NEW ANALYTICAL DATA FROM GÖLTEPE CRUCIBLES Göltepe potalarından yeni analitik veriler

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Key words: Göltepe/Kestel, Early Bronze Age, tin smelting **Anahtar Sözcükler:** Göltepe/Kestel, İlk Tunç Çağ, kalay ergitmesi

ÖZET

Niğde, Göltepe İlk Tunç Çağı kalay ergitme işliğinden daha önce komposizyonu ve mikroyapıları belirlenmemiş 11 adet pota parçası EDX ve taramalı electron Mikroskobu (SEM) ile incelenmiştir. İncelenen 11 pota parçasından sekiz adedinin iç yüzeylerinde kalay oksit ince bir bant veya granüller olarak yayıldığı belirlenmiştir. Ara tamamen metalik veya kısmen oksitlenmiş 5-20 mikron çapında kalay küreciklere rastlanmıştır. Pota parçalarının çok küçük olmasından dolayı şekilleri ve büyüklükleri belirlenememiştir. Pota parçalarının ya kalay ergitmesi sırasında pota kapağı, ya da ergitmenin yapıldığı pota olarak kullanılmıştır.

INTRODUCTION

Archaeological excavations at the Early Bronze Age site of Göltepe (Map. 1) where cassiterite from the Kestel mine was smelted yielded a large number of crucibles of many different sizes and shapes (Yener et al. 1989). Archaeometallurgical study of various crucible fragments indicated that they were used for the processing of tin containing materials (Yener and Vandiver 1993; Adriaens et al. 1999a). The eleven crucibles selected for this study were of different sizes, shapes and thicknesses. Yener and Vandiver (1993) have established that similar crucibles fragments that they have studied were generally exposed to different firing temperatures between 700 - 800°C, with a maximum of about 1000°C. Such variations may indicate that different types of thermal processing were taking place at Göltepe. Yener and Vandiver (1993) did not associate different

types of crucibles with any particular process. In 1993, a total of 28 crucible fragments from Göltepe, most of them in the form of powder from the inner accretion layer, were brought to Boğaziçi University to determine the tin content of these crucible accretions by atomic absorption spectrometry (Earl and Özbal 1996; Adriaens et al. 1999b). Four samples yielded over 1% tin with highest level at 3.65%. The remaining 24 samples had an average of 1070 ppm tin. Eleven of the 28 crucible samples were large enough for cross-sectioning. This paper presents investigations on the microstructure of the crucible cross section profiles by scanning electron microscope (SEM), optical microscope, as well as analyses on the chemical composition of various phases and inclusions using energy dispersive x-ray analysis (EDX).

DESCRIPTION OF THE CRUCIBLE FRAGMENTS

The description of the crucible fragments is given in Table 1. Due to the very fragmentary nature of the samples, it was not possible to predict the approximate size and shape of the crucibles. Thus, the crucibles are grouped according to the presence or absence of tin oxide and by comparing the microstructure, composition and the distributions pattern of tin oxide in the accretion layer on the inner surface of the crucible fragments. Even though the crucibles were constructed in different sizes and shapes and seem to have been used for different processes, the composition and microstructure of the bulk clay material seem similar. Organic fiber was used in all samples. SiO₂ and Al₂O₃ were the major components with minor amounts of CaO, MgO, Na₂O, K₂O and FeO (Table 2). TiO₂ was less then 1.0 %. The main mineral was quartz, followed by albite and muscovite. These minerals are probably derived from the local clay material. The main ceramic body of most crucible samples was overlaid by a rather thin accretion layer that contained tin oxide in the form of globules or as a very thin continuous band. Adriaens (1999a) demonstrated that tin oxide does not penetrate beyond 300-400 μ m from the surface and hardly ever found its way into the bulk of the ceramic.

The crucible fragments were recovered from trenches excavated in areas A and B (Yener and Vandiver 1993). Area A, on the southern part of the mound, had mainly subterranean and semi subterranean pit structures some of which could have been workshops. Four out of seven crucible fragments from this area (Trenches A22, A23 and A24) contained a very thin continuous layer or globules of tin oxide on the inner surface of the fragments. The remaining four fragments are from area B, located at the northwest corner of the hill from trenches B01 and B09 which are next to each other near the circuit wall. Area B yielded many fragments of crude porous ware with accretions that contain tin oxide and glassy slag discarded by the circuit wall (Yener and Vandiver 1993). This area may also be considered a workshop where cassiterite processing and smelting took place.

GROUP 1 CRUCIBLES

This group of samples (Table 3, Entries 1-4) was all rim fragments that vary in thickness between 14 and

24.1 mm. They had pale grey to brown and black scorified accretions on the inner surfaces that are about 2 to 3 mm thick. Entry 1 was a small grey to black, highly scorified porous fragment that was exposed to highly reducing conditions. Entries 2, 3 and 4 had a light brown, orange to red, dense, compacted and oxidized exterior bodies. No slag particles could be observed by visual examination or by binocular microscope. Their common characteristic was a continuous thin tin oxide layer located at the interface between the clay bulk matrix and the accretion on the inner surface. Sample MRN 1124 (Entry 1) was unique because the continuous tin oxide had also penetrated into the clay matrix of the crucible and can be seen as a light grey band across the inner surface (Fig. 1). The width of the band reaches up to about 500 μ m. The sample must have been exposed to relatively high temperatures that probably allowed tin oxide to diffuse into the bulk matrix of the crucible. Embedded in the tin-rich band, there are many globules with diameters as large as $50 \,\mu m$ that appear as bright prills. Close examination of one of the prills indicates that they are composed of SnO_2 (Fig. 2, region A) and pure metallic tin (Fig. 2, region B). It is interesting to note that no iron was detected in any of these prills. The cassiterite ore from Kestel is associated with hematite and the enriched cassiterite powder generally contains considerable amounts of iron. However, highly pure tin inclusions may indicate that it is possible to produce iron-free tin from cassiterite ore even though it contains hematite.

The remaining three crucibles in this group were rim fragments with evidence of scorified inner surfaces represented by 1-3 mm thick light grey bands. The reddish-orange color of the main bulk of the sherds indicates that they were not exposed to reducing conditions. The continuous thin band of tin oxide in these samples was restricted to the interface between the surface accretion and the main ceramic matrix. There was no evidence of diffusion into the clay matrix. Similarly, no residual tin was detected on the outer surface of the crucibles. The bright white coating of tin oxide layer varies only between 1-3 μ m. All three must have been constructed for the specific metallurgical process.

A bright thin band of tin oxide can be seen in the back-scattered electron image of sample MRN 4937B (Entry 2) where it appears to be restricted only to the interface between the surface accretion and the clay matrix (Fig 3). The sample was probably not exposed to high temperatures to facilitate diffusion. A partially oxidized metallic tin prill, with a 5μ m diameter, imbedded in the tin-rich accretion band is also observed (Fig. 4). Sample MRN 1416 (Entry 3) also displayed a tin oxide-rich band at the surface; however, the layer seems to have greater dispersion. On the surface, there are tin oxide patches which seem to have formed by the accumulation of small $(1-2\mu m)$ granules (Fig. 5). EDX analysis of this region yielded 81.3% SnO₂. On the opposite side of this agglomeration, there is a region composed of polyhedral aggregate of iron oxide grains. At higher magnification, the small iron oxide grains displayed a very fine network of tin oxide within the grain matrix (Fig. 6) which is part of the crystallization product of the smelting process. Sample MRN 1591 (Entry 4) in this group also displays a very thin and intense continuous layer of tin oxide at the interface (Fig. 7). Besides the surface coating, the tin oxide layer had also diffused into the cavities just below the surface and has coated the inner walls of the cavities. Some of the cavities were also actually filled with small spherical tin oxide prills (Fig. 8).

Yener and Vandiver (1993) suggest that such a band of tin accretion at the surface rather than within the clay matrix may be due to the precipitation of tin oxide from the vapor with very small amounts of slag during smelting. They also suggest that such a ceramic may have been used as a cover for a crucible. The group one crucibles in this study may also have been used as crucible covers.

GROUP 2 CRUCIBLES

Four fragments are assigned to the group 2 crucibles. This group shows even greater variation in structural features both in thickness and in matrix appearance (Table 1). They were all body fragments and it was not possible to estimate their original sizes and shapes. Samples MRN 1760 (Table 3, Entry 5) had a very similar appearance with the crucibles in group 1 displaying a reddish orange matrix having a scorified inner surface of few a millimeters. Sample MRN 4937C (Table 3, Entry 6) also had similar cross sectional characteristics with a light grey scorified surface; however, it was more than twice the thickness of the other members of the group 2 samples. Sample MRN 4937A (Table 3, Entry 7), on the other hand, was a black fragment with extensive pores and was tempered both with organic matter and quartz. There is a 5-6 mm reddish pale brown layer on the inner surface that does not show the scorification and the porosity of the main body. Sample MRN 4318 (Table 3, Entry 8) was composed of three small fragments. None of the fragments yielded the complete cross sectional profile of a crucible and only one fragment had a possible inner surface face. The cross section of this fragment has a brown-reddish porous matrix with a very thin dark encrustation layer.

The collection of different shaped and sized crucible fragments of group 2 all showed small clusters of tin oxide globules between the main clay body matrix and the surface accretion rather than a continuous thin band as observed in group 1 samples.

Sample MRN 1760 (Table 2, Entry 5) yield a very distinctive narrow interface band between the main ceramics matrix and a surface accretion layer that was composed of relatively fine crystalline material (Fig. 9). The tin globules as large as $50 \,\mu\text{m}$ are randomly distributed together with some iron oxides within this narrow accretion band (Fig. 10). Sample MRN 4937C (Table 3, Entry 6) also showed a similar accretion band at the interface with tin oxide globules (Fig. 11). The width of the band that contains the tin globules varies between 20 and 200 μ m and is composed of mainly aluminum silicate together with smaller amounts of calcium, iron, and phosphorus oxides with about 5.2% tin oxide (Fig. 12 area B). The chemical composition of this layer resembles that of tin smelting slag (Yener and Vandiver 1993).

One unique feature of these tin globules, especially in these two crucible fragments is that they are fused together with calcite crystals (Fig. 10 and Fig. 12, area A). EDAX analysis of most of the tin oxide globules observed in this group of crucibles yielded high levels of calcium oxide (Table 3). Such accretion layers in crucible samples MRN 1760 and MRN 4937C cannot form if tin is melted in them or if they are used as crucible covers like those of group 1. These globules must have deposited or formed in the band during a high temperature tin processing activity. Sample MRN 4937A (Table 3, Entry 7) that had a completely scorified clay matrix also had globules of tin oxide in a not well-defined accretion band with much less associated calcium oxide (Fig. 13, area A) together with iron oxide crystals (Fig. 13, area B). This sample also contained a 40μ m inclusion that was composed of 68.2% FeO and 22.1 and As₂O₃ (Fig. 14). Yener and Vandiver (1993) also report high levels of arsenic. The arsenic probably originates from the ore since some of the powdered ore samples from Göltepe contained about 5 % arsenic (Earl and Özbal 1996). The last sample of this group, MRN 4318, contained three small fragments. None of the fragments yielded a complete cross section profile. Only one fragment had a small area of inner surface that was coated with about 1.5 mm dark accretion layer. This sample also contained tin globules that also contained relatively high levels of CaO (Fig 15, Entry 8 in Table 3). The accretion layer also contained As₂O₃ inclusions.

GROUP 3 CRUCIBLES

The final three crucible fragments MRN 1006, MRN 4390 and MRN 4235 (Table 1), were grouped together since they did not yield any residual tin oxide. Sample MRN 1006 was a very small fragment without any original inner or outer surface. Since tin residues diffuse only about 500 μ m into the clay matrix, it is possible that the accretion layer was lost. A loosely attached small residue was observed on the surface of one of the sides (Fig 16). The residue was composed of mainly lead and iron oxides together with minor amounts of antimony, copper and arsenic (Table 3, entry 9). Possible source of such residue needs further investigation. Sample MRN 4390 was also highly scorified, black, and porous, extensively tempered both with organic fibers and siliceous materials and was exposed to highly reducing conditions. The inner surface was coated with a very thin brown layer. EDX analysis of individual bright inclusions showed that they were iron oxide. The final sample of this group, MRN 4235, was a flat, very thin (8 mm) body fragment with a medium grey cross section. It is difficult to decide which side is the inner surface since there was no detectable curvature. One of the faces has a grey partly scarified thin layer. The other side was covered with a thin layer of calcite, probably formed after burial. The scarified face had many metallic oxide inclusions; however, no tin oxide could be detected.

This fragment probably was not intended to be used in a metallurgical process.

CONCLUSION

The SEM images and the EDX data complement the results from previous studies and further confirm that these crucible fragments are remnants from processes involving tin metallurgy. It is also conclusively affirmed that these crucibles were not used to make bronze since there was no trace of copper which could be observed either by AA or by EDX analysis.

Kestel cassiterite ore is observed in quartz veins together with hydrothermal hematite and tourmaline (Cağatay and Pehlivan 1988, Willies 1995). In order to liberate the very fine crystalline cassiterite from the associated hematite ore, it had to be ground to a very fine powder ($< 200 \,\mu$). Cassiterite ore was enriched by washing with water on an inclined surface. It was easy to enrich cassiterite from the ground Kestel ore by a vanning shovel (Bryan and Özbal 1996). To avoid loss of fine powdered cassiterite from the crucible during smelting and also avoid loss of heat, it is very likely that the samples MRN 4937B, MRN 1416 and MRN 1591 among group 1 samples may have been used as crucible covers. Agricola (1556:411-414) describes tin smelting furnaces with a dust chamber to trap the small particles of tin oxide that may escape with the fumes if heating is fast.

The group 2 samples showed globules of tin oxide associated with calcite crystals in the accretion band that covers the inner surface of the crucibles. It is highly possible that these crucibles could have been used for smelting cassiterite where calcite may have been used as some sort of fluxing agent. Alternatively, the calcite may have from the Kestel cassiterite since most of the powdered ore samples contained both calcite and dolomite.

Sample MRN 1124 (Entry 1 in Table 2) was probably from a high temperature process where tin oxide has diffused almost 500μ m into the highly glassy upper surface of the crucible which even had a metallic tin prill.

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Sample	Group	Туре	Thickness (mm)	Description	Site location
MRN 1124	1	Rim	14	Porous body with a black <u>scorified</u> inner surface. Tempered with quartz and organic <u>fiber</u> . (7.5YR 4/0-5/0, grey dark grey)	B01-0300- 003
MRN 4937B	1	Rim	24,1	Red to orange bulk with a 2 mm light pale grey accretion on the inner surface (7.5YR 6/5-6/6 reddish yellow)	B09-0100- 999
MRN 1416	1	Rim	13,3	2 mm light pale grey accretion on the inner surface (5YR 6/6 Reddish yellow)	A24-0100- 003
MRN 1591	1	Rim	14,7	2 mm light pale grey accretion on the inner surface (7.5YR 6/6 Reddish yellow)	A24-0100- 005
MRN 1760	2	Body	16	2 mm grey accretion on the inner surface (7.5YR 5/4 brown)	A23-0100- 005
MRN 4937C	2	Body	38,5	6.5 mm grey accretion on the inner surface (5YR 5/2 Yellowish red)	B09-0100- 999
MRN 4937A	2	Body	15,8	Highly charred body with a 6 mm reddish brown clay inner surface (7.5YR 3/0 dark grey)	B09-0100- 999
MRN 4318	2	Body		Complete cross section not available. Highly tempered body with a 1.5 mm dark inner surface coating (5YR 5/4 reddish brown)	A22-0500- 005
MRN 1006	3	Body		Complete cross section not available scorified body without outer surface. Tempered with quartz and organic fiber (7.5YR 3/0 very dark grey)	A03-0234- 003
MRN 4390	3	Body	12,1	Highly scorified body without any distinctive inner accretion. 7.5YR 2.5.0 black)	A06-0400- 003
MRN 4235	3	Body	8,3	One side is encrusted with partially scorified layer, other side coated with a thin calcite layer (YR 7.5 YR 4.0 dark grey)	A24-0700- 000

Table 1: Description of crucible fragments

Sample	SiO ₂	Al ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O	FeO	TiO ₂
MRN 1124	58.6	25.8	1.20	4.13	4.04	2.25	3.02	
MRN 4937B	62,4	22,6	1,33	4,12	2,8	2,18	3,49	0,95
MRN 1416	64,4	18,2	1,81	3,72	2,24	2,23	6,68	0,71
MRN 1591	60,4	17,9	2,14	2,99	3,48	4,11	7,96	1,03
MRN1760	63,4	19,8	1,11	3,3	5,15	1,82	505	
MRN 4937A	60,4	21,1	2,42	3,27	1,95	2,81	7,35	0,73
MRN 4937C	63,8	18,2	2,72	3,11	2,36	3,12	6,14	0,51
MRN 4318	59,4	24,7	1,57	2,8	1,56	2,85	6,29	0,91
MRN 1006	63,9	19,4	1,22	2,75	3,44	3,55	5,34	
MRN 4390	65,3	17,5	3,37	2,51	1,33	3,16	6,05	0,71
MRN 4235	57,8	23,2	2,47	3,19	1,78	3,35	7,36	0,87

Table 2: Composition of the clay matrix of crucible fragments

				%	%	%	%	%	%	%	%	%	%	%	%	%	%
Sample #	Ent.	Fig.	Region	SiO ₂	SnO ₂	Al ₂ O ₃	CaO	MgO	MnO ₂	Na ₂ O	FeO	TiO ₂	As ₂ O ₃	P205	CuO	PbO ₂	SbO ₂
MRN 1124		-	V	37,9	33	9,12	16,8	1,66		1,52							
		6	A	1,36	95,5	1,24		6,0									
MRN 4937B	3	e	A	22,6	48,3	18,3	2,25	3,34			5,27				_		-
MRN 1416	m	S		6,01	813	2,12	5,02	6.0		0,61	4,03						
	-	9	_	4,92	22,3	3,12	2,53	2,11	-	0,49	64.5				-	-	
MRN 1591	4	7		34,2	35,9	17,2		3,42	3,7	1,55	4,03						
		8		27,2	49,4	14,9	-	4	-	1,37	3,18	÷					
MRN 1760	-v	6	_	18,4	75,4	2,78	_	2,91	_				_				
		10		7,8	27,4	2,29	62,5			<u></u>					-		
MRN 4937C	6	11		10,7	45,2	2,73	36,4	1,73	_		1,74			1,6			
	_	12	A	12,1	47,8	3,17	29,5	2,39			1,54			2,3			
		12	B	50,7	5,16	13,2	8,9	3,51		<u></u>	12,7	1,63		3,2			
MRN 4937A	7	13	A	7,72	88,7	1,87	_	1,75	-	<u>i</u> -	_	_		_	-	_	
		13	B	8,18	2,71	4,18	1,07	1,72	-		73,2	6.7					
		14				1,01	8,76				68,2		22,1			_	_
MRN 4318	8	15		31,3	16,6	6,13	14,5	3,69	Ľ.	0,93	25,7						
MRN 1006	6	16	7	0,71	_	_				-	37,7	_	7,54		4,1	47,7	2,3
	-	-	-	-	-	-	-	<u></u>	-	Tal	ole 3: Th	e compo:	sition of ph	ases and	l inclusio	ns in the	crucibles

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Map. 1: Kestel tin mine and Göltepe workshop.



Fig. 1: Tin oxide band (A) on the crucibles inner surface (MRN 1124).



Fig. 3: Tin oxide band (white region) (MRN 4937B).



Fig 2: Inclusion composed of tin oxide (A) and metallic tin (B) (MRN 1124).



Fig 4: Metallic tin prill (MRN 4937B).

Hadi ÖZBAL



Fig.5: Tin oxide granules (MRN 1416).



Fig. 6: Network of tin oxide (white specks) in grey polyhedral iron oxide grains (MRN 1416).



Fig. 7: Tin oxide layer coating cavities (MRN 1591).



Fig 8: Tin oxide granules in cavities (MRN 1591).



Fig. 9: Polyhedral tin oxide inclusions in the accretion band (MRN 1760).



Fig. 10: Calcite crystal impregnated with tin oxide (MRN 1760).



Fig 11: Tin oxide impregnated calcite crystal in the accretion band (MRN 4937C).



Fig. 12: Tin oxide impregnated calcite crystal (A) in the accretion band (B) (MRN 4937C).



Fig. 13: Accretion layer containing tin oxide (A) and iron oxide inclusions (B) (MRN 4937A).



Fig. 14: Inclusion composed of arsenic oxide (white specks) in light grey iron oxide grain (MRN 4937A).



Fig. 15: Tin oxide globule inclusions in surface accretion band (MRN 4318).



Fig 16: Surface grain composed of lead, iron, antimony, arsenic and copper oxides (MRN 1006).