SMELTING
POLYMETALLIC
COPPER ORES

FAHLERZ TYPE ORES

• Major copper deposits may contain arsenic and antimony as impurity.
• During the weathering of such ores, arsenic and antimony is collected in the secondary enrichment zone together with chalcosite ($\text{Cu}_2\text{S}$) and will forms minerals such as:
  Tetrahedrite: $((\text{CuFe})_{12}\text{Sb}_4\text{S}_{13})$
  Tennantite: $((\text{CuFe})_{12}\text{As}_4\text{S}_{13})$

Alloys of Copper

Ancient miners first utilized the oxidized secondary ores of copper to produce earliest extracted metals. They also came across rich deposits of primary copper ores in areas where erosion has exposed them at the surface. They were able to overcome the difficulty of extracting copper from sulfide ores. Finally they came across polymetallic ores of copper that may contain arsenic, antimony, zinc and lead together with iron. These were Fahlerz type ores form at lower levels of copper deposits.
APPEARANCE OF Cu-As ALLOYS

EARLIEST Cu-As ALLOYS
- Nahal Nishmar
- Arslantepe
- Ikiztepe

NAHAL MISHMAR
CHEMICAL ANALYSIS RESULTS OF NAHAL MISHMAR SAMPLES

<table>
<thead>
<tr>
<th>Sample</th>
<th>No.</th>
<th>% Cu</th>
<th>% As</th>
<th>% Sb</th>
<th>% Ni</th>
<th>% Bi</th>
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<tbody>
<tr>
<td>Macehead</td>
<td>61-351</td>
<td>70.0</td>
<td>2.24</td>
<td>4.20</td>
<td>0.25</td>
<td>0.30</td>
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<tr>
<td>Macehead</td>
<td>61-226</td>
<td>79.4</td>
<td>2.52</td>
<td>0.07</td>
<td>8.27</td>
<td>0.04</td>
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<td>Macehead</td>
<td>61-278</td>
<td>87.4</td>
<td>3.78</td>
<td>0.19</td>
<td>3.98</td>
<td>Tr</td>
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<tr>
<td>Macehead</td>
<td>61-311</td>
<td>88.5</td>
<td>2.18</td>
<td>0.54</td>
<td>0.09</td>
<td>0.40</td>
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<tr>
<td>Macehead</td>
<td>61-115</td>
<td>71.3</td>
<td>8.22</td>
<td>18.3</td>
<td>0.08</td>
<td>1.00</td>
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<tr>
<td>Macehead</td>
<td>61-400</td>
<td>75.0</td>
<td>3.00</td>
<td>5.90</td>
<td>0.22</td>
<td>0.38</td>
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<tr>
<td>Macehead</td>
<td>61-249</td>
<td>87.1</td>
<td>3.48</td>
<td>3.70</td>
<td>0.30</td>
<td>0.23</td>
</tr>
<tr>
<td>Standard</td>
<td>61-94</td>
<td>65.7</td>
<td>6.29</td>
<td>22.5</td>
<td>0.18</td>
<td>1.40</td>
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<tr>
<td>Crown</td>
<td>61-179</td>
<td>90.7</td>
<td>2.64</td>
<td>2.99</td>
<td>1.43</td>
<td>0.86</td>
</tr>
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</table>

DIRECT SMELTING

When the primary copper ores that contain arsenic (Copper sulpharsenide) are roasted they will turn into copper arsenate (olivenite).

\[ \text{CuAsS} + \text{O}_2 \rightarrow \text{CuAsO}_4 + \text{CuO} + \text{As}_2\text{O}_3 + \text{SO}_2 \]

Reduction of copper arsenate by charcoal will yield Cu-As alloy

\[ \text{CuAsO}_4 + \text{CO} \rightarrow \text{Cu-As (alloy)} + \text{CO}_2 \]

(olivenite)

During roasting over 50% of arsenic is lost as \( \text{As}_2\text{O}_3 \).

Reactions are not balanced.

METHODS OF PREPARING Cu-As ALLOYS

- Direct reduction
- Co-smelting
- Cementation

CO-SMELTING

Secondary copper ores are smelted together with sulfidic ores of arsenic.

\[ \text{CuCO}_3 + \text{Cu}_4\text{AsS}_4 \rightarrow \text{Cu-As} + \text{SO}_2 + \text{CO}_2 \]

enargite

\[ \text{CuCO}_3 + \text{FeAsS} \rightarrow \text{Cu-As} + \text{SO}_2 + \text{CO}_2 \]

Arsenopyrite

\[ \text{CuCO}_3 + \text{As}_2\text{S}_3 \rightarrow \text{Cu-As} + \text{SO}_2 + \text{CO}_2 \]

Orpiment

Charcoal is not necessary in this experiment because CO is not needed for reduction.

Reactions are not balanced.
CEMENTATION

A mixture of arsenic ores such as $Cu_3AsS_4$, $FeAsS$ or $As_2S_3$ with charcoal powder is added on to molten copper metal in a crucible. Arsenic is quickly reduced and incorporated into copper.

USING BOWL FURNACE

REPLICA OF İKİZTEPE CRUCIBLE

ADDING ARSENIC ON MOLTEN COPPER
**PREPARATION OF ARSENICAL COPPER**

<table>
<thead>
<tr>
<th>Experiment</th>
<th>% Cu</th>
<th>% As</th>
<th>% Fe</th>
<th>% S</th>
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<tr>
<td>1</td>
<td>82.2 (70.3)</td>
<td>9.95 (13.6)</td>
<td>5.82 (5.18)</td>
<td>1.75</td>
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<td>2</td>
<td>89.3 (90.0)</td>
<td>5.08 (10.1)</td>
<td>3.99 (3.34)</td>
<td>1.61</td>
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<tr>
<td>3</td>
<td>88.6 (86.8)</td>
<td>5.82 (7.31)</td>
<td>3.95 (3.45)</td>
<td>1.38</td>
</tr>
<tr>
<td>4*</td>
<td>96.3 (87.0)</td>
<td>2.08 (2.50)</td>
<td>0.43 (1.00)</td>
<td>1.13</td>
</tr>
</tbody>
</table>

Values in parenthesis are atomic absorption results, * Copper metal and arsenopyrite are heated together
ADVANTAGES OF CU-AS ALLOYS

- Copper that contains about 5% arsenic melts about 150°C lower temperature. Thus, casting becomes much easier and better products are produced.
- Copper that contains 4% arsenic can be hot or cold forged much easier.
- When 4% arsenic containing copper is 50% worked hardened it becomes nearly 50% harder than pure copper.
- Arsenic retards the corrosion of copper objects.
- Copper that contains over 9% arsenic attains a silvery color.

Cu-As PHASE DIAGRAM

Region where Cu and As forms Solid solution

HARDNESS OF Cu-As ALLOYS

HOROZTEPE BULL
Presently at the Boston Museum of Fine arts
Made by Hattian metal smiths around 2100 BC.
The bulk of the bull metal is bronz with less than 0.001 % arsenic.
There is a 10μ layer of arsenic rich layer of domeykite (Cu₃As) which contain about 28% arsenic and gives the bull its silvery color.

Domeykite layer is produced by cementation. In this method the bronze bull is heated in a mixture of As₂O₃, K₂CO₃ and charcoal at 450°C for some time. The reduced arsenic diffuse into copper in the solid form.
Cu-As ARTIFACTS

METAL ARTIFACTS FROM ROYAL TOMB

İKİZTEPE
**Ikiztepe Spearhead with Decoration**

**Ikiztepe Diadems**

**Spearhead with Figurine (I/80-494)**

**Analyzed Ikiztepe Metal Artifacts**

<table>
<thead>
<tr>
<th></th>
<th>Weapons</th>
<th>Tools</th>
<th>Jewellery</th>
<th>Symbols</th>
<th>Other</th>
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<tr>
<td>Spearhead</td>
<td>147</td>
<td>15</td>
<td>35</td>
<td>28</td>
<td>16</td>
</tr>
<tr>
<td>Dagger</td>
<td>27</td>
<td>22</td>
<td>5</td>
<td>16</td>
<td>6</td>
</tr>
<tr>
<td>Arrowhead</td>
<td>3</td>
<td>3</td>
<td>13</td>
<td>10</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td>Dagger</td>
<td>15</td>
<td>13</td>
<td>10</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td>Chisel</td>
<td>6</td>
<td>9</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Other</td>
<td>20</td>
<td>3</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Total</td>
<td>177</td>
<td>88</td>
<td>72</td>
<td>22</td>
</tr>
</tbody>
</table>

% Cu | % As | % Ni | % Zn | % Fe | % Sb
---|-----|-----|------|------|-----
I/80-494 | 86.4 | 9.52 | 0.15 | 0.05 | 0.09 | 0.07
ARSENIC CONCENTRATION OF IKIZTEPE METALS ACCORDING TO PERIODS

![Graph showing arsenic concentration according to periods.]

ARSENIC CONCENTRATION ACCORDING TO TYPES

![Graph showing arsenic concentration according to types.]

DISTRIBUTION OR ARSENIC CONCENTRATION IN IKIZTEPE OBJECTS

![Graph showing distribution or arsenic concentration in objects.]

As-Mass DISTRIBUTION OF IKIZTEPE SPEARHEADS

![Graph showing As-mass distribution of spearheads.]

Number of Samples

As %

0 1 2 3 4 5

LC  EB I  EB II  EB III  MB I

As %

0 1 2 3 4 5

Weapons  Tools  Jewellery  Symbols

As-Mass

0 2 4 6 8 10 12

Mass (gr)

0 100 200 300 400 500 600 700 800 900

As (%)

0 2 4 6 8 10 12

As-Mass distribution of spearheads.

Number of Samples vs. As %
IKIZTEPE CRUCIBLES

STRABO’S ANATOLIAN MAP

LOCATION OF IKIZTEPE

ARSENIC SOURCES FOR IKIZTEPE METALURGISTS
DURAGAN ARSENIC SOURCE

Realgar and Orpiment ores:
AsS and As$_2$S$_3$

TAVSANDAG ARSENOPYRITE DEPOSIT

Arsenopyrite: AsFeS

SMELTING POLYMETALLIC COPPER ORES
(Laboratory Experiments)

Tavşandağ Bakırçay valley
ORE DEPOSITS OF TAVSANDAG

MERZIFON BAKIRÇAY COPPER DEPOSITS

CHEMICAL ANALYSIS OF BAKIRÇAY SLAGS

<table>
<thead>
<tr>
<th>Sample</th>
<th>Cu</th>
<th>Pb</th>
<th>Fe</th>
<th>Zn</th>
<th>As</th>
<th>Sb</th>
<th>Ag</th>
<th>Ni</th>
<th>Bi</th>
<th>Co</th>
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</thead>
<tbody>
<tr>
<td>95/702</td>
<td>0.47</td>
<td>0.24</td>
<td>16.6</td>
<td>0.04</td>
<td>Nd</td>
<td>Nd</td>
<td>Nd</td>
<td>0.40</td>
<td>Nd</td>
<td>Nd</td>
</tr>
<tr>
<td>95/703</td>
<td>1.70</td>
<td>14.9</td>
<td>27.4</td>
<td>6.19</td>
<td>0.69</td>
<td>0.02</td>
<td>Nd</td>
<td>0.08</td>
<td>Nd</td>
<td>Nd</td>
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<tr>
<td>95/704</td>
<td>36.0</td>
<td>22.2</td>
<td>14.4</td>
<td>4.73</td>
<td>3.55</td>
<td>0.24</td>
<td>Nd</td>
<td>0.60</td>
<td>0.01</td>
<td>Nd</td>
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<tr>
<td>95/705</td>
<td>1.22</td>
<td>0.23</td>
<td>17.8</td>
<td>1.49</td>
<td>Nd</td>
<td>0.04</td>
<td>Nd</td>
<td>0.01</td>
<td>Nd</td>
<td>Nd</td>
</tr>
<tr>
<td>96/702</td>
<td>7.59</td>
<td>24.2</td>
<td>36.9</td>
<td>0.05</td>
<td>2.10</td>
<td>1.58</td>
<td>Nd</td>
<td>0.05</td>
<td>Nd</td>
<td>Nd</td>
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</tbody>
</table>
BAKIRÇAY SLAGS

METALLIC PRILL FROM BAKIRÇAY

Chemical Composition:

Cu: 56.2 %
Pb: 19.2%
Fe: 5.07%
Sb: 6.86%
Zn: 4.69%
As: 5.77%

BAKIRÇAY POLYMETALLIC ORES

CHEMICAL ANALYSIS OF SMELTING CHARGE

<table>
<thead>
<tr>
<th></th>
<th>Cu</th>
<th>Pb</th>
<th>Fe</th>
<th>Zn</th>
<th>As</th>
<th>Sb</th>
</tr>
</thead>
<tbody>
<tr>
<td>Roasted</td>
<td>21.3</td>
<td>10.5</td>
<td>19.7</td>
<td>1.90</td>
<td>Nd</td>
<td>nd</td>
</tr>
<tr>
<td>Unroasted</td>
<td>21.5</td>
<td>10.6</td>
<td>19.8</td>
<td>2.54</td>
<td>Nd</td>
<td>nd</td>
</tr>
<tr>
<td>Speiss</td>
<td>0.90</td>
<td>1.01</td>
<td>57.3</td>
<td>1.65</td>
<td>31.7</td>
<td>0.69</td>
</tr>
</tbody>
</table>
BAKIRÇAY CHALCOPYRITE AND SMELTED METAL

CHEMICAL ANALYSIS OF PRILLS FROM SMELTING EXPERIMENTS

<table>
<thead>
<tr>
<th>Element</th>
<th>Range (%)</th>
<th>Average (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>59.2-93.1</td>
<td>75.9</td>
</tr>
<tr>
<td>Pb</td>
<td>0.06-5.70</td>
<td>1.93</td>
</tr>
<tr>
<td>Fe</td>
<td>0.09-2.17</td>
<td>2.17</td>
</tr>
<tr>
<td>Zn</td>
<td>0.01-0.15</td>
<td>0.06</td>
</tr>
<tr>
<td>As</td>
<td>Nd-8,50</td>
<td>2.66</td>
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BOWL FURNACE FOR SMELTING

WHY Cu-As ALLOYS WERE ABANDONED

- Roasting of sulfide ores with arsenic caused arsenic to be lost as a sublimate.
- Due to the volatility of arsenic, its composition in copper could not be easily controlled.
- The availability of recognizable arsenic rich ores were limited.
- Toxic effect of arsenic was detrimental to the health of the smith.