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Summary

Non-destructive X-ray fluorescence analysis of copper alloy waste from this late Saxon to post-medieval site indicated that a range of different alloy types were being used. Mould fragments for casting a large artefact were found associated with a 'bell pit'. Analysis of a copper alloy deposit on one piece of mould from this context showed that it was heavily-leaded bronze containing antimony, a composition unlikely to be used in bell casting. The information is additional to that contained in AML Report 111/93.

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Analysis of non-ferrous metalworking waste from Castle Mall, Norwich, Norfolk

Catherine Mortimer

Excavations in 1989-1991 at the Castle Mall, Norwich revealed extensive deposits of metalworking waste, both ferrous and non-ferrous. An assessment of the potential for technological analysis was carried out (Bayley 1993). This showed that the bulk of the 130kg of ironworking debris was from 10th to 11th century contexts. Of the 12kg of non-ferrous metalworking debris recovered, only small amounts were found in late Saxon contexts, but this included some crucible fragments. Most of the material was identified as fired clay, mould debris and copper alloy waste, associated with a 'bell-founding pit' (context group 1/67) and a 'metalworking pit' (1/68) which overlay it, both of which have been dated to the 14th-15th century. The assessment suggested that analysis of the copper alloy waste would identify the types of alloys being worked at the site, and hence the types of artefact which could have been produced.

Material selection. 4.7kg of copper alloy waste was submitted for examination and analysis; from this material, 27 samples were analysed, including several from each of the most interesting context groups. The material analysed consisted of copper alloy waste, in the form of spillages (dribbles and dross), and a selection of the crucible and mould fragments. Only crucibles with distinctive copper-alloy metal specks or lumps were analysed in this study, because surface X-ray fluorescence (XRF) analysis of those crucibles which only have vitrification are likely to give a misleading impression of the alloys melted in them. For instance, some elements are preferentially absorbed into the crucible surface whilst others are not (*cf* Bayley *et al* 1991, 397). The analysis of moulds poses much the same problem, but an attempt was made to investigate the metals, if any, present on the surfaces of the mould.

The majority of non-ferrous metalworking evidence investigated came from the medieval (14th-15th century) metalworking deposits in area 1 – context groups 1/67 and 1/68, together with contemporary material from 1/71 and 1/72, which was also thought to be connected with non-ferrous metalworking activities. Material from context 10857 included some fragments of clay mould from casting large copper-alloy artefacts. Smaller quantities of material were available from context groups 8/5, 8/6, 8/7, 8/8 and 8/19 in area 8, further along the Castle Fee Ditch. These are late Saxon/early post-Conquest and the artefacts examined mainly come from post holes and pits. 15th-16th century contexts in areas 5 and 9 (area 5 being inside the Barbican Ditch) also provided a small proportion of the material analysed, including the two stone moulds, found in the top fills of a well (context 50321). Post-medieval crucible fragments from area 1 (context 10009, sf 5006) were also submitted for investigation.

Method. The settings used were 35kV, 100 μA, 2mm diameter collimator (oval sample spot *c.*5mm x 8mm) and 50 seconds counting time. These standard settings represent a compromise between various requirements; for example, it was necessary that all relevant elements were detectable in a single analysis, that a relatively large area of the sample should be sampled and that each analysis should be representative but not too time-consuming. Analysis was carried out on samples without any surface cleaning or preparation. The results were recorded in the form of net integrals for X-ray peaks relating to four elements (Cu, Zn, Pb and Sn). The following peaks were used for analysis; Fe Kα, Cu Kα, Zn Kβ, Pb Lα, Sn Kα. The absence of arsenic, gold, silver and antimony was confirmed in each case by looking at the spectra in the areas of the following peaks; As Kβ, Au Lα and Lβ, Ag Kα and Kβ, Sb Kα and Kβ.

Alloy types were defined by the presence or absence of zinc, tin and lead, at particular levels. An alloy was said to be leaded if the (lead Lα peak area)/(copper Kα peak area) value was more than 0.01, to contain significant tin if the (tin Kα peak area)/(copper Kα peak area) value was more than 0.01 and to contain significant zinc if (zinc Kβ peak area)/(copper Kα peak area) value was more than 0.002. This method reflects the relative efficiency of exciting the X-ray peaks for each element (*eg* lead is much more easily detected than zinc), using data from a copper alloy standard containing 5% lead, 5% tin and 5% zinc. This technique is obviously a very approximate manner of defining alloy types. More accurate analyses would merit a more careful consideration of alloy type definitions. The results of this study are recorded in Table 1.

Analysis of the crucibles was recorded by noting absence or presence of elements, and relatively strengths of signal, where possible (Table 2).

Analysis of copper alloy spillages and crucibles. Three of the copper alloy spillages found in late Saxon/early post-Conquest layers were analysed and shown to be leaded bronze and leaded copper alloys. Analysis of three crucible fragments from contexts dating to this period confirmed that they were also used for melting copper alloys. The precise alloy type cannot be determined, but high levels of zinc were discovered indicating a zinc-containing alloys (*eg* brass or quaternary alloy).

For the 14th-15th century period, twelve pieces of copper alloy waste were selected from the 'bell founding pit', contexts 10911 and 11005, and the 'metalworking pit', context 10857. Although the figures are difficult to interpret, the XRF analyses of these samples seem to show a variety of different alloy types. Most of the pieces analysed from the bell pit contexts (10911 and 11005) are bronzes or leaded bronzes. The detection of arsenic and antimony on one sample from the bell pit ('d' from context 10911) might indicate the use of a high-impurity copper alloy, such as those recently discussed by Blades (1995); this sample was also noted to be more heavily-leaded than the other pieces from this context group. Three samples from context 10857 - the metalworking pit - are quaternary alloys (Cu-Pb-Sn-Zn) and the other two are a leaded bronze and an unidentified type of copper alloy (small amounts of both copper and lead were found in this example). Four pieces of copper spillage from context groups 1/71 and 1/72 (which are also linked to this phase of metalworking) comprised three leaded bronzes and a quaternary alloy.

The medieval non-ferrous metalworking at the site therefore utilised a range of different alloy types, which could have been used for casting different types of artefacts. For example, bells are normally made with high-tin bronzes and they cannot be made satisfactorily using heavily leaded bronze or quaternary alloys. However it is known that lightly-leaded bronzes were used for bell founding (up to 4.5% Pb, Tylecote 1986, 39), although the medieval sources such as Theophilus (Hawthorne and Smith 1963) do not specifically refer to lead being added. It is difficult to suggest what sorts of lead levels might originally have been in the spillages as they are now heavily corroded, but experience in interpreting surface XRF spectra suggests that they are unlikely to be more than a few percent lead in most of the pieces from the bell pit. It is less likely that the high-impurity alloy would have been used to cast bells; most objects made of this type of alloy are domestic vessels such as cauldrons.

The variety of alloys found at the site would seem to suggest a variety of different artefacts were being cast. Although bells could have been cast using the lightly-leaded bronze found in the 'bell pit', a variety of other large or small cast artefact types could also be made. Similarly the quaternary alloys and the high-impurity alloy would also be suitable for large or small cast artefact types.

Post-medieval crucible fragments were analysed (sf 5006) and shown to have been used to melt a zinc-rich copper alloy, possibly a brass or a quaternary alloy. These have thick (more than 10mm), straight-sided walls, similar to late- and post-medieval forms seen elsewhere (*eg* Bayley 1992, Fig 5). The crucible fragments from earlier periods are too small to indicate their complete form but clearly have thinner walls.

Moulds. About 1.5kg of mould fragments from context 10857 were examined; other material from the context is fired clay but could not be clearly identified as being concerned with non-ferrous metalworking. Included amongst the mould material, there are a few pieces with copper alloy attached to it, as well as pieces of copper alloy waste, whose analyses were considered with the other copper alloy waste (above). Copper alloy attached to one mould fragment from the context was found to be a heavily-leaded bronze containing antimony. This composition suggests that the mould is unlikely to have been used for casting bells.

The 'mould' material submitted from contexts 11021 and 11026 could not convincingly be reconstructed into a bell mould. In fact, most of it was very lightly-fired, if at all, and showed no evidence for having been connected with high-temperature metalworking. None of it was heavily reduced-fired. More useful details about material from these contexts should be recoverable from the site records.

A strong lead signal was recorded from the surface of the lithographic stone mould SF7120 (context 50321), suggesting that the mould was used to cast a lead-containing artefact. Stone moulds were often used for casting low-melting temperature alloys, especially lead- and tin-rich alloys, *eg* pewter, but the lead signal could also have originated from a lead-containing copper alloy. A much less clear picture emerged from the other stone mould, SF7119, from the same context, with only a tiny amount of copper being detected. The best moulds are designed not to allow the metals to 'wet' the surfaces, so it is not surprising that only low levels of metals are found on them.

Other material examined

The whet stone SF5922 from context 90401 has a pink, mercury-rich pigment on the broken surfaces, indicating that the stone had been reused for pigment preparation. The pigment is probably cinnabar or vermillion, the natural or artificial mercury sulphides (HgS). Further analysis (by X-ray diffraction) could be carried out, if this was necessary to determine the exact composition. Mercury-containing artefacts should be handled as little as possible, as mercury is toxic. The whetstone has been re-packaged and labelled, although a further health and safety assessment should be made for long term storage purposes.

14kg of material from contexts 50295 and 50284 were submitted but these are entirely unconnected with non-ferrous metalworking; they are ironworking slag, probably smithing slag.

Conclusions

Analysis of the copper alloy spillages, crucible and mould debris from the site shows that the alloys cast at all periods were mostly bronzes with low levels of zinc. A few quaternary alloys were also found and the material found in the bell pit included a heavily-leaded high-impurity copper alloy. Convincing evidence for bell founding was not found, as most of the alloys are more likely to have been used for other purposes and the mould forms were not diagnostic.

References

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Table 1: XRF analyses on non-ferrous material from Castle Mall

Context	Group	Date	Cont. type	SF no	Type	Alloy	Other	comments
10637	1/71	14th-15th	layers rel. to metalworking?		CA spill	quarternary		
10801	1/72	14th-15th	layers rel. to metalworking?		CA spill	leaded bronze		
10801	1/72	14th-15th	layers rel. to metalworking?		CA spill	leaded bronze		
10823	1/72	14th-15th	layers rel. to metalworking?		CA spill	leaded bronze		
10857	1/68	14th-15th	metalworking pit		CA waste a	quarternary		
10857	1/68	14th-15th	metalworking pit		CA waste b	leaded bronze		
10857	1/68	14th-15th	metalworking pit		CA waste c	quarternary		
10857	1/68	14th-15th	metalworking pit	1016	CA waste d	copper alloy		
10857	1/68	14th-15th	metalworking pit		CA waste e	quarternary	Sb? Ag? As	associated with moulds
10911	1/67	14th-15th	bell pit		CA waste a	leaded bronze		SRS/191
10911	1/67	14th-15th	bell pit		CA waste b	leaded bronze		SRS/191
10911	1/67	14th-15th	bell pit		CA waste c	bronze		SRS/191
10911	1/67	14th-15th	bell pit		CA waste d	leaded bronze	As, Sb	
10926	1/162	US	pit fill		?crucible with CA	leaded bronze		
10966	1/140	<15th ?<12th	post hole		CA spill	leaded bronze		
11005	1/67	14th-15th	bell pit	5360	CA waste a	bronze		other contexts incl. fired clay
11005	1/67	14th-15th	bell pit	5360	CA waste b	copper alloy		
11005	1/67	14th-15th	bell pit	5360	CA waste c	bronze		
50308	5/23	13th-15th	well fill		CA spill ?miscast	leaded copper		
80208	8/19	c.1090-1120	bailey rampart	1067	CA spill ?object	leaded bronze		
80471	8/8	c.1068-1090	destruction/accumulation		CA spill and FAS	leaded copper		
80762	8/5	c.960-1068	post holes	5923	CA droplet	leaded copper		
90251	9/76	modern	pit fill		CA and VFL	leaded bronze		
90646	9/55	?>15th	quarries		CA spill	bronze		
90683	9/82	15th-16th	refuse pits, quarry backfill		CA spill	leaded bronze		
90716	9/82	15th-16th	refuse pits, quarry backfill		CA spill	leaded bronze		
90922	9/82	15th-16th	refuse pits, quarry backfill		CA spill	leaded copper		

CA = copper alloy, FAS = fuel ash slag, VFL = vitrified furnace lining, US = unstratified, As = arsenic, Sb = antimony

Table 2: XRF analyses on crucible, mould and fired clay from Castle Mall

Context	Group	Date	Context type	SF no	Type	Fe	Cu	Zn	Pb	Sn	comments
10009	1/99		well fill (10012)	5006	crucible		xx	xx	xx	xx	post-med form
10009	1/99		well fill (10012)	5066	crucible		xx	xx	xx	xx	post-med form
10857	1/68	14th-15th	metalworking pit		mould	xx	xxx		xxx	xxx	Sb detected
11021	1/67	14th-15th	bell pit		fired clay						no non-ferrous detected
11026	1/67	14th-15th	bell pit		fired clay						no non-ferrous detected
50321	5/24	l15th-e16th	well fill	7119	Stone mould	xxx	tr				
50321	5/24	l15th-e16th	well fill	7120	Stone mould	xxx	tr		xxx	?	
80010	8/21	12th-14th	pits		fired clay		xx		xx	xx	tiny trace of CA
80613	8/6	*c.*960-1068	pitting		crucible?		tr	xxx			heavily vitrified outside
80613	8/6	*c.*960-1068	pitting		crucible?	xx	tr				
80679	8/7	*c.*960-1068	post holes		crucible		tr	xxx			overfired, analysed outside
80674	8/8		external dump/accumul.		FC ?crucible		tr				outside has ?tool marks

number of 'x's denotes strength of signal. tr = trace. ? = possible. CA = copper alloy