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Late La Tène bronze rivets from selected sites in Bohemia: material research

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Abstract
The study presented focuses on material research of La Tène rivets and represents the very first study conducted into this class of archaeological finds from the Bohemian region. The rivets examined come from two significant archaeological sites situated in this geographical area—a hillfort Kolo near Týnec nad Labem and an oppidum in Stradonice. The sets of the rivets selected for the study were dated to the Late La Tène period (second–first century BC)—in the context of Western Europe, the term Celtic period can also be found. Thorough material research of the objects utilised a range of methods such as scanning electron microscopy with energy dispersive analyser, atomic absorption spectrometry, X-ray micro-tomography scanning, laser ablation-inductively coupled plasma-mass spectrometry, and Raman spectrometry. As a result, the research has identified and described three different technologies used to produce the rivets. The rivets uncovered there were mostly produced by casting from a bronze alloy or by putting wrought iron pins into the bronze melt of rivet heads. In addition, a minority of the rivets were produced using forged wrought iron with their heads plated with a very thin bronze plate. The results of the elemental analysis showed that several of the rivets and most of the rivet heads were made of bronze alloys with a tin content of 2–10 wt.%. The lead content of bronze alloy rivets from both sites varies from 0.2 to 10.1 wt.%. It can be assumed, that lead was intentionally added to the bronze melt used to produce the majority of the artefacts examined. Also, several bronze rivet heads were found to be decorated with enamel, which is a type of soda-lime-silica high lead glass coloured with crystals of Cu_2O (the Colour of the enamel was predominantly red). In conclusion, two different groups of enamels were distinguished: (a) enamels with PbO up to 20% and (b) enamels with a higher content of PbO reaching up to 40%.

Keywords Late La Tène period, Rivet, Bronze, Enamel, Wrought iron, Bohemia

Introduction

Multiple finds of bronze rivets have been uncovered in former European settlements dating to the Late La Tène period (second–first century BC). As for the terminology, the term Celtic period can also be found, but this term is generally not used in the context of Central Europe. The rivets typically contain engraved decorations, where traces of enamel are rarely preserved. Although such bronze artefacts have been known for long, only marginal attention has been paid to them, primarily focusing on the typological analysis of the decoration [1]. However,

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the issue of the production processes applied has been neglected so far.

The La Tène period saw the development of a wide range of specialised crafts, whose activities were concentrated at the so-called central sites. Owing to very complicated production processes applying enamel to decorate bronze artefacts, those objects were likely produced in specialised workshops concentrated at the central sites only. These locations truly served as the centres of large networks of long-distance trade routes, and the trade concentrated around them provided both initial raw materials and opportunities to distribute finished goods [2]. Raw glass needed to produce enamel decorations of bronze artefacts was probably imported to the La Tène Central European glassworks from primary workshops located in the Eastern Mediterranean and Egypt [3]. For instance, the use of decorative enamel rivets is well documented for the La Tène period due to the discovery of opulent wagons from Boé or Dejbjerg [4]. Here, the rivets could have played a decorative role, but at the same time they may also have been used to fix decorative plates, as evidenced by the remains of iron or bronze openwork plates and the rivets found there [4] (Fig. 1).

These rivets could also have served the identical function when attaching decorative fittings to wooden furniture or wooden vessels/buckets. Smaller rivets decorated with enamel are also known from other artefacts: e.g., helmets, or knife and sword fittings [4, 5]. Furthermore, rivets are well documented in belt hooks or decorative horse harness phaleras. Rivets were also applied to yokes (e.g., of the Titelberg type) and guide rings for horse reins (e.g., the Hoppstädten type) [4]. Another use of rivets may have possibly lied in attaching handles or other components to metal vessels, as confirmed by the discovery of a zoomorphic handle from the site of Bělohošt' [6]. Used as decorations, larger decorative enamelled rivets have been found in greater numbers at central sites/oppida, representing the most characteristic finds from phase LT D [4, 7]. One of the most numerous sets of rivets uncovered in the region of Central Bohemia comes from the oppidum of Stradonice [8] and is characterized by considerable variations of shapes and decorative motifs. A minor set of decorative rivets is also known from an oppidum located in Závist (Bohemia), and rivets were also found in smaller numbers at the sites of Staré Hradisko (Moravia) and Třísov (Bohemia) [9] (Fig. 2). Similar finds have

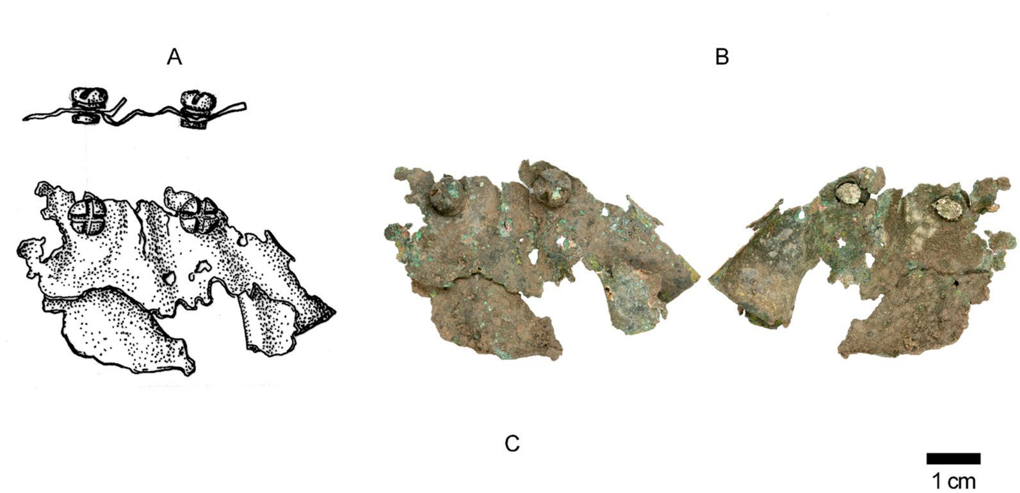

Fig. 1 Rivets fixed in metal sheet **a** Staré Hradisko (Museum of the Boskovice Region), **b** Staré Hradisko (Museum of the Boskovice Region), **c** Vyšehořovice (Prague-East Region)

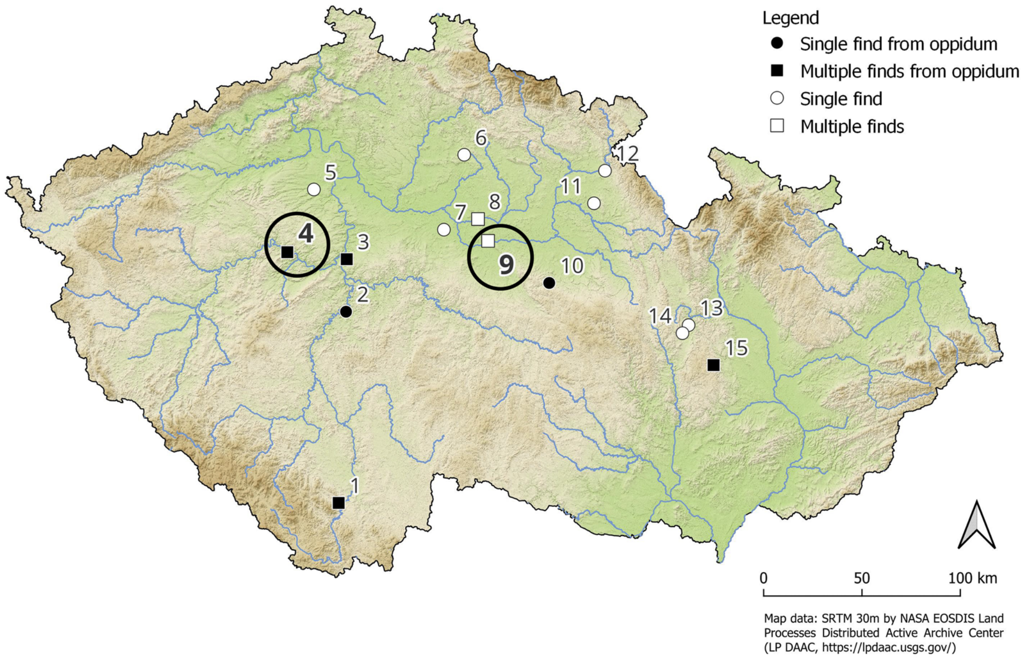

Fig. 2 Location of Finds of Rivets from La Tène Period in Czech Republic: 1. Třísov, 2. Hrazany, 3. Lhota u Dolních Břežan - Závist, 4. Stradonice, 5. Ješín, 6. Markvartice. 7. Ratenice, 8. Žehuň, 9. Týnec nad Labem, 10. České Lhotice, 11. Bolehošť, 12. Nové Město nad Metují – Hradiště, 13. Chornice, 14. Jevíčko, 15. Staré Hradisko

been documented in other places in Europe as well, for instance, at the Manching oppidum (Germany).

In the context of Central Europe, decorations of rivets, made of a copper alloy, were predominantly produced using red enamel, thus creating an attractive contrast with their metal base. On the other hand, the decoration of iron objects with enamel appears to be relatively rare. Still, enamel decoration on iron artefacts has been described e.g., in the already mentioned wagons from Boé and Dejbjerg [4]. We can also mention the discovery of an iron linchpin from Plavecké Podhradí in western Slovakia containing an iron rivet with enamel decoration. To date, the only centres of enamel production confirmed in the context of the La Tène cultural circle are the workshops from an oppidum at Bibracte (Mont-Beuvray) in France, with preserved finds of both finished products, including rivets, as well as semi-finished products and iron tools, coupled with a set of grinding and polishing stones [10]. The production process applying enamel onto the surface of bronze rivets has also been suggested by small fragments of glass "shells" with negative imprints of grooves, well known from the La Tène rivets. Furthermore, manufacturing waste has also been recorded in the workshops of the Bibracte oppidum containing amorphous lumps of red glass together with fragments of raw glass [10]. It would, of course, be misleading to assume that this was the only manufacturing centre dedicated to the production of enamelled bronze rivets in the entire La Tène Europe. In fact, the decorative spectrum of the finds from the Bibracte oppidum does not coincide with the finds known from the Czech sites. Therefore, it is not surprising that a wide range of decorative motifs of enamelled rivets can also be observed in the finds from the Stradonice oppidum (Bohemia), because, in many respects, it was a site of supra-regional importance. Compared with the Stradonice oppidum, a rather monotonous assortment of rivets has been found at other sites, such as hillfort Kolo near Týnec nad Labem (Bohemia), or oppida in Staré Hradisko (Moravia) and Manching (Germany), where merely one or occasionally two types of decoration were observed [11]. Most likely, the Stradonice oppidum could have been one of the production centres of enamelled rivets in the La Tène period, just as the Bibracte (Mont-Beuvray) oppidum in France. In Stradonice, semi-finished bronze rivets have been uncovered [8], but no direct evidence exists confirming the existence of a local enamel workshop. Therefore, it cannot be ruled out that the Stradonice oppidum was just a centre of trade, supplied, among other things, with enamelled bronze rivets from various production centres in Europe.

In the region of the Czech Republic, the existence of a pre-oppidum glass workshop (2^{nd} half of third century–1^{st} half of second century BC) is documented for the site of Němčice nad Hanou, where fragments of raw glass have been found together with the waste characteristic of glass production [12]. Both Němčice and the oppidum of Staré Hradisko are well known for the finds of coloured raw glass (blue and opaque green fragments), quite likely indicating the import of pre-coloured ingots of raw glass from primary Egyptian and/or Middle Eastern workshops [3].

This study aimed to conduct material research into small connecting components—rivets, which were frequently used in the La Tène period. Although rivets are found at the corresponding sites rather frequently, they have been neglected so far in terms of their detailed research. For the archaeological and material study of rivets coming from the Late La Tène Age, two sets of finds were selected from two different archaeological sites in Bohemia, namely the Kolo hillfort near Týnec nad Labem and the Stradonice oppidum (Fig. 2). The material research primarily concentrated on the production technology of rivets and their enamel decoration. This research represents the very first study conducted into this class of archaeological finds from the Bohemian region.

Experimental

Archaeological and typological research focused on two sets of decorative metal rivets dating from the Late La Tène Period (second–first century BC), uncovered during the field survey of the archaeological sites of Kolo near Týnec nad Labem and Stradonice (Fig. 2). Namely, a set of 67 rivets comes from the Kolo hillfort near Týnec nad Labem, 17 of which could have been originally decorated with enamel.[1] This collection is one of the most complete sets of metal rivets known in the territory of the Czech Republic. For subsequent material research, 30 rivets were selected from the set described (the Kolo hillfort near Týnec nad Labem) (Fig. 3). The archaeological and typological study was complemented by 15 rivets coming from another extensive set of rivets found in the oppidum of Stradonice. Eleven of them were probably decorated with enamel[1], and all of them were used for subsequent material research (Fig. 3).

The following devices were used to determine the chemical elemental composition of the metal rivets: Tescan Vega 3 scanning electron microscope (SEM) with an Oxford Instruments INCA 350 LMU energy dispersive analyzer (SEM/EDS) and an AGILENT 280 FS AA atomic absorption spectrometer (AAS). Metallographic samples were prepared by casting them in epoxy resin Buehler EpoxiCure 2. Subsequently, the samples were ground with SiC P400–P2000 abrasive papers, and the final pieces were polished with diamond pastes of D2 and D 0.7 grit. The structure of the metal matrix was highlighted by etching in the Ratin's solution with the following composition: 5 ml H_2O, 5g $FeCl_3$, 25 ml HCl and 37 ml ethanol. A Nikon Eclipse MA 200 optical microscope and a Tescan Vega 3 scanning electron microscope (SEM) were applied to observe both the structure of the metal matrix of the rivets and their enamel decoration. The internal structure of the metal rivets was examined using X-ray with an YXLON Smart EVO 160D X-ray tube with an operating voltage of up to 160 kV and a current of 4.6 mA (X-ray). The transmission was performed applying memory foils with a 40 µm detection layer and a digital scanner. The design of the selected metal rivets selected was investigated using computed micro-tomography scanning (micro-CT). Micro-CT scans were carried out at the laboratory of the Institute of Experimental and Applied Physics, CTU in Prague, using an in-house built scanner. The scanner was equipped with an X-ray tube Hamamatsu L12161-07 and a hybrid-pixel semiconductor detector $\text{WidePIX}_{2\times5}$. WidePIX devices are based on technology of hybrid-pixel photon-counting detectors Timepix developed within the scope of Medipix Collaboration at CERN [13, 14]. The detector unit features a 1 mm thick CdTe sensor and provides a pixelated array of 1280 × 512 pixels with 55 µm pixel pitch. An X-ray beam of 140kVp filtered with 1mm Cu and 1 mm Al foils was used for the measurements presented. CT scans were carried out using spiral geometry with the pixel resolution of 15.1 µm. CT reconstructions and data visualisations were conducted with VG Studio MAX and ORS Dragonfly software, respectively.

For the basic observation of the condition of the preserved enamel, the Olympus SZX9 stereomicroscope was selected, and the data were processed using the QuickPHOTO INDUSTRIAL program.

Major, minor and trace element contents of archaeological samples were determined using an LA-ICP-MS (laser ablation-inductively coupled plasma-mass spectrometry) system consisting of Agilent 7900 quadrupole (Q)-ICP-MS (Agilent Technologies Inc., USA) coupled with an Analyte Excite Excimer 193 nm LA system (Photon Machines, USA), equipped with a two-volume HelEx ablation cell. The gas system of the laser includes nitrogen clearing the path of the laser beam and helium carrier gas. Agilent 7900 Q-ICP-MS was equipped with a standard nickel sampler, skimmer cones and a quartz torch with a 2.5 mm injector. The samples were measured in the form of polished resin pucks (small fragments of glass embedded in epoxy resin blocks, which were ground and polished).

The diameter of the laser beam ("spot size") was 85 µm. Applied laser fluence was 4.71 J/cm^2 with a laser pulse

[1] The assumption is based on the specific decoration being in the form of engraved ornaments, which could have been filled with enamel.

Fig. 3 Rivets from archaeological sites at Kolo Hillfort Near Týnec Nad Labem and Stradonice

rate of 10 Hz. A analysis consisted of 20s of background acquisition (gas blank), 60 of sample ablation, and 60 of wash-out time. The Iolite 4.0 software package was used for data reduction to determine trace element concentrations, analytical errors, and detection limits. Internal standardization was based on ^{29}Si concentrations established with the SEM–EDS. For external calibration, NIST 610 and 612 glass reference materials and Corning B and C were applied. The standards were analysed at the beginning and the end of the analytical sessions, and also after every 5 measurements to monitor the drift in instrumental sensitivity.

SEM/EDS experiments were performed with all the samples embedded in resin blocks, polished and covered with a conductive gold coating. For measurements, scanning electron microscope Hitachi S4700 was used, coupled with an SDD detector. For each glass sample, three X-ray spectra were acquired at different spots in the samples using voltage of 20 kV and 100 s acquisition time. Corning B and C glasses were analysed as reference standards. The results obtained indicate relative errors below 5% for most of the elements present at concentrations above 1 wt %.

Several methods (SEM/EDS, LA-ICP-MS) were used to examine 5 samples taken from rivets 620, 1068, 1875, 3754 and 3900 (Fig. 3) from the sites of Kolo hillfort near Týnec nad Labem and 3 samples taken from rivets 1052, 80,231 and 226,455 from the locality of Stradonice (Fig. 3). Owing to the clouding of the enamels, the opacifier detected was also measured by Raman spectrometry (RM). Raman spectra were examined with a Thermo Scientific Raman dispersive spectrometer—model DXR Microscope, equipped with an Olympus confocal microscope. The excitation source was a 532 nm Nd:YAG laser with an input power of 10 mW utilising a grid of 900 notches/mm. As a detector, a multichannel thermoelectrically cooled CCD camera was used. The samples were measured at 50 × magnification with a measurement footprint of approx. 1 μm through the aperture of a 50 μm pinhole. Omnic 9 (Thermo Scientific) was employed to process all the spectra obtained.

Results and discussion

Typological research

The rivet sets from both archaeological sites (Kolo hillfort and Stradonice) were divided into five groups according to the shape of their heads (Fig. 4):

A—semispherical
B—semispherical with frame
C—convex with frame
D—highly profiled/spherical
E—flat

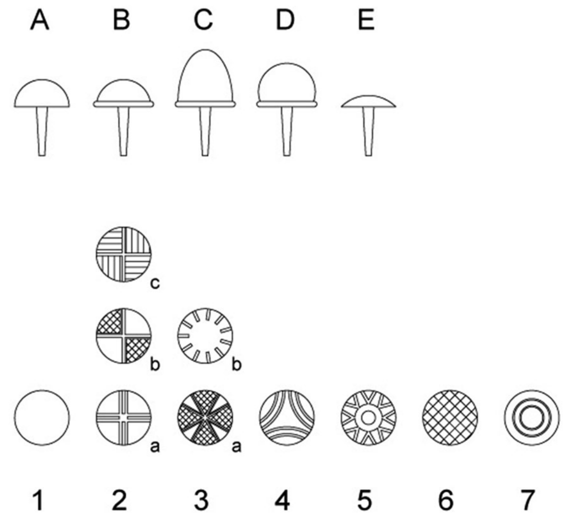

Fig. 4 Classification of rivets according to shape and decoration of rivet heads

On the basis of decorations of rivet heads, originally serving as a base for enamel filling, all the rivets examined were classified into seven groups (Fig. 4):

1. No decoration
2. Cross-shaped decoration
3. Radial decoration
4. Geometrical decoration
5. Central circle with radial decoration
6. Grid-like decoration
7. Centred circle

The results of the typological survey show that most of the rivets from the archaeological site of Kolo near Týnec nad Labem have a semispherical head or semispherical head with a frame (Figs. 4, 5), and they have either no decoration or are decorated with symmetrical cross-shaped decorations (Figs. 4, 6). Decoration of the heads was mostly engraved. Only a minority of the rivets had heads with cast decorations (namely rivets No. 3465, 864 and 561.918). The relation between a type of decoration and production technology of the rivets was not observed.

Based on the typological data evaluated,[2] the set of rivets from the Stradonice site appears to have a predominant head shape very similar to that of the rivet heads from the Kolo hillfort near Týnec nad Labem. Rivet heads from both sites are frequently without decoration or contain symmetrical cross-shaped decorations. Moreover, in

[2] For the comprehensive typological evaluation of the rivets from the archaeological site of Stradonice, a complex analysis of the entire set is needed. However, the set is very extensive and has not been fully processed or registered in respective museums.

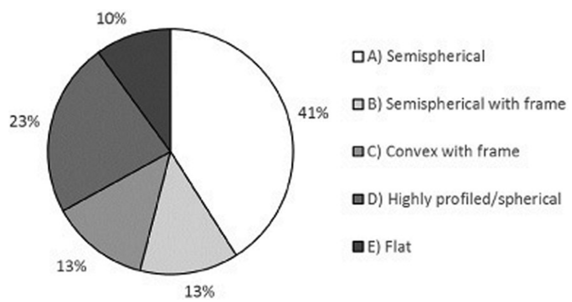

Fig. 5 Rivets from Kolo Hillfort near Týnec nad Labem according to shape of heads

the examined set of rivets from Stradonice, it is also possible to find decorations of rivet heads with grid-like and centred circle motifs (Fig. 4), which, in contrast, do not occur in the set of rivets from the Kolo hillfort (Fig. 4).

Material research

The following three production technologies were identified at both Kolo hillfort near Týnec nad Labem and in Stradonice. The rivets produced there were either made by casting or putting a forged wrought iron pin into a bronze melt. Only several rivets were made of forged wrought iron with their head plated with a bronze plate.

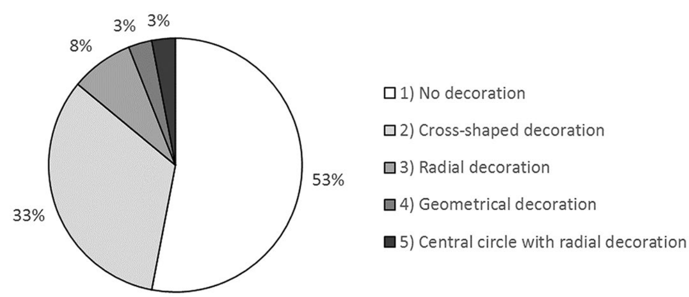

Fig. 6 Rivets from Kolo Hillfort near Týnec nad Labem divided according to decoration of rivet heads

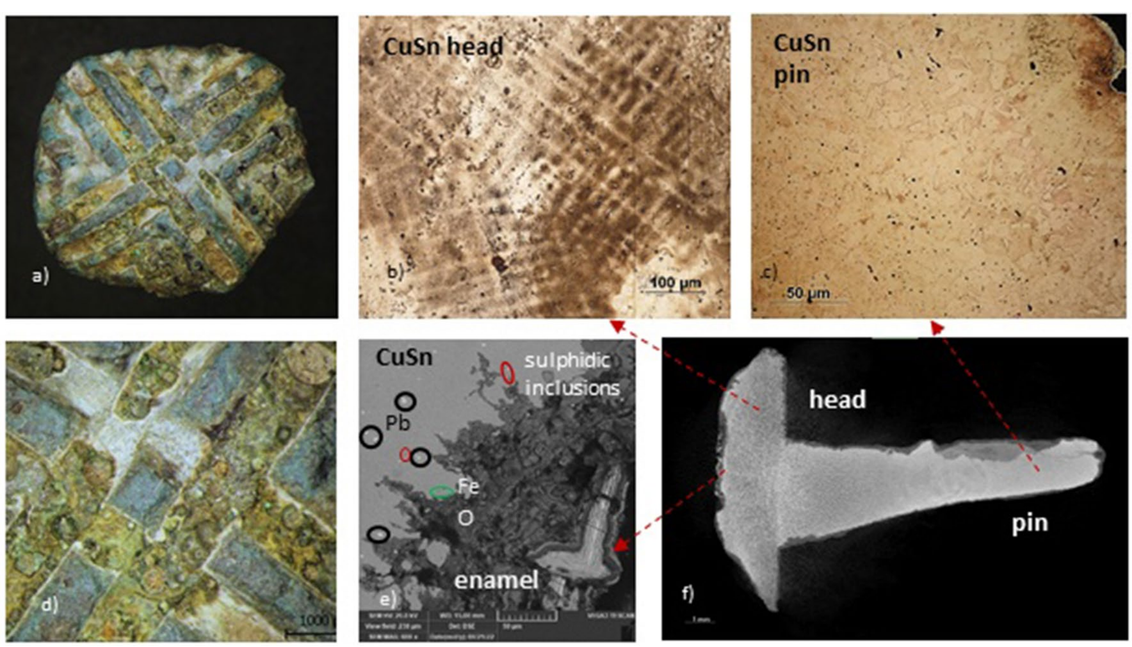

Fig. 7 Results of Material Research of Cast Bronze rivets—Cross Section. **a** Rivet head with cross-shaped decoration; **b** Dendritic structure of Cast Bronze rivet Head; **c** mechanically hardened and Heat-treated rivet pin; **d** corroded Enamel Decoration; **e** detail of bronze matrix and corroded enamel; **f** micro-CT slice of Cast Rivet

The cast rivets are made of a bronze alloy with mostly small contents of Pb, Fe, and Zn. Sulphidic and FeO inclusions together with spherical Pb particles are well visible in the bronze matrix (Fig. 7). The pins of the cast rivets were mechanically hardened by hammering and subsequently treated with recrystallization annealing (Fig. 7).

The rivets were made by casting or putting a forged wrought iron pin into a bronze melt (Fig. 8 a-c).

The rivet heads were cast from a bronze alloy containing small amounts of Pb, Bi, Fe, and Sb. In the bronze matrix, the intermetallic phase δ ($Cu_{41}Sn_{11}$) can be seen together with sulphidic inclusions and spherical Pb particles (Fig. 9). Iron pins of the rivets examined are often wholly corroded. Still, a ferritic structure of the forged wrought iron is clearly visible in the remains of the pins, which is also true for tiny particles of fayalite slag found in the corroded iron matrix (Fig. 9).

Several rivets were made of wrought iron with their heads plated with a bronze plate (Fig. 10 and Video 1).

Video 1 Plated Rivet Head.

This type of rivets was forged from wrought iron. A number of inclusions of fayalite and wüstite were detected in the ferritic structure of iron (Fig. 11). The inclusions are well oriented in the direction of forming. A bronze plate with an average thickness of 300–500 µm was applied to plate the heads of the rivets. The bronze plates were treated by recrystallization annealing (Fig. 11). The bronze alloy used was found to contain small amounts of Pb, Bi, and Fe. Sulphidic and FeO inclusions together with spherical Pb particles were also observed in the bronze matrix (Fig. 11).

In the set examined, two rivets were identified as not belonging to either of the above groups (Fig. 3, rivets No. 3353 and 4036). One of them is made of wrought iron, and its head is not plated with bronze (Fig. 12 a). It is possible that, in this case, the bronze plate was lost from the rivet head due to its long stay in the ground.

The second rivet was somewhat surprisingly found to have been cast from an almost eutectic SnPb alloy with an approximate Sn content of 60 wt % and Pb content of 40 wt % (Fig. 12 b).

All types of the rivets described above were identified at both settlement sites (Kolo hillfort near Týnec nad Labem and Stradonice). However, the prevalent production technology of the rivets was the application

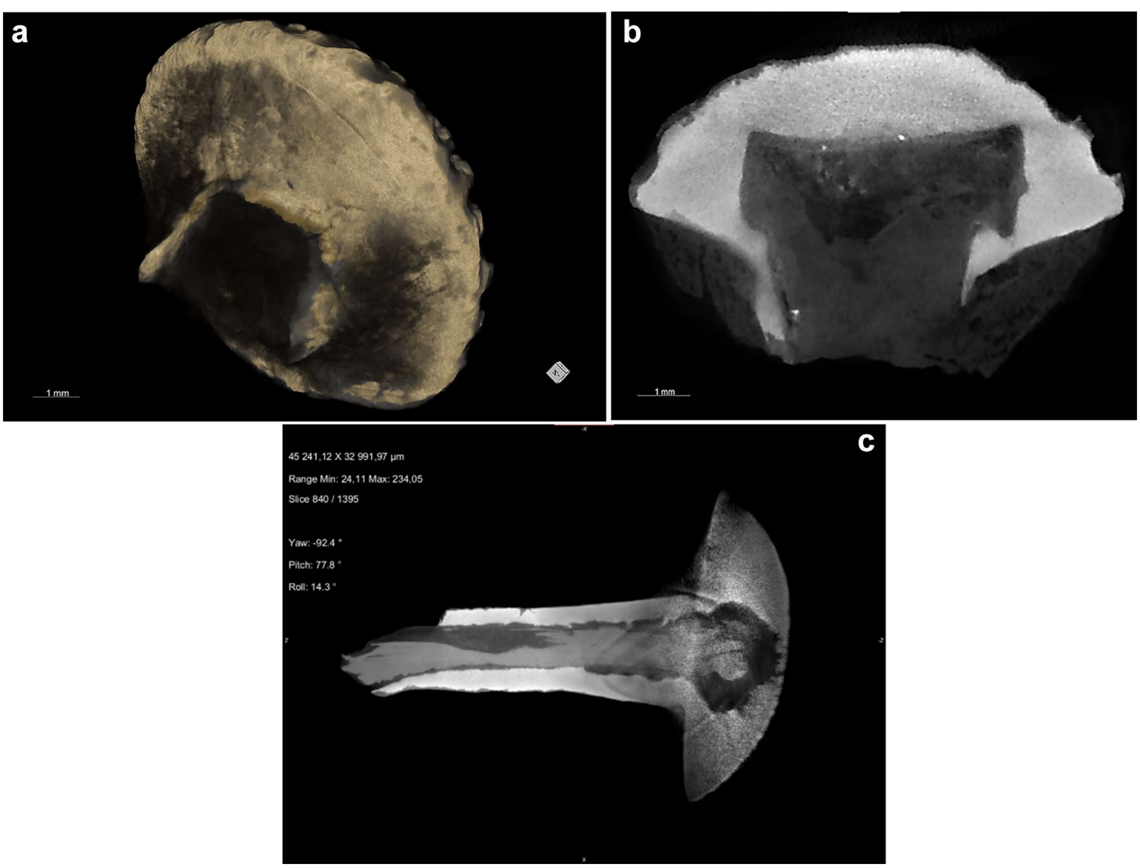

Fig. 8 a-c Principle of putting forged wrought iron pin into bronze melt

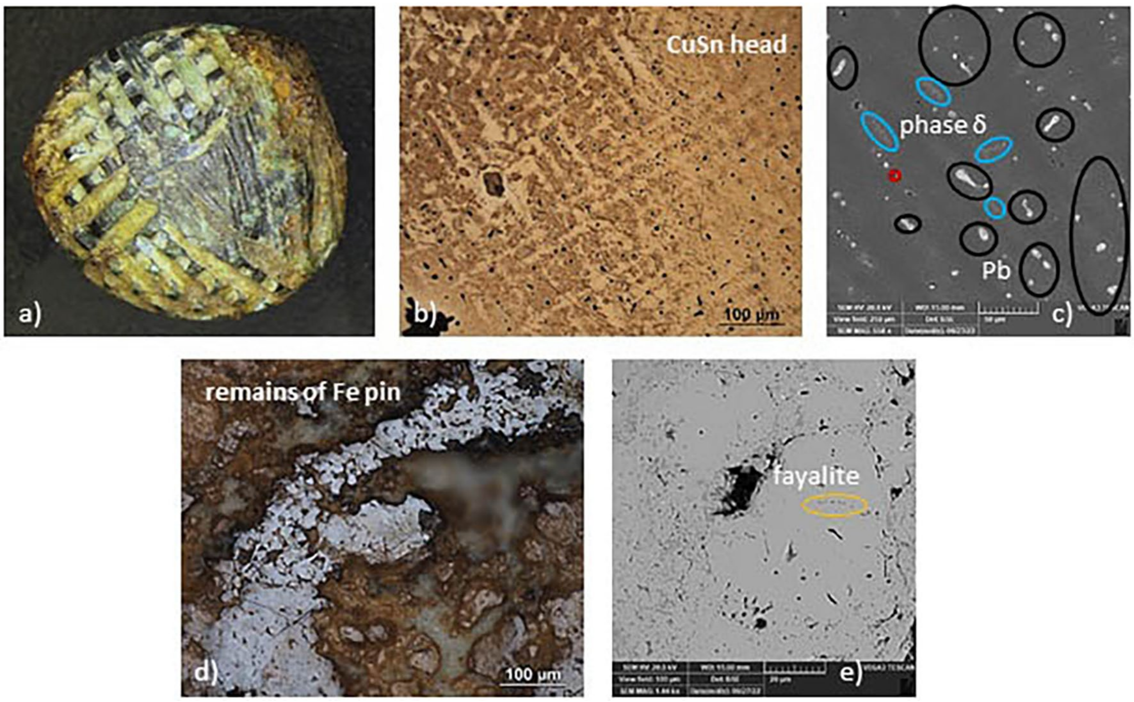

Fig. 9 Results of Material Research of Bronze Rivet with Pin Made of Forged Wrought Iron–Cross Section. **a** Rivet Head with Radial Decoration; **b** Dendritic Structure of Cast Bronze Rivet Head; **c** Detail of Chemical Composition of Bronze Matrix; **d** Ferritic Structure of Iron Pin Remains; **e** Detail of Fayalite Slag in Iron Pin Remains

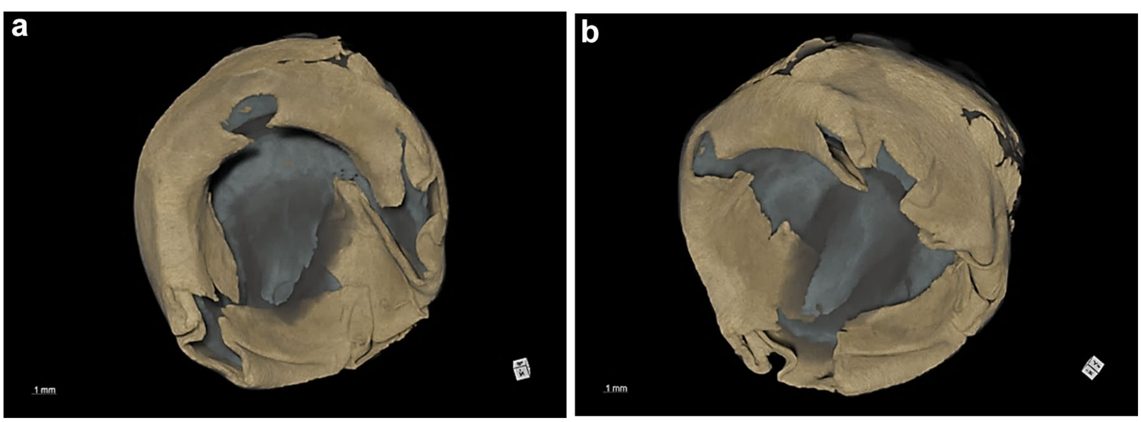

Fig. 10 **a, b** Detail of Plated Rivet Heads

of a forged wrought iron pin into a bronze melt (Figs. 7, 8, 13).

The elemental composition of the bronze parts of the rivets is comparable for both archaeological sites (Tables 1, 2; Fig. 14 a, b).

The lead content of bronze alloy rivets from both sites varies from 0.2 to 10.1 wt % (Tables 1, 2). In case of the lead content in the bronze matrix reaching above 1 wt.%, it can be assumed that lead was intentionally added to the bronze melt (Tables 1,2 highlighted in bold) [15, 16]. The presence of a higher lead content in the bronze alloy improves the fluidity of the melt, the runnability of the alloy into casting moulds and slightly lowers the melting temperature of the alloy. The results of the analyses show that approximately 3/4 of the rivets examined were deliberately alloyed with lead (Tables 1 and 2, marked in bold). Lead in the other rivets is

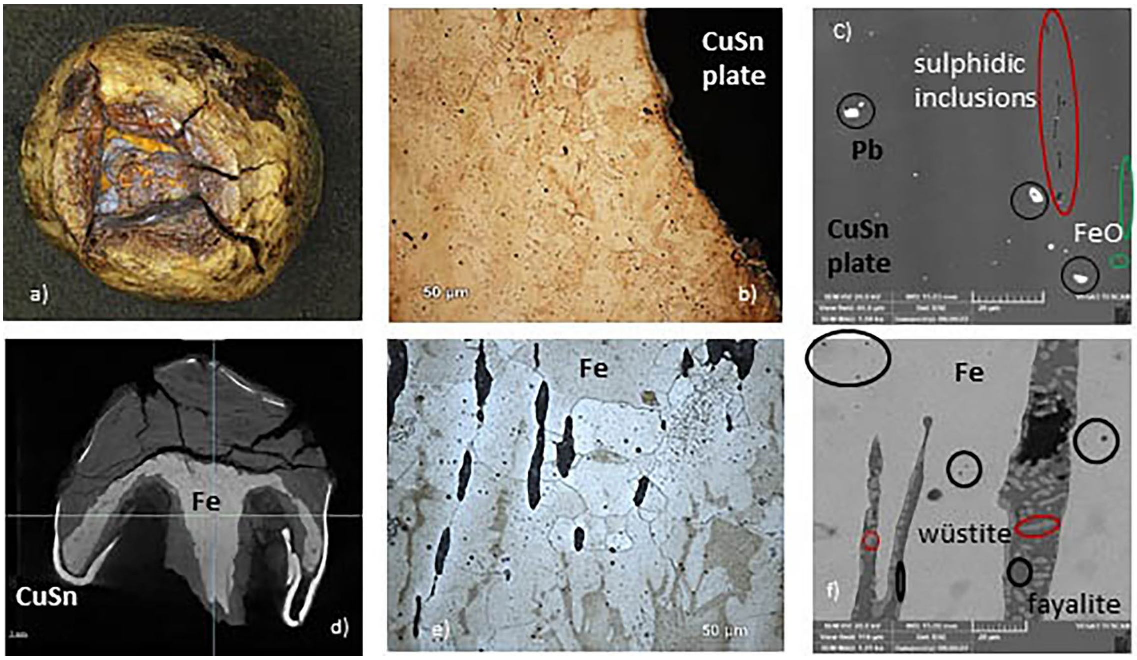

Fig. 11 Results of material research of plated wrought iron rivet–cross section. **a** Rivet Head without Decoration; **b** Mechanically Hardened and Heat-Treated Plate Structure; **c** Detail of Chemical Composition of Bronze Matrix; **d** micro-CT slice of Plated Wrought Iron Rivet; **e** Ferritic Structure of Wrought Iron; **f** Detail of Fayalite and Wüstite Slag in Wrought Iron

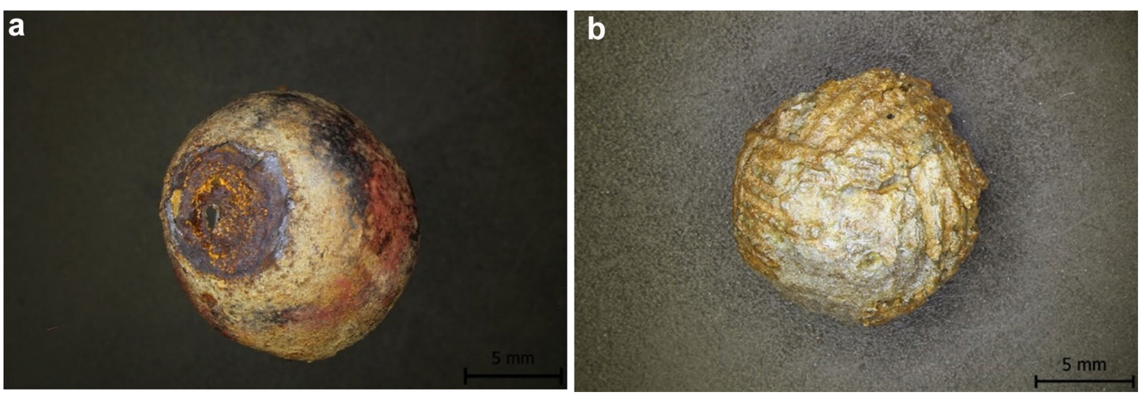

Fig. 12 **a** Rivet made of wrought iron. **b** Rivet cast from SnPb alloy

probably just an impurity element originating from tetrahedral copper ores [15, 16].

Other impurity elements identified in the bronze alloys from both archaeological sites are namely Fe and Zn (Tables 1, 2). Silver, as an impurity, was confirmed only in three rivets coming from Stradonice and one rivet from the Kolo hillfort near Týnec nad Labem (Tables 1, 2). The last impurity element identified is nickel, which was detected just in four rivets from the Kolo hillfort near Týnec nad Labem (Tables 1, 2). In contrast, nickel was not detected in any of the rivets from Stradonice. The possible presence of any other impurity elements in the bronze alloys (used for the production of the rivets) lies beyond the detection limits of the instruments employed for the analysis.

The contents of the impurity elements recorded show that the bronze parts of the rivets were made from tetrahedral copper ores most likely coming from two

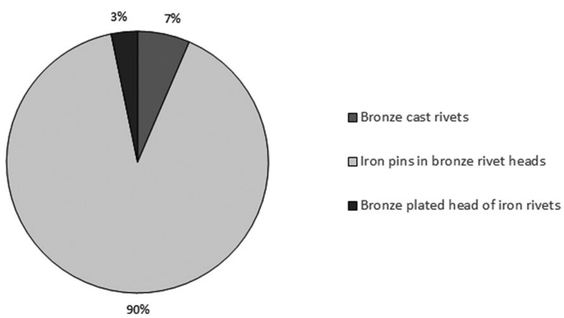

Fig. 13 Percentage of production technology used in rivets from Kolo Hillfort near Týnec nad Labem

different areas. Tetrahedral copper ores containing nickel may possibly originate from the western part of the Alps [16], whereas the source of tetrahedral copper ores without nickel and containing some or no silver may lie in the region of the western Carpathians, for instance, in the area of the Špania valley or around today´s Kremnice in Slovakia [17–19].

The bronze matrix of the rivets from both archaeological did not display the presence of arsenic and antimony. This means that the bronze alloy used to produce the rivets examined was pre-melted several times, as arsenic and antimony are known to create

Table 1 Elemental composition of bronze parts of rivets from Kolo Hillfort near Týnec nad Labem (SEM/EDS)

Rivet No./wt %	Sn	Pb	Fe	Zn	Ni	Ag	Cu
612	1.3	**5.6**	0.4	0.3			92.4
620	6.7	**4.0**	0.4	1.3	0.7		86.9
645	7.8	**2.5**					89.7
646	6.0	**2.5**	2.9	0.3			88.3
687	5.4	**2.9**					91.7
790	12.8	0.7	0.4	0.1			86.0
901[a]	5.8	**9.5**	0.8	0.4			83.5
1068	6.0	**2.1**					91.9
1746	4.8	**4.1**	0.3	0.5			90.3
1781	4.6	**1.9**	0.7	0.2	0.5		92.1
1871	5.3	0.5	0.4	0.3			93.5
1875	8.2	**10.1**	0.2	0.3	1.1		80.1
1876	3.1	0.7	0.2	0.7			95.3
1884	7.6	**5.5**	0.3	0.2			96.4
1891	6.3	**3.1**	0.2	1.1			89.3
1896	4.8	1.2	0.3	0.1			93.6
3312	11.5	1.2	0.3	1.4	0.2		85.4
3328	8.6	**3.5**					87.9
3382	3.5	**1.5**	0.5	0.4		0.8	93.3
3425	5.3	**1.8**	1.7	0.6			90.6
3463[b]	4.8	1.3					93.9
3465[a]	8.9	**3.1**	0.4	0.3			87.3
3493	4.8	0.6					94.6
3544	8.4	0.7					90.9
3669	9.5	**3.6**					86.9
3754	9.7	**7.1**					83.2
3825	6.0	**3.0**	0.2	0.1			90.7
3901	9.1	**3.0**					87.9
4050	7.3	**2.0**					90.7
4068	8.5	0.4					91.1

In case of the lead content in the bronze matrix reaching above 1 wt.%, it can be assumed that lead was intentionally added to the bronze melt (Table 1,2 highlighted in bold) [15, 16].

Rivet no. corresponding to Rivet No. in Fig. 3

[a] Bronze cast rivets

[b] Bronze plated head of iron rivet

Table 2 Elemental composition of bronze parts of rivets from Stradonice (SEM/EDS)

Rivet No./wt %	Sn	Pb	Fe	Zn	Ag	Cu
188–76[b]	6.8	0.2	1.2			91.8
864[a]	8.7	**4.2**	0.2	0.2		86.7
959	11.4	**3.5**	0.2			84.9
960–814	4.9	**6.6**				88.5
1052[a]	7.7	**1.4**	0.2	0.1		90.6
1014[a]	4.2	**4.3**	0.3	1.1	0.3	89.8
1023[a]	6.0	**1.6**	0.3	1.2	0.3	90.6
1029	6.3	**2.0**		0.2		91.5
1071[a]	10.1	0.8	0.1			89.0
80.231	4.8	**1.3**	0.2			93.7
561.371	5.0	**3.4**		0.2		91.4
561.372	4.7	0.7	0.4	0.2	1.2	92.8
561.374	7.2	1.1	0.2	0.1		91.4
561.918[a]	7.6	**4.8**	0.4	0.1		87.1
266.455	7.6	**3.3**	0.2	0.1		88.8

In case of the lead content in the bronze matrix reaching above 1 wt.%, it can be assumed that lead was intentionally added to the bronze melt (Table 1,2 highlighted in bold) [15, 16].

Rivet no. corresponding to Rivet No. in Fig. 3

[a] Bronze cast rivets

[b] Bronze plated head of iron rivet

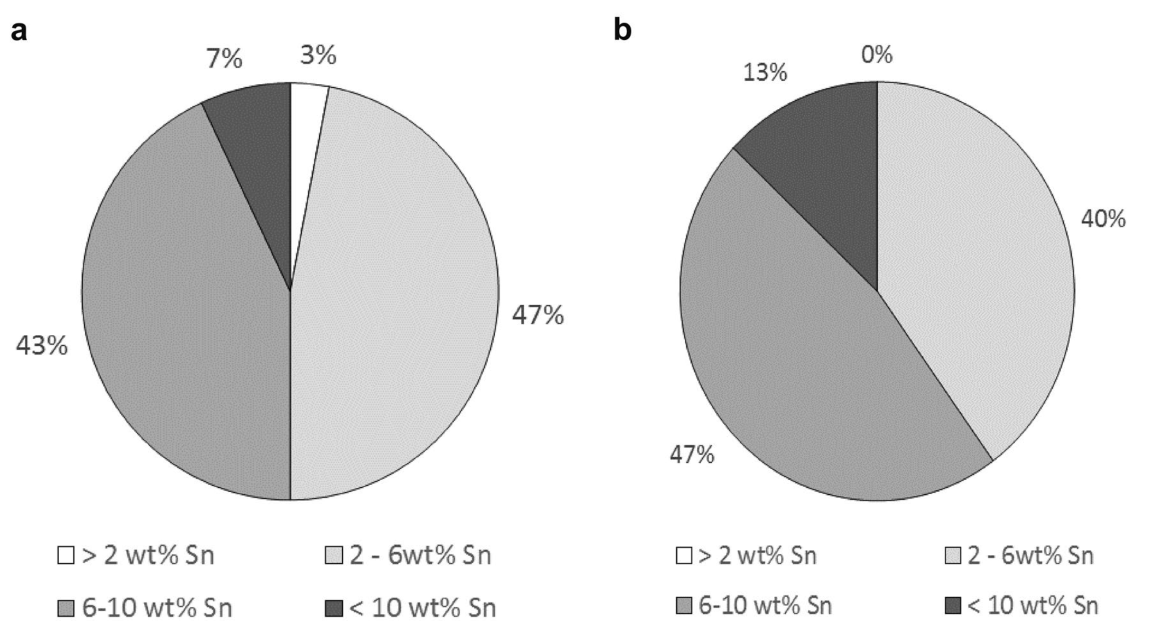

Fig. 14 **a** Sn Content in Bronze Matrix of Rivets from Kolo Hillfort near Týnec nad Labem. **b** Sn Content in Bronze Matrix of Rivets from Stradonice

oxides at higher temperatures. Gaseous As_2O_3, or As_4O_6, already occurs at temperature > 600 °C and Sb_2O_3 melt, or Sb_4O_6, being lighter than the bronze melt and also more volatile, occurs at ca. 700 °C [20, 21], which means that the repeated melting of bronze ingots reduces the concentration of arsenic and antimony in cast objects [15, 22].

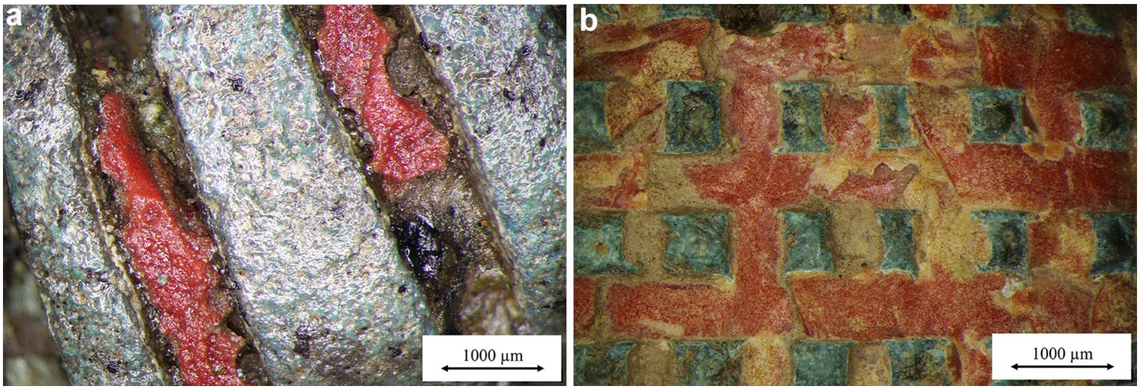

Fig. 15 Remains of Enamel Production. **a** Rivet No. 3754—Kolo Hillfort near Týnec nad Labem; **b** Rivet No. 1052–Stradonice Site. **Rivet No. corresponding to Rivet No. in* Fig. 3

Table 3 Chemical composition of enamel samples analysed by LA-ICP-MS

Rivets No	620	1068	1875	3754	3900	1052	80.231	226.455
Typological types	2	2	2	2	5	6	2	3
Site	Týnec nad Labem					Stradonice		
	Oxides (wt %)							
Na_2O	11.51	9.22	8.88	13.51	7.41	7.65	8.43	8.06
MgO	0.26	0.30	0.30	0.24	0.30	0.41	0.30	0.33
Al_2O_3	1.55	1.61	1.57	1.47	1.32	1.74	0.99	1.74
SiO_2	42.83	42.95	41.03	50.33	41.30	43.95	43.65	43.59
P_2O_5	0.05	0.06	0.05	0.07	0.05	0.05	0.04	0.07
K_2O	0.42	0.55	0.50	0.47	0.38	0.41	0.25	0.56
CaO	3.99	4.66	5.01	2.68	3.76	4.26	2.63	4.08
TiO_2	0.07	0.06	0.06	0.09	0.06	0.08	0.07	0.06
MnO	0.03	0.01	0.01	0.26	0.27	0.02	0.02	0.31
Fe_2O_3	1.43	1.85	1.62	0.62	1.60	1.52	1.33	1.37
Cu_2O	6.45	6.43	1.55	8.87	6.87	8.32	9.84	6.42
PbO	32.74	33.67	40.87	19.73	33.75	35.16	39.46	37.61

Rivet No. corresponding to Rivet No. in Fig. 3. Described Typological Types: 2—Cross-Shaped Decoration, 3—Radial Decoration, 5—Central Circle with Radial Decoration, 6—Grid-like Decoration (according to 3.1 Typological Research)

Chemical composition of enamel

The term enamel designates a glass coating melted onto a metal base. All enamels obtained from the samples examined are in shades of red or red and orange (Fig. 15), well corresponding with relevant data from the literature dealing with objects with enamel dated to the La Tène period [23]. Enamel was particularly found in rivets with iron pins in bronze heads. Regarding the shape of the rivet heads (Fig. 4), 4 types are represented, and the prevailing type of decoration is a cross shaped decoration (Table 3). A notable connection between the type of the head and the composition of enamel was not observed. For instance, all three types of composition (according to the origin of glass, see the text below) were detected in Type 2 decoration (cross-shaped). Other shapes cannot be assessed with respect to a small number of samples.

The elemental composition of the samples analysed is provided in Tables 3 and 4. It is obvious that the enamels have high contents of PbO.

As a flux, mineral soda (so called natron) was used together with sand. In general, sand tends to contain a certain portion of shells serving as a source of calcium, which works as a stabilising agent in glass [3, 24, 25]. The use of natron may be assumed due to low contents of K_2O and MgO up to 1.5 wt.% as noted, for instance, by Sayre and Smith [26], Brill [27], Freestone [25] and also Rolland—Venclová [3]. The content of most

Table 4 Chemical composition of enamel samples analysed by LA-ICP-MS—elements

Rivets No	620	1068	1875	3754	3900	1052	80,231	226,455
Site	Týnec nad Labem Elements (ppm)					Stradonice		
Li	2.42	1.82	2.99	3	2.59	2.83	4.43	2.58
B	60.17	63.27	59.95	64.92	62.29	50.43	187.52	94.83
V	7.88	9.62	7.43	13.29	10.08	9.88	8.81	8.96
Cr	7.51	8.37	6.61	8.87	6.77	12.41	6.65	6.68
Co	25	14	20	140	39.09	7	2	35
Ni	48.59	128.99	122.37	107.27	96.96	41.1	163.45	159.6
Zn	12.14	15.62	16.97	30.9	22.1	20.96	23.26	29.14
As	100.57	59.37	86.94	133.21	107	37.27	157.82	69.92
Rb	4.82	7.32	7.26	5.52	6.94	6.21	3.65	7.28
Sr	213.32	285.41	296.28	164.08	240.51	226.49	89.65	247.75
Y	4.24	4.75	5.03	4.01	3.6	4.62	3.97	3.99
Zr	58.98	45.14	44.75	34.25	38.82	49.78	82.28	35.3
Ag	25.6	5.03	1.81	18.42	7.91	13.38	356.28	4.85
Sn	40.35	14.52	312	405.7	7.98	4.8	9	10.3
Sb	58	66	142	8394	877.65	2090	511	3555
Ba	105.53	119.93	121.47	101.84	132.05	111.6	45.77	138.04
La	3.61	4.29	4.26	3.45	3.52	4.18	4.44	3.91
Ce	5.97	7.57	7.13	6.27	6.6	7.11	8.4	6.68
Nd	3.7	4.47	4.4	3.6	3.64	4.31	4.66	4.02
Hf	1.52	1.16	1.11	0.83	1	1.31	2.08	0.95
Th	0.59	0.8	0.75	0.56	0.73	0.75	1.24	0.77
U	0.47	0.49	0.46	0.5	0.65	0.54	0.48	0.59

Rivet No. corresponding to Rivet No. in Fig. 3

dominant elements found in natron glass is specifically mentioned by [3] as follows: 15–20% Na_2O and ca. 8% CaO. This type of raw soda-lime-silica glass is known to have been imported to La Tène Europe from the Middle East.

If the so-called reduced composition (the recalculation of the values without colourants, decolourants and opacifiers) is used, several samples display lower values of Na_2O and CaO than those just stated above. However, even the cited study on La Tène glass [3] sets, for the glass examined, the range of Na_2O values from 8.5 to 19.3.wt %, i.e., lower values of Na_2O. Similarly, the content of CaO is also listed below 6%, which indicates a certain degree of compositional variability.

Generally, two main contemporary areas producing soda-lime-silica glass can be distinguished – Egypt and the Levant. According to [3], the glass from the area of Egypt is characteristically represented in the finds dating from the period of 250 BC (LT C1) until the transition LTC1b/LTC2 in the early second century BC. In contrast, the glass from the Levant region is usually

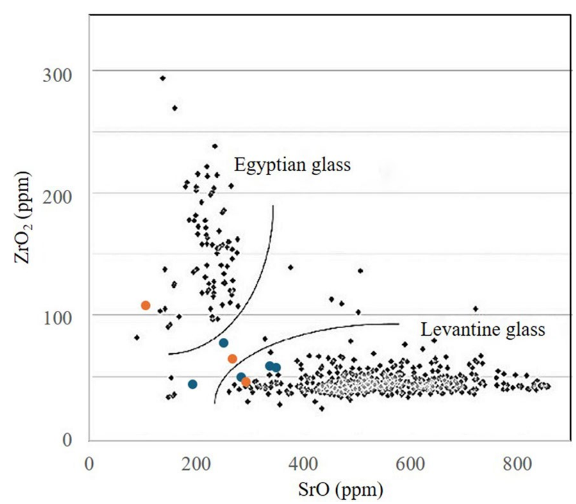

Fig. 16 Scatter Plot of ZrO_2 and SrO Contents in Enamels Compared with La Tène Glasses; Graph Modified according to Study [30]. Blue–Samples from Týnec nad Labem, Orange–Samples from Stradonice

linked to the period between the early second century BC and the late first century BC (LTC2-D period).

The criterion that can be used to further specify primary production workshops of natron glass is namely the content of zircon (Zr) and strontium (Sr). To distinguish the glass of the Egyptian or Levantine origin, the work of Kemp [28] and Shortland [29] lists (besides Zr and Sr), also the contents of Cr, La and Ti. Typically, Egyptian glass has a relatively low ratio of Cr/La and a higher content of Zr (for Mesopotamian glass, it is quite the opposite).

Specific limits for the La Téne glass examined are provided, for instance, by Rolland-Venclová [3; Table 3]. This work specifies the values for Egyptian glass as follows: the content of SrO below 270 ppm, and ZrO_2 levels exceeding 90 ppm. In contrast, the same study states the values of ZrO_2 lower than 60 ppm as being typical of Levantine glass. Using these criteria in our work, only sample 80 231 from Stradonice can be classified as Egyptian glass. However, several of our samples seem to be somewhat "borderline" (e.g., samples 620 and 1052 display the content of ZrO_2 higher than 60 ppm but lower than 90 ppm). In the study [30], Rolland elaborated more on the topic of La Téne glass, once again specifying the composition of Egyptian and Mesopotamian glass (Fig. 15). Based on the graph in Fig. 16, the following groups can be distinguished in our dataset: a) glass of Egyptian origin (80 231/Fig. 3), b) Levantine glass (1068/Fig. 3, 1875/Fig. 3, 3900/Fig. 3 a 226.455/Fig. 3), and c) the combination of both (620/Fig. 3, 1052/Fig. 3, 3754/Fig. 3). With respect to the dating of our samples and the above-mentioned information on the occurrence of glass from Egypt, this type of glass should not be represented in our dataset. Also, as our dataset contains the combination of both glass (Egyptian and Levantine), the recycling of older raw material may be inferred here.

As stated earlier, the enamels in our set display a high content of PbO (often exceeding 30%), and it is worth mentioning that quite similar values are also provided for "Celtic" enamels by [23]. The only exception in our set is rivet 3754 (Fig. 3) containing ca. 20% PbO. However, even such low values have already been published, in particular for the enamels uncovered in the oppidum of Mount Beuvray in France [23] The enamels from this region also show a lower content of Fe_2O_3 (0.4%), and, indeed, a lower value (0.6% Fe_2O_3) was detected in our rivet (No. 3754) too. Another characteristic of the region is the content of MnO being in tens of percent, which also corresponds well with our sample No. 3754.

Additionally, in comparison with common natron glass, virtually all our samples contain atypically high levels of CuO (ca. 8.6%). Based on the contents of PbO and CuO, the enamels from our set can be defined as so called high-copper-high lead glass, sometimes also called a „sealing wax " red variety. This designation comes from the literature focused on red glass in archaeological artefacts [23, 31]. Another group of red glass identified is the so called "low-lead and low-copper", whose colour usually results from the presence of metallic copper [32].

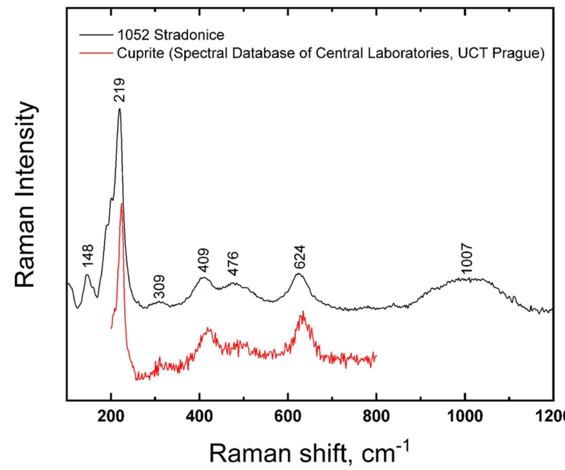

Fig. 17 Raman spectrum of sample enamel from rivet head No. 1052 Compared to card ID: R050374 of spectrum database RRUFF

With respect to enamels, other interesting elements discussed in literature [23] are antimony, iron, and tin. The question remains whether or not these elements are admixtures introduced to enamels in raw materials prevalently based on lead or copper. Our content of tin was found to be generally lower (max. 406 ppm Sn, sample 3754), but the level of Fe_2O_3 reached up to 1.9% (sample 1068). Brun [23] states a hypothesis that iron could have been added to the melt on purpose as a reduction agent. Davis and Freestone [33] attributes higher contents of iron, together with aluminium, to the contamination of enamels by the material of crucibles (however, our work has not identified such a relation in the samples analysed).

Glass coloured with copper

When melting glass containing copper, the equilibrium is reached between the pyrosol of copper atoms and mono- and di-valent ions. Reduction conditions and suitable glass composition (today, namely the presence of Sn) shift the equilibrium towards metal copper. Whereas Cu^{2+} ions colour glass with shades of turquoise or green (depending on glass composition), Cu^{+} ions are colourless. In contrast, red shades are typically caused by copper particles of colloidal dimensions being in the equilibrium with Cu^{+} [34]. Another copper phase that can occur and cause red colouring is cuprite (cuprous oxide/copper(I) oxide/Cu_2O).

Often, particles of cuprite (Cu_2O) are linked to the above-mentioned group of high-copper high-lead glass, while particles of metal copper (Cu°) with dimensions below 1 µm are typically linked to low-lead glass [31]. High contents of PbO positively affect the nucleation velocity of Cu_2O and shift the CuO/Cu_2O equilibrium towards Cu_2O. To create a dendritic structure of Cu_2O, the melt needs to contain not only high contents of lead but also copper. As mentioned before, the enamels investigated in our study meet both criteria well. Moreover, an increased content of PbO in glass improves its meltability (decreases melting temperature) and even lowers viscosity. All these effects were, of course, utilised when applying enamels on objects, because one of the techniques suggested is heat softening of the glass and its subsequent shaping or inlaying into metal voids or recesses [31]. It is also worth mentioning that the content of lead affects even the coefficient of thermal expansion, which is important for the stability of the complex enamel—metal.

The presence of opacifiers, or crystals of red colour could be well observed even under the microscope. To identify them more precisely, Raman spectrometry was applied, clearly revealing the presence of Cu_2O (Fig. 17) with its characteristic peak at 219 cm^{-1} in red/orange regions of the samples.

Positions of peaks at 220, 305, 407 and 620 cm^{-1} for Cu_2O are well described in [32]. The peak position at 476 cm^{-1} could be assigned to the SiO_4 tetrahedral deformation mode of the glass (spectra recorded with green excitation on red glass show a strong intensity increase of the ~500 cm^{-1} assigned to the Si–O bending component) and 1007 cm^{-1} to the Si–O vibrational mode [32, 35]. The spectra of all samples were identical (see Supplementary Material), their representative is shown in this figure. No other phase was determined for enamels. The red colour can also be caused by Cu° particles, however metallic copper is not active enough for Raman spectrometry. The unique presence of a mixture of cuprite with Cu° nanoparticles was observed by TEM [36].

Conclusion

The material survey conducted shows that the rivets from both archaeological sites (Kolo hillfort near Týnec nad Labem and Stradonice) were produced using three different technological procedures. Most of the rivets analysed were made by inserting a forged wrought iron pin into a bronze melt, or by casting rivets from a bronze alloy. In contrast, a small number of rivets from the set examined were found to have been cast from forged wrought iron with subsequent plating of their heads with a bronze plate. The plating of iron rivet heads with a thin bronze plate is rather unique and has not been described in the region of Bohemia for the finds from the Late La Tène Period until now. The bronze parts of the examined rivets from both archaeological locations are made of bronze alloys with a tin content of 2–10 wt % and content of lead from 0.2 to 10.1 wt %. Lead was probably intentionally added to the bronze melt used to produce the majority of the artefacts examined. The presence of impurities of nickel and silver in the bronze alloys of several rivets indicates two different places serving as the source of tetrahedral copper ores used for bronze production. The first site is probably located in the Western Alps, while the second site lies most likely in the Špania Valley or the area around present-day Kremnica in Slovakia in the Western Carpathians. The absence of arsenic and antimony in the bronze alloys examined indicates that they were re-melted several times. The shape of the heads of the rivets coming from the Kolo hillfort near Týnec nad Labem site is mostly semispherical or semispherical with a frame and, in most cases, the heads are decorated with symmetrical cross-shaped decorations or they are not decorated at all. Moreover, the set of rivets from the Stradonice site contains rivets with heads decorated with grid-like and centred circular decorations, whereas these motifs were not identified in the finds from the Kolo hillfort. Since also semi-finished products of similar rivets were found in the Stradonice oppidum, the existence of a contemporary local workshop can be assumed producing rivets with this type of decoration at the time (heads with motifs of centred circles). The analysis of the chemical composition of enamels found on the rivets has revealed that all of them can be described as high-copper-high lead glass. The only exception is an enamel sample with a composition indicating the use of material from a European workshop in the Mount Beuvray area (lower PbO content detected in the sample). The particular sample of the enamel comes from rivet head No. 3750, which was found at the Kolo hillfort site near Týnec nad Labem.

As a result of the extensive research conducted in this study, the data acquired provide the information both on manufacturing technology as well as the material composition of the artefacts. It is also worth mentioning that this work, employing a wide range of imaging and analytical methods, is the first-ever study examining La Tène artefacts of this type coming from Bohemia.

Abbreviations

SEM	Scanning electron microscope
SEM/EDS	Scanning electron microscope with an energy dispersive

	analyser
AAS	Atomic absorption spectrometry
X-ray	Projectional radiography
CT	Computed tomography
RM	Raman spectrometry
LA-ICP-MS	Laser ablation inductively coupled plasma mass spectrometry

Supplementary Information

The online version contains supplementary material available at https://doi.org/10.1186/s40494-024-01338-7.

Additional file 1.

Author contributions

MS (main author) material research of metal parts of rivets primarily using SEM/EDS and AAS with interpretation of results in the archaeological context. ZZC material research of enamel decoration of rivets primarily using SEM/EDS with interpretation of results in the archaeological context. VC archaeological research and typological analysis of rivets with interpretation of results. ZB archaeological research and typological analysis of rivets with interpretation of results. JD CT reconstruction and data visualisation. JZ CT reconstruction and data visualisation. VT CT reconstruction and data visualisation. JK X-ray examination of internal structures in rivets. JM analysis using LA-ICP-MS. JS drawing visualisation of rivets and graphic editing. All the authors have read and approved the final manuscript.

Funding

The research was supported by Czech Science Foundation Grant No. 22-00828S named Enamelled Archaeological Objects—Archaeometry Contribution to the Knowledge of Production Technologies.

Availability of data and materials

The dataset analysed in the study is available from the corresponding author on request.

Declarations

Competing interests

The authors declare that they have no conflict of interest.

Received: 3 January 2024 Accepted: 22 June 2024
Published online: 24 July 2024

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