COPPER AND COPPER BASE ALLOYS - PART I

H.F. Nanayakkara
Former Deputy Chief Engineer/
Foundry Manager
J.I.C.A Foundry Technology
Development Project

Introduction

The origination of the art of making sculptures in Sri Lanka has a very long history, and is old as her civilization. The sculptures are objects made by carving from rock or shaping it from wood, clay, or any other material. Casting of the same also makes it from metals or alloys of metals. These technologies were transferred to Sri lanka from India during the period of King Devanampiyatissa.

With the present day technology even the patterns are cast from different types of waxes or plastics. The moulds are made from steel or copper alloys. This method is practiced in production shops. It is worthy to note that bronze castings which contain over 85 percent copper could be gilded with 24 carat gold. Most of the valuable religious images cast during the Anuradhapura and Polonnaruwa periods were done so. As for gilding purpose the surface has to be finished to an extreme smoothness. The jeweller's gilding alloys is 94 percent copper and 6 percent Zinc.

High conductivity copper alloys

Cast pure copper and high copper alloys have been used for many years in the applications requiring high electrical conductivity. It is not easy to obtain sound castings from pure copper unless the correct melting and fluxing techniques are known and applied. This causes much difficulty in obtaining quality castings with copper thus reducing its electrical conductivity.

Porosity due to gases

Any cavities or unsoundness present in the metal will reduce the conductivity to a great extent. Such defects can result from liquid shrinkage and gas evolution during solidification. Molten copper of (98 - 99) percent purity, at 100°C above its melting point can hold in solution 10 cubic centimeters of hydrogen per 100 grams molten metal. About half of this quantity is expelled from the solution as the molten copper cools to its solidification temperature. During the phase change from liquid to solid a further 3 cubic centimeters hydrogen per 100 grams of metal which is maintained in solid solution. Porosity due to hydrogen is most likely to result from that which comes out of solution during phase change.

Another gas, which must receive consideration, is oxygen, which combines with molten copper to form cuprous oxide. If hydrogen comes out of solution in the presence of cuprous oxide it reacts with it to form water vapor or steam.

This is known as "steam reaction" and causes gross porosity in high conductivity copper castings. Therefore, to avoid steam reaction it is sufficient to ensure that the molten metal is free from one of the gases.

Fluxing and deoxidation techniques

The standard procedures were developed aiming to keep the cuprous oxide formation to the lowest possible level. Thus melting is performed in some cases under cover of a reducing flux, which inhibits pick up of oxygen, followed by complete deoxidization. The oxidizing technique means simply that of all the fuel oil or the gas-fired furnaces must be burned thoroughly and has more than 0.5 percent residual oxygen left in the products of combustion. It is also possible to provide oxygen to the liquid metal by the use of oxygen containing chemicals in fluxes and covers designed for this purpose.

The bulk of oxygen introduced by the oxidation treatment must be removed just before pouring by the addition of deoxidizer. This deoxidizer must have a higher affinity for oxygen than copper. Deoxidents, which have received some consideration, include aluminium, beryllium, boron carbide, calcium, calcium boride, lithium, magnesium, phosphorous, strontium, titanium, zinc.

Of all deoxidents phosphorous in the form of phosphorous copper has been frequently used as it is cheap, convenient and very effective, although it suffers from the disadvantage of adversely effecting the conductivity when present in amounts exceeding mere traces. Although in commercial practice residual phosphorous content is 0.05 percent, it is preferable to have 0.02 percent.

A residual phosphorous content of 0.022 percent is left in the melt when just 0.025 percent phosphor copper as 15 percent phosphorous copper is added. With a reduced phosphor addition of 0.1 percent which gives residual phosphorous content of 0.007 percent the oxygen content of the metal is still sufficiently high (0.010 percent) to promote gas porosity.

For high conductivity applications demanding electrical conductivity value greater than 80, a duplex deoxidizing treatment using phosphor copper and calcium boride or lithium may be economically utilized. Cadmium (0.5-1) percent has also been used in conduction with approximately 0.01 percent phosphorous.

In the duplex method a major part of the oxygen content is removed by partially deoxidizing with relatively inexpensive phosphor copper to a point where the residual phosphorous could exit only in trace. Then the deoxidization process is completed with an addition of a more expensive deoxidant efficient and economical. Another practice could be the molten metal first flushed by nitrogen gas for removing hydrogen and then deoxidized by phosphor copper.

Tin bronzes and leaded tin bronzes

Tin bronzes are copper base alloys containing (2-20) percent tin, with zinc less than tin and with lead less than 0.5 percent. The leaded tin bronzes are similarly defined but with lead contents over 0.5 percent and under 6 percent. Under equilibrium condition tin is soluble in copper up to about 16 percent at $(510\text{-}520)^0$ C. The presence of oxygen in bronzes limits the amount of hydrogen that can exist in equilibrium with it. However the presence of zinc lowers the solubility of oxygen if it is present above 0.5 percent, if so the degassification by oxidation becomes less effective.

Melting practice

Metal should be melted under a slightly oxidizing atmosphere if the charge has been melted and heated to pouring temperature under sufficiently oxidizing conditions, the hydrogen content will be held to a minimum. The speed of melting is the most important factor. The solution of hydrogen in the liquid metal is a function of both time and temperature. The metal should be melted as rapidly as possible and raised only slightly over the necessary tapping temperature.

Covers can be divided into two groups; natural and reacting type. A natural cover is simply a layer of slag inert to the melt, protecting it from the atmosphere. It helps to reduce the melt losses. Glass is sometimes used for this purpose. Flux can offer some protection against careless and improper melting procedures. These materials react with the melt or with elements in the melt.

A simple deoxidization treatment with phosphor copper should put the metal in proper condition for pouring. The amount required for deoxidization will vary according to the metal composition, melting process, and types of furnace. It is customary to add 60 grams of 15 percent phosphor copper per 45 kilograms of metal to perform this function. Thus equivalent to adding 0.02 percent of phosphorous. An alternative procedure for melting bronze and gunmetal can be used. It consists of the use of a natural or reducing flux cover and subsequent degassing of the melt with nitrogen at a rate of 1 liter per kilogram melt.

Properties and application

The tin bronze has excellent resistance to corrosion and wear and tear. It is used for valve and pump - bodies steam fittings, paper machinery, bearings and pump impellers. The leaded tin bronzes are basically same as the tin bronzes but 2 percent lead is added. The addition of this relatively small amount of lead greatly improves machinability.

High leaded tin bronze

The high leaded tin bronzes are basically alloys of copper, tin and lead containing up to 20 percent tin and lead over 6 percent. Lead in a few cases may reach the 50 percent level. These combinations are not alloys in the true sense because in the solid state they exist as a mechanical mixture of copper with lead.

Lead is insoluble and should be distributed uniformly throughout the copper to impart good anti friction properties and a high lead carrying capacity The high leaded tin bronzes also possess excellent corrosion resistant properties, which markedly expand their field of application. It is necessary for even dispersal of the lead which is the main problem in producing satisfactory lead bronze castings.

All combinations of copper and lead up to 36 percent of lead form a homogeneous melt at temperatures above 1080^{0}C. On cooling below this temperature, crystals of copper solidify and separate out from the liquid. This process continues until the temperature reaches about 950^{0}C when all the copper will have solidified to form a network of primary copper crystals. The lead still in the molten state will occupy the space between copper crystals. Finally at about 320^{0}C both metals will be solid and co - exist as separate constituents. If the cooling time is prolonged, as it may be when thick section castings are made in stand moulds, the lead which is of a higher density tends to coagulate and segregate to from flakes. Therefore it is advantageous to cast into chill moulds. With high lead bronzes containing more than 36 percent lead the conditions become somewhat more complex. Two to four ounces per hundred pounds of metal is stirred into the metal in the pouring ladle.

Melting practice

For highest and most consistent quality castings these high leaded alloys should be melted under slightly oxidizing atmosphere. Melting of these high lead bronze alloys actually starts at about (320^0 - 330^{0}C) the melting point of lead. During melting it is essential to ensure the complete solution of the lead in the copper. To accomplish this the alloys must be heated to a high temperature (1220^0 - 1300^{0}C) although not necessarily poured from this temperature range.

First copper is melted and then thoroughly deoxidized with 15 percent phosphor copper. The lead (and if tin is required) is pre heated to about 200^{0}C and introduced into the copper. The melt is covered with a flux based on feldspar and phosphate which is capable of dissolving lead oxide, and then charge through up to the super heating temperature in accordance with its lead content. The best structure for lead bronzes is achieved by preparing in the first place, an 80 - 20 copper lead melt which stirred thoroughly, super headed to 1350^{0}C and cast into pigs which are used as the main ingredient of the charge. Heavy oxidation of the lead must be avoided or irregular cavities containing a grayish powder may be present in the castings. Silicon and phosphor residuals are also to be avoided as they combine with lead oxide to form heavy fluid silicates and phosphates, which do not separate readily from the molten metal.

Suggested pouring temperatures are,

15 percent lead	-	1080^0 to 1100^0 C
20 percent lead	-	1050^0 to 1070^0 C
30 percent lead	-	1030^0 to 1050^0 C

Phosphor Bronzes

The phosphor bronzes are relatively pure copper - tin alloys with less than 0.5 percent of zinc and rarely more than 0.5 percent phosphorous. The low zinc levels make these alloys much less sensitive to hydrogen porosity from metal mould reaction. Melting may be performed under somewhat less oxidizing condition. Often called "tin sweet", this condition may occur in phosphor bronzes of high phosphorous and tin contents. It appears as beads of oxides on the outside of the castings. These oxides have tin phosphorous. The tin and phosphorus ratios are much above the average levels of the parent alloys. Gassy melt, pouring temperature, speed of solidification, high temperature gradients and a wide freezing range are all factors influencing this effect. Pouring temperatures are in the range of 1040^0 C - 1100^{0}C.

Copper Silicon Alloys

These alloys were developed as an alternative to tin bronzes. In recent years they have gained popularity because of their low tin content, high physical properties and corrosion resistant properties. Alloyed with copper, silicon, are bout 2 1/2 times as effective as tin in strength and hardness.

Silicon brasses contain over 0.5 percent silicon and over 5 percent zinc. Silicon bronzes are defined as those alloys containing over 0.5 percent silicon and less than 5 percent zinc except that copper content shall not be over 98 percent.

The best known composition contain about 4 percent of silicon. Although tin, iron, manganese and aluminium may sometimes be present, the mechanical properties of these alloys are primarily dependent on the amount of silicides precipitated during solidification.

Melting Practice

The best results are obtained when the alloys are melted under slightly oxidizing conditions. The metal should be melted as rapidly as possible, superheated about 60°C above the pouring temperature. Use of charcoal, as a cover is not recommended and fluxes are usually not necessary. If desired, however, lead free glass or fused borax may be used as a cover. Deoxidization is unnecessary because of the high silicon content, but if gas is absorbed some degassing treatment is necessary. Pouring range for these alloys vary from 1010°C - 1177°C, depending on the size of the castings and the section thickness. Silicon brasses and silicon bronzes are quite fluid and need not be poured as hot as other alloys. Tin increases hardness slightly and improves corrosion resistant action of silicon bronzes.

Copper Nickel Alloys

Nickel brasses contains over 10 percent zinc, nickel in amounts sufficient to give a white colour to the metal, and lead under 0.4 percent. The leaded nickel brasses conform to the same requirements, but contains over 0.5 percent lead. Leaded nickel bronzes contain 0.5 percent or more of lead.

The cast cupro - nickel alloys are generally of solid solution type requiring no head treatment. These alloys can be hardened and strengthened with small amounts of silicon, columbium, aluminium, titanium or beryllium or combinations of these elements.

Silicon and Colombian are the most commonly used alloying elements when properly balanced, yield alloys having a good combination of castability and mechanical properties.

Melting Practice

These alloys should be melted in slightly oxidizing atmosphere. Superheat as rapidly as possible to an adequate temperature, which depends on the nickel content, with 2 percent, heat to 1400°C and for monel metal (60 percent) nickel a temperature as high as 1650°C is required.

It is specially important that cutting compounds or any other organic materials should be removed before melting. There is no standard or ideal melting method in which gas will not be absorbed by the alloys and many degssifiers are sold under various trade names. The other nickel tin alloys require 56 grams phosphor copper per 45 kilograms of melt just prior to pouring. The nickel silvers require five ounces 70 - 30 copper manganese shots, 28 grams of magnesium and 85 grams of phosphor copper per 45 kilogram of melt. The cupro nickels require 150 grams of magnesium per 45 kilograms of melt.

Pouring temperatures range from 1120°C - 1400°C, depending on the casting size and section thickness.

(Part II will appear in the Next Issue)