Melt treatment of Copper – „Ways to a high tech material“

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Copper is presumably the first metal used technically by mankind. First archaeological discoveries date back 10.000 years. During time the application fields for Copper and its alloys diversified and changed drastically, especially in the last century. The biggest change of its use was initiated with the discovery of electricity; Copper is the second best electric conductor besides Silver. Today the major part of Copper (approx. 50%) is used in conductivity applications, either as pure metal in wires or as alloys in connectors. Early in the development phase it was discovered, that even very small amounts of impurities decrease its electrical conductivity significantly. In 1913 the International Annealed Copper Standard (IACS) was defined with 58 MS/m as minimum conductivity for high conductivity Copper [1]. Today qualities with 102.5% IACS and more are available. An increase of conductivity leads to a decrease in ohmic heat generation, this is especially important in the microelectronics industry.

Besides the use as electrical conductor, Copper is used in a variety of other applica-tions. Major fields are fresh water tubing, roofing, heat exchangers, as moulds for continuous casting of Aluminium and Copper, in power generators, in wire etc. In these cases other positive characteristics of Copper like superior heat conductivity and an outstanding corrosion performance are taken advantage off.

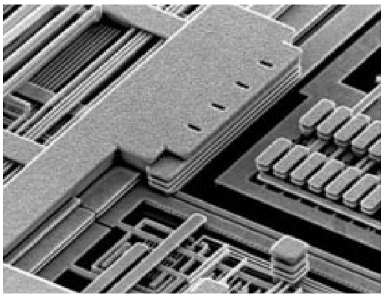
As starting material for Copper products Copper cathodes have the highest purity. This material can only be degraded during remelting by absorbing gases and solid inclusions. In secondary materials besides dissolved gases also alloying elements can be present as dissolved impurities that lower the properties. In this paper melt treatment technologies for the refining of secondary Copper melts are discussed. Especially the removal of gases from secondary Copper, the removal of dissolved metallic impurities as well as the treatment of solid inclusions are reviewed in detail.

Copper high tech applications

As mentioned above, Copper is mainly used for electrical conductivity applications. Besides the day-to-day household uses there are some fields where extreme product cleanliness is necessary. One example is the use as a cladding material for superconductors as shown in Figure 1. In case of cooling failure (most superconductors still need very low temperatures) the Copper matrix takes over the conduction because of good deep temperature conductivity until the system is shut off. Contrarily to the superconductors Copper does not reveal a sharp resistance step at a certain temperature.

Another example for Copper in high-tech industries is the application in the micro electronics industry. The electronic industry boomed with the development of the so called printed circuit boards (PCBs): a Copper foil is applied onto a non conducting substrate; alternatively the Copper is deposited electrolytically on the substrate. Then the circuit lines are printed with a special colour, the excess Copper is etched away and the conductor lines remain. Nowadays layers of only 50 µm Copper are applied. The boards with these thin Copper layers can also be made flexible. This is a great challenge for the material: it has to combine a high conductivity with good mechanical properties and elasticity.

One last example for a Copper high-tech application is the use in connector pins, an every day's, but often not recognised application. In modern automobiles numberless electronic helpers are connected to one central site. Therefore tens of connectors are combined in one connector system. The pins need a high conductivity but also a flexibility that allows to assemble and disassemble them often. At the same time they should be stiff enough to guarantee the electrical contact even at temperatures in an



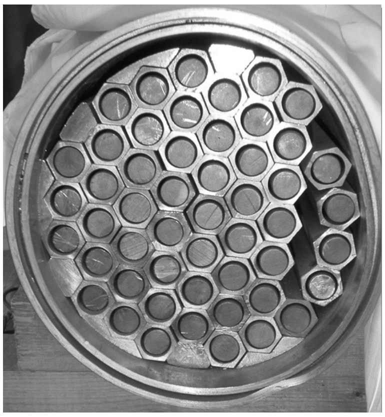


Figure 1: Copper in super conductors applications

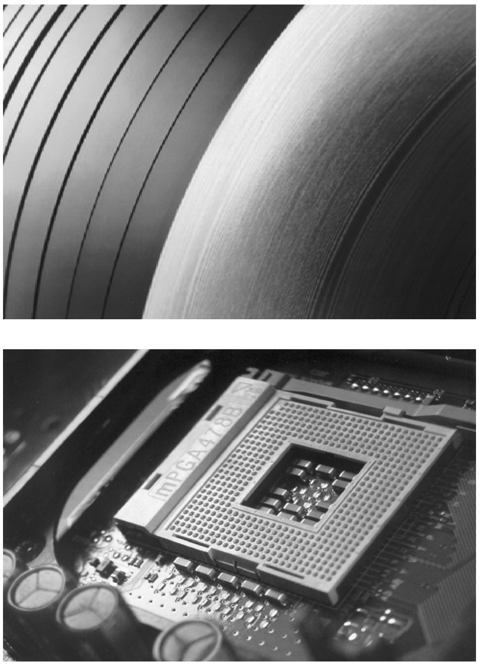


Figure 2: Copper strip and connectors

engine compartment and should have the same lifetime expectance as the automobile.

These three fields of application are, of course, only a very small extract of the Copper world. Copper and its alloys are also used in vacuum switches, vacuum capacitors, electron beam tubes, welding electrodes, heat exchangers, as moulds for con-tinuous casting of steel, Aluminium and Copper, in generators of power plants and wire and so on.

Processing of liquid Copper

The processing of primary Copper usually starts with the melting of Copper cathodes in a shaft furnace. For melting of Copper scrap in general induction furnaces or drum furnaces are applied. After the preliminary melting furnace the melt is either casted directly or subjected to a casting furnace where the melt is stored, (alloyed) and heated to casting temperature. For Copper the continuous wire casting by casting wheels or Hazelett casters is especially important. Besides wire casting also vertical and horizontal slab casting is applied as well as mould casting etc.

Impurities in Copper melts

The issue of impurities in Copper can be separated in two parts: impurities in primary Copper remaining or collected after refining electrolysis and impurities in secondary not electrorefined Copper scrap. The refining electrolysis produces cathodes with min. 99.995 wt. % Cu, the major remaining impurities are Silver, Sulphur, Nickel and Iron. But the contents are usually so small that they are not detrimental to the properties of Copper. The more critical elements in this sense namely Hydrogen and Oxygen as well as inclusions enter the primary Copper usually during the remelting and casting process.

In secondary materials the impurity matter is more complicated. Remelting of Copper scrap makes sense ecologically and economically because the material does not have to be lead back into the energy intensive primary electrolysis. There are two types of scrap, the sorted and mostly clean production scrap which is easily and directly reusable and end of lifecycle scrap (="old scrap") consisting often of a mixture of different alloys or even compounds with other metals and materials. In the process of producing a clean and specified alloy the undesired elements either have to be removed or diluted. In case they are not removed they can e.g. form intermetallic phases in the Copper matrix and as a result decrease the mechanical properties like the ultimate yield strength and the ductility. Due to the noble character of Copper, most elements like Silicon, Aluminium and Iron can easily be removed from a Copper melt by selective oxidation up to a very low concentration (activity). Physically and chemically more similar elements like Nickel, Cobalt, Tin and Lead have to be treated with more attention. Elements and compounds typically occurring in Copper melts are summarised in Fig.ure 4. Dissolved metallic impurities in small amounts mostly are not detrimental to the properties of Copper, but some elements as for example Lead and Arsenic precipitate at the grain boundaries of the Copper materials and lead to embrittlement of the material.

Generally an Oxygen and Hydrogen pick-up can lead to very negative effects. The two gases have a high solubility in liquid Copper that decreases sharply during solidification. This can lead to a bubble formation, i.e. porosity in the solid material. Oxygen can also form cuprous oxide (Cu_2O) above its solubility level that immediately reacts with the hydrogen of an annealing or welding atmosphere forming water vapour during annealing or welding, this phenomenon is called Hydrogen embrittlement. Dissolved Hydrogen and Oxygen (or Cu_2O) will react to water under extreme pressure in the

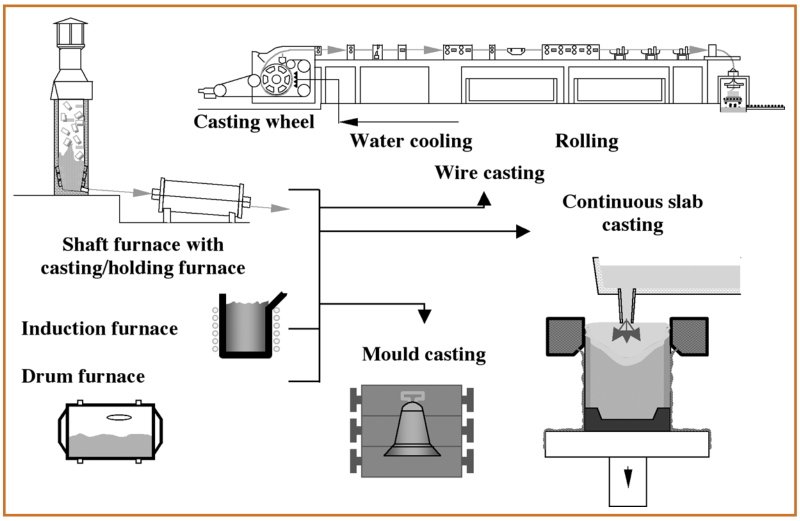


Figure 3: Processing of molten Copper to semi finished products

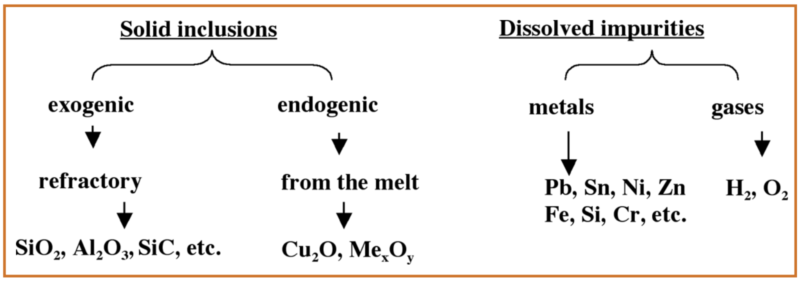


Figure 4: Impurities in Copper melts

lattice and will form cracks and lead to embrittlement.

Solid inclusions like intermetallics or oxides from alloying elements or the refractory material usually do not have a negative impact on Copper and Copper alloys. Because the density difference between the Copper melt and the particles is very high the particles tend to float to the surface (e.g. the density of Copper at 1100°C is 7.96 g/cm^3 while Iron oxide has a density of 5.25 g/cm^3 [2]). However Stokes law predicts that even at high density differences very small particles tend to stay suspended (In case of FeO particles the diameter smaller than 10 µm rise with 0.59 m/h). This leads to problems where wires with a very small diameter are drawn, for thin Copper foils or where small connector pins are made from thin Copper strip, being etched or punched.

Requirements for clean Copper melts

The most frequent impurity in refined Copper is Oxygen. If the alloy is not molten un-der Oxygen free atmosphere, Copper melts will always pick up Oxygen. Copper melts hyper saturated with Oxygen lead holes or the so called Hydrogen embrittlement during casting and welding in case Hydrogen is present in the material or the atmosphere. Dissolved Oxygen can also oxidise less noble elements which leads to the formation of brittle oxides in the material. In technically alloys, an Oxygen content of a few hundred ppm is accepted whereas in special grade materials the content has to be lowered below one ppm, some grades and their respective tolerated Oxygen content are shown in Figure 5.

In technical alloys the limit for specified metallic impurities mainly varies between 0.03 wt. % and 0.05 wt. %. A typical requirement for DHP-Cu is for example all ele-ments except for Phosphorous <0.05 wt. %, specified elements (Fe, Ni, Zn) max. 150 ppm all remaining elements max 50 ppm [3]. For high quality products lim-its of < 90 ppm Pb, < 50 ppm Sn and < 150 ppm Ni are required.

Solid inclusions are especially a problem in thin wire drawing and thin sheets rolling. Equation 1 describes the critical inclusion size, any particle bigger will initiate wire breaks:

$$d_{critical} \geq \frac{D \cdot K}{T^n} \qquad \text{Eq. 1}$$

with $d_{critical}$: inclusion size that leads to a break, D: wire diameter, K is a material con-stant, T: applied pulling tension, n: reduction ratio.

That means that the possibility for a wire break increases sharply with the size reduction ratio and the pulling tension. In foil production inclusions lead to a foil break in the worst case. Smaller inclusions lead to surface defects and elongated holes in the material.

Refining by melt treatment

The mentioned impurities can be reduced to an uncritical content by an appropriate melt treatment before casting. Different melt treatment technologies of Copper were developed for different impurities. The “classical” melt treatment of Copper is the oxidation by air or Oxygen injection or top blowing. With this technique elements that are less noble than Copper can be removed from the melt. Today this technique is often combined with a specific slag that can take up the impurity oxides and supplies a certain Oxygen potential to improve the impurity separation.

To remove dissolved gases especially Hydrogen and Oxygen the oldest method is first of all the right melt handling. That means that the open melt surface has to be shielded and melt transfer has to be in a laminar flow in order to inhibit turbulences. Hydrogen can be removed by an excess of Oxygen in the melt. After the removal of Hydrogen by oxidising conditions, the melt has to be treated under reducing conditions to remove the Oxygen. A new pick-up of Hydrogen has to be avoided by shielding of the melt with slags, coal layers or shielding gases. Oxygen is usually added by blowing air on the melt surface. For the reduction since

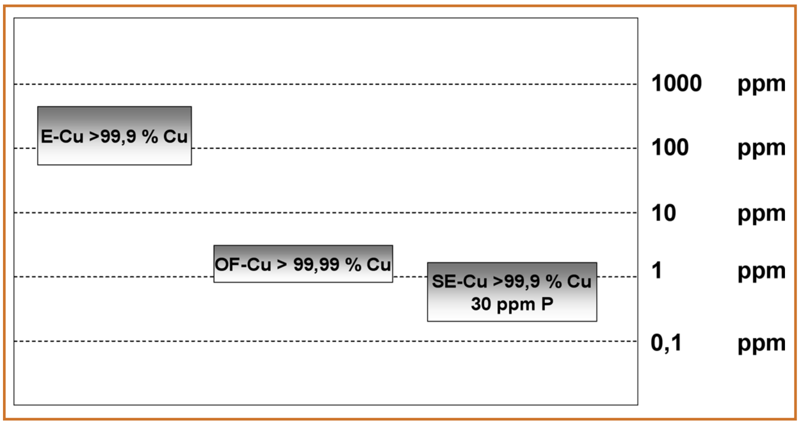


Figure 5: Requirements for Oxygen contents in Copper

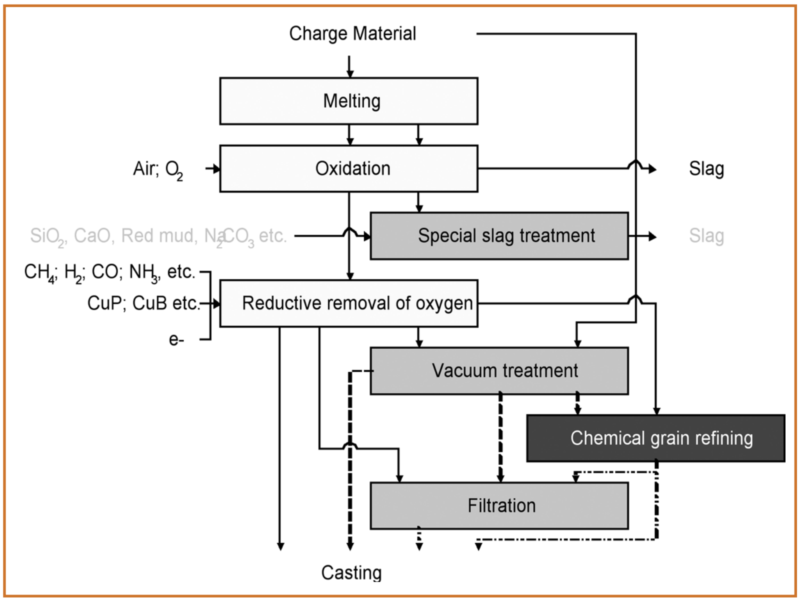


Figure 6: Flow chart of possible melt treatment steps

former times the so called poling by tree trunks, especially birch, is used [4]. This technique is still used today in some places. An advantage of the tree trunks is that they have a CO2 emission of zero, as plants are considered to be regenerative. Alternatively to this classical procedure, modern techniques reduce the partial pressure in the surrounding atmosphere; this led to vacuum and gas purging technologies. A flow chart of possible melt treatment routs is shown in Figure 6.

The removal of dissolved metals in Copper is an upcoming problem because of the increasing recycling material volume not being treated by refining electrolysis. Metals like Zinc, Arsenic and Antimony can be evaporated by a vacuum treatment, for others like Nickel, Cobalt, Tin and Lead a special slag treatment is more economic. Nevertheless very often the high specifications of high tech applications cannot be met using only one refining technique.

To remove solid particles from Copper melts a simple settling is usually enough for standard qualities. But the increasing requirements, e.g. for wire production, led to the development of filtration and floatation techniques. Typical filter materials made of alumina or silicon carbide are shown in Figure 7.

All the melt treatment techniques are actually batch processes. They have to be im-plemented in the existing process routes in a way that their effect is not lost before casting and solidification of the metal. That means that after deoxidation, a pick up of Oxygen has to be avoided by proper casting gutters protected by a coal or coke cover or a shielding gas. After filtration a laminar flow of the melt through the launder has to be assured to avoid turbulences that promote abrasion of the refractory and formation of oxides.

Deoxidation

A deoxidation has to be conducted after all melt treatments that enclose an oxidative refining. As deoxidation agents be applied gases, certain reagents and electricity.

Deoxidation by gas purging

Gas purging of Copper alloys can be divided into purging with inert gases and purg-ing with reactive gases. The purging with inert gases is based on a low partial pres-sure of the gas that needs to be removed. This process is diffusion controlled, i.e. the speed depends on the diffusion constant and the specific surface area of the melt-bubble interface. A diffusion controlled mass transfer can be influenced by rising temperatures (technically not feasible) and a decrease in the thickness of the Nernst layer. Thus the process can be significantly intensified by an increase of the surface of the gas bubbles by an appropriate gas supplying technique. The principles for the gas purging with an inert gas was described by Friedrich et. al. [5] elsewhere. Argon and Nitrogen are appropriate inert gases for purging Copper, especially for Hydrogen removal. Their solubility in liquid Copper is negligible.

Gas purging methods for Copper deoxidation were developed to replace the poling with tree trunks that goes back at least to the year 1200 AD when it was mentioned in "De Re Metallica". In the 1960s extensive research was conducted on reactive gases with different gaseous and solid reducing agents. Reducing gases were tested like different carbonhydrates (Methane, Propane, Butane) [6], Carbon monoxide as well as Hydrogen. Ammonia for gas purging was investigated in the 1970s [7]. Also oil or coal dust were used as reducing agents, the problem of these substances was their impurity content, especially Sulphur that enriches in the Copper melt.

Natural gas as a reducing agent was tested by Klein [8] but the process was found to be very ineffective and slow. In comparison a reformed, partially oxidised natural gas where the carbon hydrates are reacted to carbon monoxide and Hydrogen leads to a fast deoxidation of the Copper melt. This process was implemented at the

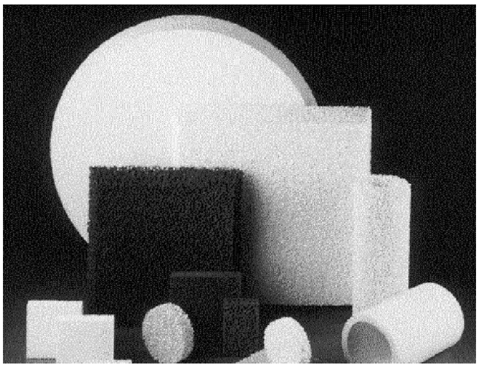


Figure 7: Typical CFF filter plates for melt filtration (CFF= ceramic foam filter)

Phelps Dodge refining works in the 1960s according to US-patent 2,989,397. An intensive investigation on the kinetics of the Copper deoxidation by carbon monoxide was carried out by Andreini et al. in 1977 [9]. The chemical gross equation of the deoxidation with carbon monoxide is

$$\underline{O}_{Cu} + CO \Leftrightarrow CO_2 \qquad \text{Eq. 2}$$

It was found that the Oxygen diffusion in the liquid Copper to the gas bubbles is the rate controlling step, valid in a concentration interval of 50 to 1000 ppm. Below 50 ppm the kinetics of the Oxygen removal decreases sharply. This can not be explained by equilibrium reasons, it is possibly due to interactions with Sulphur in the melt. This study agrees fairly well with an older study from Nanda et al [10] which also found a sharp decrease of the deoxidation speed below a concentration of 50 ppm Oxygen. The lowest Oxygen concentration in liquid Copper that could be achieved by this process was 10 ppm.

As an alternative to carbon hydrates, ammonia was investigated as a possible re-ducing agent by Henych et al.[7]. The gross equation of this reaction is:

$$3\underline{O}_2 + 4NH_3 = 2N_2 + 6H_2O \qquad \text{Eq. 3}$$

The reducing element in this case is the Hydrogen. The developing Nitrogen is an inert gas and does not dissolve in the Copper melt. The lowest Oxygen concentration in liquid Copper that could be achieved by this process was 200 ppm. Ammonia is very expensive and at room temperature a liquid, therefore it has to be gasified which increases the complexity of the process. Therefore this technology never achieved industrial scale.

It is also possible to use a Nitrogen-Hydrogen mixture instead of ammonia. The ad-vantage is that the purging media are already gaseous [11]. But pure Hydrogen is quite expensive and mainly produced from natural gas, so there is no advantage in comparison to natural gas.

Up till now the favoured gas injection technology in the Copper industry is tuyeres/injectors even though in other industries different gas supplying techniques are used as rotary vaned dispersers and porous plugs.

Deoxidation by addition of solid additives

Besides deoxidation with reactive gases also deoxidation procedures with a solid element- or compound-additive exist. For Copper the insertion of Phosphorous, Lith-ium, Calcium, Boron, Beryllium, Aluminium, Silicon, Magnesium and Zinc as well as Calcium-Boride [11];[13] were investigated starting in the 1930s. The deoxidising agents are added in stoichiometric amounts or with a very slight excess related to Oxygen. The oxides of the added elements should evaporate, float and form or dissolve in a slag. Any excess agents unfortunately dissolve in Copper or form compounds and harm the properties of the material. For example Phosphorus leads to a decrease in the conductivity of Copper as shown in Table 1. Lithium in Copper does not result in such a drastic loss of conductivity but it is rather expensive and reacts with refractories and carbon bearing shielding layers. Some multiple-step processes were developed for exotic applications, e.g. two step processes with Zinc and Magnesium, Zinc and Beryllium, Calcium boride and Magnesium, Phosphorous and Lithium or Calcium boride as well as processes with three steps as for example Zinc, Calcium boride and Beryllium [13]. With these techniques Oxygen contents of below one ppm can be obtained. But the lower the achieved Oxygen content is, the higher is the concentration of the dissolved deoxidation agent causing a lower conductivity. Table 1 Shows relevant properties of possible deoxidation agents.

The general equation of the deoxidation of Copper melts by solid reducing reactants (R) is

$$x\underline{O}_{Cu} + yR \Leftrightarrow R_yO_x \qquad \text{Eq. 4}$$

Most of the oxidic compounds resulting from deoxidation have a high melting point. So as a result besides the deoxidation treatment also a slag forming constituent like SiO_2/FeO/CaO has to be added to obtain a slag with a low viscosity and melting temperature that can be easily and entirely removed. The only elements forming low melting oxides are Boron and Phosphorus. Because of the higher price of Boron in comparison to Phos-

Element	Resulting resistance at 0.1 wt. % in Cu	Max. solubility in Copper	Oxide compound formed by deoxidation	Density of the oxide	Melting temperature of the oxide
	/µΩcm	/wt. %		/g/cm³	/°C
Al	1.89	5.7	Al_2O_3	3.423	2290
B	2.435	0.3	B_2O_3	2.44 (hex)	460
Be	2.1	16.4	BeO	3.02	2575
Ca	1.726	<0.001	CaO	3.4	2927
Li	2.2	2.8	Li_2O	2.013	1560
Mg	1.876	3	MgO	3.576	2831
P	3.04	2	P_2O_5	2.93	580
Si	2.344	5	SiO_2	2.648	1550
Zn	1.709	38.27	ZnO	5.66	1975
Cu	1.5	-	-	8.96	1085
O	1.673 at 0.01 wt%	$20*10^{-4}$	Cu_2O	6.00	1244

Table 1: Properties of deoxidising agents and their oxides [2];[13];[14]

phorous, Phosphorous is the deoxidation element of choice until today. Phosphorous is usually added as a master alloy with the composition 90% Cu and 10% P in the form of waffle plates, which are dumped into the furnace. For a fine adjustment of the P-content during continuous casting Phosphorous may be added in cored wire or as granulates.

In practice for deoxidation multiple steps are applied as for example deoxidation by tree trunks, followed by deoxidation with phosphorous and then shielding by carbon layers on top of the melt and burners with reducing conditions.

Electrochemical deoxidation

Besides the known and proven deoxidation techniques more recently galvanic deoxidation was investigated. With Calcium oxide doped Zirconium oxide was proposed as a high temperature oxygen ion conductor already in 1957 [15]. The technique for electrochemical oxidation or reduction was firstly used to determine the oxygen solubility in metal melts especially in Copper [16].

The electrochemical that is applied cell can be written as

Cu $ZrO_2 + CaO(Y_2O_3)$ Pt, air
O (at p'_{O2}) solid electrolyte
(p''_{O2}=0,21 atm)

The heart of this technique is the solid electrolyte oxygen ion conductor. Through this conductor an Oxygen exchange between a closed melt and for example the atmosphere can happen but only in the ionic form. So at one side of the electrolyte the Oxygen is supplied with electrons and is ionised to O^{2-} and at the other side it leaves electrons. For charge equilibrium the electrons have to move the other way. This can only happen by an electron conductor. The electron movement results in a voltage that can be measured, it is dependent on the oxygen concentration difference between melt and surrounding atmosphere. In case the voltage is zero there is no Oxygen concentration difference between melt and atmosphere. Vice versa if a voltage is supplied externally oxygen can be pumped in or out of a melt. The scheme is shown in Figure 8. In case the oxygen exchange is due to concentration differences, the process is called galvanic oxidation/reduction, in case a voltage is supplied it is an electrochemical oxidation/reduction.

On this principle are based also for example the Lambda probe in cars or the technology of fuel cells. It is also very common for batch wise oxygen measurements in Copper melts.

In the 1970´s first trials for deoxidation of metal melts were conducted. In Copper melts a value of 7 ppm O_{Cu} could be achieved. It was soon discovered that diffusion is not fast enough to supply the electrolyte with sufficient Oxygen and sever mechanical or inductive stirring is necessary to achieve a fast deoxidation. R. R. Odle achieved on laboratory scale a reduction from 500 ppm O_{Cu} to 25 ppm O_{Cu} in 80 min [16].

In the end of the 1990´s pilot scale test runs for electrochemical deoxidation cells were conducted by P. Soral [16]. In this pilot scale unit as electrolyte Yttria stabilised Zirconia was used (YSZ) with a Ni-YSZ cermet as an anodic electron conductor on the inside of electrolyte and stainless steel rods as the cathodic current supplier in the melt. It was found that the electrolyte tubes are very prone to thermal shock and therefore a not complete deoxidation was obtained. But future research is ongoing to find more thermal shock resistant electrolytes for the use in industrial environments.

Impurity removal by slag treatment

Slags in Copper refining have the task to take up the impurity oxides, that means they should have the following properties:

- High solubility for impurity oxides
- Low solubility for Copper and Copper oxide
- Low melting temperature close to the melting temperature of Copper
- High thermal stability
- Low interaction with the refractory material

Before or during a slag treatment the Copper melt has to be oxidised for example by top blowing of air. A slag that is industrially used is the so called "Fayalite" slag that is also applied in the primary flash smelting furnace. It is based on the system FeO – Fe_2O_3 – SiO_2. It is effective for the removal of Cd, Fe, Pb, Sn and Zn especially for elements with the valence of two that can be trapped as silicates. This slag can be used in furnaces with silica refractory [16]. This is the slag mainly used today.

On laboratory scale other slag types were investigated as for example Calcium-ferrite slags that are based on the ternary system FeO – Fe_2O_3 – CaO. They remove the elements Al, As, Fe, Sb and Sn, especially elements which exhibit an acidic character in a slag [16] at their highest oxidation levels. Another system is based on CaF_2 – CaO – MgO – SiO_2 this slag shows the same behaviour as the "Calcium-ferrite" slag but with a lower solubility for Copper oxide.

Oxide slags often contain by-products from the deoxidation treatment with solid reactants. That means especially B_2O_3 and P_2O_5. These compounds can further influence the activity of impurity metals like Lead, Nickel and Tin. Here the research is ongoing on the influence of these compounds.

As slag additions for oxide slags besides pure oxides like SiO_2 or CaO also so called residues can be applied as for example red mud from the bauxite processing during Aluminium production.

Also investigated by researchers on laboratory scale were salt slags that

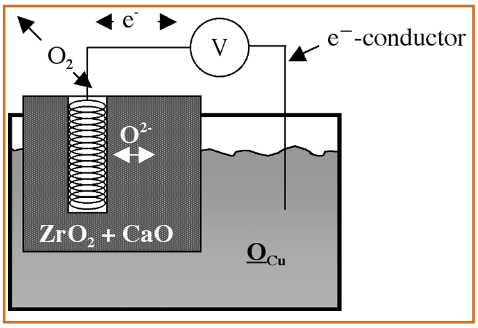


Figure 8: Scheme of a electrochemical cell with solid electrolyte

are mainly based on Sodium carbonate (Na_2CO_3) but also on other alkaline carbonates like lithium and Potassium carbonates (Li_2CO_3) and (K_2CO_3). They are very effective refining slags, but they all attack "usual" refractories of the Copper industry. It was found that by fluxing with a sodium carbonate slag the amount of arsenic and antimony could be lowered below 0.1 ppm. The problem that occurred was, that the binary solution of Sodium carbonate and Antimony oxide let to an increase of solubility of Copper oxide in the slag and therefore let to higher Copper losses [21].

For fluxes on other salt bases mainly fluorides can be used because their melting and evaporation point is very high. Here especially systems on Calcium fluoride (CaF_2) base with a mixture of Aluminium fluoride (AlF_3) or Sodium fluoride (NaF) are possible candidates. All salt fluxes operate in the best way when the reaction surface between metal and slag is increased for example by solid flux injection in the metal melt [23] instead of an addition to the surface.

Vacuum treatment

The vacuum technology in the Copper industry is mostly used for the production of low alloyed alloys with reactive elements and for the production of master alloys on Copper base with reactive elements like Chromium, Zirconium, Magnesium and Beryllium. Qualities with an Oxygen content below one ppm are also produced by this method [27]. The amount of vacuum produced Copper materials is very small com-pared to the total amount of produced Copper. Vacuum treatment for special products of Copper alloys mainly is used to remove dissolved gases like Hydrogen and Oxygen or less frequently to evaporate volatile elements like Zinc, Bismuth and Arsenic etc. First trials for the removal of Oxygen, Hydrogen and Sulphur from Copper melts were conducted by R.A. Stauffer et. al. in 1948 [24]. They started by melting Copper in a retort using a graphite boat. The carbon is necessary because the decrease of the pressure during the vacuum treatment is not sufficient to remove Oxygen to low values, a CO formation/removal is much more effective. After three hours the chemical analysis showed a reduction of Hydrogen to 0.1 ppm, of Oxygen to 3.8 ppm and of Sulphur to 1.9 ppm. Despite these good results the vacuum technology for gas removal was never implemented for the production of technical materials due the high investment costs for vacuum equipment and its maintenance. Only the company Hitachi patented a continuous process in 1989 that is in use until today [21].

In the 1970s the possibility to remove other elements than dissolved gases by means of vacuum was investigated. In the focus were mainly Bismuth, Antimony and Arsenic because they often accompany the Copper ores and are difficult to remove during the refining electrolysis. These elements have a negative effect on the properties of Copper and its alloys, so their removal is of great importance [26]. The removal of Bismuth, Lead, Arsenic and Antimony from Copper [26] was investigated and it was found that for Copper alloys the Bismuth content could be reduced to 70 ppm, Arsenic to 1260 ppm and Antimony to 310 ppm. The distillation of volatile elements is not very common industrially.

For the removal of gases three different setups of furnaces can be used.

Figure 9: Vacuum furnace [27] (VIM)

Usually the heating source in vacuum furnaces is an induction heating. The vacuum induction melting (VIM) furnace consists of a cold walled chamber in which all equipment like moulds etc. is stored. The induction coil can be tilted so that inside the material can be casted inside the furnace under vacuum. In the vacuum induction degassing system (VID) a lid is positioned on the top of the furnace. Before casting the lid has to be removed, and the melt is subjected again to the atmosphere. The advantage of this system is the small size in comparison to the VIM. The third system is the so called vacuum induction degassing pouring (VIDP). The cold walled container of the induction coil can be tilted so that the melt flows in a launder and leaves the cold walled system through a closed launder chamber. This system avoids the contact to the air during casting and combines the advantages of VIM and VID.

Summary

In this paper the possibilities for the melt treatment of Copper and Copper alloy melts are discussed. Gas purging, deoxidation by chemical reaction, slag treatment and vacuum treatment were reviewed in more detail. The review shows that wood poling can achieve oxygen contents to a few hundred ppm, cracked natural gas can reduce the Oxygen down to a few tens of a ppm and a deoxidation by solid reactants leads to below 1 ppm of Oxygen in a Copper melt. A vacuum treatment can also reduce the oxygen level to ~ 1 ppm.

With a melt treatment with a slag dissolved metallic impurities can be reduced below critical values. Fayalite slags that are the most common can remove elements with the valence of two as silicates as for example Pb, Cd, Sn and Fe. Carbonate slags can remove As and Sb below 1 ppm, but are not technically used.

With The results show that nearly all elements can be removed from Copper melts in the molten state, avoiding the energy intensive refining electrolysis. Because all melt treatment technologies in the Copper industry are batch processes their implementation has to undergo critical consideration to fit them into the existing process lines. Also the effect of the different treatment technologies has to be maintained until the metal is casted and chilled. Therefore effective shielding measures by carbon layers and shielding gases have to be added to the actual melt treatment process.

The state of the art of the existing melt treatment process technologies enables the Copper industry to achieve the dire demands of the semi finished product consumers.

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