

# 1 Introduction

Copper is a marvelous metal for studying several metallurgical phenomena, in particular high temperature mechanisms, like dynamic recovery and dynamic recrystallization. This thesis work shows the findings after studying three fire-refined coppers, which had a purity of 99.9%. Before presenting the scientific work an explanation will proceed that ties the properties of copper with human needs, in an attempt to show this work's relevance in society.

## 1.1 Coppers and Civilization

Across the ages copper has remained one the principal materials chosen by human kind to fulfill necessities and thereby improving the quality of life. From early uses in ornamentation (a malachite pendant found in Shanidar, Iraq, dated around 8000 B.C.) and the first metallic tools to modern age, copper has been preferably selected for its availability, formability, relative corrosion resistance and, lately for its electrical and thermal conductivity. Even when the Bronze Age ended at about 1200 B. C. copper consumption gradually continued to increase, however copper consumption did not increased noticeably until the Industrial Revolution and then with the progress of the electrical industry in the late 19<sup>th</sup> and early 20<sup>th</sup> centuries. Commercially 99.9% pure coppers were classified into several standard designations, which now help in selecting the most suitable copper according to the desired properties without having to keep track of the residual elements responsible of the property modification. Among the different designations four major grades can be singled out: Electrolytic Tough Pitch (ETP) copper, Phosphorus Deoxidized (DHP or DLP depending on a high or low P content) copper, Oxygen-Free High Conductivity (OFHC) copper and Fire-Refined copper. ETP Cu may have from 100 to 650ppm of O. The OF Cu may have up to 10ppm of O. The latter distinctions are due, in part, to the electrical efficiency and the solderability requirements (to be explained) of more recent times. Humanity has progressed much since the dawn of metallurgy and commercially pure coppers will continue to have an important role in civilization. This work will be concerned with high phosphorus fire refined coppers, which fit into the A.S.T.M. Unified Number System C12200, but other designations may also be applicable. However first an understanding will be presented of the role different commercially pure coppers have in our present lives.

When economic cost, formability, thermal or electrical conductivity are required, then copper ranks high among other metals, however within commercial purity coppers the end use needs particular attention before a selection is made. Another property of copper is a good corrosion resistance, but this property is not as excellent as in other metals and alloys. Table 1.1 shows the thermal and electrical conductivity values of several pure metals and grades of pure copper taken from ref [1]. Only Ag has higher thermal and electrical conductivities than copper, but because Ag costs more Cu tends to be the preferred choice. Specific applications of copper are numerous but the general areas include: building wire, plumbing and heating, air-conditioning and refrigeration units, power utilities, telecommunications, automotive electrical systems, in-plant equipment, appliances, business electronics, industrial valves and fittings, lighting and wiring devices, automotive non-electrical, and others like jewelry and mintage. Table 1.1 shows that for electrical purposes the optimal grades of coppers are the purest coppers

## Chapter 1 Introduction

Table 1.1. Thermal and Electrical Conductivities of different elements taken from ref. [1]

	Pure Cu	ETP Cu	DHP Cu	Al	Fe	Ni	Ag	Au	Zn	W
Thermal Conductivity W/m·K	398	391	339	247	80.4	82.9	428	317.9	113	160
Electrical Conductivity %IACS*	103.06	101	**	65	17.6	25.2	106	73.4	28.27	30

\* International Annealed Copper Standard (IACS) and 100% IACS represents a conductivity of 58 MegaSiemens per meter (MS/m); this is equivalent to a resistivity of 1/58 Ohm per meter for a wire one square millimeter in cross section.

\*\* The electrical conductivity or resistivity decreases sharply with the content of P, see also fig. 1.1

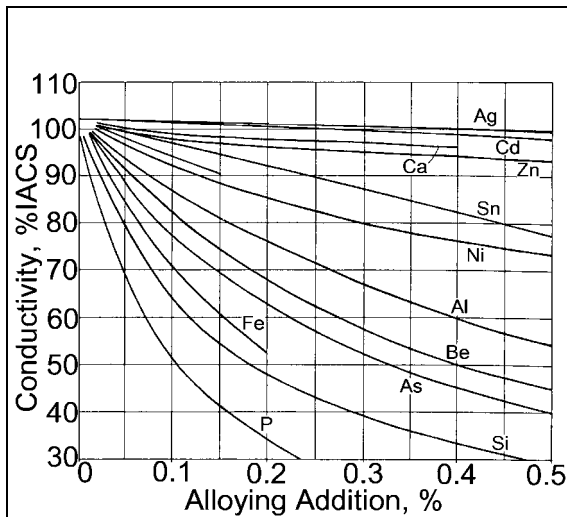


Fig. 1.1. The effect of alloying elements on the electrical conductivity of copper [2]. The plot shows that most alloying elements or residual elements (if present in low quantities) decrease the conductivity. Phosphorus, which is an element used as deoxidant, reduces substantially the conductivity even in dilute amounts. Coppers that contain phosphorus are not destined for electrical purposes.

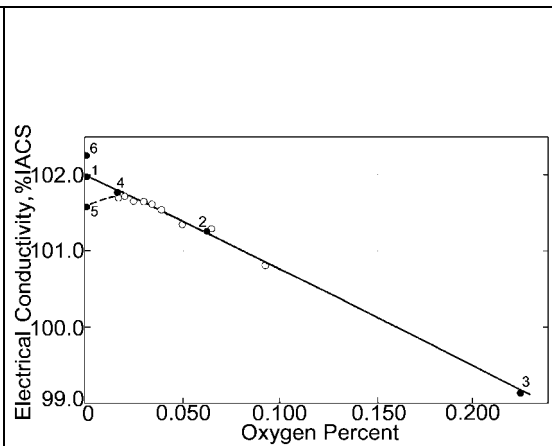


Fig. 1.2. Oxygen initially raises the conductivity of 99.9% pure copper, but beyond 200ppm the conductivity decreases [3]. The open circles are commercial Tough Pitch coppers. Point (1) is 99.9% pure melted and casted in vacuum. Points (2) and (3) are the same as (1) but were allowed to absorb oxygen. Point (4) is a Tough Pitch copper. Point (5) is a commercial Oxygen Free copper and point (6) is a laboratory 99.999% pure copper.

and ETP Cu and the reason is the decrease in conductivity when other residual elements are present, except oxygen.

Our present civilization depends largely on electrically driven devices and 99.9% pure coppers have been classified to address the requirements. Plots of the electrical

conductivity versus alloying addition more clearly explain the need for creating standard designations (see figures 1.1 and 1.2). The plot on fig. 1.1 from [2] shows the deleterious influence on the electrical conductivity by most other elements, however the influence of oxygen seen on fig. 1.2 from [3] shows that the conductivity increases up to about 200ppm and then decreases. Oxygen may also cause a similar behavior in the conductivity of 99.9% pure copper, however the peak is lower and depends on the residual elements present and the type of precipitates or inclusions formed [4, 5, 6]. A high purity copper of the Oxygen Free type is excellent for electrical requirements especially for electronic devices, and also where no inclusions are allowed like in the manufacture of fine wire. However a higher purity increases costs. ETP copper is used instead when cost and conductivity are jointly compromised, but higher oxygen content may cause hydrogen absorption if exposed to higher temperatures.

Oxygen is deliberately added during the melt not only to increase conductivity but also to reduce hydrogen absorption. When ETP copper is soldered, for example, hydrogen from the torch combines with cuprite ( $\text{Cu}_2\text{O}$ ) to form water vapor bubbles that causes the structure to weaken [2, 7, 8]. When molten the solubility equilibrium between oxygen and hydrogen follows the line shown on fig. 1.3. The water vapor reaction occurs above the line denoting the equilibrium concentration, but not below. Excess oxygen in ETP copper precludes hydrogen absorption while molten and minimizes porosity while solidifying. If a high conductivity copper needs to be soldered then the OFHC copper would be the choice, because no cuprite is available to react with hydrogen.

Fire-refined coppers and phosphorus-deoxidized coppers are preferably used for their thermal conductivity and corrosion resistance, despite that some fire-refined coppers with low phosphorus may reach the electrical conductivity values of ETP copper [5]. Fire refined coppers owe their name to the production method and are characterized not by their oxygen content but by the types and amounts of residual elements, which tend to include Ag, As, Sb, P, Te and several other elements (coppers C12500 and C12900 are some examples). The oxygen amount may vary from as low as 26ppm, which is the amount in one of the coppers of this study, to 508ppm in other fire-refined coppers [9, 10]. The standard designation allows fire refined coppers to have a minimum purity of 99.88%, however some fire-refining processes are capable of achieving higher purities rendering an up-grade in designation number. As will be explained phosphorus is a widely used deoxidant of molten copper, but also serves to

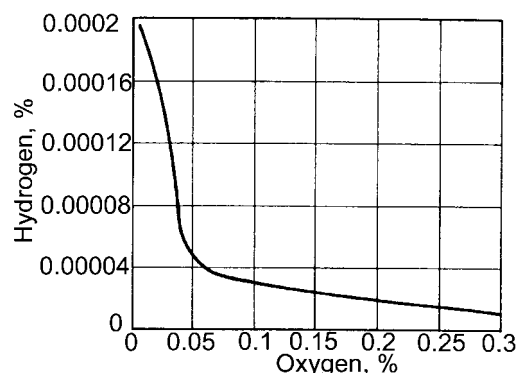


Fig. 1.3. The plot shows the Hydrogen / Oxygen equilibrium in molten copper taken from ref. [2]. An excess of oxygen precludes the absorption of hydrogen, which can react to form water vapor. If the concentration is below the equilibrium line then no vapor forms.

## Chapter 1 Introduction

Table 1.2. Typical applications of DHP copper C12200.

Category	Use	Reason
Architecture	Downspouts, flashing, gutters, roofing	Appearance, corrosion resistance, formability,
Automotive	Air Lines, hydraulic lines, oil lines	Pressure tight, solderability, corrosion resistance, corrosion resistance to salt water, thermal conductivity
Building	Air conditioner tubes and condenser sheets, gas lines, heater lines, oil burner tubes	Corrosion resistance, formability, solderability, thermal conductivity, pressure tight,
Consumer	Air conditioners, refrigerators	Brazability, corrosion resistance, pressure tight, thermal conductivity, formability, solderability,
Electrical	Heater elements, wire connectors	Corrosion resistance, electrical conductivity, thermal conductivity
Industrial	Air lines in airplanes, anodes for electroplating, brewery tubes, casting molds, condenser tubes, dairy tubes, distiller tubes, evaporator tubes, expansion joint tubes, gage lines, gasoline lines in airplanes, heat exchanger shells, heat exchanger tubes, hydraulic lines in airplanes, kettles, oil coolers in airplanes, oil lines in airplanes, paper lines, paper rolls, plating anodes, plating hangers, plating racks, plumbing tube, print rolls, pulp lines, rotating bands, steam lines, sugar house refinery lines, tanks, water lines	Corrosion resistance, pressure tight, solderability, electrical conductivity, thermal conductivity, appearance, brazability, moderate strength, formability, corrosion resistance to chemicals, electrical conductivity, plateable, weldability, creep resistant, retains strength at high temperatures,
Marine	Gasoline lines, oil coolers	Corrosion resistance, pressure tight, solderability, corrosion resistance to salt water, thermal conductivity
Plumbing	Plumbing fittings, plumbing pipe	Corrosion resistance, corrosion resistance to hydrogen embrittlement, formability, solderability, brazability,

avoid the explained hydrogen reaction when soldered or brazed [11] or exposed to a combustion environment. If the residual composition is too high then formability is affected [9, 10, 12], as is the case with fire-refined coppers of lower purity.

This study, on the other hand, worked with higher purity fire-refined coppers obtained from scrap and formability was also investigated through the examination of

the stress and strain when forming at higher temperatures (600°C-950°C). Aspects of formability in fire-refined coppers and phosphorus-deoxidized coppers are indeed important if one takes into account the variety of intricate shapes produced to serve the necessities of our modern lives. Table 1.2 outlines the variety of different products whose standards require a phosphorus-deoxidized copper (C12200) like the ones used on this study. The applications presented on table 1.2 demonstrate the impact a copper like the C12200 has had in our present civilization. However perhaps an explanation is needed of the copper extraction process, which allows a fire-refined copper from scrap (commonly considered impure) to be classified as a phosphorus-deoxidized copper without being electrolytically refined. The fire-refined coppers of this study contain residual elements some of which are deliberately added and some are the result of the refining process. As is known, hot forming directly influences the plasticity of the purest copper at room temperature. On this study the behavior of fire-refined coppers at higher temperatures was found that changed with the residual chemical composition and consequently the final room temperature properties were also modified.

## 1.2 Copper Production

Several complete [13] and detailed [11, 14] works exist that describe the copper extraction process, however a concise but comprehensive explanation can be given of the process along with an account of the residual elements in copper. If copper production starts from the ore then the process depends on the type of ore being exploited. Sulfide ores follow a smelting and electrolytic refining process whereas oxide ores follow a leaching and electrowinning process. Table 1.3 details the different mineral sources from where copper is extracted. However through the use of bacteria capable of dissolving the copper from sulfide ores into a sulphuric acid solution, increasingly sulfide ores are also being leached and then electrowon [15, 16]. After the mined mineral has been crushed into golf-ball size pieces then a grinding process produces a powder that normally contains 0.5-2.0% copper, depending on the mine. Oxide mineral powders are acid leached in tanks or on hill size heaps, producing a weak copper sulfate solution (5-35 kg Cu/m<sup>3</sup>). On the other hand sulfide mineral is concentrated using a bubble floatation process that captures metal containing grains into a slurry of 20-30% Cu. The slurry is dried and then various smelting processes produce a liquid matte (two

Table 1.3. Principal copper mineral ores that are exploited [11].

Mineral	Theoretical Composition	Distribution Site
<b>Sulfurs</b>		
Chalcopyrite	CuFeS <sub>2</sub>	widely present
Chalcocite	Cu <sub>2</sub> S	widely present
Bornite	Cu <sub>5</sub> FeS <sub>4</sub>	widely present
Covellite	CuS	African copper belt
<b>Oxides</b>		
Malachite	CuCO <sub>3</sub> ·Cu(OH) <sub>2</sub>	Congo, Zambia
Azurite	(CuCO <sub>3</sub> ) <sub>2</sub> ·Cu(OH) <sub>2</sub>	Congo, Zambia
Cuprite	Cu <sub>2</sub> O	widely present
Chrysocolla	CuSiO <sub>3</sub> ·2H <sub>2</sub> O	Congo, U.S.A.
Antlerite	Cu <sub>3</sub> SO <sub>4</sub> (OH) <sub>4</sub>	Chuquicamata (Chile)

separable phases one of which has 35-65% Cu), blister copper (98.5% Cu) and fire-refined copper (99.5-99.9% Cu), which is normally casted into anodes that are then electrolytically refined (ASTM standard specification B115-00). Electrolytic refinement (0.25-0.3V for 250Amp/m<sup>2</sup> of anode) turns the anodes into 99.99% Cu cathodes, which are casted into wire rod, billets, cakes or ingots. If the process reaches the latter casting procedure then oxygen may deliberately be introduced to produce ETP Cu. Or if OFHC Cu is to be produced then a carbon, lithium or boron based deoxidant (see table 1.4) may be used, because electrical conductivity is not reduced substantially. The origin of the residual composition in ETP and OFHC coppers can be easily understood, however the residual composition in fire-refined coppers, phosphorus deoxidized and coppers from electrowinning processes depends on the process and uncontrollable situations.

The minerals that have been leached normally pass by an electrowinning process (2-2.5V for 250Amp/m<sup>2</sup> of anode), which is less efficient than the electrolytic process, because a lower purity is achieved (99.9% Cu) and more electric energy is needed. The copper sulfate solution used during electrowinning contains other metals that end up on the electrowon cathode. The cathodes are melted, casted and destined for non-electrical purposes, because impurities might reduce conductivity. In some operations the copper in the copper sulfate solution is precipitated over iron scrap through a substitutional chemical reaction that requires no electricity, then the precipitated copper is smelted as previously described. The copper sulfate solution also contains dissolved precious metals, which are extracted using other techniques. The impurities in electrowon copper cathodes come from two main sources (1) the incomplete dissolution of particles in the copper sulfate solution and (2) the corrosion products (lead sulfides or oxides) of the lead alloy anodes (Pb plus 0.06% Ca or 6-15%Sb). The type of undissolved particles in the solution will depend on the source of the mineral, so for example Chuquicamata (Chile) may have Fe and Pb whereas Baghdad (Arizona) may have Ag, As, Bi, Fe, Ni, Pb, S, Sb and Te, for more information see ref. [11]. However the most important source of impurities during the electrowinning process comes from the lead alloy anode, which forms PbO<sub>2</sub> particles that flow to the copper cathode.

Table 1.4. Theoretical capabilities of common deoxidizers used in copper melts [2]. The boron-copper master alloy is theoretically the most efficient deoxidizer however in practice lithium is more effective, but handling of lithium requires precaution.

Deoxidizer	Reaction Products	Amount of deoxidizer required to remove 0.01% oxygen (g/100kg)
Carbon	CO	7.5
Carbon	CO <sub>2</sub>	3.8
Phosphorus	P <sub>2</sub> O <sub>5</sub>	7.5
Phosphorus	2Cu <sub>2</sub> P <sub>2</sub> O <sub>5</sub>	5.6
Cu-15P	P <sub>2</sub> O <sub>5</sub>	49.3
Cu-15P	2Cu <sub>2</sub> P <sub>2</sub> O <sub>5</sub>	36.8
Boron	B <sub>2</sub> O <sub>3</sub>	4.4
Boron	2Cu <sub>2</sub> OB <sub>2</sub> O <sub>3</sub>	2.5
Cu-2B	B <sub>2</sub> O <sub>3</sub>	224.5
Cu-2B	2Cu <sub>2</sub> OB <sub>2</sub> O <sub>3</sub>	134.7
Lithium	Li <sub>2</sub> O	8.7
Magnesium	MgO	15.0

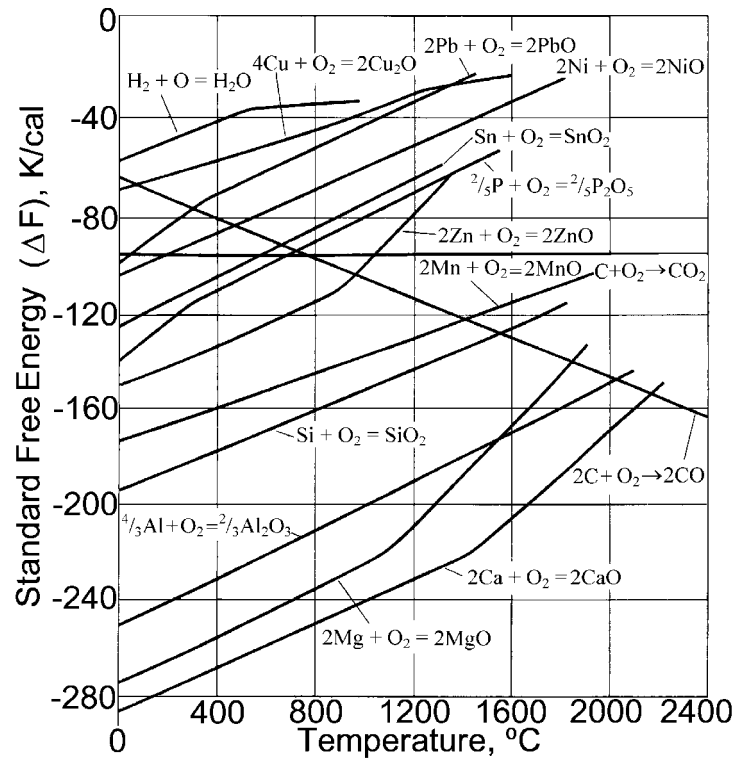


Fig. 1.4. A free energy diagram taken from ref. [2] shows the energy changes for various metal oxidation reactions. A lower energy change value means a higher probability of oxidation in the melt. On the diagram, however, the free energies of formation of oxides were calculated using pure condensed phases and gases at 1atm.

An increasingly important source of copper that is also smelted and fire-refined is copper scrap. While using copper scrap the process begins by melting the pieces in an adequate furnace [17] depending on the grade of the scrap. The Institute of Scrap Recycling Industries (ISRI) recognizes several classes (about 53) of copper scrap, however the major categories are No. 1 scrap, which consists of scrap containing a minimum of 99% Cu and No. 2 scrap, which contains a minimum of 96% Cu. Light-copper scrap contains between 88% and 92% Cu. The name “new scrap” refers to scrap generated in the process of manufacture and the name “old scrap” refers to scrap derived from used products. A reverberatory or rotary furnace is used to melt and then fire-refined No. 1 and No. 2 copper scrap. However reverberatory furnaces have almost been replaced by flash-furnace technology [16, 17], which in primary smelting facilities combines the steps of partially oxidizing the concentrate and producing a molten matte while using the exothermal energy provided by oxidation reactions.

Fire refining refers to the oxidation of metallic impurities, the use of fluxing agents to agglomerate the metal oxides formed and a final deoxidizing procedure to produce a refined product (99.9% Cu). If low-grade copper scrap is used then the process begins by first forming a matte as with concentrate from mineral ore. When oxidizing, air or oxygen-enriched air is injected to the molted copper. Several metal oxidation reactions have a lower standard free energy of formation,  $\Delta F$ , than  $\text{Cu}_2\text{O}$  and are hence oxidized first. A free energy diagram for oxide formation, also called Ellingham Diagram [18,

19], is shown on fig. 1.4 from ref. [2]. According to the diagrams metallic impurities are oxidized in the following order: Al, Mn, Si, P, Fe [20], Zn, Sn and Pb. Figure 1.5 also from ref. [2] shows the effect of blowing oxygen on the impurity content of the melt. The plot shows that the concentration decreases with blowing time, however the time necessary to reduce Pb is the longest. Most inclusions found in fire-refined copper contain Pb, as was corroborated in the results section of this study. A neutral cover flux (borax, boric acid or glass) is needed [2] to reduce copper loss by providing a liquid slag cover that also agglomerates and absorbs nonmetallic impurities from the charge. Fluxes containing sodium carbonate (Na<sub>2</sub>CO<sub>3</sub>) or potassium carbonate (K<sub>2</sub>CO<sub>3</sub>) are also added to control impurities containing S, As, Se, Sb, Bi and Te. Silicate fluxes or slags help remove Pb from the melt, however phosphor copper or the use of phosphate or borate fluxes along with agitation increases the rate of Pb removal [2]. Other Pb removal techniques have also been developed [21]. At the end of the oxidizing stage the metallic impurities that were not oxidized or agglomerated in the slag-cover will remain in the melt, because the concern during the deoxidizing stage is not only to extract the oxygen, but also to avoid hydrogen absorption due to a lower oxygen content (see fig. 1.3).

The origin of metallic impurities and inclusions found in fire-refined copper is partly explained from the purity achieved during oxidizing, however other impurities might be introduced while deoxidizing. Several deoxidizing treatments may be selected based on actual efficiency, economics, ease of use and specific metallurgical requirements. The free energy diagram on fig. 1.4 shows several possible elements that could be effective scavengers of oxygen. Common deoxidizers are listed in table 1.4. Phosphorus is usually the least problematic and most economical [2]. Some refineries inject natural gas, fuel oil, propane or a combination of these as a source of carbon, however in this case the combustion forms large quantities of water vapor and hydrogen absorption may be a problem. When using phosphorus, the liquid slag of cuprous phosphate ( $2P + 4Cu + 7O \rightarrow 2Cu_2 \cdot P_2O_5$ ) is easily skimmed from the melt, however an

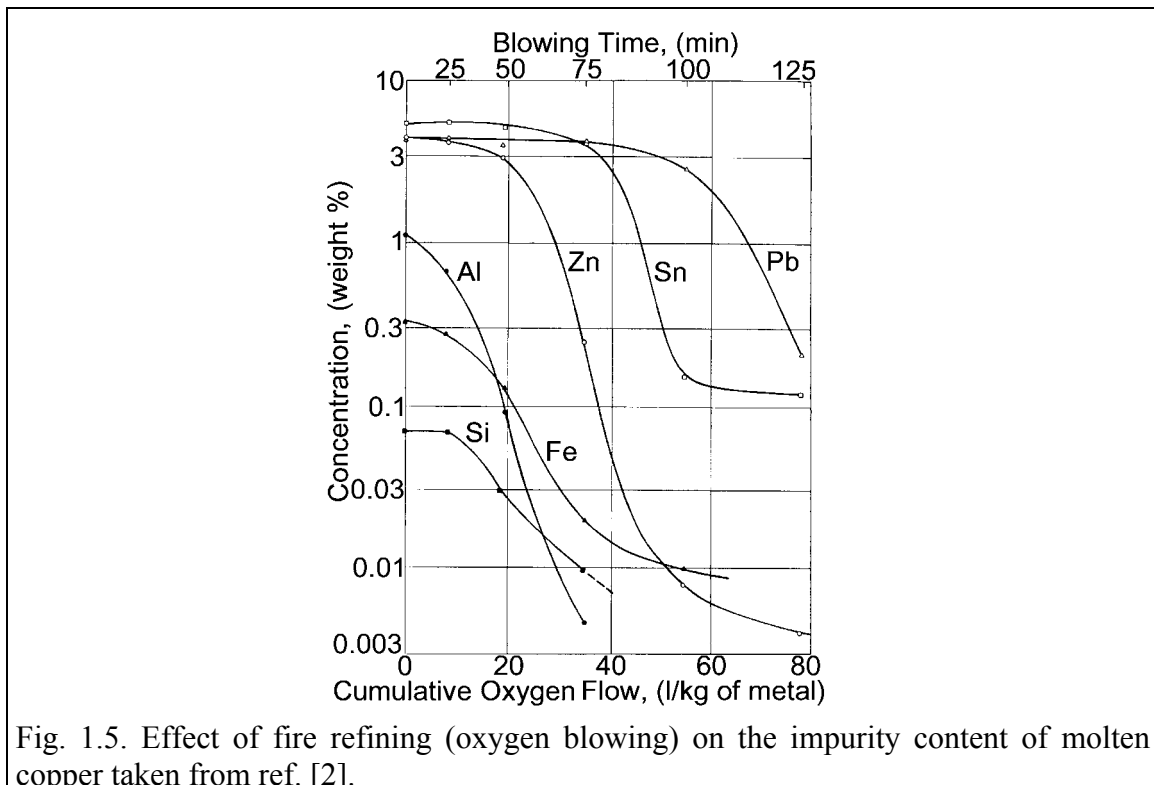


Fig. 1.5. Effect of fire refining (oxygen blowing) on the impurity content of molten copper taken from ref. [2].



excess of phosphorus causes a lack of oxygen, which may invite hydrogen resulting in the steam reaction during casting. A mentioned drawback of phosphorus is the reduced electrical conductivity. If the metallurgical requirement calls for high conductivity then boron (copper-boron master alloy or  $\text{CuB}_6$ ) or Li can be used for deoxidizing without reducing appreciably the electrical conductivity. The phosphorus deoxidized fire-refined coppers used on this study were 99.9% pure with 26ppm, 46ppm and 62ppm of residual oxygen, however few micron size inclusions were found, whose origin has been explained.

### 1.3 The Copper Market

The size of the copper market is another argument that justifies continued research in copper, especially during recent hard times for producers. In 2003 the world copper consumption was of 15 454 600 metric tons [22] and if the average London Metal Exchange (LME) price is taken as a reference [17], then an estimate of the amount of money that changed hands is of U.S.\$26 575 839 080°. Despite that in recent years the world's copper production has exceeded demand, the transactions of money involved certainly have an impact on the world's economy. Copper producers have seen the price go down (see fig. 1.6), most probably as a direct effect of a lower demand and a surplus in production (see fig. 1.7). Contrary to a downsizing policy the situation calls for more investment in research to reduce production and manufacturing costs and also to expand the range of products where copper can compete.

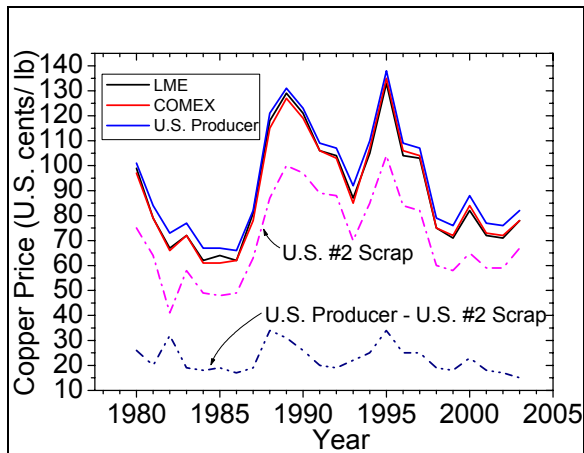


Fig. 1.6. The plot shows the variation of the yearly average price of copper according to the London Metal Exchange (LME) grade A cash, Commodity Metals Exchange (COMEX) HG 1<sup>st</sup> Post and the U.S. Producers price [17]. Also the U.S. buying price of #2 copper scrap is shown. The lowest line corresponds to the difference between the U.S. Producers price and the cost of #2 copper scrap. Since 1995 prices had been dropping, however in 2003 a modest increase occurred.

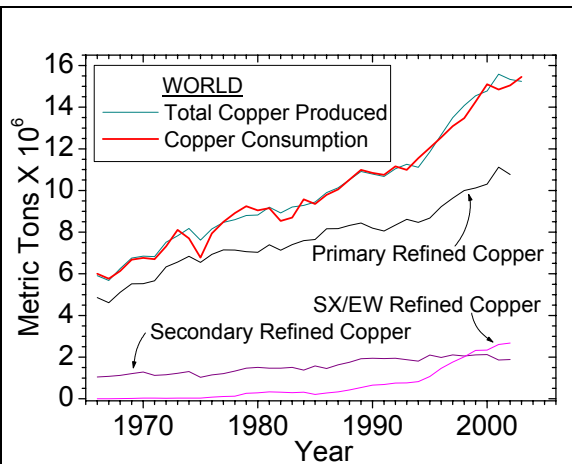


Fig. 1.7. The world production and consumption of copper continue to increase however a consumption drop in 2001 and the over production of past years has carried the copper producer industry into a decline [17]. In 1999 copper refined through solvent extraction and electrowinning (SX/EW) surpassed copper refined from secondary sources such as scrap. However scrap in 2001 and 2002 maintained a 12% share of the total copper produced.

### 1.4 Challenges and Outlook

The recuperation of copper consumption is the largest challenge facing the industry. New copper applications, higher energy consumption and growing markets, like China, are starting to turn the tide. From a technological standpoint a long lasting challenge is the implementation of decades of research in copper related phenomena into existing and new products. An example of research that has not yet entered the production line is the investments made to produce nano-crystalline copper. A nano-size grain promises elevated resistance and formability without rupture, however commercial large-scale production is not yet available. Probably the technical problems facing the copper manufacturers require lower technology, however the paths to channel the accumulated knowledge are not readily available. Unquestionably the residual composition changes the properties of 99.9% pure copper, however countless studies have been published about copper without specifying the residual composition. A challenge for researchers is to report data in a more compatible manner by identifying the initial conditions of a copper such as: residual composition, initial grain size, initial texture and other unique conditions. A better description will allow reproducible results and more compatible values. Several areas about copper that are still being researched should already form part of a text or manual, but the lack of compatible results has prevented a larger database for comparison.

The copper on this study is extensively used to make tubing, which in past years has faced strict certification requirements before being sold. Concerns about the quality of potable water and mechanical behavior while in use have prompted governments to pass laws regulating the use of copper tubing. In 1996 when the United States accounted for 20.8% of the world consumption [17], the Safe Drinking Water Act (SDWA) was amended and required the U. S. Environmental Protection Agency (EPA) to establish a performance standard to govern the leaching of Pb from devices intended to dispense water for human consumption. The EPA requires that copper tube (C12200) be certified by the American National Standards Institute or by the National Sanitation Foundation (ANSI/NSF) with Standard 61- Drinking Water System Components-Health Effects. Once copper tubing meets the SDWA and the EPA Lead and Copper Rule (56FR 26460, June 7, 1991) then the tubes should bear a label along with a limitation statement. Addition of ortho- and polyphosphates as corrosion inhibitors and an adjustment of the water between pH 6.5 and 8.5 assures noncorrosive drinking water. The tap water concentrations of Pb and Cu must be below 15 $\mu\text{g/l}$  and 1300 $\mu\text{g/l}$ , respectively. The limitation label informs that a pH less than 6.5 may require corrosion control to limit copper solubility in drinking water. The ASTM standard B 306 governs the mechanical performance of copper C12200 intended for sanitary drainage, waste and vent piping (DWV). The ASTM standard E 53 verifies the copper plus silver content and E62 verifies the phosphorus content. The ASTM standards E 8 and E 18 establish the tensile and hardness requirements. The ASTM B 306 also requires the ASTM practice E243 of electromagnetic examination/eddy-current test and the ASME section 16.2.3 for pneumatic test. Seamless copper water tube also requires ASTM standard B 88 for chemical composition, temper, mechanical properties, dimensions, mass, roundness, standard lengths and tolerances and squareness of cut. The challenge to meet the latter requirements on every tube during the manufacturing process has indirectly conducted to the present investigation.

The outlook for copper depends on the area of application [23]. On the building market, the increasing electricity consumption in homes, commercial and industrial buildings is forcing an upgrade for thicker wires (AWG 14 to AWG 12 in homes using

the U.S. National Electric Code), which has been estimated to increase copper wiring by 20-40%. On the second largest market, the plumbing and heating, despite the proven reliability of copper other materials like plastic and steel are holding a strong competition. However Copper Development Associations are strongly promoting the benefits of copper in plumbing and heating through technical literature and installation training programs.

On the automotive market the outlook is uncertain because no one knows how the technological advancements might affect the copper industry. The Copper Development Association predicts that the consumption increases should outweigh the consumption decreases and the result will be an increase in copper content for the vehicle. The strive for more efficient motors and transformers has driven the power utilities market to have a larger and larger share of the total market. More efficient electrical motors use coils made of thicker copper wires and a copper squirrel cage instead of the usual aluminum cage. However technological advancements for injecting copper without reducing conductivity and maintaining an acceptable cost still require optimization. The outlook on the air conditioning and refrigeration market is expected to continue growing.

A recent study by Keevil and Noyce [24] of the University of Southampton, U.K., compared the life expectancy of antibiotics resistant organisms over the surface of three copper alloys (C19700, C24000 and C77000) and AISI 304 stainless steel and found that a higher copper content drastically reduced the survival rate. The latter study might boost the use of copper alloys in hospitals and healthcare facilities where the bacteria commonly causes problems.

### 1.5 Purpose

When manufacturing hot-formed products using copper the process conditions (temperature and strain rate) vary, which causes slight differences in the room temperature mechanical properties of the product. Copper is not normally used for having strong structural properties and consequently, room temperature mechanical properties are not normally of concern, however some intermediate steps during manufacturing do require a minimum of resistance. For example hot extruded tube, which is then cold drawn, needs to be produced with a minimum of ductility if rupture during drawing is to be completely avoided. Knowing quantitatively the limiting process conditions, which will produce a hot formed product that is not destined to an early failure, is most desirable and in the case of tube manufacturing would save money and plant time. The initial grain size before cold forming is a determining condition of the mechanical properties of a single phase metal. A finer grain size in general produces a higher mechanical response [25, 26, 27]. The use of phosphorus deoxidised fire-refined 99.9% pure copper, which may contain up to 1000ppm of residual elements, may be of additional influence during the hot-forming operations. The variations of temperature, strain rates and residual composition may cause undesirable intermediate products. A company, Tertub Tubo Técnico Europeo, located in Les Masies de Voltregà (Barcelona, Spain) agreed to fund research oriented to explain the occasional appearance of intermediate tubes that are not drawn with ease. The purpose of this research is to learn about the extents temperature, strain rate and particularly the residual composition of a copper may have on the hot-forming process and eventually the room temperature mechanical properties.

### 1.6 Hypotheses

- 1) Fire-refined 99.9% pure coppers probably behaved differently than coppers with less chemical residual content (OFHC or ETP coppers). The hot flow characteristics and room temperature mechanical properties of fire-refined copper might be different.
- 2) The synergetic effect of several residual elements would require studying several fire-refined coppers to observe a trend.
- 3) If temperature and strain rate conditions were optimized then acceptable dynamically recrystallized grain sizes would be produced and thereby room temperature mechanical properties would be optimized.
- 4) The dynamically recrystallized grain size was assumed to grow to undesirable sizes while cooling and consequently worsening the final mechanical properties.
- 5) The steady state stress should be reached on most hot flow curves and a constant stress should be noticed.
- 6) A hypothesis is that inclusions may be the particles responsible for the increased strain hardening during warm working temperatures (600-800°C).

### 1.7 Objectives

- 1) The research was to determine the dynamically recrystallized grain size for the tested hot flow conditions.
- 2) Improve the quality of the observed metallographic samples.
- 3) Discover the influence of the residual composition has over the values that characterize the constitutive relations used to describe the hot flow of 99.9% pure copper.
- 4) Discover the true onset of dynamic recrystallization (not the peak strain on the stress-strain curve) and the conditions that could affect the onset of dynamic recrystallization in other coppers similar to the ones studied.
- 5) Improve the established constitutive relations for hot flow investigating the appearance of multiple peak dynamic recrystallization and proposing a model. Also study why stress decreases without stabilizing during the supposed steady state stress.
- 6) The research would study the kinetics of static grain growth at different temperatures for the fire-refined coppers in study. The grain growth study would help determine the initial grain size of the annealed samples before hot compression tests.
- 7) Research would obtain a volume and radius distribution of the inclusions found in the 99.9% pure coppers.
- 8) Determine the stoichiometric formula of the possible precipitates that harden the copper matrix during warm temperature compression tests. And then make a correlation between the precipitates and the increased stress (back stress) during hot flow.

## 1.8 References

- [1] Davis J.R. (editor), ASM Specialty Handbook: Copper and Copper Alloys, (2001), ASM International, Metals Park, Ohio, U.S.A., pp. I-600.
- [2] Stefanescu D.M. (chairman), Metals Handbook: Casting, 9<sup>th</sup> Edition, Vol. 15, (1988), American Society for Metals, Metals Park, pp. 448-494.
- [3] Armstrong Smith G., Some Observations on the Electrical Conductivity of Commercial Electrorefined Copper, Journal of the Institute of Metals, Vol. 100, (1972), pp. 125-130.
- [4] Aoyama S., Onuki M., Miyake Y., Urao R., Effects of Lead on Annealing Properties of Cold-Drawn Copper Wire, Journal of Materials Science 26, (1991), pp. 3775-3779.
- [5] Esparducer, A., Segarra, M., Espiell F., García, M., Guixà, O., Effects of Pre-Heating Treatment on the Annealing Behavior of Cold-Drawn Fire-Refined Coppers, Journal of Materials Science 36 (2001), pp.241-245.
- [6] Pops Horace, The Metallurgy of Copper Wire, Essex Group Inc, <http://64.90.169.191/innovations/1997/Dec1997/wiremetallurgy.html>
- [7] Nieh T.G., Nix W.D., Embrittlement of Copper Due to Segregation of Oxygen to Grain Boundaries, Metallurgical Transactions A, vol. 12A, may (1981), pp. 893-901.
- [8] Nieh T.G., Nix W.D., The Formation of Water Vapor Bubbles in Copper and their Effect on Intergranular Creep Fracture, Acta Metallurgica, Vol. 28, (1980), pp. 557-566.
- [9] Camurri C., López M., Sánchez M., Soto J., Impurities in Fire Refined Copper. Effect of Oxygen on Ductility, EDP Congress 1994, The Minerals, Metals & Materials Society (1993), pp.601-613.
- [10] Camurri C., López M., Soto J., Influence de la teneur en oxygène sur la ductilité du cuivre raffiné au feu entre la température ambiante et 800°C, La Revue de la Métallurgie-CIT/Science et Génie des Matériaux, Decembre (1994), pp. 1797-1803.
- [11] Biswas A.K., Davenport W.G., El Cobre Metalurgia extractiva, Pergamon Press, Limusa, México D. F., (1993), pp. 1-471.
- [12] Camurri C.P., López M.J., Leon P.C., Rheology and Metal Forming of Fire-Refined Copper, Materials Characterization 47 (2001), pp. 253-257.
- [13] Herenguel Jean, Metalurgia Especial Tomo II El Cobre y sus Aleaciones, Ediciones Urmo, Espertero 10, Bilbao, (1970), pp. 1-166.
- [14] Tseidler A. A., Metallurgy of Copper and Nickel, Israel Program for Scientific

Translations, Jerusalem, Keter Press, (1970) pp. 1-320.

- [15] Rodríguez Y., Ballester A., Blázquez M.L., González F., Muñoz J.A., Mecanismo de Biolixiviación de Sulfuros Metálicos, Rev. Metal. Madrid, 37, (2001), pp.665-672.
- [16] Riekkola-Vanhanen Marja, Finnish Expert Report on Best Available Techniques in Copper Production and By-Production of Precious Metals, Edita Ltd, Helsinki, <http://www.vyh.fi/eng/orginfo/publica/electro/fe316/fe316.htm>, ISBN 952-11-0506-2,(1999), pp.1-74.
- [17] Jolly Janice L., The U.S. Copper-base Scrap Industry and Its By-products, 4<sup>th</sup> Edition, December (2003), Copper Development Association Inc., 260 Madison Avenue, New York, pp. i-74.
- \*[18] Ellingham H.T., J. Soc. Chem. Ind. 63, 125 (1944).
- \*[19] Richardson F.D., Jeffes J.H.E., J.I.S.I. 160, 261 (1948).
- [20] Gilchrist J.D., Extraction Metallurgy Third Edition, Pergamon Press, Headington Hill Hall, Oxford OX3 OBW, England, (1989).
- [21] Schutt H.U., Toguri J.M., Removal of Impurities in Copper by a Halide-Carrier Technique, Transactions of the Metallurgical Society of AIME, vol. 236, February (1966), pp. 230-231.
- [22] World Bureau of Metal Statistics, 27A High Street, Ware, Hertfordshire, SG12 9BA, United Kingdom.
- [23] Milker, Emil W., Opportunities in North America's Copper Market, International Copper Study Group in Santiago Chile, March 22, (2002) Copper Development Association Inc., [www.copper.org](http://www.copper.org)
- [24] Keevil William C., Noyce J.O., The Antimicrobial Effect of Copper and Copper-based Alloys on Methicillin Resistant Staphylococcus aureus, May 24, 2004, Copper Development Association Inc., to be published.
- [25] Kok S., Beaudoin A.J., Tortorelli D.A., On the Development of Stage IV Hardening Using a Model based on the Mechanical Threshold, Acta Materialia, 50, (2002), pp. 1653-1667.
- [26] Hansen N., Ralph B., The Strain and Grain Size Dependence of the Flow Stress of Copper, Acta metall. Vol. 30, (1982), pp. 411-417.
- [27] Juul Jensen Dorte, Thompson Anthony W., Hansen Niels, The Role of Grain Size and Strain in Work Hardening and Texture Development, Metallurgical Transactions A, Vol. 20A, December (1989), pp. 2803-2810.