

17th Century bronze cannon: How can they be magnetic?

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ABSTRACT

During investigations into the cause and type of corrosion on salvaged 17th century cannon, it became apparent that some of the bronze pieces were ferro magnetic. In this paper we investigate the possible cause for this phenomenon.

KEYWORDS

Bronze, Cannon, Dutch East India company, Golden Age, Magnetic, Metallurgy, 17th century.

Introduction

Salvaged bronze cannon from 17th century Dutch vessels were found to be magnetic: a magnet would stick at the surface. This is remarkable since bronze in itself is not magnetic. Magnetism in 17th century Dutch cannon has also been described by Guildmartin (1983). Recently, researchers at the Western Australian museum in Fremantle (Au) have confirmed that some of the bronze cannon from the Batavia also have magnetic properties (Vicky Richards, *pers. comm.*). The phenomenon may therefore be much more widespread.

Possible causes

This phenomenon could have several causes:

1. During casting, the mould for the bore in the cannon is commonly held in place with iron reinforcements. Iron bars from these reinforcements ("crown irons" or "cruzeta") could be the magnetic parts of the cannon (Guilmartin 1983).
2. Magnetic iron minerals like magnetite (Fe₃O₄) or greigite (Fe₃S₄) may have been formed during corrosion when the cannon were on the sea floor.
3. Iron particles or scrap iron could be included in the bronze melt, maybe as a result of the melting and re-use of old bronze cannon.

In the 17th century bronze cannon typically contained 90wt% copper and 10wt% tin. Sometimes small additions of lead to improve casting, or zinc for a more golden appearance were added (Kennard 1986). Normally, no iron was added during the process.

Methods

In order to test these hypotheses, we investigated the composition of six 17th century cannon from the collections of RCE and Bataviawerf in Lelystad (table 1) with hand-held XRF (pXRF), a Niton XL3t equipped with a large area silicon drift detector. Multiple measurements were done on different parts of each cannon on corroded and non-corroded areas.

In addition to the hand-held XRF one metallurgical sample from a trunnion cap (cannon made by Ouwerogge, nr RCE DW 2.1-002, 4200lb) was taken with a hollow diamond drill (0.8cm), cooled with cutting oil. The magnetic sample was then cast in epoxy resin and carefully cut with a fine jeweller's saw. After that, both sides were polished with SiC paper with a final grain of 4000 and subsequently polished with a 1µm Al suspension.

Both cut sides were investigated under high vacuum with a JEOL JSM 5910 LV SEM equipped with an Noran EDX system.

Table 1. Investigated cannon. Additional information about the AvdP and CO 4200lb cannon in Vos 2009 and 2010.

Maker	Year	Weight	Origin	Magnetic?
Arent van der Put (AvdP)	1623	1638 kg	S. North Sea c. 1988	+
Cornelis Ouwerogge (CO)	1631	4200 lbs	Euro-Maasgeul 1996	+
Cornelis Ouwerogge (CO)	1631	4275 lbs	Euro-Maasgeul 2008	+
Everhardus Splinter (ES)	1632	3480 lbs	Eurogeul	+/-
Wouter Wegewaert (WW)	1652	1875 lbs	Eurogeul	-
Coenraet Wegewaert (CW)	1654	2200 kg	Euro-Maasgeul 1999	-

Results

In table 2 the results of the pXRF measurements from the non-corroded, mechanically cleaned parts of the cannon are summarized. From table 2 it is clear that the magnetic cannon contain significantly more iron than the non-magnetic cannon. Although the amount of samples is very limited it is remarkable that the cannon from before 1632 are magnetic and the younger cannon are not. The composition of the cannon appeared to vary between the different makers: some have tin contents that are much lower (less than half) than the 10% that was prescribed. Magnetic cannon have systematically higher iron contents than non-magnetic cannon. Moreover, the iron content varies between the makers.

Table 2. pXRF major element results. * indicates cannon also analysed with SEM.

Maker	AvdP	CO 4200 lb*	CO 4275 lb	ES	WW	CW
Year	1623	1631	1631	1632	1652	1654
Magnetic?	+	+	+	-	-	-
Cu	82	78	89	92	85	84
Sn	9.7	3.6	3.3	5.1	8.0	8.4
Fe	2.1	6.6	3.4	0.5	0.3	0.4
Pb	0.7	1.9	0.9	0.8	2.3	1.7
Zn	1.7	0.5	0.4	0.1	1.4	1.2
Sb	0.2	0.5	0.4	0.4	0.3	0.7
Si	2.2	5.8	1.8	ND?	1.6	3.1

Microstructure

During the SEM investigation of the samples no deformation caused by sampling was observed, nor differentiation in microstructure between the outside and inside of the sampled cylinder (Fig. 1). This was not to be expected because the sample was taken in the middle of the trunnion cap. Dendrites or compositional differences caused by diffusion were also absent. As a cannon is a fairly large piece of bronze to cast, cooling rates are low, explaining the absence of dendrites and other phenomena that could be attributed to rapid cooling.

From fig. 1 it is clear that many impurities are present in the bronze. The inclusions can be categorized into three types. Type 1 inclusions are star shaped without a substructure, approximately between 2 µm and 5µm in diameter. Type 2 inclusions are spherical (fig. 2), often with substructure, and about 20µm in diameter. Finally, type 3 inclusions have low sphericity but are well rounded, mostly without a substructure and about 50µm in diameter. The morphology of the less sphere shaped and spherical inclusions looks fairly similar; however, they have a different composition. The inclusions are not deformed and do not form texture-like patterns, indicating that after casting the metal was not

further worked. The white areas in the BSE image are most probably edge charging artefacts.

Composition as measured with SEM-EDX

The results of the pXRF analyses are confirmed by the analyses of the matrix with SEM-EDX. The copper content is higher (93 versus 78wt%) but the tin content is quite similar. One of reasons for the deviation in the copper content is that the inclusions are also included in the pXRF measurements and not in the SEM-EDX analyses. The iron content measured with pXRF is however significantly higher than the values from the SEM matrix measurements, indicating that iron is mostly present in inclusions and not in the matrix of the cannon.

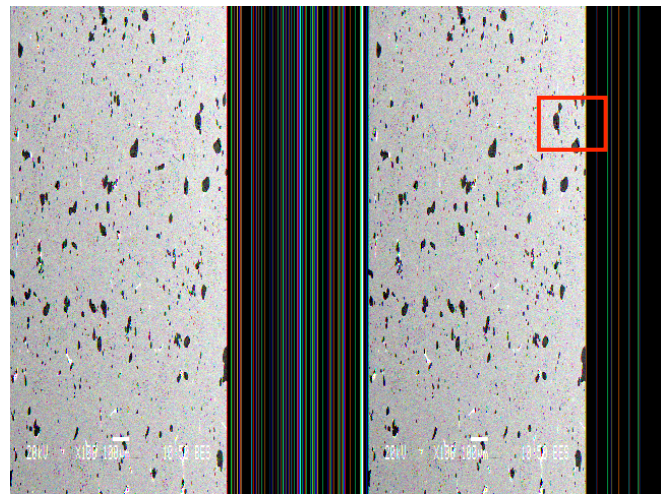


Fig. 1. SEM BSE image of a magnetic sample. The dark phases have a lower density than the lighter bronze matrix. The red insert is the area of fig. 2.

The elemental composition of the various inclusions can be found in table 3. On the basis of their composition, again three groups of inclusions can be distinguished. These are pure metallic iron inclusions; copper-iron-sulphur inclusions, with a stoichiometric ratio of bornite (Cu_5FeS_4) and an iron-zinc sulphide. These three groups do not directly seem to correspond with the morphological types. The star-shaped particles were too small to analyse. Lead and antimony were not detected with SEM. This is due to the higher detection limits for SEM-EDX (0.5wt% in general) than pXRF (0.01-0.05wt%) for these elements.

Discussion

Origin of iron particles

Before the industrial age copper artefacts and their alloys, always contained up to ~0.3% iron (Cooke and Aschenbrenner 1975, Craddock and Meeks 1987). Three components could be responsible for the addition of iron towards the finalized copper product. These are the ore, added flux and fuel.

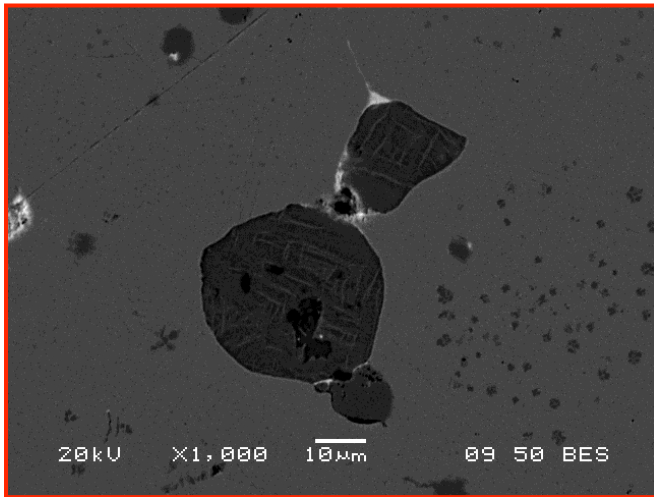


Fig. 2. SEM-BSE image of a spherical inclusion. The dark phase has a lower density than the lighter bronze matrix. Note the substructure in the spherical structure.

Table 3. SEM analyses results L.sph means low sphericity.

Shape	Cu (wt%)	Sn (wt%)	Fe (wt%)	S (wt%)	Zn (wt%)
Matrix	93.3	3.3	2.5	ND	ND
Matrix	94.5	3.3	1.6	ND	ND
Spherical	63	<DL	12.4	24.6	ND
Spherical	67.5	0.8	25.8	5.7	ND
Linear	53.6	<DL	19	27.4	ND
L. sph.	57.8	<DL	16.7	25.5	ND
Spherical	59.6	<DL	14.5	25.9	ND
L. sph.	60.7	<DL	14.6	24.7	ND
L. sph.	71	<DL	6.6	22.4	ND
Point	81.7	3.7	14.5	<DL	ND
L. sph.	<DL	ND	100	ND	ND
L. sph.	<DL	ND	100	ND	ND
L. sph.	<DL	ND	100	ND	ND
Spherical	7.1	ND	92.9	ND	ND
Spherical	8.2	ND	91.8	ND	ND
Spherical	<DL	ND	23.4	34.1	42.6
L. sph.	<DL	ND	24.1	34.5	41.5
L. sph.	<DL	ND	24.1	33.7	42.3
Spherical	10.2	ND	21.9	31.6	36.3
Spherical	12.3	ND	21.7	31.3	34.6

In sulphidic copper ore, as is most probably the case here, iron is, in general, more abundant than copper because the main ore minerals often contain iron, such as chalcopyrite (CuFeS_2), that are often associated with pyrite (FeS_2) (Ayres *et al.* 2002). Silicon dioxide (sand) is sometimes used to remove iron from the melt into the slag and thus refine the

copper. During this process, reducing conditions can develop as a result of the addition of an excess of charcoal as fuel and a high-volume air blast. In such a case iron oxides can be reduced to metallic iron. Also during roasting, metal sulphides oxidize and iron oxides form. During the separation stage these oxides may become reduced again and metallic iron particles may form, depending on the temperature of the process. During the matte forming process (conversion of chalcopyrite into a sulphidic mixture of Cu, S, and Fe), copper sulphur iron globules may form; these remain soluble due to their low melting point, while cooling the matte (Ryndina *et al.* 1999). In addition primary sulphides may survive the smelting process and be preserved in the final product. Furthermore, magnetite (Fe_3O_4) is also commonly found in prehistoric copper ingots (Hauptmann *et al.* 2002). In the case that the copper ore also contained associated metals such as zinc and lead, these metals can also remain in the final product. During the early 17th century metal refinement was not at the level that impurities at these levels could be prevented (Tylecote 1976, 71). Zinc and lead were therefore probably also introduced into the cannon by the copper ore.

At room temperature the solubility of iron in copper is less than 1% and the remaining part will precipitate (Campbell and Clark 1974). In copper with more than 5wt% iron, the iron will be concentrated in star-shaped ferritic-dendrites. Ferritic iron can easily be magnetised. Therefore, the iron in the cannon is most likely ferritic iron.

It is not very likely that scrap iron or iron parts – like *cuizetta* – used in the casting process are responsible for the high iron content. As mentioned before, the solid solubility of iron in a copper matrix is very low and the melting point of iron is far above that of the bronze melt. Furthermore, the iron would be largely removed during the different refinement processes. Again, this confirms the hypothesis that a not very high-grade copper was used for the manufacture of the cannon.

The results of the metallurgical investigations indicate that the source of iron, zinc and lead, is the copper ore used. Unfortunately, the provenance of the ore is not known. However, in the early 17th century, Sweden had a monopoly on European copper (Ayres *et al.* 2002). The largest operating copper mine at the time was the copper sulphide deposit in Falun, Sweden, at Kopparberg (Tylecote 1976, 94). It is estimated that about 90% of the copper in Europe came from Falun in the early 17th century (Ayres *et al.* 2002). It is therefore most likely that the copper used for the cannon came from this deposit. Remarkably, until 1620-1625, the product exported from Falun was so-called black copper, a non-refined copper with about 90% copper (Ayres *et al.* 2002). After 1620-1625 the copper was refined with charcoal and oxidised with air blasting resulting in copper with a purity of 97-99.7% (Tylecote 1976). Interestingly, the black copper also contained significant amounts of impurities, mainly iron, zinc, lead and sulphur (Ayres *et al.* 2002, ANNEX1). These are the same impurities as found in the investigated cannon. The main copper mineral at Falun was chalcopyrite. The deposit had two different types of ore. One part was a mix of pyrite, chalcopyrite and other metal sulphides, as lead and zinc minerals. The other part was a

mixture of quartzite and chalcopyrite (Ayres *et al.* 2002). It is therefore possible that the silicon content measured with pXRF is the result of quartzite still present in the black copper used for the cannon.

The consequences of having magnetic cannon on board an early 17th vessel could be large. The magnetic field of 10 or more magnetic cannon on a wooden ship could easily affect the compass readings if not compensated for. This may have been an additional factor for the wreckage of the Batavia (1629), which had several magnetic cannons, and is thought to have been stranded due to bad navigation.

Conclusions

Magnetism in the investigated bronze cannon is caused by pure iron inclusions up to 50µm in diameter. This iron was most probably introduced during the smelting process of the copper. The copper was most likely produced in Falun, Sweden, the largest copper producer in the early 17th century. The poor quality of the copper in the cannon can be explained by the use of black copper that only had a 90% grade.

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