The use of antimony bronze in the Koban culture
A W G Pike, M R Cowell and J E Curtis

Abstract

As part of a program of analyses of Caucasian metalwork in the British Museum, a group of five Late Bronze Age-Early Iron Age Koban ornamental copper-alloy objects were analysed using inductively coupled plasma optical emission spectrometry. They were found to contain high levels of antimony, but had relatively low arsenic, nickel and silver contents. This differs from some other occurrences of antimony bronze which are highly polymetallic in character and are believed to have been obtained from secondary enriched fahlerz. It is concluded therefore that Koban antimony bronze was made either from the co-smelting of relatively pure antimony and copper ores, or from the addition to copper of metallic antimony.

Introduction

The Koban culture, named after the well-known site in Northern Ossetia, developed out of the existing Late Bronze Age culture of the Central Caucasus in the late 2nd millennium with the initial stage of cultural development dating to the 12th century BC (see Fig 1). The culture is best known for its outstanding bronzes, primarily from cemetery sites. Graves were richly endowed with weapons such as daggers, axes and maces together with horse-bits, cheek-pieces and costume elements such as pendants, fibulae, bracelets, beads etc.

Most of the Koban material in the British Museum was presented by Prince Noruz Orouzbekov in 1913, although subsequent acquisitions have augmented the collection. It currently consists of some 75 Koban objects, including rattles, zoomorphic, anthropomorphic and cross-shaped pendants, beads, pins and weapons such as axes. A full catalogue of these and the other Caucasian objects in the collection is in preparation (Curtis and Kruszynski, forthcoming). As part of this catalogue, a qualitative X-ray fluorescence (XRF) survey of all the Museum’s Caucasian metalwork was undertaken, along with quantitative inductively coupled plasma atomic emission spectrometry (ICP-AES) analyses of selected objects.

The complete data will be published in the catalogue. The survey identified several Koban objects of metallurgical interest with high antimony contents, in particular five pendants, which are presented here.

Copper-Antimony alloys

The alloying of copper with antimony increases its hardness although, according to Charles (1980), with antimony contents above a few percent it becomes brittle, to the extent that it cracks on working. It is therefore essentially a casting alloy. The phase diagram of the Cu-Sb system (Smithells 1967, 479) shows that antimony is a useful addition for casting because it rapidly lowers the liquidus temperature of the alloy with a maximum solubility of 10.9% and a eutectic temperature of 645°C. It also increases its fluidity and expands slightly on cooling, thus filling intricate details in moulds (Halse 1925, 20). Perhaps one of the most obvious and desirable properties of copper-antimony alloys, especially for antimony contents above 10%, is their colour. Experimental preparation of copper-antimony alloys has shown that with antimony contents of about 10% a golden colour is obtained, with a silver colour at about 20% antimony (P Maclean, pers comm).

Fig 1: Map showing the site of Koban on the north slopes of the Caucasus mountain range.
The brittleness of high antimony alloys might have limited their application by ancient metalworkers unless the alloy was in fact being exploited for its other useful properties. For example, the high antimony content (up to 18% in a complex Cu-As-Sb-Ni alloy) of some of the objects in the hoard found at Nahal Mishmar, Israel, would have given the metal a silver/grey appearance, and was no doubt exploited for its colour (Northover et al 1992) rather than any mechanical properties. As noted above, the antimony would also impart useful casting properties, and may contribute corrosion resistant properties to the alloy (Maclean 1993, 14). These alloys were clearly chosen because they exploit the properties of high antimony complex alloys and the antimony should not be considered as an adventitious impurity. Thus, antimony copper was a deliberate alloy in the past, and needs to be placed within the prehistory of metallurgy rather than mentioned in passing as an accidental curiosity.

Nevertheless, the occurrence of antimony as an alloy in copper is relatively rare, although one of the few areas in which it is found with any frequency is the Caucasus. Other notable occurrences come from Velem St Vid, Hungary (Davies 1935), Hasanlu, northwest Iran (Maclean et al 1992), central Europe and the Nahal Mishmar hoard (see above). Early occurrences of antimony bronze in the Caucasus date to the 3rd millennium BC (Early to Middle Bronze Age) in Transcaucasia, although these are usually complex copper-arsenic-antimony alloys (Chemykh 1992, 101ff) and were probably produced from smelting fahl ores. However, Selimkhanov (1975) gives analyses of metallic antimony objects, one of which dates from the end of the 3rd millennium BC. Although these objects are small and may be of native antimony (Tylecote 1987, 144) suggests that native antimony occurs in the Caucasus), it is unlikely that the native metal was a major source of antimony for the alloying of copper. Metallic antimony may have been produced by smelting antimony ores. By the 17th century BC there is evidence that the antimony ore deposits of the Gornaya Racha ridge were being mined (Chemykh 1992, 113) and both the large-scale mining of antimony minerals and the production of antimony bronze are evident from the beginning of the Late Bronze Age (mid 2nd millennium).

The objects reported here are two bird-shaped pendants and three Maltese cross pendants (Fig 2). Zoomorphic pendants such as these, incorporating characteristics of birds and various animals particularly dogs, are especially diagnostic of the Koban culture. In the large cemeteries, thousands have been found. Tekhov (1977) associates them with the bird cult practised by the Central Caucasian tribes of the Late Bronze Age although their religious importance is difficult to assess. The Maltese cross pendants are commonly found in graves in the Caucasus, many were found, for example, in the female inhumations at Tli (Tekhov 1977, 166-7), where they may have been part of female costume. They are also known from the Koban necropolis.

This paper looks at the composition of these antimony alloys, in comparison to other known analyses of copper-antimony objects, and comments on the production of the alloys. In particular the degree of control in the manufacturing process is discussed: whether they were made simply by the careful selection of a poly-metallic ore or by co-smelting of a mixture of minerals, or even by the addition of metallic antimony.

Analysis

A qualitative survey of all the metal objects in the collection was undertaken using non-destructive X-ray fluorescence. These results showed that various alloys were used in the Koban artefacts, including tin-bronze, arsenical copper and antimony bronze. The full details will be presented elsewhere, but five objects which showed particularly high antimony contents were drilled and analysed using ICP-AES.

A small sample was removed (c10-20mg) from each object using an electric hand drill with 0.6-0.8mm high speed steel bits. The drillings from any corrosion/patina and from the first 0.5mm of surface metal were discarded to avoid problems with surface enrichment and contamination. The drillings were weighed and then dissolved in aqua regia, heating gently on a hot plate. The
solution was then diluted with distilled water to 20ml (Hughes et al 1976).

The analyses were performed on an ARL 3410 sequential spectrometer, and 15 elements were quantified with reference to prepared standard solutions, and solutions of dissolved standard metals (see Hook, forthcoming, for detailed procedure). The precision of the technique is about ±1-2% for copper; ±5% for major elements (ie those present at levels >10%); ±10% for minor elements (present at 1-10%) deteriorating to about ±50% at the detection limit.

One element, bismuth, is not easily measured in copper-based solutions by ICP-AES and this was determined by atomic absorption spectroscopy (AAS) using the solution remaining after ICP-AES analyses, following the method of Hughes et al (1976).

Results

Table 1 gives the quantitative ICP-AES and AAS results. The most likely sources of error in these results are from the effects of corrosion that has penetrated into the heart of the object. In these cases inaccuracies will occur because the sample includes corrosion products rather than pure metal. Elements such as oxygen, chlorine and carbon that have not been analysed are present from carbonates, chlorides and other compounds that make up the corrosion products. In general, these inaccuracies can be seen as a total of significantly less than 100% after allowing for overall precision, ie less than 97%. Although two of the objects have low totals they all fall within the general precision of the technique.

Discussion

The results of the quantitative analyses in Table 1 show antimony as the major alloying component (in the range 5-10%), and apart from about 1-3% tin are otherwise relatively pure. In other cases of high antimony-copper alloys, for example the Nahal Mishmar hoard (Shalev and Northover 1993) and four British LBA artefacts analysed by Craddock (1979), the antimony is accompanied by high arsenic, nickel and silver contents (Table 2). This has been seen as indicative of the use of secondary enriched sulphide ores (grey ores or fahlerz). Both antimony and arsenic can substitute for each other in the grey copper minerals, eg enargite Cu₃(As,Sb)S₄ or tetrahedrite/tennantite (Cu₄(Cu,Fe)₁₄(Sb,As)₂S₁₃), which often occur in the secondary (enriched) sulphide zone of an ore body. In addition, other metals such as silver, nickel and cobalt leach from the overlying minerals, and in the presence of sulphide reducing bacteria are precipitated below the water table (Barnes 1988, 20). The copper smelted from this particularly metal-rich but impure ore would be polymetallic, with high concentrations of antimony and arsenic, and probably relatively high concentrations of other leached metals (eg nickel, silver and cobalt).

In many cases, groups of arsenical or antimony-copper artefacts show a correlation between these elements. For example, regression analysis of data published by McKerrell and Tylecote (1972) for British Bronze Age rivets has shown a strong correlation between silver and arsenic. This relationship probably reflects the composition of the ore body and any attempt to deliberately modify the arsenic content during the finishing of the artefact (eg by oxidative working as McKerrell and Tylecote suggest), would disrupt this relationship. A similar regression analysis also shows a correlation between silver and antimony in the Nahal Mishmar hoard analyses. In these cases, it is probable that the control the smelter and metalworker exercised was simply over the selection of a particular ore for a particular task and a particular metal for a particular manufacturing process. Experimental smelting of polymetallic ores found on archaeological sites in southeast Spain has shown that similar alloys to those in contemporary artefacts can be produced simply by smelting, without complex processing, mixing or alteration of the furnace charge (Delibes et al 1991).

The Koban antimony alloys do not show significant nickel, silver, cobalt or bismuth contents and are markedly different from both the Nahal Mishmar objects and the analyses given by Craddock for LBA antimony bronze (see Fig 3 and Table 2). The arsenic content of the
Table 1: ICP-AES results for the Koban antimony bronze artefacts (wt%).

<table>
<thead>
<tr>
<th>Reg No</th>
<th>Description</th>
<th>Ag</th>
<th>As</th>
<th>Au</th>
<th>Bi</th>
<th>Cd</th>
<th>Co</th>
<th>Cu</th>
<th>Fe</th>
<th>Mn</th>
<th>Ni</th>
<th>P</th>
<th>Pb</th>
<th>S</th>
<th>Sb</th>
<th>Sn</th>
<th>Zn</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>18</td>
<td>Bird pendant</td>
<td>0.07</td>
<td>0.13</td>
<td>&lt;0.005</td>
<td>&lt;0.02</td>
<td>&lt;0.003</td>
<td>83.1</td>
<td>0.012</td>
<td>0.0006</td>
<td>0.017</td>
<td>&lt;0.03</td>
<td>0.16</td>
<td>0.26</td>
<td>10.71</td>
<td>3.43</td>
<td>&lt;0.014</td>
<td>97.8</td>
<td></td>
</tr>
<tr>
<td>28</td>
<td>Dog-bird pendant, small</td>
<td>0.05</td>
<td>0.05</td>
<td>&lt;0.008</td>
<td>&lt;0.03</td>
<td>&lt;0.005</td>
<td>93.6</td>
<td>0.020</td>
<td>0.0011</td>
<td>0.081</td>
<td>&lt;0.05</td>
<td>0.13</td>
<td>0.49</td>
<td>5.22</td>
<td>&lt;0.02</td>
<td>&lt;0.023</td>
<td>99.5</td>
<td></td>
</tr>
<tr>
<td>33</td>
<td>Maltese cross pendant</td>
<td>0.08</td>
<td>0.07</td>
<td>&lt;0.008</td>
<td>&lt;0.03</td>
<td>&lt;0.005</td>
<td>89.6</td>
<td>&lt;0.010</td>
<td>&lt;0.0010</td>
<td>0.011</td>
<td>&lt;0.05</td>
<td>0.13</td>
<td>0.17</td>
<td>8.14</td>
<td>2.01</td>
<td>&lt;0.022</td>
<td>100.1</td>
<td></td>
</tr>
<tr>
<td>32</td>
<td>Maltese cross pendant</td>
<td>0.11</td>
<td>0.12</td>
<td>&lt;0.005</td>
<td>&lt;0.02</td>
<td>&lt;0.003</td>
<td>90.1</td>
<td>0.030</td>
<td>&lt;0.0007</td>
<td>0.028</td>
<td>&lt;0.03</td>
<td>0.08</td>
<td>0.11</td>
<td>8.24</td>
<td>0.85</td>
<td>&lt;0.014</td>
<td>99.6</td>
<td></td>
</tr>
<tr>
<td>35b</td>
<td>Broken maltese cross</td>
<td>0.03</td>
<td>0.20</td>
<td>&lt;0.005</td>
<td>&lt;0.02</td>
<td>&lt;0.003</td>
<td>86.2</td>
<td>0.009</td>
<td>&lt;0.0007</td>
<td>0.018</td>
<td>&lt;0.03</td>
<td>1.83</td>
<td>0.16</td>
<td>7.74</td>
<td>1.82</td>
<td>&lt;0.015</td>
<td>97.9</td>
<td></td>
</tr>
</tbody>
</table>

Registration numbers of all these artefacts are preceded by 1913-12-15.
The precision of the technique is about ±1-2% for copper, ±5% for major elements (>10%), ±10% for minor elements (1-10%) deteriorating to about ±50% at the detection limit. '<' denotes a concentration below the given detection limit.

Table 2: Atomic absorption analyses for antimony alloys from other cultures for comparison.

<table>
<thead>
<tr>
<th>Source</th>
<th>ID number</th>
<th>Description</th>
<th>Ag</th>
<th>As</th>
<th>Au</th>
<th>Bi</th>
<th>Co</th>
<th>Cu</th>
<th>Fe</th>
<th>Ni</th>
<th>Pb</th>
<th>Sb</th>
<th>Sn</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>Craddock, 1979</td>
<td>106</td>
<td>Spearhead</td>
<td>0.12</td>
<td>1.50</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Craddock, 1979</td>
<td>62</td>
<td>Looped socketted axe</td>
<td>2.65</td>
<td>0.95</td>
<td>0.005</td>
<td>0.075</td>
<td>0.003</td>
<td></td>
<td>88.5</td>
<td>0.010</td>
<td>0.65</td>
<td>0.11</td>
<td>6.4</td>
<td></td>
</tr>
<tr>
<td>Craddock, 1979</td>
<td>155</td>
<td>Socketted looped chisel</td>
<td>1.30</td>
<td>1.60</td>
<td></td>
<td>0.010</td>
<td>0.035</td>
<td>84.5</td>
<td>0.004</td>
<td>0.11</td>
<td>4.10</td>
<td>4.8</td>
<td>2.3</td>
<td></td>
</tr>
<tr>
<td>Craddock, 1979</td>
<td>161</td>
<td>Sword Chafe</td>
<td>0.80</td>
<td>2.50</td>
<td></td>
<td>0.055</td>
<td>0.030</td>
<td>90.0</td>
<td>0.280</td>
<td>0.07</td>
<td>0.18</td>
<td>5.3</td>
<td>1.5</td>
<td></td>
</tr>
<tr>
<td>Shalev &amp; Northover,</td>
<td>61-373 (AAS)</td>
<td>Mace head</td>
<td>0.43</td>
<td>2.25</td>
<td>tr.</td>
<td>0.47</td>
<td>n.d</td>
<td></td>
<td>88.5</td>
<td>0.08</td>
<td>0.30</td>
<td>0.33</td>
<td>4.8</td>
<td>tr.</td>
</tr>
<tr>
<td>Shalev &amp; Northover,</td>
<td>61-400 (AAS)</td>
<td>Mace head</td>
<td>0.45</td>
<td>3.00</td>
<td>0.02</td>
<td>0.38</td>
<td>n.d</td>
<td></td>
<td>75.0</td>
<td>0.18</td>
<td>0.22</td>
<td>0.90</td>
<td>5.9</td>
<td>tr.</td>
</tr>
<tr>
<td>Shalev &amp; Northover,</td>
<td>61-162 (AAS)</td>
<td>Basket-like vessel</td>
<td>0.98</td>
<td>6.56</td>
<td>n.d</td>
<td>0.83</td>
<td>0.010</td>
<td>62.5</td>
<td>0.23</td>
<td>0.25</td>
<td>0.32</td>
<td>10.3</td>
<td>0.13</td>
<td></td>
</tr>
</tbody>
</table>

'n.d.' - not determined, 'tr.' - trace, blanks - not detected.
Three analyses from Shalev and Northover (1993) have been selected as typical of the high antimony alloys found in the Nahal Mishmar hoard.

Table 3: 30/1 1996
Koban objects is relatively low (<0.2%) compared to 1% and above for the comparative material. Unless a relatively pure Cu-Sb mineral was widely available, the two most likely explanations for the compositions seen are the co-smelting of copper minerals with a relatively pure antimony mineral (eg stibnite Sb2S3), or the addition of metallic antimony (or perhaps an antimony mineral) to copper. There is evidence for antimony mining in the Gornaya Rachka region (Chernykh 1992, 276), and as noted above, a few relatively pure antimony objects have been found dating from the 3rd millennium in the Northern Caucasus. Antimony from Redkin in Transcaucasia had arsenic as its major impurity, but never more than 1.2% (Selimkhanov 1975). If metallic antimony was being produced, there is no reason why it could not have been added to molten copper. This would produce a purer and more controlled alloy than the smelting of enriched polymetallic ores. According to the literature, no antimony ingots have been found, but this should not be taken to mean none were produced: consider the case for tin where tin-bronze was being produced in great quantities but finds of tin ingots are very scarce.

Conclusions

The production of antimony bronze within the Koban culture does not seem to have been through the fortuitous use (albeit deliberate selection) of polymetallic fahl ores. Rather, a relatively pure antimony mineral seems to have been co-smelted with copper, or reduced to metallic antimony which was added to copper. To some extent this may have been prompted by the lack of tin in the Caucasian region (Selimkhanov 1978, Smirnov 1989), or the colour of antimony bronze (mimicking gold, silver or even iron) was sufficiently desirable to generate a technology and an industry.

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The authors

Alistair Pike is a graduate in Archaeological Sciences from Bradford University, currently undertaking a one year post at the British Museum’s Department of Scientific Research. Mike Cowell is a Principle Scientific Officer at the Department of Scientific Research. John
Curtis is Keeper of Western Asiatic Antiquities, The British Museum.

Authors Addresses: Alistair Pike and Mike Cowell, The Department of Scientific Research, The British Museum, London WC1B 3DG.
John Curtis, The Keeper of Western Asiatic Antiquities, The British Museum, London WC1B 3DG.