



MILITARY ID TAG 5668-MXX-1008-1 - ZN PB ALLOY - MODERN TIMES - FRANCE

Artefact name Military ID tag 5668-MXX-1008-1

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Url /artefacts/213/

▼ The object



Fig. 1: German military ID tag from First World War, recto and verso, 2013

▼ Description and visual observation

Description of the artefactFragments from an oval shaped plate with two circular holes at the central upper edge. Information

concerning the soldier were given in the centre of the plate. The plate is covered with sediments.

Dimensions (70 x 50 mm initially): L = 65mm; W = 50mm; T = 1 mm; WT = 6.3g.

Type of artefact Military tag

Origin German army, 94th Infantry Regiment, 1918, Carspach, Alsace, France

Recovering date Recovered in 2011

Chronology category Modern Times

chronology tpq 1915 A.D. ✓

chronology taq

Chronology comment 1915

Burial conditions / environment Soil

Artefact location Pôle d'Archéologie Interdépartemental Rhénan, Sélestat, Alsace

Owner Pôle d'Archéologie Interdépartemental Rhénan, Sélestat, Alsace

Inv. number 5668-MXX-1008-1

Recorded conservation data Not conserved

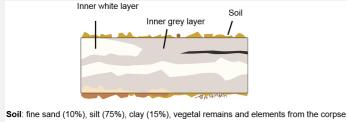
Complementary information

This 1915 model is the oldest standardized model (Directive 594 of the Ministry of War referenced 1085/7.15.B3). Burial conditions (loess sediments, collapsed shelter (Killianstollen) in March 1918 after a French bombing buried the tag at a depth between 3.5 and 6 meters).



Fig. 2: Location of sample,

The schematic representation below gives an overview of the corrosion layers encountered on the military tag from a first visual macroscopic observation.

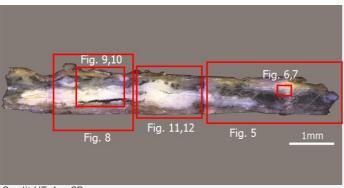


Soli, line sailo (10%), siit (10%), ciay (10%), vegetai remains and elements from the corps (hairs, tissue fibres)

Inner layer grey: translucent and compact, heavily cracked Inner layer white: opaque and powdery heap, heavily cracked Credit HE-Arc CR, M-J.Scholl.

Fig. 3: Stratigraphic representation of the military tag in cross-section by macroscopic observation,

Fig. 4: Micrograph of the cross-section showing the locations of Figures 5-12. Unetched, dark field, 50x,



Credit HE-Arc CR.

Description of sample This sample was cut out of fragment b in Fig. 1. The cross-section shows the entire thickness of the plate (L

= 8 mm, W= 1 mm). The corrosion goes through the whole metal thickness but a metallic core remains

(Fig. 4).

Alloy Zn Pb Alloy

Cold worked (laminated) Technology

Lab number of sample

Sample location HE-Arc CR, Neuchâtel, Neuchâtel

Responsible institution Pôle d'Archéologie Interdépartemental Rhénan, Sélestat, Alsace

Date and aim of sampling 2013, metallography and chemical analyses

Analyses performed:

Metallography (etched with HCl 10 M reagent), XRF, SEM/EDX, FTIR and Raman spectroscopy.

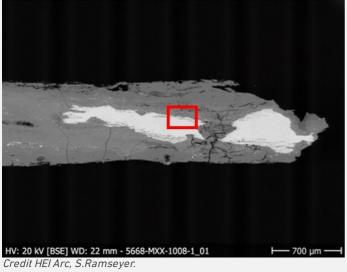
The remaining metal is an almost pure zinc alloy (Table 1) containing 1.8% in weight lead. Lead appears in the metal in the form of small flattened white Pb inclusions (Figs. 5 and 6), confirming the manufacturing technique, namely lamination. The etched metal does not show any specific microstructure (Fig. 7).

Elements	Zn	Pb
mass%	98.2	1.8

Table 1: Chemical composition of the metal. Method of analysis: SEM-EDX, Lab of Electronic Microscopy and Microanalysis, IMA (Néode), HEI Arc.

Fig. 5: SEM image of the cross-section, from Fig. 4 (detail), BSD-mode. Note the presence of Pb inclusions all through the thickness of the heavily cracked corrosion layers,





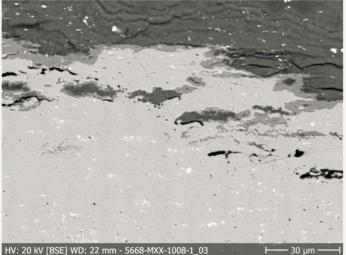
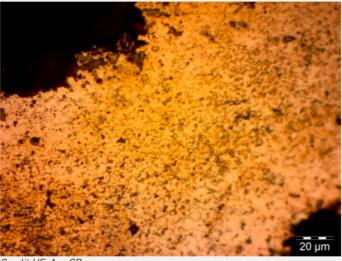


Fig. 6: SEM image of the cross-section, from Fig. 5 (detail), BSD-mode,

Credit HEI Arc, S.Ramseyer.



Credit HE-Arc CR.

Microstructure First metal element Zn

Other metal elements Pb

Fig. 7: Micrograph of the cross-section, etched, bright field, 500x,

The corrosion spreads on the entire thickness of the plate and different forms of corrosion within the same plate may occur (multiform corrosion). Sometimes the metal core still remains, sometimes not.

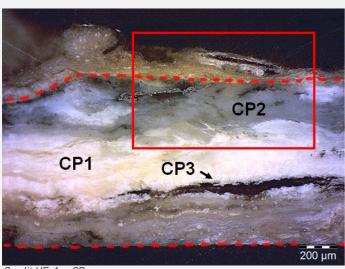
The corrosion structure is multi-layered: several corrosion products overlap. However they are not all continuous layers, since some of them are isolated. Most of the corrosion products layers show structural voids (up to $100 \mu m$ thick) and some cracks inside. Three layers can be distinguished (Fig. 8) which have the same elements but in different proportions (Figs. 9, 10 and table 2):

- <u>Inner grey layer</u> CP2 (up to 1 mm thick) is a translucent, compact layer and constitutes most part of the corrosion products. Corroded metal appears inside this layer as lead inclusions within a black corrosion product (Figs. 11 and 12). Sulphur has also been detected by SEM-EDX inside this layer, near the surface, where the colour turns into grey-orange (zinc sulfide or sulphates but to be confirmed, table 2).
- <u>Inner white layer CP1</u> (up to 0.6 mm thick) is an opaque and powdery heap, occurring in different places inside inner grey layer and sometimes near the surface, as pitting corrosion. The interface between inner layers grey and white is diffuse. Localized aggregates showing a crystalline microstructure of thickness of 50 µm are located against the walls of a structural void, inside the white corrosion product (Fig. 12).
- <u>Inner black layer CP3</u> (up to 0.1 mm) is an opaque and compact layer with a composition similar to inner white layer (Table 2). On top the metal is covered with non-metallic materials (fine sand (10%), silt (75%), clay (15%), vegetal remains) and elements from the corpse (hairs, tissue fibers)). An outer corrosion product has not been identified, but may occur, because zinc combined with sulphur was detected at the surface (Table 2).

The inner grey layer has been identified by FTIR as a zinc carbonate (smithsonite), mixed with other unidentified corrosion products. Raman spectra seems to confirm it (Fig. 13). The exact composition of inner white layer is unknown. Inner white layer shows a bluish fluorescence under UV light and has been identified by FTIR as a mixture of zinc oxides and carbonates, that could be zinc hydroxycarbonates (hydrozincite). Raman spectroscopy shows also a mixture of carbonates and other corrosion products (Fig. 14). The inner black layer is a zinc carbonate as well, identified by FTIR and Raman spectroscopy (Fig. 15) appearing as a vein between layers grey and white (Fig. 8).

Elements	0	Zn	Pb	
Inner grey layer (CP2)	++	+++	+	
Black inclusions		+	+++	
Inner white layer (CP1)	++	+++	+	
Inner black layer (CP3)	++	+++	+	
Inner grey-orange layer	+	++		++
Remnant metal phase		+++	+	

Table 2: Chemical composition of the different corrosion layers from Fig. 11. Method of analysis: SEM-EDX, Lab of Electronic Microscopy and Microanalysis, IMA (Néode) (+++: high concentration, ++ medium concentration, + low concentration, nd: not-detected).



Credit HE-Arc CR.

Fig. 8: Micrograph of the cross-section, from Fig. 4 (detail), unetched, dark field, 50x. View of the inner layers and the limit of the original surface (red line). We can see that the interfaces between the different layers are not well defined: some of the white corrosion product is found inside the inner grey layer. The micrograph of Fig. 9 is marked by a rectangular,

Fig. 9: SEM image of the cross-section from Fig. 8 (detail), BSD-mode. The mapped area (Fig. 10) is marked by a rectangle,



Credit HEI Arc, S.Ramseyer.

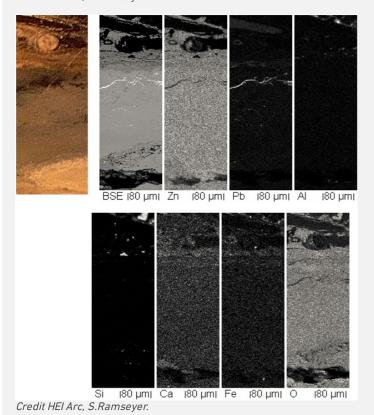
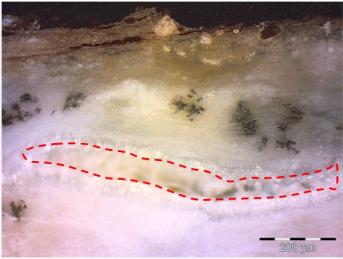


Fig. 10: SEM image of the cross-section from Fig. 9 (detail), SE-mode, and elemental chemical distribution. Method of examination: SEM/EDX, Lab of Electronic Microscopy and microanalysis, IMA (Néode), HEI Arc,



Fig. 11: Micrograph of the cross-section, from Fig. 4 (detail), unetched, dark field, 50x. The micrograph of Fig. 12 is marked by a rectangular,

Fig. 12: Micrograph of the cross-section, from Fig. 9 (detail) unetched, dark field, 100x. Structural void (dotted red line) with aggregates,



Credit HE-Arc CR.

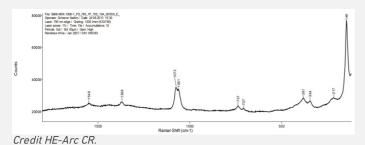


Fig. 13: Raman spectrum of inner grey layer (ZnCO3 – smithsonite?). Settings: laser wavelength 532nm, acquisition time 10s, one accumulation, filter D2 (0.75-0.8mW), hole 500, slit 80, grating 600. Method of analysis: Raman spectroscopy, Art Technological Laboratory, Departement Conservation HKB,

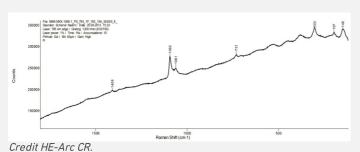


Fig. 14: Raman spectrum of inner white layer (zinc hydroxycarbonate?). Settings: laser wavelength 532nm, acquisition time 10s, one accumulation, filter D2 (0.75-0.8mW), hole 500, slit 80, grating 600. Method of analysis: Raman spectroscopy, Art Technological Laboratory, Departement Conservation HKB,

| \$2,00000 | \$\text{Fig. 1000-MOV-1004-} \cdot \

Fig. 15: Raman spectrum of inner black layer (zinc carbonate?). Settings: laser wavelength 532nm, acquisition time 10s, one accumulation, filter D2 (0.75-0.8mW), hole 500, slit 80, grating 600. Method of analysis: Raman spectroscopy, Art Technological Laboratory, Departement Conservation HKB,

Corrosion form

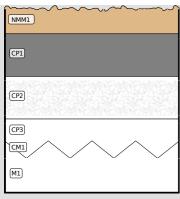
Credit HE-Arc CR.

Multiform - transgranular

Corrosion type

?

Fig. 5: Stratigraphic representation of the object in cross-section using the MiCorr application. This representation can be compared to Fig. 10.



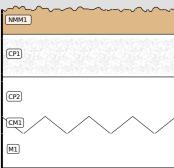
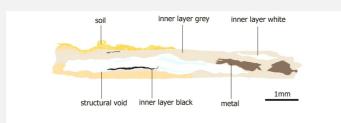


Fig. 6: Stratigraphic representation of the object in cross-section using the MiCorr application. This representation is different from Fig. 10 due to the inversion of CP1 and CP2. Furthermore, CP3 is not represented.

▼ Synthesis of the binocular / cross-section examination of the corrosion structure

Based on the analyses carried out, the schematic representation of the stratigraphy of the military tag has been corrected.



	1
Strate	Composition
Soil (S)	Elements from soil, organic elements
Grey corrosion product (CP1)	Zinc carbonate (smithsonite) + S
White corrosion product (CP2)	Zinc hydroxycarbonate + mixture of CP
Black corrosion product (CP3)	Zinc carbonate
Corroded metal (CM)	
Metal (M)	Zn-Pb

Credit HE-Arc CR, M-J.Scholl.

Fig. 16: Improved stratigraphic representation of the stratigraphy of corrosion layers on the military tag from visual observations and analyses,

▼ Conclusion

The military tag is made of a laminated sheet of zinc-lead alloy. The corrosion has entirely penetrated the objet leaving though some spots of remaining original metal inside the corrosion products. Lead particles are not affected by the corrosion process. The main corrosion products are zinc carbonates (smithsonite) and hydroxycarbonates (hydrozincite) but mixtures of different corrosion products can occur. These corrosion products are intermixed and heavily cracked.

▼ References

References on object and sample

Reference object

1. Scholl, M.-J. (2013) Caractérisation des plaques d'identification militaires en zinc provenant du site de Carspach (Alsace, Haut-Rhin, F). Travail de Bachelor Filière Conservation-restauration, Haute Ecole Arc de Conservation-restauration, Neuchâtel.

Reference sample

2. Scholl, M.-J. (2013) Caractérisation des plaques d'identification militaires en zinc provenant du site de Carspach (Alsace, Haut-Rhin, F). Travail de Bachelor Filière Conservation-restauration, Haute Ecole Arc de Conservation-restauration, Neuchâtel.

References on analytic methods and interpretation

- 3. Moser, Z., et al. (1994) The Pb-Zn (Lead-Zinc) System. In Journal of Phase Equilibria, vol.15, n°6, p.643-644.
- 4. Goodwin, F. E. (2010) "Corrosion of Zinc and its Alloys". In Cottis, R. A. Shreir's corrosion. vol.3 Corrosion and degradation of engineering materials. Elsevier Science, Oxford, 2078–2093. 5. De Zoubov, N. et Pourbaix, M. (1963) « Zinc », In Pourbaix, Marcel. Atlas d'équilibres électrochimiques. Gauthier-Villars, Paris, 406-413.