Structural examinations of selected copper castings

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Received: 26.02.2010; accepted in revised form: 30.03.2010

Abstract
Studies were undertaken to examine the copper metallurgy and casting, taking into account both the historical problems of copper fabrication as well as modern technology. Examinations were carried out on copper from archaeological sites and on copper produced nowadays as cast parts for the power engineering industry.

Keywords: copper Alloy; structure

1. Introduction
Modern science often requires analyses made by an interdisciplinary research team. Acting according to this principle, at the Faculty of Foundry Engineering, AGH University of Science and Technology in Cracow, studies were undertaken on the copper metallurgy and casting process, taking into consideration both the history of copper fabrication and modern technology. The point of departure for the studies was investigation of the technology by which high-quality copper castings were manufactured, carried out after an analysis of the old and modern refining operations. The examinations were carried out on copper originating from the archaeological sites and on copper produced nowadays in the form of castings for power engineering industry.

2. Examinations of old copper findings
Copper is one of the oldest metals known to mankind, and the history of its metallurgy is one of the most important in the development of economy. Copper was known and used by, among others, Egyptians, Phoenicians, Greeks, Spaniards, Celts and Galls, and also by the inhabitants of Germany and of the Czech and Polish lands \cite{1, 2}. Various proofs for the local process of copper smelting have been acquired as a result of archaeological studies of the fragments of crucibles made from clay, of tuyères and copper products. An important group of the earliest copper objects includes tools and weapons, and ornaments like bracelets, spaulders and rings, as well as various cult objects \cite{2, 3}. A trade route was running through Poland making transport of copper to sea ports possible. An important place on this route was Cracow, where raw materials were transported from mines and old metallurgical plants located in Slovakia. From Cracow, copper was carried to Gdańsk, and further by sea to Antwerp.

Along with the development of metallurgical processes, smelting of different polymorphous ores became possible. The individual components were separated at a final stage of the process. The ores of lead and copper often contained high content of the most desired metals, i.e. silver and gold, both of which were recovered \cite{4}. In Middle Ages, shaft furnaces were already used, mainly for smelting of copper and copper concentrate; also furnaces for the separation of lead and silver and for metal refining were designed \cite{3}.

Nowadays, owing to its electrical and thermal conductivity as well as good corrosion resistance, pure copper is used in the manufacture of castings for power engineering industry. These properties are obtained through proper treatment of molten metal, mainly the removal of gaseous impurities.

Studies of old technologies used in copper metallurgy and casting, based on archival sources and historical excavations, were completed with analyses of the historical material. The
metallic material acquired for investigations mainly originated from the excavation works carried out at archaeological sites in the Main Market Square in Cracow in the period of 2005-2010. It was enriched with some objects from the collections of Central Marine Museum in Gdańsk and from the Archaeological Museum in Cracow and its local division at Nowa Huta.

The archaeological material, dated by experts to the 14th-15th century, was subjected to quantitative and qualitative analyses and examinations. The following examinations were made: macro- and micrometallographic examinations by optical microscopy and scanning electron microscopy. The structural examinations were performed on scanning electron microscope with X-ray microanalyser JEOL 5500LV equipped with EDAX attachment for non-dispersive X-ray analysis. Trace elements were analysed by the method of Induced Coupled Plasma Atomic Emission Spectroscopy – ICP AES – using ELAN 6100 mass spectrometer with inductively coupled plasma made by Perkin Elmer. Samples of modern copper examined for the content of trace elements were prepared for the examinations carried out on a GDS 850A (LECO) emission spectrometer.

Table 1. The results of chemical analysis of copper samples (wt. %) K0, M0, M1, M7, P5-P8 modern copper casting, G2-G3 archaeological samples; the analysis done by emission spectrometry.

<table>
<thead>
<tr>
<th>Element</th>
<th>K0</th>
<th>M0</th>
<th>M1</th>
<th>M7</th>
<th>P5</th>
<th>P6</th>
<th>P7</th>
<th>P8</th>
<th>G2</th>
<th>G3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn</td>
<td>0.0392</td>
<td>&lt;0.0092</td>
<td>0.0245</td>
<td>0.0617</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>&lt;0.0016</td>
<td>&lt;0.0016</td>
</tr>
<tr>
<td>Pb</td>
<td>0.0238</td>
<td>0.0062</td>
<td>&lt;0.0039</td>
<td>&lt;0.0044</td>
<td>0.01</td>
<td>0.009</td>
<td>0.004</td>
<td>0.007</td>
<td>0.837</td>
<td>0.809</td>
</tr>
<tr>
<td>Sn</td>
<td>0.0260</td>
<td>0.0238</td>
<td>0.0119</td>
<td>0.0140</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.108</td>
<td>0.0682</td>
</tr>
<tr>
<td>P</td>
<td>&lt;0.0001</td>
<td>&lt;0.0001</td>
<td>&lt;0.0001</td>
<td>&lt;0.0001</td>
<td>0.015</td>
<td>0.014</td>
<td>0.005</td>
<td>0.012</td>
<td>0.0008</td>
<td>0.0005</td>
</tr>
<tr>
<td>Mn</td>
<td>0.0005</td>
<td>&lt;0.0003</td>
<td>&lt;0.0003</td>
<td>&lt;0.0003</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>&lt;0.0003</td>
<td>0.0012</td>
</tr>
<tr>
<td>Fe</td>
<td>0.0251</td>
<td>0.0124</td>
<td>0.0172</td>
<td>0.0229</td>
<td>0.00</td>
<td>0.002</td>
<td>0.00</td>
<td>0.00</td>
<td>0.0036</td>
<td>0.0142</td>
</tr>
<tr>
<td>Ni</td>
<td>0.0035</td>
<td>&lt;0.0035</td>
<td>&lt;0.0035</td>
<td>&lt;0.0040</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.0327</td>
<td>0.0383</td>
</tr>
<tr>
<td>Si</td>
<td>0.0005</td>
<td>&lt;0.0005</td>
<td>&lt;0.0005</td>
<td>&lt;0.0005</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>&lt;0.0005</td>
<td>&lt;0.0005</td>
</tr>
<tr>
<td>Al</td>
<td>0.0112</td>
<td>0.0027</td>
<td>0.0038</td>
<td>0.0034</td>
<td>0.001</td>
<td>0.001</td>
<td>0.00</td>
<td>0.001</td>
<td>&lt;0.0008</td>
<td>&lt;0.0008</td>
</tr>
<tr>
<td>S</td>
<td>0</td>
<td>0</td>
<td>0.0003</td>
<td>0</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.0508</td>
<td>0.0808</td>
</tr>
<tr>
<td>Total</td>
<td>0.1298</td>
<td>0.0451</td>
<td>0.0577</td>
<td>0.1021</td>
<td>0.026</td>
<td>0.026</td>
<td>0.009</td>
<td>0.02</td>
<td>1.0329</td>
<td>1.0120</td>
</tr>
</tbody>
</table>

Fig. 1. Microstructure of copper castings, 500 x, etched with Mi15Cu, (a) archaeological copper from Central Marine Museum in Gdańsk, (b) modern copper casting.
Fig. 2. Microstructure of copper castings, 500 x, etched with Mi15Cu, (a) casting made from cathode copper, (b) modern copper casting

Fig. 3. SEM images of archaeological samples of the smelted copper, 1500 x, (a) copper from the Main Market Square in Cracow, (b) copper from Central Marine Museum in Gdańsk. [7]
Table 2. Chemical analysis (wt%) based on X-ray microanalysis of 2a.

<table>
<thead>
<tr>
<th>Analysis range</th>
<th>Cu</th>
<th>S</th>
<th>Fe</th>
<th>Pb</th>
<th>Al</th>
<th>O</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>51.8</td>
<td>36.8</td>
<td>9.8</td>
<td>-</td>
<td>-</td>
<td>1.6</td>
</tr>
<tr>
<td>2</td>
<td>55.8</td>
<td>35.8</td>
<td>7.3</td>
<td>-</td>
<td>-</td>
<td>1.1</td>
</tr>
<tr>
<td>3</td>
<td>97.8</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.5</td>
<td>1.7</td>
</tr>
</tbody>
</table>

Table 3. Chemical analysis (wt%) based on X-ray microanalysis of 2b.

<table>
<thead>
<tr>
<th>Analysis range</th>
<th>Cu</th>
<th>S</th>
<th>Sb</th>
<th>Pb</th>
<th>As</th>
<th>Sr</th>
<th>O</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>9.7</td>
<td>-</td>
<td>5.9</td>
<td>42.1</td>
<td>27.8</td>
<td>2.2</td>
<td>12.3</td>
</tr>
<tr>
<td>2</td>
<td>15.9</td>
<td>-</td>
<td>3.5</td>
<td>35.1</td>
<td>31.7</td>
<td>1.5</td>
<td>12.2</td>
</tr>
<tr>
<td>3</td>
<td>96.8</td>
<td>0.2</td>
<td>0.4</td>
<td>-</td>
<td>1.9</td>
<td>0.3</td>
<td>0.4</td>
</tr>
</tbody>
</table>

Fig. 4. SEM images of corrosion-affected layers present in archaeological samples of the smelted copper, (a) copper from the Main Market Square in Cracow, corrosion in soil, 1000 x, (b) copper from Central Marine Museum in Gdańsk; corrosion in seawater, 2500 x.

The analysis of historical material shows that, as early as in the period of the Middle Ages and Renaissance, copper smelting from ore was already at a relatively advanced level of technology. The investigations of copper honeycombs revealed high purity of the smelted material with copper content reaching even 99%. The multi-stage processes used at that time resulted in the manufacture of raw materials characterised by very low content of the impurities. This has been confirmed by the performed analyses (Table 1), where the total of impurities was comprised in a range of 0.84 - 2.17%. Special attention deserves the fact that the most desired noble elements contained in copper ores, i.e. silver and gold, have remained there in a very low content only, i.e. in the range of Au 0.0001-0.0002% and Ag 0.019-0.035%. On the other hand, prominent differences were observed in the content of iron, which in samples 1-3 was comprised in a range of 0.034-0.06% and in sample 4 amounted to 1.29%. Similar differences in the chemical composition of honeycombs were also observed during examinations carried out by the method of X-ray fluorescence analysis in microregions (Figs. 2a, 2b, Table 2,3) [7]. The structure shows the presence of fine inclusions of sulphides and oxides and of metallic elements forming various impurities in the copper material.

Another problem, strictly related with the investigations of the pieces of art and archaeological monuments, is corrosion of metallic objects. This problem is most serious in the excavated monuments. The archaeological copper samples were examined for surface changes caused by corrosion due to a long stay in soil (samples collected in the Main Market Square in Cracow) and in seawater (samples collected in the Bay of Gdańsk). Some attention deserves the fact that, depending on the environment, the metal objects were undergoing different types of corrosion. In the medium of seawater, mainly pitting and intercrystalline corrosion was observed, while in the environment of atmosphere and soil, the general and local corrosion types prevailed. The analyses enabled detailed assessment of similarities and differences caused by the corrosion process. The electrochemical investigations
carried out in parallel, comparing the susceptibility to corrosion of both the historical and modern copper objects, have proved high corrosion resistance of the historical material and high quality of the examined samples [7, 8].

3. Examinations of copper castings

Copper castings were examined to evaluate the effect of selected deoxidisers on copper properties and conductivity. The effect of selected deoxidisers and modifiers on the structure and properties of cast primary copper windings used in power engineering industry was also investigated. Examinations were carried out on a SIGMA TEST 2.067 conductivity tester made by Fürster. The examinations were completed with an analysis of the gas content before and after the application of deoxidiser, using a LECO apparatus in measurements of the content of gaseous impurities. Examples of the results obtained on deoxidised copper are compared below (Table 4).

<table>
<thead>
<tr>
<th></th>
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<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>50, 51, 50, 51</td>
<td>50</td>
<td>Cu</td>
<td>-</td>
<td>305</td>
</tr>
<tr>
<td>2</td>
<td>53, 54, 53, 53, 53</td>
<td>53</td>
<td>Logas</td>
<td>3,5</td>
<td>136</td>
</tr>
<tr>
<td>3</td>
<td>53, 54, 54, 54, 54</td>
<td>54</td>
<td>Logas</td>
<td>8</td>
<td>173</td>
</tr>
<tr>
<td>4</td>
<td>50, 46, 50, 46, 47</td>
<td>48</td>
<td>Cu</td>
<td>-</td>
<td>350</td>
</tr>
<tr>
<td>5</td>
<td>53, 54, 55, 54, 54</td>
<td>54</td>
<td>P3</td>
<td>3,5</td>
<td>244</td>
</tr>
<tr>
<td>6</td>
<td>54, 54, 55, 56, 56</td>
<td>55</td>
<td>P3</td>
<td>8</td>
<td>93</td>
</tr>
</tbody>
</table>

Similar as historical material, modern copper castings are often characterised by the presence of numerous impurities, mainly the gaseous ones. The source of these impurities includes metallic charge, furnace atmosphere, atmosphere in foundry shop, and tools not dry enough. Atmosphere is the first source of impurities present in melt.

Gases entering in reaction with molten metal can be divided into simple and complex. Simple gases include H₂, O₂, N₂, Cl₂, while complex gases include, among others, H₂O, SO₂, CO, CO₂ [6]. From data obtained on the deoxidising and modifying effect of refiners it follows that high deoxidising effectiveness combined with minimum influence on conductivity can offer the low-phosphorus materials. The time necessary for the molten metal/deoxidiser reaction to take place should be considered as well. From the investigations it follows that in most cases this time amounts to 2-4 minutes. The effect of copper deoxidising with deoxidisers and/or deoxidising-modifying agents is very intense and, when done with complex compounds, has relatively strong effect on both microstructure and oxygen content.

4. Conclusions

Studies of the historical metallic samples, including the metallographic analysis and testing of corrosive behaviour, have contributed a lot to better knowledge of these objects. They have also proved the high level of mediaeval copper metallurgy manifested by the high quality of final products. At the same time it should be mentioned that a comparison of the content of trace elements in archaeological samples and in modern electrolytic copper of the M1E type has revealed a 1% difference in the content of impurities. This proves that the technology of molten metal fabrication was quite well mastered by the old copper metallurgical works; it also depicts the difficulties in maintaining a high level of the copper purity.

Owing to technical progress, modern techniques of molten copper fabrication for the subsequent manufacture of castings characterised by high technological properties have been improved quite considerably and nowadays enable us to produce materials of nearly ideal purity, reaching 99.994% Cu.

The investigations based on archaeological material are expected to further enrich our knowledge of the history of old findings and related technological processes as well as corrosion phenomena. Studies of the structure of copper and its alloys and of the modern metal refining technologies, combined with archaeometallurgical investigations, can help us a lot in understanding the properties of historical objects and in the selection of best preservation means and best technology for the manufacture of high-quality copper castings.
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