

Metallography for the European Copper Age: Research on the Axe-Blade of the Glacier- Mummy from the Ötztaler Alps in Tyrol

Gerhard O. Sperl

Universities of Leoben, Innsbruck and Vienna: researcher at the Erich-Schmid Institut für Materialwissenschaft der Österreichischen Akademie der Wissenschaften, Leoben (retired 2002). Now: Institute for Historical Materials, Leoben, Austria

sperl@unileoben.ac.at

This article is dedicated to Prof. Hein Peter Stüwe, Leoben, Austria, on the occasion of his 75th birthday on September 14, 2005.

The late-Neolithic Copper Age

The beginning of metallurgy in the Old World is characterized by hammering native metals such as gold, copper and meteoric iron. Owing to the need of annealing the metal, for softening it after cold working, pyrometallurgy [1], the use of fire for producing metals from ores, could have been found by trial and error. Parallel to the rise of metallurgy is the use of a campfire (low temperature: max. 800°C) for baking clay-objects, which also seems to be an additional origin of metallurgy. The very first piece of molten copper-ore, dating back to the 7th millennium BC, was found in Catal Höyük, Turkey, together with hammered native copper and beads made of galena (PbS), initially mistakenly thought to be metallic lead [1].



Fig. 1: The glacier-mummy from the Ötztaler Alps (Similaun-Hauslabjoch) in Tyrol, commonly called "Ötzi"

The technology of copper-smelting in the European Bronze-Age (1,800-800 BC) had its height around 1,000 BC (urnfield-time), with ore-roasting and slagging of iron by soft-reducing smelting. Its signature characteristics can be found at excavations of smelting sites and analyzed by metallographic analysis of slags and other smelting by-products, such as frequently observed bun-shaped ingots of black-copper [2]. In the central European Copper-Age (4,000-1,800 BC) the most interesting piece of worked copper is the axe (Fig. 2) found with the glacier-mummy from the Ötztaler Alps (Similaun-Hauslabjoch) in Tyrol, commonly called "Ötzi", or "Frozen Fritz," dating from 3,300 BC. The well-preserved body was found with various tools, clothing and weapons in September 1991 near the Austro-Italian border in the Ötztal Alps by a couple of mountaineers. The initial analysis of the axe-blade was undertaken in Leoben, Austria at the "Erich-Schmid-Institut für Materialwis-



Fig. 2: "Ötzi's" axe-blade is 94 mm long and weighs 174 grams. The material is naturally alloyed copper (99,1% Cu) with some arsenic, silver and oxygen.



Fig. 3: The axe-blades in Fig.3 are either reconstructed by experimental casting and hammering (left), or axe-blades from the same period, one of them mounted in the handle (IN=Inventory-number of the Institute for Prehistory at the University of Vienna (Institut für Ur-und Frühgeschichte). They can be researched by metallography for comparison—allowing the method and quality of producing the axe-blade to be determined.

senschaft" (Institute for Materials Science) of the Austrian Academy of Sciences [3].

Metallographic research on historical copper-based objects

In the European Copper-Age, copper implements were produced either by melting native copper in the early stages or, later, by reducing the metal from the ore, mainly oxides or hydroxides (cuprite, malachite, and azurite). Due to the use of highly reactive

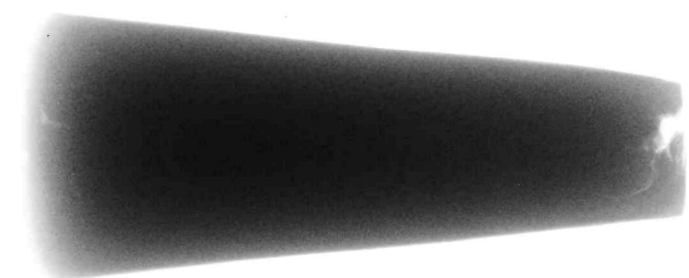


Fig. 4: Defects in the axe-blade made visible by X-ray photography: left: crack in the cutting edge; right: casting-pipe cavity, deformed by hammering for shaping the neck.

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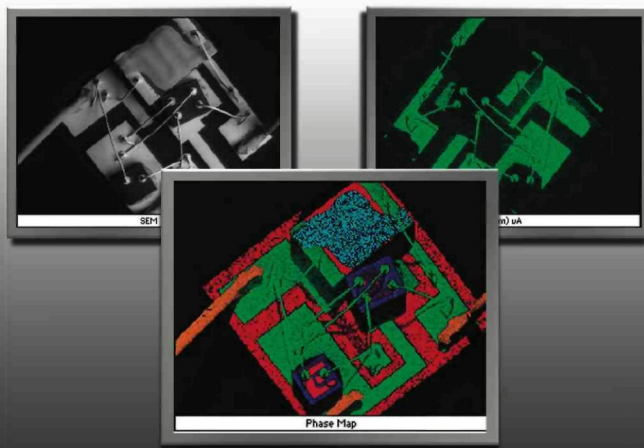
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Fig. 5a: the cutting edge (slightly polished near the crack)



Fig. 5b: the defect on the neck and the polishing on the side-flange

charcoal for heating the ore, minor elements, with lower reducing potential than copper and trace elements like silver, gold, arsenic, antimony and nickel, enter the metal. The concentration of these elements in the copper metal can locate and characterize the original ore deposit and/or the type of ore used. Therefore, chemical analysis of the trace-elements is a very important tool for revealing the provenance of the object. By metallographic research, the presence and quantity of sulfur (in sulfides) or oxygen (in cuprite CuO) can be estimated. The main aim of this archeological metallography is the investigation of the metallurgical process: solidification after casting, plastic deformation by hot and cold-working, and recrystallization.

Boundary conditions of metallographic research

Because of the singularity of the object it was not possible to cut metallographic specimens, so research was confined to the natural surface of the axe, after a very slight surface polishing (Fig. 2) only. Therefore, the results of XRF and X-ray-diffraction analyses are only applicable to the object's surface. Additional parts of the research were done by weight-control, scanning electron microscopy and by neutron scattering [4].

Chemical analysis of the axe

The first examination of the axe-blade was carried out at the Römisch-Germanisches Zentralmuseum, Mainz, Germany, where the other objects (bow, arrows, tools, clothes, and shoes) were preserved in the laboratory of Dr. Markus Egg, a Tyrolean like the iceman. After its finding in September 1991, the body was stored at the University of Innsbruck, Tyrol, Austria until it was moved to a permanent home at the museum in Bozen/Bolzano, South-Tyrol/Alto Adige, Italy.

The results of the analysis are not surprising:

a. XRF- RGZ-Mainz (D)

0.2 wt.-% arsenic (As)

0.1 wt.-% silver (Ag)

<0.1 wt.-% others

b. Microscopy.(ESI) (A)

~0.5 wt.-% oxygen (O₂)

99.1 wt.-% Cu by difference

By EDS analysis in the scanning electron microscope of the ax surface, some small grains (less than 3 microns wide), showing the presence of arsenic (As) and bismuth (Bi), but no antimony

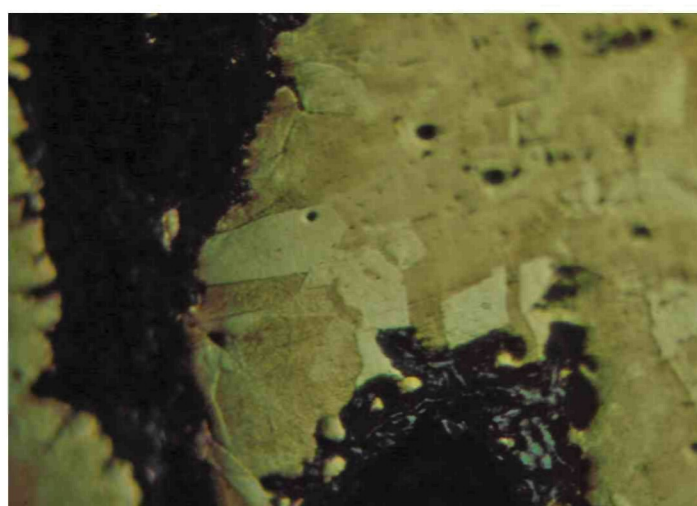
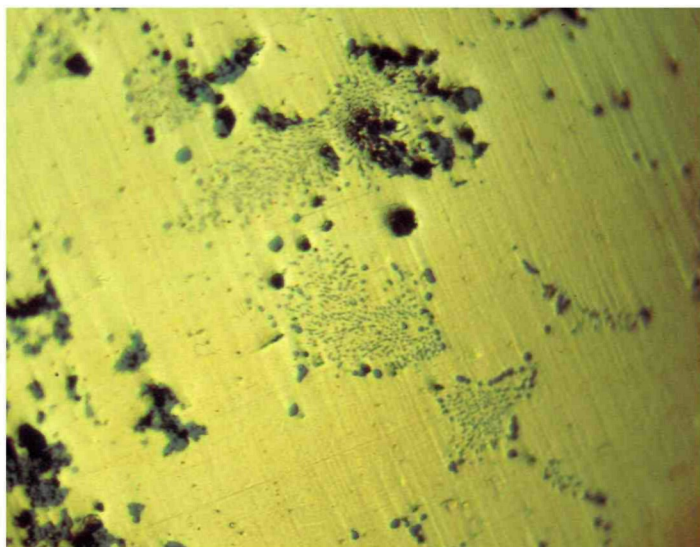
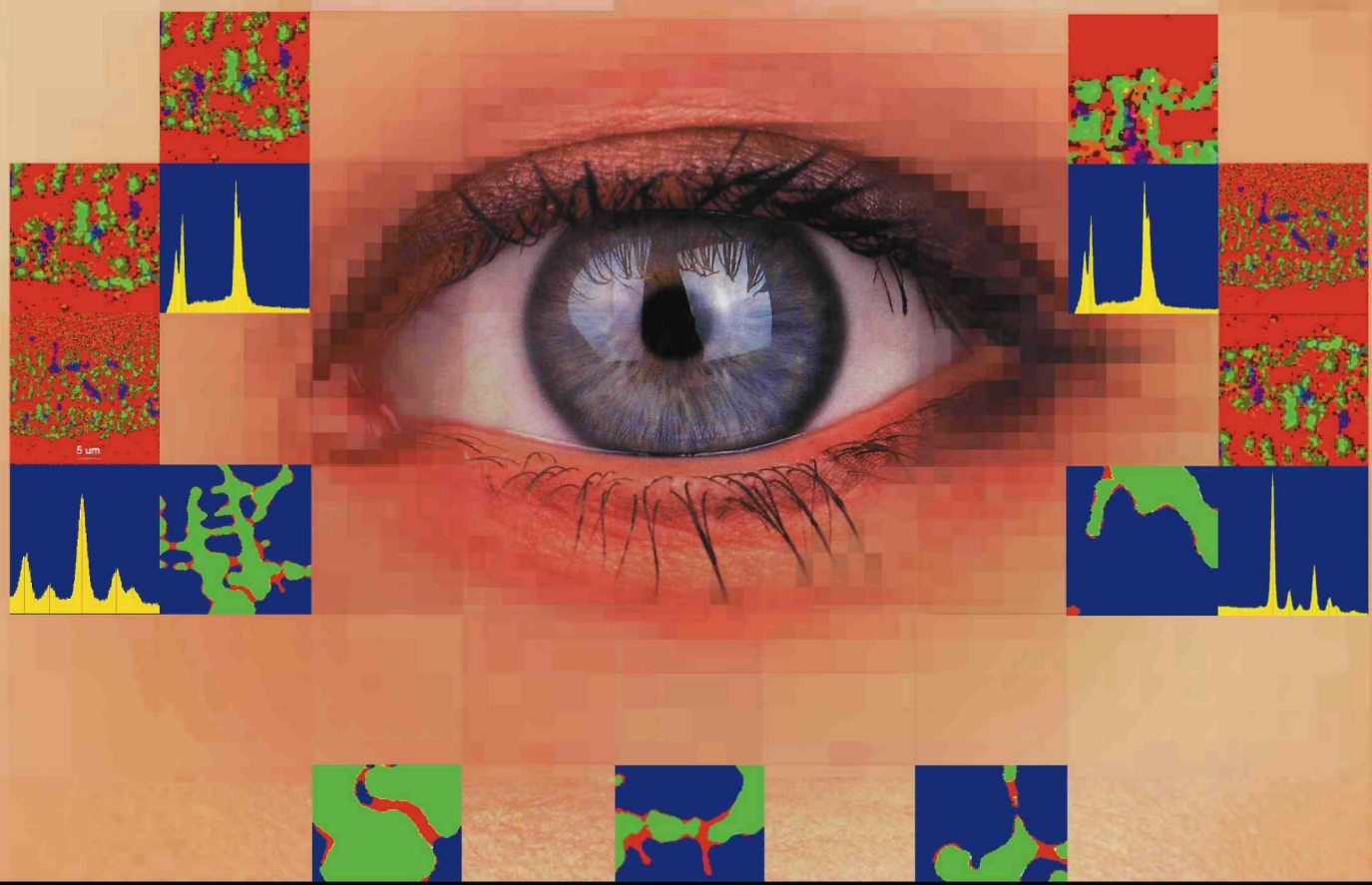


Fig. 6: Polished parts near the cutting edge of the icemans axe-blade (magn. 100x): left (Fig. 6a): Cuprite (fine) and corrosion products (coarse) in a homogeneous matrix; right (Fig. 6b): after etching: coarse recrystallization grains (twinning)

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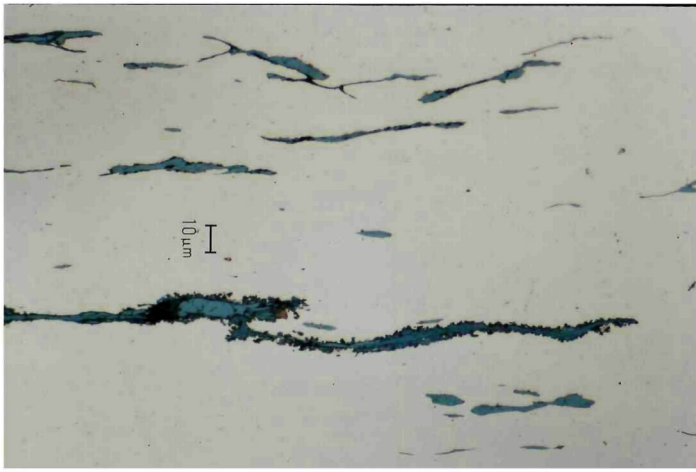


Fig. 7: Deformation of oxide-inclusions near the cutting edge in a prehistoric axe-blade (IN 9036) (magn. 200x)

(Sb) were found. This composition, with the diagnostic absence of antimony (Sb), excludes the provenance of the metal from the later famous copper deposits of Tyrol (Schwaz-Brixlegg, Austria) [5] and also the deposits of Prentau-Ahrntal/Valle Aurinia, Italy. The source of copper seems to be the deposits in the area near Trento (Val Sugana), Italy, as the flintstones of the arrow-heads can also be attributed to the south, specifically, the Monti Lessini region near Lake Garda, south of Trento.

The axes of the copper-age, often made of stone, rarely of copper, were mounted in a wooden handle. Such handles are often found in the lake dwellings in Austria and Switzerland. The best example is this axe of "Oetzi" from 3,300 BC. In Fig. 3 the reconstructed handle shows how the axe-blade was fastened by gluing it with birch-tar and fixing it with a strip of leather.

The Axe-Blade of the Iceman

Macroscopic Examination

In Fig. 2 the shape and dimensions of the blade can be seen: it is 94 mm in length and the maximum thickness (less than 10 mm) was very common in the European Copper-Age (Fig. 3). X-ray analysis revealed two defects: The cutting edge is partly deformed, but seems hammered for sharpening ("dengeln") (Fig. 5a); and there is a crack (Fig. 4, left,) not visible from outside, as result of hammering the oxygen-containing copper. The opposite end, the neck, shows a flaw (Fig.4, right; Fig. 5b). This is the pipe-cavity that proves that the cast was poured into a vertical standing (clay-) mold. The flaw is slightly concealed by hammering. The sides of the blade are deformed by hammering intended to form side-flanges, typical for advanced Copper-Age tools.

Many blades of the same typology (flanged axes, Randleistenbeile) are found in northern Italy, typical for the Remedello-culture, coeval with the Mondsee-Altheim-culture in southern Germany and Austria. Three of them (Fig.3), from the Institute für Ur- und Frühgeschichte (Prehistory) at the University of Vienna, were at the authors disposal for comparative research at the Erich-Schmid-Institut für Materialwissenschaft (Materials Science) of the Austrian Academy of Sciences in Leoben.

The Metallography of the Axe-Blades

As can be seen, the surface of the blade could be polished only slightly at two locations (Fig. 6 a, b): The edge near a crack visible in the x-ray-photograph (Fig. 6a) and on one side adjacent to the hammered flanges. (Fig. 6b)

From metallographic research, which was possible only in a very reduced scale, three conclusions can be drawn:

1. The copper contains, on average, 0.5% oxygen, as can be estimated from the quantity of cuprite (CuO) in the areas investigated (Fig. 6a).
2. Etching revealed a structure of typical recrystallized grains (Fig. 6b)
3. In the grains, some deformation bands, showing cold-working after recrystallization were observed (micro-hardness $HVM(30g)=120 \text{ kp/mm}^2$).

For comparison, the sections of the contemporary axes (Fig. 2) were examined (Figs. 7, 8); they showed severe deformation of the cuprite-inclusions (Fig. 7) and clear deformation-bands after etching (Fig. 8).

Summary

Metallographic examination of prehistorical objects often is handicapped by their historical value. That fact hinders the sampling necessary for exhaustive metallurgical analysis. In the case of the late-Neolithic axe from the glacier-mummy (5,300 years old) found in the Ötztaler Alps (border Italy-Austria) only slight surface polishing was possible. Therefore comparison with axe-blades of lower value (no finding conditions available) was useful for understanding the results from the primary object.

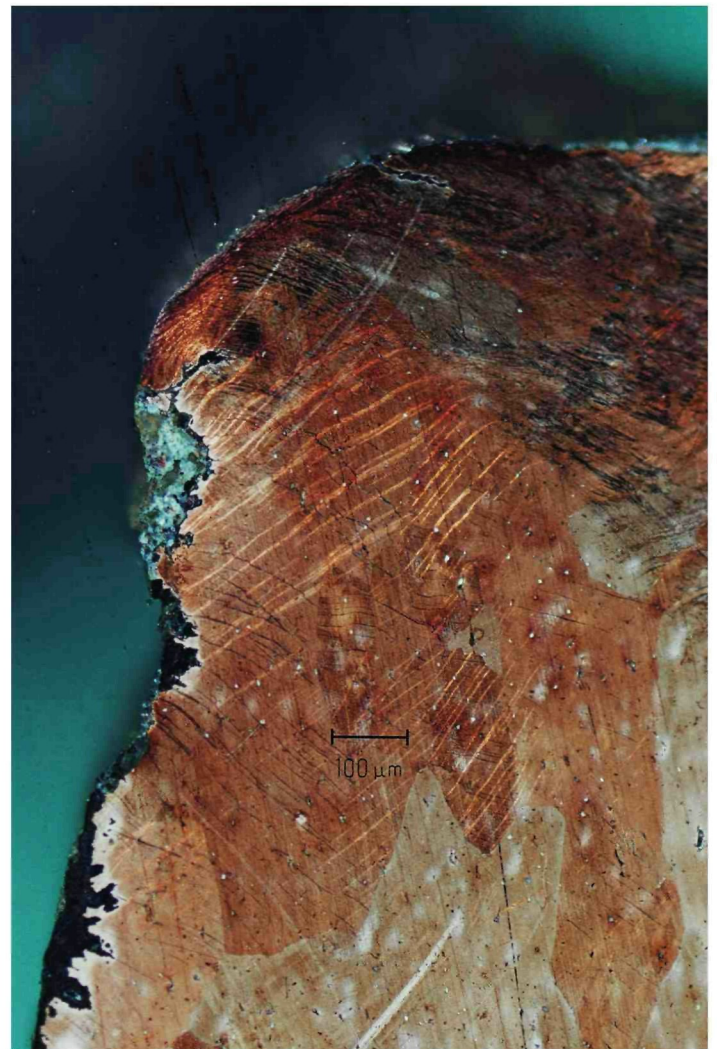


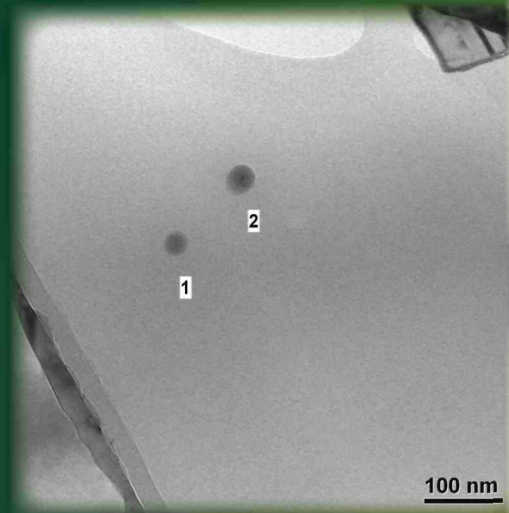
Fig. 8: Slip-bands in the cutting edge of a prehistoric axe-blade (IN 9036) (etched, magn. 100x)

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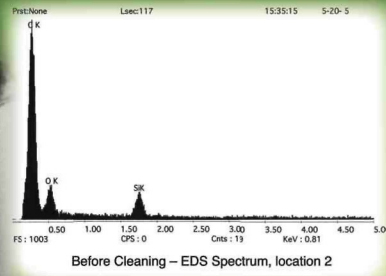
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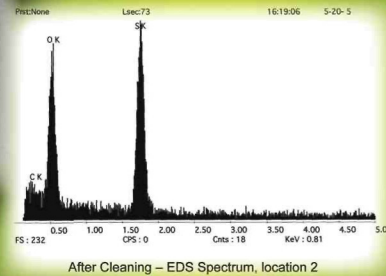
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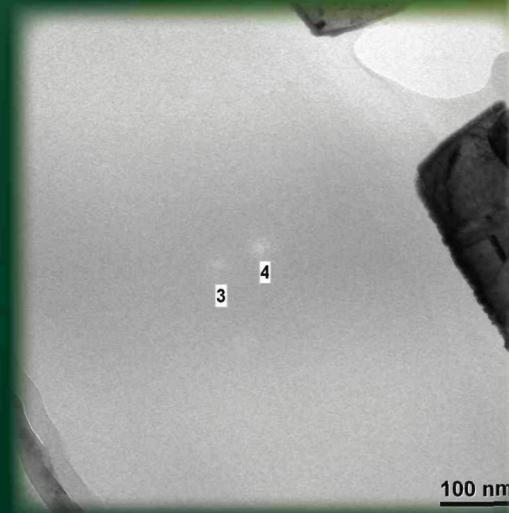
Before Cleaning - Wedge polished silicon sample + 10min PIPS ion milling. Contamination grown during spectrum collection times of 74 sec



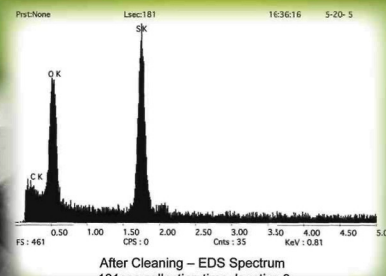
Before Cleaning - EDS Spectrum, location 2



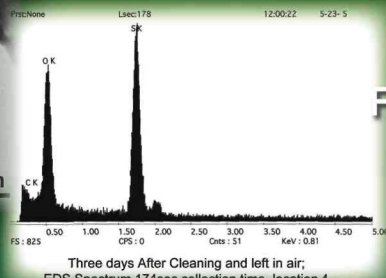
After Cleaning - EDS Spectrum, location 2



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The axe-blade was cast in the vertical position in a slow-cooling mold of sandstone or baked clay (for dendritic crystallization). The reducing condition during the casting process was not very carefully observed. The presence of a remarkable amount of oxygen (0.5% O₂ as cuprite CuO) could have removed a portion of the highly volatile original arsenic content. Therefore, a higher content of arsenic (more than 2% As) in the metal of origin seems reasonable.

After taking the rough blade from the mold, it was cleaned at the sides, and then hammered for forming the cutting-edge and the side-flanges. It was re-heated (over 600°C) for softening (by recrystallization) and finally hammered again at the cutting edge for sharpening and hardening by cold working (in German: dengeln).

The chemical composition is characterized by the presence of low amounts of arsenic (0.19% As) and silver (0.09% Ag), and the absence of antimony—in neither the XRF-analysis nor in the small As-Bi-containing inclusions. So the provenance of the copper from deposits in Alpine Northern Italy near Trento (TN) is very likely. ■

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References:

- [1] G. Sperl, Zur Urgeschichte des Bleies; in: Zeitschrift für Metallkunde, 81 (1990), H.11, .799-801; On the prehistory of lead, paper prepared for Historical Metallurgy (GB)
- [2] G. Sperl, Das Beil vom Hauslabjoch; in: Der Mann im Eis, Band 1, Universität Innsbruck 1992, S. 454-461
- [3] G. Sperl, Metallurgie des urgeschichtlichen Kupferwesens im Alpenraum; in: BHM 133 (1988), H.11, S.495-498
- [4] Lutterotti L., Artioli G., Dugnani M., Hansen T., Pedrotti A., Sperl G., "Crystallographic texture analysis of the Iceman and coeval copper axes by non-invasive neutron powder diffraction". In: Die Gletschermumie aus der Kupferzeit 2. Fleckinger A. (ed.), Bozen - Wien: Folio Verlag, 2003. p. 9-22
- [5] Höppner B., Bartelheim M., Hujsmans, M., Krauss R., Martinek K.-P., Pernicka E., Schwab R., Prehistoric Copper Production in the Inn Valley (Austria), and the Earliest Copper in Central Europe; in: Archaeometry, Vol. 47/2(2005) p.293



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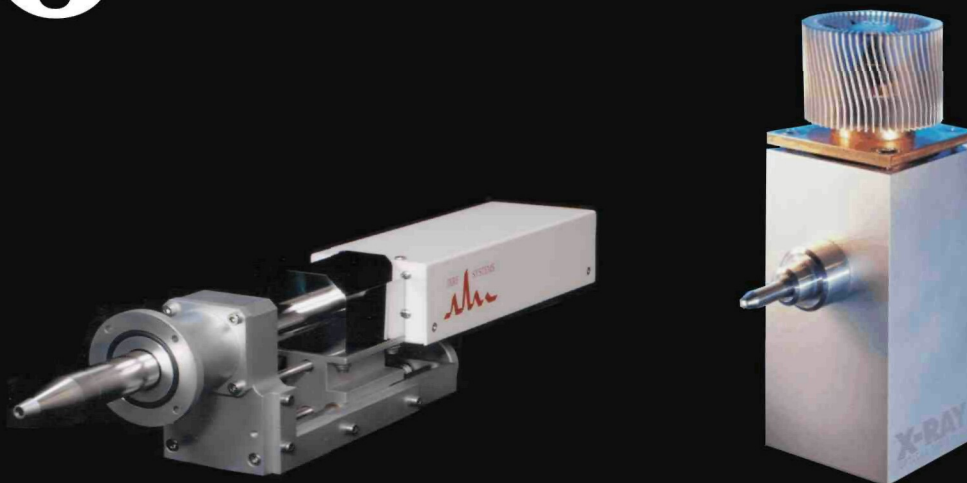


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