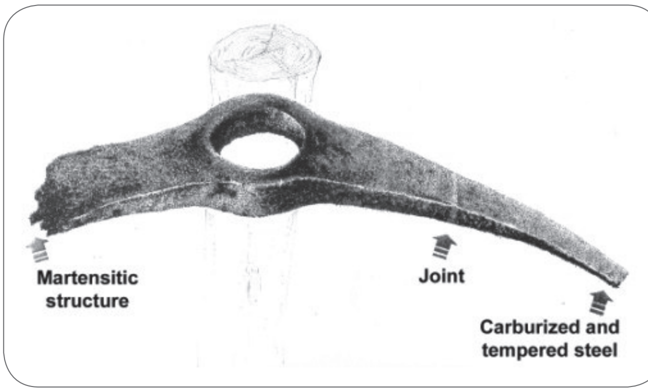

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Fig. 11
R. Maddin work on pick found in Palestine in XII b.C.
Piccone ritrovato da R. Maddin in Palestina e risalente al XII a.C.

the metal which undergo cold forming process. The formation of particular orientation textures does not influence only the strength properties but also the ductility and thoughness of the alloys [15]. The final orientation of the observed crystallite depend on [16]:
- the direction of the stresses imposing the deformation;
- the applied strain rate;
- the temperature of the imposed deformation;
- the presence of alloying elements present in the chemical composition of the alloys;
- the temperature and the duration time of the annealing.

Particularly the difference in the chemical composition has been exploited by the ancient artisans, which certainly know the different behaviour of metal alloys produced starting from metal ores extracted by different mines. One of the most significant example is related to the arsenicum present in the copper (Fig. 10). Beside being a easily melting alloy, the arsenicated copper is features by a higher hardening rate and after successive annealing treatments and recrystallizations the arsenicate copper is interested by the formation of favourable grain orientations.

FIRST FINDINGS OF CARBURIZED OBJECTS

It is difficult to state precisely the beginning of the carburizing treatment. On the basis of the archeological findings performed up to now, we can identify with a certain reliability the Middle Eastern as the birth place of such a practice. And the most ancient carburized findings are dated at XII b.C.. The first marvellous example of the development and affination of the carburizing treatment is the famous pick (Fig. 11) found by Maddin during the digging on Adir Mountain in Palestine.

After the metallographic examinations and on the basis of the hardness measurements it is possible to recognize the presence of martensite in the rounded shaped region while the sharpened zone - welded to the previous one by hammering - was carburized on the surface and quenched. This the first object witnessing an aware treatment aimed at realizing a different carbon concentration in the metal pieces through the thermo-chemical process carbon diffusion. A dagger found in Pella (Jordany) [17] going back to the same period is featured by a bainitic structure, while an axe coming from Sardi, in Turckey, dated at X b.C., layers featured by high carbon content welded to the one featured by low carbon concentration has been pointed out. Several blades found in Cyprus prove that the carburizing is not an occasional result of anomalous treatments but that it was consciously performed (Tab. 1).

During the X b.C. the carburizing practice an increasing success for its application on pieces obtained from hammered sponge iron. This statement proves that the ancient artisans become progressively more conscious that a correct application of the carbon enrichment by diffusion and the following quenching allowed to obtain materials featured by improved properties. This represents certainly a technological revolution, because it makes possible to

Site	No.	Date	Object	Carburizing
Lapithos	420/46	XI century	Knife end	Low
Lapithos	411/27	X century	Knife tip	Low
Lapithos	409/17°	X century	Knife tip	Extended
Lapithos	409/6	X century	Sward	Extended
Idalion	106	XI century	Knife tip	Extended
Idalion	517	XI century	Dagger	Extended
Amathus	21/19	X century	Knife centre	Extended
Amathus	25/4	X century	Knife tip	Extended

▲
Tab. 1
Metallographic results on several object found in Amato, Lapito and Idalon (Cyprus) ancient tombs.
Risultati dell'analisi metallografica svolta su reperti ritrovati in tombe antiche presso Amato, Lapito and Idalon (Cipro).

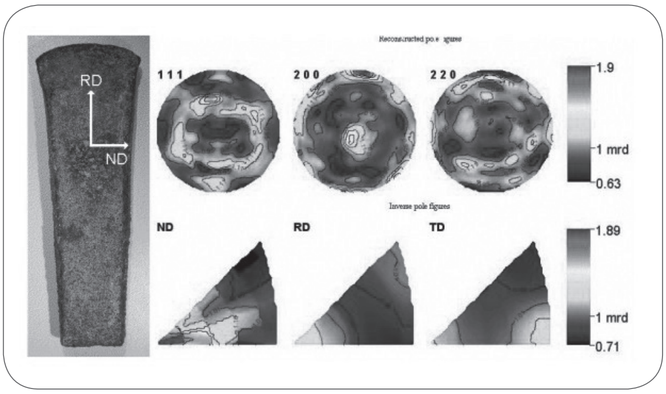

Fig. 12
Crystallographic texture detected on a axe found in n.78 Remendello tomb [Autor: Gilberto Artioli - Università degli Studi di Padova].
Tessiture cristallografiche osservate sull'ascia ritrovata nella tomba n.78 di Remedello (Autore: G. Artioli dell'Università degli Studi di Padova).

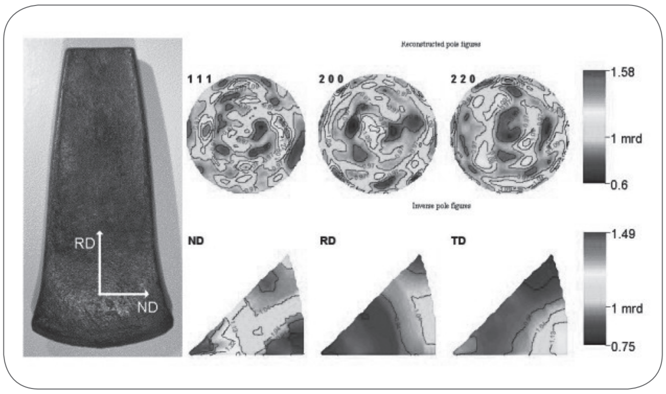

Fig. 13
Crystallographic texture detected on a axe found in n.62 Remendello tomb [Autor: Gilberto Artioli - Università degli Studi di Padova].
Tessiture cristallografiche osservate sull'ascia ritrovata nella tomba n.62 di Remedello (Autore: G. Artioli dell'Università degli Studi di Padova).

realize a wider range of products to improve the quality and the efficiency of the tools and of the shipping device permitting an intensification of trading across the Mediterranean Sea. Phoenicians and Greeks took important advantage from the described technological innovation.
The increase of the efficiency in the steel objects realized between XI-X b.C. is proved by the rapid substitution of the bronze for the realization of several objects [18].

EXAMINATIONS ON DIFFERENT BLADES

The blades, probably represent one of the most interesting typology of products for the evaluation of the evolution of the metallurgical technique, because of the required combination of properties (strength-thoughness-hardness). Especially the blades of the axes and the ones of the sword are heavily loaded also in the impulsive modality.
The investigation performed on the thermo-mechanical properties performed on copper axes belonging to the Eneolitic Age can a be significant clue to understand the role played by the thermo-mechanical properties on the designing of such a type of working tools. The neutronic diffraction performed by G. Artioli [19] has allowed to point out the texture developed also at the core of the axes without implementing any destructive procedure. Some prehistoric axes going back between 3200b.C. and 1900b.C., have been analysed and show a crystallographic texture certainly induced through cold forming and only in some cases clear recrystallization textures have been recognized.
The core of axe belonging to the Similaun man (3200b.C.) and the axe of Kolmann, do not point out any particular intense texture probably for the presence of an equiaxed grain structure formed only by casting and solidification without the application of significant successive plastic deformation. Actually, the very weak texture indication seems to make reliable the hypothesis of a static recrystallization following the application of a only slight plastic reduction (5-10%) probably aimed at restoring the shape and functionality of the tool after a certain working period.
A clear presence of texture components {001}<110> (Rotated Cube) and {001}<100> (Cube) in the axes coming from tombs n.78 and 62 at Remedello suggests that the realization of a thermal treatment led the crystallite of the axes to orientate themselves along the Rotated Cube component (Fig. 12, Fig. 13).
It is extremely significant that the most sharp texture components belongs to the axes going back to the Copper Age. Actually, this texture needs the imposition of a high thermal level applied for long time which could be reached only by the efficient refractories and combustion technique which are not typical of the first steps of Copper Age.
Other samples - nearly contemporary to the Remedello ones – usually show texture developed by textural features produced by an annealing treatment which has produced incomplete recrystallization: {211}<11-1> (Copper), {321}<41-2> (S), {110}<-112> (Brass), {110}<001>(Goss) often organized along α-fiber, β-fiber and γ-fiber (Fig. 14, Fig. 15, Fig. 16).
It is possible that the partial recrystallization was due to the attempt to modulate the mechanical properties of the axes through a compromise between the hardening featuring the plastically strained crystallite and the softening undergone by the recrystallized grains. The axes certainly represent a good example of the thermo-mechanical treatment applied to a mono-phase alloy in order to impose a particular combination of mechanical properties.

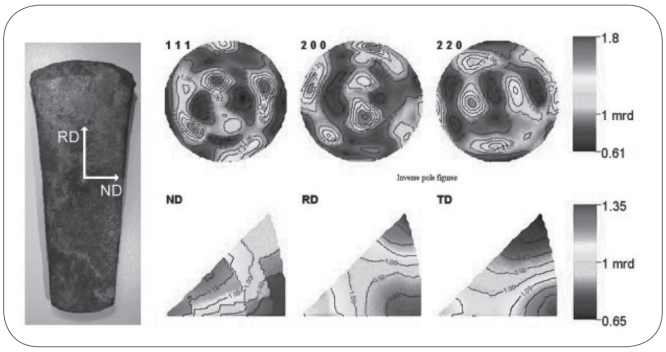

Fig. 14
Crystallographic texture detected on Ponte Enza axe (11.6x4.9x1.1 cm3) [Autor: Gilberto Artioli - Università degli Studi di Padova].
Tessiture cristallografiche osservate sull'ascia ritrovata in una tomba di Ponte Enza (11.6x4.9x1.1 cm3) (Autore: G. Artioli dell'Università degli Studi di Padova).

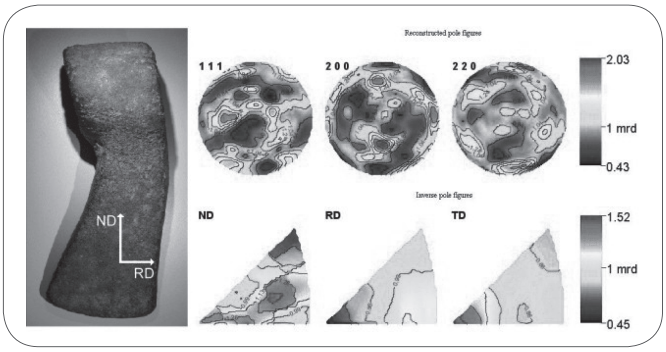

Fig. 15

Crystallographic texture detected on Acquafredda (13.1x5.4x1.9 cm3) axe [Autore: Gilberto Artioli dell'Università degli Studi di Padova].

Tessiture cristallografiche osservate sull'ascia ritrovata in una tomba di Acquafredda (13.1x5.4x1.9 cm3) (Autore: G. Artioli dell'Università degli Studi di Padova).

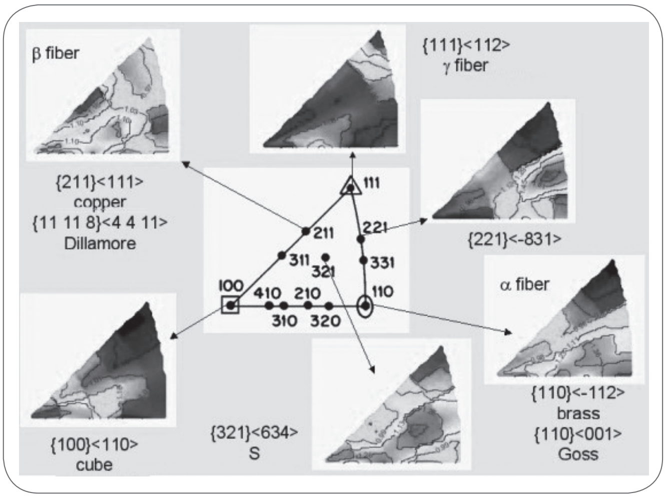

Fig. 16

Crystallographic texture detected on a axe found in n.102 di Remedello di Sotto tomb [Autore: Gilberto Artioli dell'Università degli Studi di Padova].

Tessiture cristallografiche osservate sull'ascia ritrovata nella tomba n.102 di Remedello di Sotto (Autore: G. Artioli dell'Università degli Studi di Padova).

The analysis of the blades going back to the Iron Age reveals not only the application of particular thermo-mechanical process, but also the introduction of specific heat treatments. This development is associated to further increase of the thermal regime which can be produce and supported by the furnaces and forging devices built during the Iron Age.

The sword from Vetulonia (Fig. 5) and from Chiusi (Fig. 17-A) are two emblematic example of heat treatment and thermo-mechanical processing, performed at high temperature on metallurgical solid system characterized by the presence of different structural constituents (Fig. 5, Fig. 17 -B).

In the case of the sword from Chiusi there is the presence of perlitic structure induced by the carburizing process, which clearly indicates the formation of a reducing atmosphere which can at partially carburize the metal during the reduction process itself.

The sword from Vetulonia is a clear example of packed blade composed by five different layers joined together by a diffusion

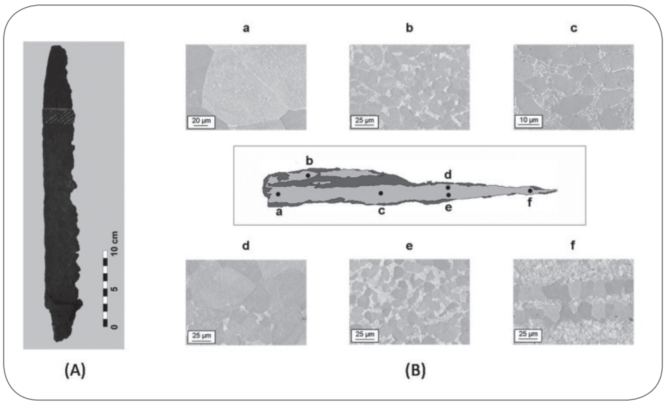

Fig. 17

(A) Sword from Chiusi (III century b.C.); (B) different structural constituents detected in the sword section.

(A) Spada di Chiusi (III d.C.), (B) differenti costituenti strutturali identificati lungo una sezione della spada di Chiusi.

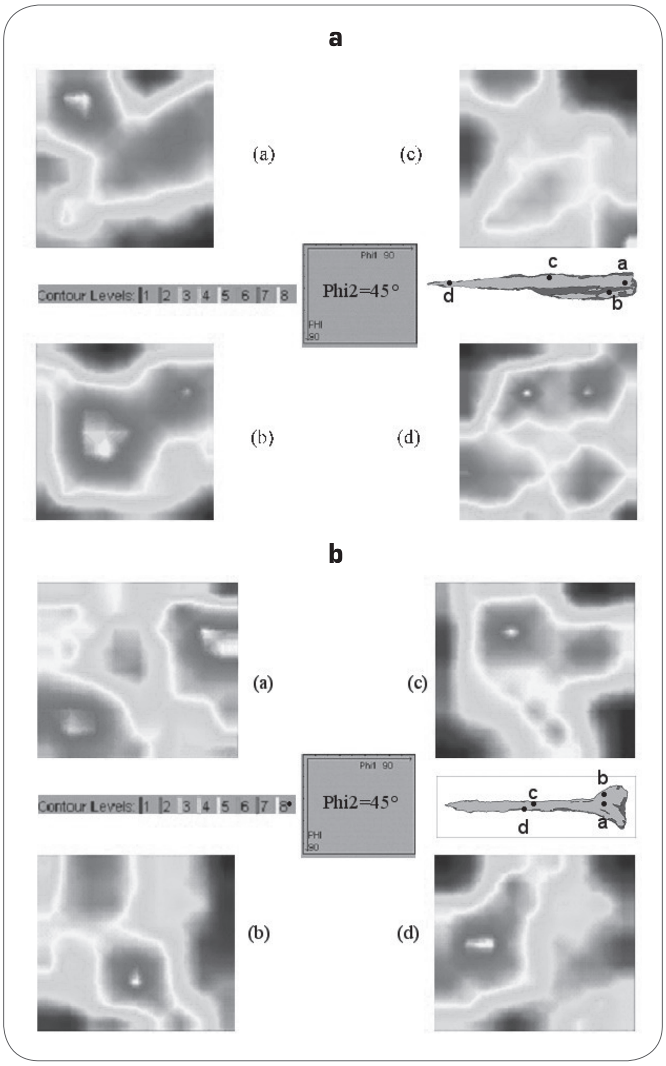

Fig. 18

ODF observed on Chiusi sward (A); and on Vetulonia sward.

Diagrammi ODF ottenuti dalle misure cristallografiche operate (A) sulla spada di Vetulonia, (B) sulla strada di Chiusi.

promoted welding realized during the forging of the different layers. The different layers during the forging and welding treatment were covered by a fluid fayalite slag saturated by FeO in order to protect the surface to be welded from the oxidation. In both the blades a strong formation of textures featured by {111} planes perpendicular to the blade line has been pointed out and this crystallographic situation certainly leads to a simultaneous increase of resistance properties and of the thoughness. This favourable mix of properties certainly has been reached, although the contextual presence of such detrimental crystallographic components i.e. { 13}, especially in sword from Vetulonia. However, the revealed component could be developed only through straining at high temperature in the austenitic phase and by the austenite-ferrite phase transformation before the recrystallization of austenite. Actually, in the sword from Chius the cooling rate was fast enough to cause the formation of acicular ferrite which can improve the yield strength of the blade (Fig. 18).
The high concentration of misorientation angles toward the high-

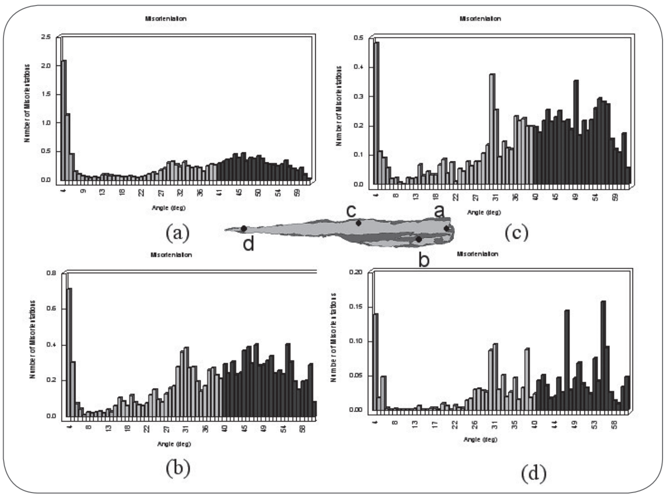

Fig. 19
Misorientation distribution in the Chiusi sword.
Distribuzione della misorientazione osservata nella spada di Chiusi.

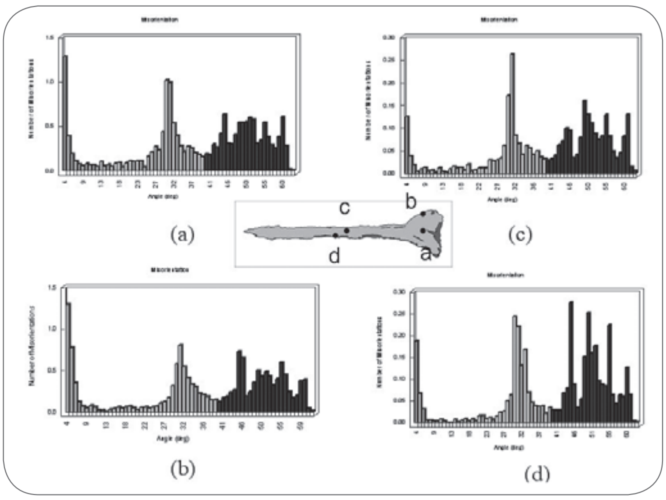

Fig. 20
Misorientation distribution in the Vetulonia sword.
Distribuzione della misorientazione osservata nella spada di Vetulonia.

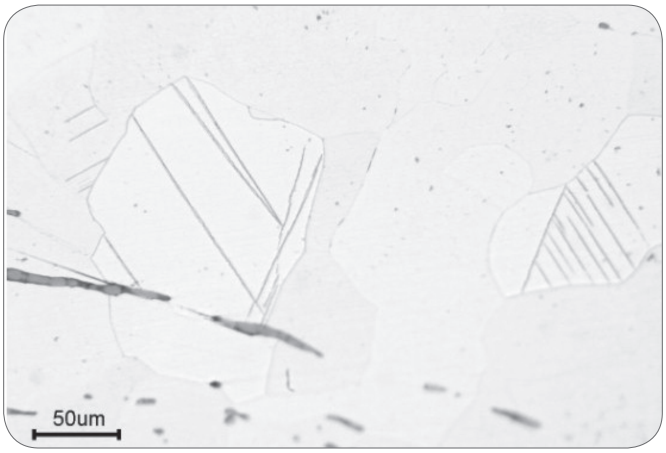

Fig. 21
Neumann lines detected on Vetulonia sword.
Linee di Neumann osservate nella spada di Vetulonia.

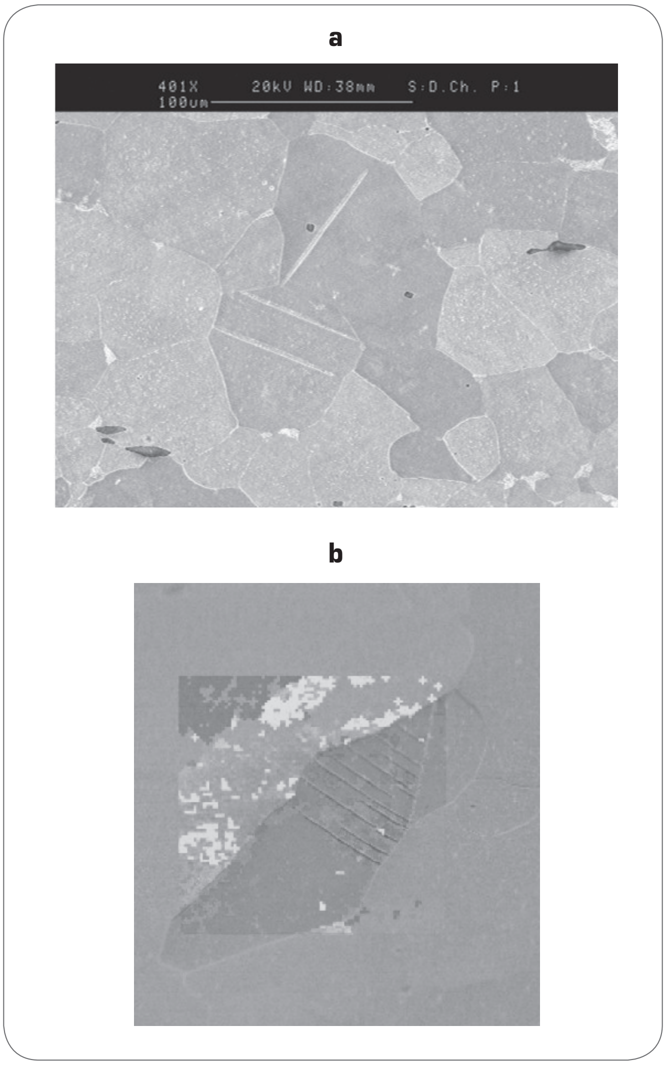

Fig. 22
Neumann lines detected on Chiusi sword (a); EBSD analysis underline twins (b).
(a) Linee di Neumann rilevate nella spada di Chiusi e (b) fenomeni di geminazione evidenziati dall'analisi EBSD.

est values prove the incomplete recrystallization featuring the core regions of the two examined blades (Fig. 19, Fig. 20).
The same blades have certainly undergone a final cold hammering process which has produced a hardening associated to the formation of twinnings, as witnessed by the clear presence of the Neumann bands, so the thermo-mechanical process was featured by a final step implying the cold plastic deformation (Fig. 21, Fig. 22).
It is very interesting and suggestive that the same process has been applied some centuries later in the Himalayan and Indonesian regions for the production of the Kris pamor, produced a route very similar to the Etruscan-Roman one.

CONCLUSIONS

The first significant innovations in the human social evolution is certainly related to the revolution promoted the application of the different metals, actually the different Ages has been called with the name of the metal which has been exploited. On the other hand, the birth of the mechanical metallurgy before the extractive has implied that the plastic deformation and the annealing processes have covered a fundamental role for the realization of the first artefacts. Thus the annealing can be recognized as the first heat treatment systematically applied in the metallurgical activities. During the beginning and the development of the Iron Age the landscape of the heat treatment procedure has been enriched by the application of carburizing procedure and to more complex thermo-mechanical processes. The modern techniques of investigation involving also the characterization of the crystallographic aspects have pointed out that the microstructural features and the related mechanical properties are the fruit of systematic thermo-mechanical treatment applied to copper-based products as well as to carburized and composite steel objects.

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ABSTRACT

UN SALTO AGLI INIZI DELL'ETA' DEI METALLI: RICRISTALLIZZAZIONE E CARBURAZIONE

Keywords: storia della metallurgia, trattamenti termici, deformazione plastica

Contrariamente ad una diffusa quanto poco attendibile opinione l'inizio dell'attiività metallurgica non può essere fatta coincidere con l'inizio dell'attività estrattiva. Infatti, sembra accertato che l'avvio delle lavorazioni metallurgiche sia da associare alla deformazione plastica di metalli presenti in forma ridotta allo stato nativo e all'applicazione dei processi di trattamento termico. Attraverso tali tecniche gli antichi artigiani metallurgici hanno prodotto anche pregevoli pezzi di gioielleria finemente lavorati (Fig. 1, Fig. 2). La necessità di realizzare deformazioni plastiche profonde volte ad ottenere cambiamenti di forma significativi ha indotto all'applicazione di trattamenti termici in grado di ripristinare le proprietà di formabilità del materiale, che sono interessate da una diminuzione durante il processo di foggiatura (Fig. 3, Fig. 4). Comunque, lo sviluppo di attività metallurgiche sistematiche è da ricondurre all'Età del Ferro, anche se i ritrovamenti del contesto hittita, il primo in cui compaiano oggetti ferro, non sembrano provare la messa a punto di tecniche in grado di carburare significativamente il materiale. Il vero salto tecnologico è da associare allo sviluppo di trattamenti in grado di arricchire in carbonio la composizione chimica degli acciai e di favorire in primo luogo un rafforzamento grazie all'aggiunta di elementi chimici in soluzione solida, ma in un secondo momento l'incremento del tenore di carbonio verrà sfruttato per realizzare la tempra dell'acciaio (Fig. 5, Fig. 6). Si possono riconoscere tre stadi successivi nel livello evolutivo delle tecniche e dei prodotti realizzati:
- indurimento ed addolcimento
- carburazione
- realizzazione di componenti compositi.
Uno degli aspetti discriminanti da chiarire quando si osserva un manufatto antico è proprio capire se un processo di deformazione plastica sia stato applicato o meno (Fig. 7) (Fig. 10). Come ampiamente noto, la deformazione plastica (Fig. 8) oltre che un cambiamento di forma provoca un incrudimento del materiale. I primi trattamenti termici applicati sono stati certamente trattamenti di ricottura volti a ripristinare la deformabilità a seguito dei processi di incrudimento indotti dalla formatura plastica. Le analisi cristallografiche svolte su asce antiche realizzate in lega a base di rame mostrano il progressivo affinamento delle modalità di ricottura all'avanzare del tempo e con il miglioramento dei sistemi di riscaldamento (Fig. 12, Fig. 13, Fig. 14, Fig. 15, Fig. 16). Trattamenti termici ancor più complessi ed articolati vengono messi a punto nell'Età del Ferro, che prevedono la diffusione del carbonio (Fig. 11) e la realizzazione di strutture composite caratterizzate dall'alternanza di strati ferritici e di strati carburati (Fig. 5, Fig. 17). Anche nel caso di manufatti in acciaio sembra essere evidente la realizzazione di trattamenti termo-meccanici in grado di indurre tessiture cristallografiche favorevoli (Fig. 18, Fig. 19, Fig. 20). Dall'osservazione dei manufatti in acciaio emerge la realizzazione di un ciclo piuttosto strutturato, terminante, almeno nel caso di manufatti sofisticati come la spade e le lame in genere, in un processo finale di deformazione plastica posto in evidenza da chiari fenomeni di geminazione (Fig. 21, Fig. 22).