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The Assessment of the Cast Quality of Monuments on the Basis of the Analysis of the Copper Alloy Casting Properties

The quality of large cast sculptures depends first of all on the foundrymen. The skills of the foundrymen were based on the theory and practice of foundry manufacture of a certain time and on the availability and quality of materials, which depended on different facts like the political and economic situation in different countries. There are only a few descriptions of casting technologies of large cast monuments, e.g. those included in the scientific program "COPAL" but they are not detailed enough.

It is most important to understand that the expert foundryman will be able to do the scientific analysis of the cast features of the monuments by the knowledge of the chemical composition of an alloy from which the sculpture was cast. The availability of the data on the chemical composition of the alloys of the COPAL monuments allows an analysis of the different casting properties on the basis of the modern theory of casting processes, mainly by postulates, that connect alloy properties with information from the phase diagrams of the alloys. The author presents the analysis on the data for 6 alloys, from which the monuments, investigated under the program "COPAL" were cast. These alloys could be divided into two groups: Cu – Sn – Pb and Cu – Zn – Sn (Fig. 1).

The main technological properties of casting are:
– Fluidity and castability;
– Shrinkage (linear and volumetric);
– Hot-shortness;
– Liquation;
– Scabformation;
– Interaction with gases.

The quantitative values of the casting properties for specified alloys were taken from modern literature and the author's works. Some of them were investigated at the laboratory of casting at the Moscow State Evening Metallurgical Institute, where the author works. The values of the casting properties of the alloys, according to the modern theory of casting processes, are first of all correlated with the values of the crystallization range of the alloys: $\Delta T = T_{liquidus} - T_{solidus}$ (that is in the temperature range where the metal exists in liquid and solid state).

Fluidity and Castability

Fluidity and castability are the ability of a liquid metal to fill the mold. The significance of the crystallisation temperature range and the fluidity of six alloys are indicated in Figure 2. The alloys with the narrow crystallisation temperature range (Cu – Zn) have a higher value of fluidity than alloys with the broad temperature range (Cu – Sn).

How could this affect the quality of casting?

The filling of the molds with the liquid Cu – Zn alloys (brass) occurs with increased volumetric and linear speeds of cast, i. e. it takes less time when the other parameters of cast like pouring temperature, mold properties, value of pressure of a liquid metal are constant. By this way cavities of the mold will be filled be-
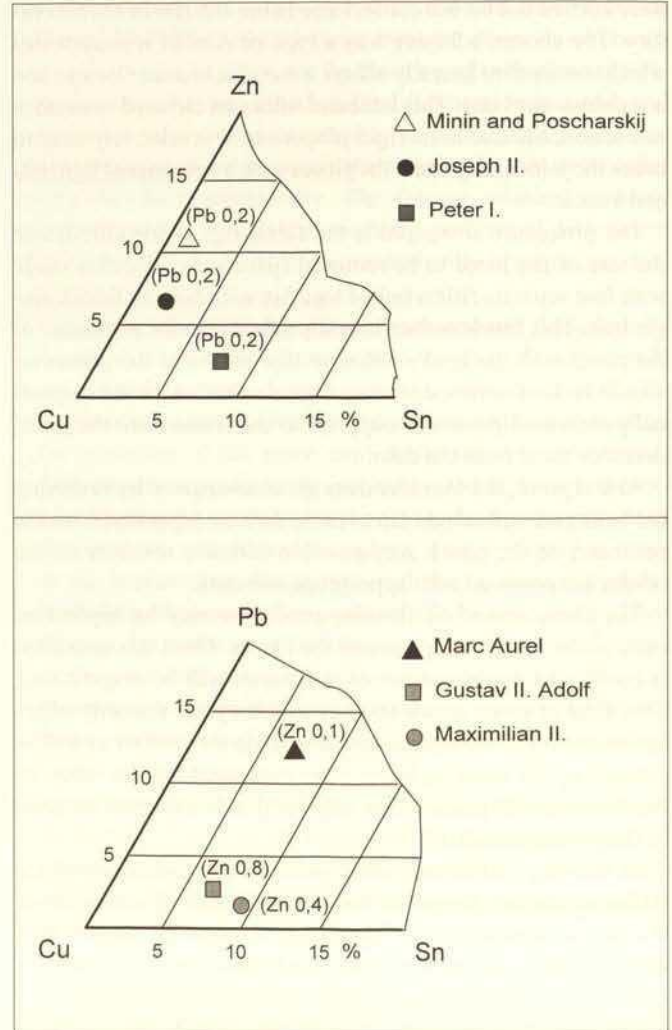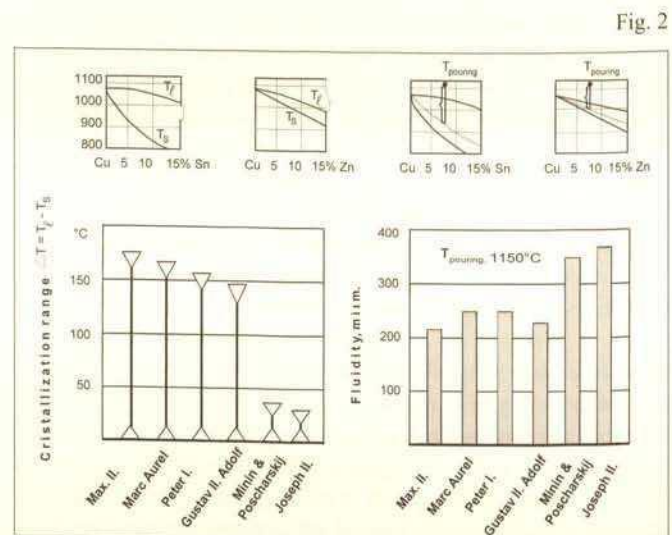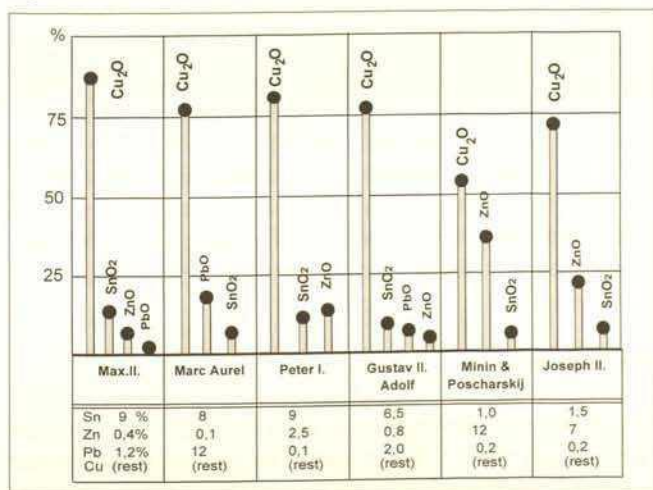

Fig. 1

Fig. 2

fore the metal loses its fluidity. However, the high speeds give a stream filling of molten metal. This could result in the unfilling of separate casting fragments (especially of lateral fragments of the castings). Therefore casting defects like small-sized underfills, misruns and runs will be detected.

The alloys with a wide crystallization range (Cu – Sn) require a longer pouring time to obtain the same sizes of casting, but the filling of the molds occurs more quietly and with smaller linear and volumetric speeds of filling than in the case of brass. This fact seems to be positive, but on the other hand the molten metal can lose its fluidity. During the cooling of the metal there is a danger of partial filling with the formation of significant cavities in the castings. It is difficult to cure these defects. Therefore, tin bronze cast requires an increased overheating of the liquid metal or the mold. This was inconvenient and did deteriorate the surface quality of the castings.

The quality of filling of the molds with a liquid metal depends not only on its fluidity, but also on the structure and properties of oxide films, which are formed on the surface of the liquid metal. The use of zinc, instead or together with tin in copper art alloys was caused not only by economical reasons (zinc was always cheaper than tin), but also by the necessity to improve the casting properties of art alloys. Until the application of phosphorus as a deoxidation additive in tin bronze (~ 1860), the presence of viscous films ($Cu_2O + SnO_2 + PbO$) on a surface of bronze made the filling of a thin-walled casting difficult. On Fig. 3 the composition of oxide films is presented, removed from surface of melts of 6 types of copper alloys (without addition of phosphorus). Oxide inclusions not only reduce the fluidity of the bronze, but also form inclusions in the volume and on the surface of the castings. This reduces the quality of casting and the macrogeometry of the surface of a sculpture. These allocations are the centres of local corrosion due to being more hygroscopic stains. The availability of zinc in tin bronze reduces the strength of oxide films and promotes the increase of fluidity of a metal. The cast of alloys in Cu – Zn system has its own features. At the temperatures of pouring evaporation of zinc occurs, which interacts with oxygen from the air and forms solid flaky oxides of white colour. The small-sized zinc oxide inclusions are partially removed from the mold. However a significant part of them remains on the casting surface in the shape of small-sized stains. As time passes the major part of these inclusions is removed by atmospheric precipitations, however their traces re-

main. In Figure 4 details of the sculpture of M. and P. are shown with this kind of traces. These traces are caused by the named defects explained by the author.

Shrinkage Processes

The interval of crystallization affects the mode of solidification, the form and the extent of shrinkage. The alloys with narrow crystallization range (brass) form predominant concentrated shrinkage in those places where the metal solidifies at the last moment. Tin bronze poured in the molds solidifies in the vol-

Fig. 4
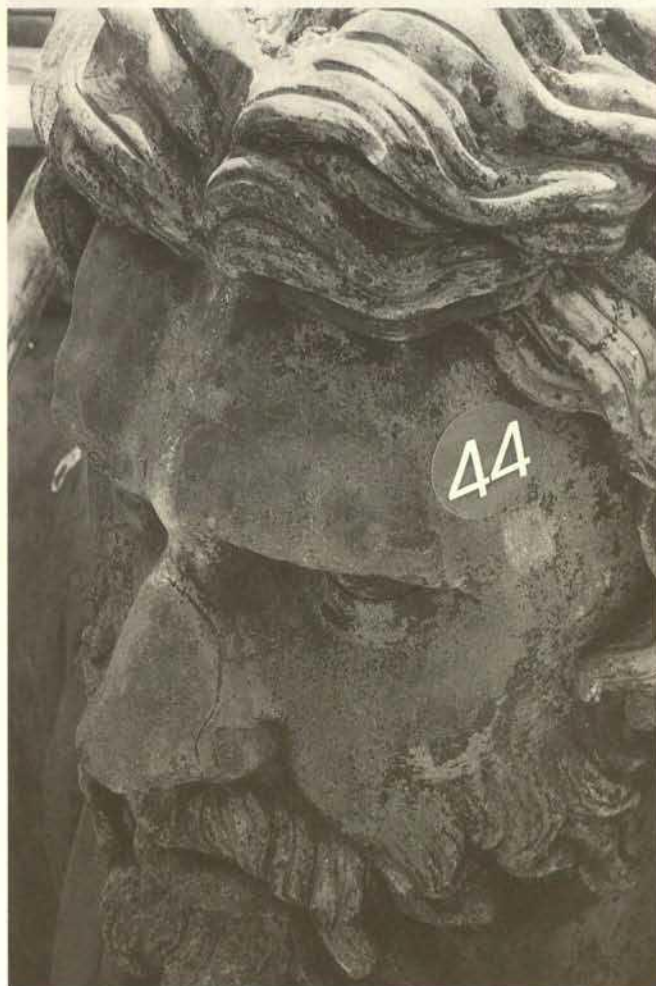
ume mode and shrinkage is realized in the shape of a scattered shrinkage porosity: micro (20-400 µm) and macro (0,1-1,0 mm). In Figure 6 the significance of linear and volume shrinkage is compared for the six alloys. The microstructures of the cross sections (Colour Plate IV.1-6)[1] of separately cast specimens (thickness 5 mm) show that alloys with wide crystallization range have the heaviest shrinkage porosity.

The ratio of the values of scattered and volumetric shrinkage in casting depends also on temperature parameters of casting technology. The majority of large art castings were poured over hot (300-700 °C) molds. This promotes the occurrence of the partially scattered porosity in alloys (brass) with narrow crystallization range. In alloys with wide crystallization range

Fig. 3

	Max.II.	Marc Aurel	Peter I.	Gustav II. Adolf	Minin & Poscharskij	Joseph II.
Sn	9 %	8	9	6,5	1,0	1,5
Zn	0,4%	0,1	2,5	0,8	12	7
Pb	1,2%	12	0,1	2,0	0,2	0,2
Cu	(rest)	(rest)	(rest)	(rest)	(rest)	(rest)

Fig. 5a

Fig. 5b

cal composition of the alloys, the thickness of casting walls and other technological parameters of cast. In certain conditions the surface skin could be absent or mechanically removed during the primary and subsequent processing. The castings of this type have a large surface area with porous structure. The state of the cast surface skin is especially important for art castings made from tin bronze (Cu – Sn). The availability of cast micro- and macroporosity can influence the corrosion rate of copper alloys. The rates determined on specimens and presented in the literature are about $8 – 30 \times 10^{-4}$ mm per year. With regard to cast porosity, coalescence of profile, streamlining of form, general configuration, the availability of hollows and some other factors, in real casting the corrosion rate of copper alloys could increase by one order of magnitude. The availability of macro and micro porosity in cast sculpture is especially dangerous in northern re-
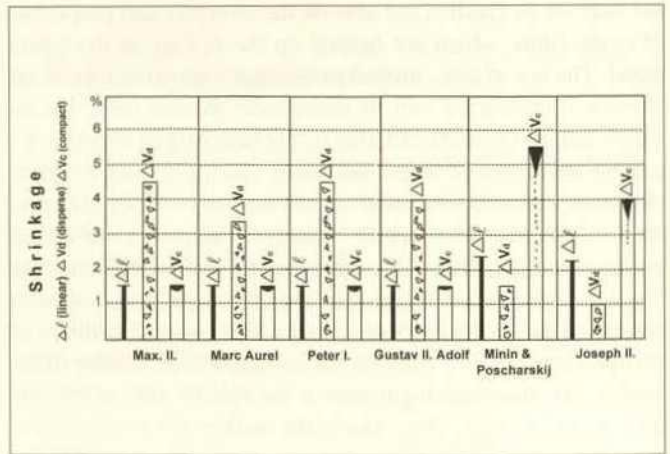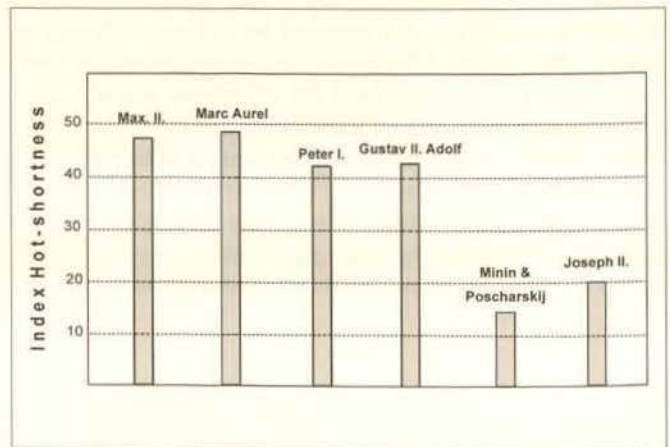

Fig. 6

Fig. 7

(tin bronze) the macro and micro shrinkage porosity is increased. The transit microporosity is the most dangerous for the quality of metal. These volume areas of the castings are permeable for water and gases (ungermetic?). Above all the presence of micro- and macroporosity results in an increased contact surface of the castings with the aggressive and damp environment. The type of macrostructure of the casting is of importance. The casting structure consists of a small dense layer of cast surface of metal (thickness 0,1-2,0 mm) and an internal part with an equiaxial structure of casting grains possessing a lower density. The ratio of the sizes of these two zones depends on the chemi-

gions with extreme temperature fluctuations during the winter periods. The conversion of moisture into ice in macro- and micropores, accompanied by increase of volume, lowers the tightness of cast metal and reduces its corrosion resistance.

Hot-Shortness

Hot-shortness results in the cracks in castings. The "hot" and "cold" cracks must be distinguished. The "hot cracks" are formed in crystallization range (in solid-liquid state) and connected with

the chemical composition and structure of alloys. The "cold" cracks are formed below solidus temperature due to the internal stress arising in the metal at shrinkage. In Figure 7 the indexes of hot-shortness for the considered alloys are indicated. Hot-shortness of tin-bronze is higher than hot-shortness of brass. The risk of formation of "cold" cracks is higher for the brass.

In large art casting the cracks are found in places where thin sections of the castings meet thick sections. These cracks will also be formed in places where the shrinkage of the metal in the mold is hindered (inner core of mold, metal skeleton). All these cracks concern to "hot" and their formation is directly connected with hot-shortness of alloys.

The "cold" cracks reasonable will be seldom formed at cast tin-bronze. The thermal internal stress arising at the solidification of art castings poured in hot molds is usually small and does not exceed the strength of alloys.

Liquation – Inhomogenity of the Chemical Composition in Casting

Direct and inverse liquation must be distinguished. Inverse liquation results in casting defects, direct liquation does not. Inverse liquation is displayed in extrusions on the surface of a casting where low temperature liquid parts formed at solidification of alloys with wide crystallization range: for example, tin bronze contains the increased concentration of tin (8-12%) and lead (10-15%). The availability of increased concentration of tin in casting surface skin can be considered as a positive phenome-

non, as the surface corrosion resistance of the castings is increased. If the segregation of high tinbronze occurs in the shape of discrete sphere deposition ("tin-sweat") or plates, this has to be considered as a casting defect. In a body casting, where "tin-sweat" has been formed, there are blanks channels in the form of transit porosity. This porosity lowers the corrosion properties of castings. Therefore, such plates should be closed by mechanical way (strain hardening).

Gases in Copper Alloys

Apart from the oxidation during the melting and pouring of copper alloys the dissolution of hydrogen into the metal has to be taken into consideration. The hydrogen allocation in shrinkage increases them in size.

Conclusion

On the basis of the connections between casting properties and chemical compositions of the alloys it is possible to get additional information about the cast quality of historic bronze monuments.

Citation

1 The cross sections were prepared by Prof. Dr. Bernhard Pichler, Institut für Silikatchemie und Archäometrie, Vienna.