1.0 Structure of the copper atom, physical properties and thermodynamics of alloys

1.1 Atomic structure

Copper, with atomic number 29 and atomic weight 63.54, occupies the first position of subgroup IB in the periodic chart of the elements. Subgroup IB also includes silver and gold, and in fact, copper shares many characteristics with these other noble metals as a results of its atomic and electron structure.

1.1.1 Electronic structure

The copper atom is composed of a positively charged nucleus containing 29 protons and 34 to 36 neutrons surrounded by 29 electrons. The electrons are arranged in a structure described by the notation $1s^22s^22p^63s^23p^63d^{10}4s^4$, which implies that the 1s and 2s energy states contain two electrons each, and the 3s state contains two electrons; the 2p states contain six electrons and so forth. The structure is essentially that of an argon atom core plus the filled 3d state and the one 4s electron; it is sometimes written as Ar$3d^{10}4s^4$. The single “outer shell’ 4s electron is responsible for many of copper’s important physical properties, including its high electrical conductivity, its chemical stability, and its reddish color. In metallic crystalline copper, as with other metals, the 4s electron does not remain associated with any particular atom but becomes part of the electron cloud that pervades the crystal lattice [Ref: 29]

The ionization potential of the 4s electron, 7.724 eV, is relatively low, and the “cuprous” ion Cu$^+$, is easily formed. The ionization potential of the 3d state is only slightly higher, and copper, therefore, also displays a “cupric“ valence state, Cu$^{2+}$ [Ref: 29, 6, 30]

Brillouin zones:
Quantum theory limits the allowable energy of electron to specific values, or “quanta”. According to quantum theory, electrons can be described as wave functions of wavelength $\lambda=h/mv$, where $h$ is Planck’s constant and $mv$ is the momentum of an electron. A free electron, therefore, has kinetic energy of $E=1/2mv^2$, which by
substitution is \( h^2/2m\lambda^2 \) or \( h^2k^2/2m \), where \( k \) is the wave number, \( 1/\lambda \). Free, or valence electrons occupy states of increasing energy, for example, of increasing \( k \). Within a metal crystal, however, there exist certain critical wavelengths, and corresponding critical \( k \) values, for which electron energies satisfy the Bragg condition for reflection, \( \lambda=2d\sin\Theta \), and electrons having such energies are in effect excluded from the crystal. These forbidden energies are depicted as the gaps \( b_1-a_1 \) and \( b_2-a_2 \) in the plot of energy versus \( k \) shown in figure 1.1.

![Fig. 1.1.](image1.png)

*Fig. 1.1. Allowable energy states for a single electron in a periodic field, such as a crystal lattice as a function of the wave number \( k \) [Ref: 1]*

When extended to the three-dimensional structure of the face-centered cubic (fcc) crystal structure exhibited by copper, the excluded energy state take the form of a polyhedron shown in figure 1.2. This is the first Brillouin zone for the fcc crystal structure [Ref: 582].

![Fig. 1.2.](image2.png)

*Fig. 1.2. Polyhedron representing the first Brillouin zone for a face centered cubic metal such as copper [Ref: 1]*

According to Pauli’s exclusion principle, only two electron states are available within a Brillouin zone. In a univalent metal like copper, the single valence electron occupies one-
half of the zone, and its position may be visualized by a model such as that depicted in figure 1.3, where the ruled area is the spherical Fermi surface bounding the occupied energy states. Under simplified electrical and thermal conduction theory, the space, for example, energy between the Fermi surface and the Brillouin polyhedron represents the allowable free electron displacement. Because it is related the lattice dimensions, the Brillouin zone shrinks under the influence of applied compressive stress. [Ref: 1]

Fig. 1.3 Spatial relationship between the Fermi surface and the first Brillouin zone in copper [Ref: 1]

The most important consequence of the electronic structure of copper is that copper behaves like a monovalent by the existence of the filled d-shell states at an energy about 2 eV below the unfilled 4s valence state. For example, the filled d states cause the compressibility of copper to be much smaller than that of other monovalent metals, such as the alkali metals. Since the electrical resistivity of copper at room temperature and above is dominated by the scattering of electron by thermal vibrations, the low amplitude of these vibrations resulting from the metal’s low compressibility gives rise to the observed high electrical conductivity [Ref: 584].

1.1.2 Nuclear properties

The copper nucleus has a diameter on the order of $10^{-15}$ m. The nominal radius of the electron cloud surrounding an atom can be taken as the “diameter” of the atom; it is nominally five orders of magnitude larger than that of the nucleus. The radius, which depends in part on the number of nearest atomic neighbors, can be determined from the dimensions of the unit cell. Thus, for crystalline copper in the fcc structure, the distance of closest approach (Burgers vector) is $2.556 \times 10^{-10}$ m, and the so-called Goldschmidt atomic radius for twelve-fold coordination is $1.28 \times 10^{-10}$ m [Ref: 2]. The international atomic weight of copper is 63.546, although the value 63.54 is adequately precise for common calculations and is more commonly used. Copper has two stable isotopes: Cu$^{63}$ (occurring 69.09 % in nature) and Cu$^{65}$ (30.91 %). The unstable isotopes of copper include: Cu$^{58}$, Cu$^{59}$, Cu$^{60}$, Cu$^{61}$, Cu$^{62}$, Cu$^{64}$, Cu$^{66}$, Cu$^{67}$ and Cu$^{68}$; these
have half lives of 7.9 min, 81.6 s, 23.4 min, 3.33 h, 9.8 h, 12.88 h, 5.07 min, 58.6 h and 32.0 s, respectively [Ref: 3, 4, 5].

The absorption cross section of copper, \( \sigma \), with respect to low energy proton bombardment is \( 10^{-27} \) barns (1 barn = 1 cm\(^2\)). For high energy (134 \( \pm \) 4 MeV) protons, \( \sigma = 725 \pm 68 \) barns. The absorption cross section for fast neutrons is \( 10^{-24} \) barns, while for thermal neutrons, values of 3.63 and 3.8 barns have been reported [Ref: 5, 6].

### 1.2 Physical properties

#### 1.2.1 Mass constants

**Compressibility:**

Compressibility is a measure of the ease with which atoms of the metal can be brought closer together. Since the process is reversible, a low compressibility at zero pressure indicates strong bonding. Like other subgroup IB metals, copper has highly compressibility. When the temperature of a crystal is raised, the amplitude of the atomic vibrations is increased and the crystal expands. Generally, the stronger the bonding forces, the smaller the coefficient of expansion. Figure 1.4 shows coefficient of expansion of copper to other elements. The coefficients follow the same general trend as compressibilities; however the two terms cannot be compared directly since corrections are required to allow for the effect of temperature on the coefficient of expansion.

![Fig. 1.4. Coefficient of thermal expansion of copper relative to other metals]({ref: 1})

**Density:**

The density of copper varies from 8.90 to 8.95g/cm\(^3\), depending on the metal’s thermomechanical history (table 1.1). Density initially decreases with increasing degrees of cold work owing to the generation of vacancies and dislocations. It then increases to a value higher than that of recrystallized copper. This has been explained by the presence of persistent subgrain boundaries. The accepted value for the density of copper is 8.94g/cm\(^3\) at 298 K (25°C, 77°F). This density is slightly different from that used in electrical standards, as described below [Ref: 16].
Table 1.1. Densities of copper at 20°C [Ref: 7]

<table>
<thead>
<tr>
<th>State</th>
<th>$\rho$ [g/cm$^3$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Single crystal</td>
<td>8.95285</td>
</tr>
<tr>
<td>Melted and solidified in vacuum</td>
<td>8.94153</td>
</tr>
<tr>
<td>Commercial soft-drawn wire, annealed at 970 °C (1778 °F) in vacuum for 12h</td>
<td>8.92426</td>
</tr>
<tr>
<td>Sample reduced by 67.90% in it's cross section by cold drawing</td>
<td>8.90526</td>
</tr>
<tr>
<td>Diameter of sample reduced by 96.81%</td>
<td>8.91187</td>
</tr>
<tr>
<td>Sample annealed at 880 °C (1616 °F) in vacuum for 12 h</td>
<td>8.93003</td>
</tr>
<tr>
<td>Sample annealed at 1035 °C (1895 °F) in vacuum for 12 h</td>
<td>8.92763</td>
</tr>
</tbody>
</table>

1.2.2 Electrical properties

Conductivity and resistivity:
In 1913, the standard conductivity of pure annealed copper was fixed by the International Electrotechnical Commission (IEC) as that of an annealed copper wire 1 m long, weighing 1 g and having a density of 8.89 g/cm$^3$. The wire exhibited a resistance of exactly 0.15328 $\Omega$. This value was assigned a volume conductivity of 100% of the International Annealed Copper Standard, written 100% IACS. It corresponds to a volume resistivity of 17.241 n$\Omega$m [Ref: 8].

Electrical conductivity and resistivity depend strongly on purity. Purity levels and processing techniques have improved considerably since the IACS was established, and a more precise value for density has also been measured. However, the standard value continues to be used in engineering practice. Currently, the highest measured room-temperature (20 °C, 68 °F) volume conductivity for very pure copper is about 103.6% IACS; the corresponding volume resistivity is 16.642 n$\Omega$m [Ref: 8, 9, 10].

Current practically attainable conductivity values for electrolytic tough pitch and deoxidized low residual phosphorus coppers stand at about 101% IACS. Oxygen-free (OF) copper is certified under ASTM B 170 to meet this as a minimum value. Conductivity data for

It should be noted that the highest currently available value of conductivity for electrolytic copper and copper deoxidized with phosphorus is around 101% IACS. Whereas oxygen-free copper (Cu-OFE) based on the ASTM B 170 standard is characterized by the abovementioned value (101% IACS) at the minimum.

Matthiessen's rule:
This rule states that the product of a metal’s specific electrical resistance and its temperature coefficient of resistance is equal to a constant. In effect, the rule relates the effect of thermal vibrations, foreign atoms in solid solutions (as alloying additions or impurities), and plastic deformation on electrical and thermal conductivity. All of these factors lower the electrical and thermal conductivities of copper. Ordinarily, the electrical conductivity of copper decreases with increasing temperature. The effects produced by small amounts of alloying elements in solid solution and by cold deformation are
independent of temperature and are additive to the effect of thermal vibrations. The increase in resistivity brought about by small amounts of secondary elements in solid solution are shown in table 1.2 (see also fig. 4.1 - 4.3). [Ref: 2, 7]

Table 1.2.Increase in resistivity of copper due to small solute additions [Ref: 7, 12]

<table>
<thead>
<tr>
<th>Solute</th>
<th>Room temperature solubility [wt %]</th>
<th>Resistivity increase per 1 wt % addition [μΩcm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag</td>
<td>0.1</td>
<td>0.355</td>
</tr>
<tr>
<td>Al</td>
<td>9.4</td>
<td>2.22</td>
</tr>
<tr>
<td>As</td>
<td>6.5</td>
<td>5.67</td>
</tr>
<tr>
<td>Au</td>
<td>100.0</td>
<td>0.185</td>
</tr>
<tr>
<td>B</td>
<td>0.06</td>
<td>8.25</td>
</tr>
<tr>
<td>Be</td>
<td>0.2</td>
<td>4.57</td>
</tr>
<tr>
<td>Ca</td>
<td>&lt; 0.01</td>
<td>4.77</td>
</tr>
<tr>
<td>Cd</td>
<td>&lt; 0.5</td>
<td>0.172</td>
</tr>
<tr>
<td>Co</td>
<td>0.2</td>
<td>7.3</td>
</tr>
<tr>
<td>Cr</td>
<td>&lt; 0.03</td>
<td>4.9</td>
</tr>
<tr>
<td>Fe</td>
<td>0.1</td>
<td>10.6</td>
</tr>
<tr>
<td>Ga</td>
<td>20.0</td>
<td>1.27</td>
</tr>
<tr>
<td>Ge</td>
<td>11.0</td>
<td>3.2</td>
</tr>
<tr>
<td>Hg</td>
<td>-</td>
<td>0.32</td>
</tr>
<tr>
<td>In</td>
<td>3.0</td>
<td>0.615</td>
</tr>
<tr>
<td>Ir</td>
<td>1.5</td>
<td>2.0</td>
</tr>
<tr>
<td>Mg</td>
<td>1.0</td>
<td>4.2</td>
</tr>
<tr>
<td>Mn</td>
<td>24.0</td>
<td>3.37</td>
</tr>
<tr>
<td>Ni</td>
<td>100.0</td>
<td>1.2</td>
</tr>
<tr>
<td>O</td>
<td>0.0002</td>
<td>21</td>
</tr>
<tr>
<td>P</td>
<td>0.5</td>
<td>14.3</td>
</tr>
<tr>
<td>Pb</td>
<td>0.02</td>
<td>1.02</td>
</tr>
<tr>
<td>Pd</td>
<td>40.0</td>
<td>9.57</td>
</tr>
<tr>
<td>Pt</td>
<td>100.0</td>
<td>0.635</td>
</tr>
<tr>
<td>Rh</td>
<td>20.0</td>
<td>1.5</td>
</tr>
<tr>
<td>S</td>
<td>&lt; 0.0025</td>
<td>18.6</td>
</tr>
<tr>
<td>Sb</td>
<td>2.0</td>
<td>2.9</td>
</tr>
<tr>
<td>Se</td>
<td>&lt; 0.002</td>
<td>8.5</td>
</tr>
<tr>
<td>Si</td>
<td>2.0</td>
<td>7.0</td>
</tr>
<tr>
<td>Sn</td>
<td>1.2</td>
<td>1.65</td>
</tr>
<tr>
<td>Te</td>
<td>&lt; 0.0005</td>
<td>4.0</td>
</tr>
<tr>
<td>Ti</td>
<td>0.4</td>
<td>21.6</td>
</tr>
<tr>
<td>Zn</td>
<td>30.0</td>
<td>0.286</td>
</tr>
<tr>
<td>Zr</td>
<td>&lt; 0.01</td>
<td>8.0</td>
</tr>
</tbody>
</table>

Temperature and pressure coefficients of resistance:

Thermally induced lattice vibrations reduce electrical conductivity by shortening the mean free path for electron movement and by distorting the crystal structure, for example, by changing the shape of the Brillouin zone. Thermally induced stresses can also give rise to the formation of crystallographic twins, which can be interpreted as another form of lattice distortion. The rate of rise in electrical resistivity with temperature follows Matthiessen's rule and is independent of alloy content and the state of deformation if both of these factors are small. For pure copper, the temperature coefficient of resistance
is 0.068 nΩm/K at 20 °C (68 °F). The pressure coefficient of resistance is -0.228 aΩm/Pa (0.013 fΩin./psi) for pressures from 100 kPa to 9,8 GPa (1.45 psi to 1420 ksi) [Ref: 10, 11].

1.2.3 Thermal properties

The thermal properties of pure copper at 1 atm pressure are:
- Melting point: $t_m = 1084.88$ °C (1984.78 °F) [Ref: 12], 1083 ± 1 °C [Ref: 7],
- Heat of fusion: $\Delta H_f = 134$ J/g (57.7 Btu/lb) [Ref: 2]; 205 J/g (88 Btu/lb) [Ref: 6]; 204.9 J/g (88.07 Btu/lb) [Ref: 13]; 206.8 J/g (88.89 Btu/lb) [Ref: 14]; 12.804 J/mol (201.49 J/g, 86.61 Btu/lb) [Ref: 10],
- Heat of vaporization: $\Delta H_v = 3630$ J/g (1463 BTU/lb) [Ref: 2],
- Heat of sublimation at 1299 K: $\Delta H_s = 3730$ J/g (1606 Btu/lb) [Ref: 2],
- Boiling point: $t_b = 2595$ °C (4703 °F); 2567 °C (4652 °F) [Ref: 6]; 2565 °C (4649 °F) [Ref: 2],
- Vapor pressure: $p_v = 6.9214 - 17546/T(K) - 0.0001659T(K)$ atm [Ref: 7]; 1.3·10⁻¹ atm 1141 °C (2086 °F) [Ref: 6],
- Thermal conductivity: 398 W/m·K at 27 °C [Ref: 6]; (226 Btu/ft²/ft/h°F at 68 °F) [Ref: 15],
- Coefficient of thermal expansion at 20 °C (68 °F): 16.7 μm/m°C (9.4 μin./in./°F) [Ref: 6, 15],
- Specific heat: $C_p = 0.092$ cal/g°C at 20 °C; 0.092 Btu/lb°C at 68 °F (383 J/kg·K) [Ref: 15]; 384.6 J/kg·K [Ref: 6], otherwise: $C_p,0-1+\theta = 0.009619 + 6.139·10^{\theta t} + 1.928·10^{\theta t^2}$ (cal/g°C). $C_p,1033°C = 0.11 + 45.6t^{-1}$ (cal/g°C). At higher temperatures and solidification and cold worked structures, $C_p$ can be calculated by the formulae: $C_p = 0.092 + 0.000025t$ cal/g°C for solid state between 0 and 1083 °C. For molten copper, $C_p = 0.112$ cal/g°C [Ref: 7].

Thermal conductivity:

The thermal conductivity of pure copper ranges from 2780 W/m·K (1607 Btu/ft²/ft/h°F) near 0 K to 177 W/m·K (102 Btu/ft²/ft/h°F) at 2273 K (3632 °F), with the maximum of 19,600 W/m·K (11300 Btu/ft²/ft/h°F) at about 10 K [Ref: 6, 14]. Alloying copper reduces its thermal conductivity. In practice terms, however, alloying markedly improves other characteristics such as mechanical properties and corrosion resistance, and the value of these effects override losses in thermal conductivity for many applications. The changes thermal conductivity induced by alloying are of the same relative magnitude as those for electrical conductivity [Ref: 6, 14].

Surface area and film coefficients frequently affect total heat flow more than the inherent thermal conductivity of the bulk metal. This is shown in figure 1.5 in which heat transfer coefficients are compared for samples of six alloys of the same size and wall thickness. Inhibited admiral metals C44300 or C44400 are among the most commonly used materials for heat exchangers because of their high heat transfer coefficients. Copper-nickel alloys such as C71500 are also used for this purpose; these alloys have lower conductivity than copper0zinc alloys, but their higher corrosion resistance and their especially high erosion-corrosion resistance makes the more cost-effective choices for long-term service [Ref: 16].
Fig. 1.5. Heat transfer coefficients for selected copper alloys [Ref: 16]

1.2.4 Optical properties

Reflectance and emission:
The reflectivity of copper decreases continuously with wavelength from the infrared through ultraviolet regions. For incandescent light, the spectral reflection coefficient of copper is 0.63. Table 1.3 list indices of refraction, extinction coefficients, and reflectance values for several types of copper surfaces [Ref: 14].

Among copper’s other optical properties are:
- Nominal spectral emittance for polished copper at \( \lambda = 655 \text{ nm} \) and 800 °C (1470 °F): 0.15,
- Coefficient of absorption (absorptivity) for solar radiation: 0.25,
- Emissivity of heavily oxidized copper surfaces: \( \sim 0.8 \).

Table 1.3. Optical properties of copper: normal-incidence reflectance of freshly evaporated mirror coating copper [Ref: 14]

<table>
<thead>
<tr>
<th>Wavelength [( \mu \text{m} )]</th>
<th>Reflectance [%]</th>
<th>Wavelength [( \mu \text{m} )]</th>
<th>Reflectance [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.22</td>
<td>40.1</td>
<td>0.75</td>
<td>97.9</td>
</tr>
<tr>
<td>0.24</td>
<td>39.0</td>
<td>0.80</td>
<td>98.1</td>
</tr>
<tr>
<td>0.26</td>
<td>35.5</td>
<td>0.85</td>
<td>98.4</td>
</tr>
<tr>
<td>0.28</td>
<td>33.0</td>
<td>0.90</td>
<td>98.4</td>
</tr>
<tr>
<td>0.30</td>
<td>33.6</td>
<td>0.95</td>
<td>98.4</td>
</tr>
<tr>
<td>0.315</td>
<td>35.5</td>
<td>1.0</td>
<td>98.5</td>
</tr>
<tr>
<td>0.32</td>
<td>36.3</td>
<td>1.5</td>
<td>98.5</td>
</tr>
</tbody>
</table>
1.2.5 Magnetic properties

Susceptibility and permeability:
Magnetic susceptibility ($\chi$) is defined as the ratio of induced magnetization to applied magnetic field, for example: $\chi = M/H$, where $M$ - magnetization (magnetic momentum per volume unit), H is the applied magnetic field. Each material has a characteristic magnetic susceptibility, although the property varies somewhat with thermomechanical history. Copper is diamagnetic because its magnetic susceptibility is negative. Data on this subject coming from several sources are presented in table 1.4. The magnetic susceptibility of several copper-nickel alloys is given in table 1.5. Note that the magnetic behavior of alloys varies from diamagnetic to paramagnetic between various nickel content at the level of 0.94 % and 5.0 %. [Ref: 17]

Table 1.4. Magnetic susceptibility of pure copper [Ref: 13, 17, 18]

<table>
<thead>
<tr>
<th>Temperature [$^\circ$C]</th>
<th>$\chi \cdot 10^6$ [cgs]</th>
</tr>
</thead>
<tbody>
<tr>
<td>-267</td>
<td>-0.0836</td>
</tr>
<tr>
<td>from -259 to -253</td>
<td>-1.22</td>
</tr>
<tr>
<td>-250</td>
<td>-0.0856</td>
</tr>
<tr>
<td>-242</td>
<td>-0.0863</td>
</tr>
<tr>
<td>-233</td>
<td>-0.0879</td>
</tr>
<tr>
<td>-211</td>
<td>-0.0873</td>
</tr>
<tr>
<td>-174</td>
<td>-0.0869</td>
</tr>
<tr>
<td>-171</td>
<td>-0.0867</td>
</tr>
<tr>
<td>-65</td>
<td>-0.0863</td>
</tr>
<tr>
<td>-26</td>
<td>-0.0859</td>
</tr>
<tr>
<td>18</td>
<td>-1.08</td>
</tr>
<tr>
<td>19</td>
<td>-0.0855</td>
</tr>
<tr>
<td>20</td>
<td>-0.086</td>
</tr>
<tr>
<td>300</td>
<td>-0.085</td>
</tr>
<tr>
<td>600</td>
<td>-0.082</td>
</tr>
<tr>
<td>900</td>
<td>-0.079</td>
</tr>
<tr>
<td>1080 (solid)</td>
<td>-0.077</td>
</tr>
<tr>
<td>1080</td>
<td>-0.97</td>
</tr>
<tr>
<td>1090</td>
<td>-0.68</td>
</tr>
<tr>
<td>1090 (liquid)</td>
<td>-0.054</td>
</tr>
</tbody>
</table>

Table 1.5. Magnetic susceptibilities of copper-nickel alloys at 22$^\circ$C [Ref: 17, 19]
Some copper alloys and intermetallic compounds, such as Cu₈Sm and the alloys Cu-Ni-Fe and Cu-Ni-Co show ferromagnetic behavior. The so-called Heussler alloys based on the elements Cu-Mn-Al are also ferromagnetic. These materials have a maximum permeability from 100 to 1000, saturation induction of 6 T, saturation hysteresis from 300 to 450 erg/cm³, and coercitive force ranging from 79.6 to 15,900 A/m. In this case, ferromagnetism results not from the presence of copper, but from the superstructure, where manganese atoms are distributed in the proper locations [Ref: 585].

"CuNiFe" is an alloy with 80% Cu and 20% Ni. When heat treated (quenched from 1000 °C, 1830 °F), the alloy contains ferromagnetic iron- and nickel-rich clusters in a copper-rich matrix. The clusters apparently arise through spinodal decomposition. By cold working and aging, the alloy develops a crystallographic (and magnetic) texture [Ref: 19].

In industrially applied copper and copper alloys, magnetic susceptibility depends mainly on iron content present in the material as impurity. In oxygen free copper Cu-OF, small amounts of this element in a solid solution has only slight impact on magnetic properties. In electrolytic tough-pitch (ETP) copper containing about 200 ppm of oxygen, iron is present in the form of oxide Fe₃O₄, which has a much greater impact on the material's magnetic properties than iron in solid solution. Iron in alloys has a similarly small impact when it is present in the abovementioned solid solution, e.g. after heat treatment at high temperatures and rapid cooling or strengthening. It is worth noting that it is then responsible for complete magnetic susceptibility when precipitated in an iron-rich phase.

Magnetic permeability (μ) is a value that determines the material's (medium's) capacity to change magnetic induction subject to magnetic field. It is expressed as μ = B/H, where B is the flux density and H is the applied magnetic field or magnetizing force. It is a momentary inclination of magnetization. In pure copper, μ is very low. This is most beneficial, since low permeability in the presence of a magnetic field allows for avoiding energy losses in such applications as electric motors and generators.

Hall effect:

It is based on the difference of potentials in a conductor with electric current, when the conductor is placed in a magnetic field transverse to the current. This voltage, referred to as the Hall effect, appears between planes limiting the conductor, transverse to the plane designated by the direction of the current and the magnetic induction vector. This is caused by Lorentz force affecting charges moving within the magnetic field. Hall voltage for pure copper is $-5,24 \times 10^{-4}$ V at melting point from 0,30 to 0,8116 T⁰m, whereas the Hall coefficient is $-5,5$ mV·m/T.

Influence of heat treatment:

Heat treatment has no impact on magnetic properties of pure copper, although it is helpful in the formation of ferromagnetic phases in such alloys as Cu-Ni-Fe and Cu-Ni-Co. Ferromagnetic phases may also result from strengthening with precipitation, spinodal decomposition or the order-disorder transition.

<table>
<thead>
<tr>
<th>%Ni</th>
<th>$\chi \times 10^6$ [cgs]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>-0.080</td>
</tr>
<tr>
<td>0.94</td>
<td>-0.062</td>
</tr>
<tr>
<td>5.0</td>
<td>-0.042</td>
</tr>
<tr>
<td>10.0</td>
<td>0.185</td>
</tr>
<tr>
<td>11.0</td>
<td>0.221</td>
</tr>
<tr>
<td>20.3</td>
<td>0.55</td>
</tr>
<tr>
<td>30.0</td>
<td>1.28</td>
</tr>
<tr>
<td>35.6</td>
<td>1.99</td>
</tr>
<tr>
<td>38.0</td>
<td>2.84</td>
</tr>
<tr>
<td>50.2</td>
<td>11.8</td>
</tr>
</tbody>
</table>
1.2.6 Acoustic properties

Brittle fracture occurs when the velocity of a propagating crack exceeds the velocity of sound in a material, for example, when fracture energy is dissipated faster than (flexible) acoustic energy. The speed of sound in pure annealed copper is 4759 m/s for longitudinal waves, 3813 m/s for transverse waves, 2325 m/s for shifted waves and 2171 m/s for Rayleigh waves [Ref: 17]. These are very high values. As a result, fracture and fatigue cracking rarely occur in pure metals. However, this possibility should be taken into account in while working with hard copper alloys.

1.3 Properties in solid state

Copper is characterized by a face-centered cubic structure throughout the entire range of temperatures below melting point (symbol of lattice: A1; space group: O₃, Fm3m, cF4). The existing parameters of lattices are a = 0.3615090 ± 0,000004 Nm [Ref: 6], a = 0.36147 nm at 293 K (20 °C or 68 °F) [Ref: 2], a = 0.36073 nm at 290 K (17,8 °C or 64 °F) [Ref: 14, 20]. Based on values reported by Weast [Ref: 6], the closest distance or Burgers vector in the direction (110) at 293 K is 0.255625.

Slip systems:

In metals with face-centered cubic structure, such as copper, octahedral surfaces {111} and directions contain the closest atomic packing, and thus are the most active slip systems. There are four independent (111) slip surfaces per face-centered volume unit. Every surface (111) includes three (110) directions; therefore, copper has 12 possible slip systems. A slip occurs when shear stress in the direction of the slip along the slip surface reaches the critical value $\tau_{cr}$.

Twinning:

Metals with regular face-centered cubic structure, such as copper are subject to deformation through Twinning; for example, they may deform by creating orientations with mirror reflection directions - transverse surface {111} in direction (112). Twinning is a less significant mechanism deforming metals with face-centered cubic structures than in case of body-centered cubic structure and hexagonal structure, which have less favorable anti-slip systems. Nevertheless, copper has the ability to create annealing twins in order to adjust to the deformation due to cold plastic processing and the resulting process of recrystallization which is a direct continuation. Therefore, the presence of annealing twins in the microstructure proves that the metal has been mechanically deformed prior to the annealing process.

Stacking faults:

The energy of alignment errors in copper, i.e. bound energy with imperfect distribution of adjacent planes is approximately 40 erg/cm². The energy of alignment error is also associated with such properties as yield stress and strengthening through deformation. With the use of X-ray diffraction, it has been shown that the energy of alignment error decreases in brass with the increase of zinc content, and the observation also indicates that alpha brass has a greater number of mechanical twins than copper.

1.3.1 Copper Alloys
Solid solutions:
It is likely that the majority of alloys used on an industrial scale are those that may be found in the form of solid solutions. A solid solution is when atoms of different elements may occupy random location in a lattice. Such additions make substitution solid solutions. Such phenomenon is the most likely (although may not always occur), when atoms of the dissolved ingredient are of a different size than solvent by no more than 14 - 15 %. If the mismatch in atom size is smaller than 8 %, complete mutual solubility is possible. (It should be noted that the size of an atom also depends on the closest surroundings, in which the atom is located. In other words, it is convenient to assume that the size of atoms in crystalline state of a metal is constant as well as assume the match degree of 15%). Solubility in solid state is preferred when metal components have the same number of valence electrons, although this is not always the limit, as well as when they have the same lattice.

Copper and nickel, whose atom sizes differ by only 2,5 %, and which have a face-centered structure, create a number of solid solutions in the entire two-component range of solubility. This is illustrated in the phase equilibrium diagram in figure 1.6.

Copper alloys with gold, presented in figure 1.7, as well as other divalent transition metals, such as palladium and platinum, also show complete solubility in copper at high temperatures; however, transition alloys made of these metals dissociate into one or more phases at lower temperatures. During arrangement, Cu and Au atoms leave their random locations in network nodes to take preferred positions in the lattice. The atomic arrangement in this ant analogus cases is such that the closest neighboring atom is of a different kind. Such atomic arrangement is referred to as the superstructure.

![Fig. 1.6. Cu-Ni phase equilibrium system](image-url)
Fig. 1.7. Cu-Au phase equilibrium system

Similar sizes of atoms of elements do not guarantee complete solubility in solid state, as is the case in figure 1.8 presenting the Cu-Ag phase equilibrium system. Although cases of complete solubility in solid state are a rarity among copper alloys, partial or limited solubility is a common thing. Among the major (from an application point of view) copper alloys with limited solubility in solid state, it is worth noting copper-zinc alloys (brass), copper-tin alloys (tin or phosphor bronze) and copper-silicon alloys (silicon bronze).

Fig. 1.8. Cu-Ag phase equilibrium system

Interstitial solid solutions. When dissolved atoms have a significantly shorter radius, they form interstitial solutions in the solvent metal. They are formed when the difference in the size of atoms is big enough to place smaller atoms in gaps between the solvent atoms within the lattice. Such solubility occurs, for instance, when relatively small hydrogen, oxygen, nitrogen or carbon atoms are dissolved in a metal lattice. Although
interstitial solid solutions have a key role in case of steel and other metals, their practical application in commercial copper alloys is very small. The presence of interstitial solid solutions often brings more harm than good. For example, oxygen and hydrogen easily form interstitial solid solutions and, with the exception of oxygen-free copper, small amounts (up to several dozen ppm) of oxygen are then present in the material, which is used in many applications. The abovementioned oxygen and hydrogen can combine at high temperatures and cause cracking pressure in copper along grain boundaries (hydrogen embrittlement). It is worth nothing that carbon and boron are almost insoluble in copper.

The ways of strengthening copper, subject to analysis in the second part of this paper, are very important from the viewpoint of forming properties of metallic materials.

### 1.4 Thermodynamics of copper alloys

The thermodynamic of copper alloys is of great technological and commercial importance, especially due to the possibility to understand the essence of the created metallic systems, structure-properties dependencies and corrosion phenomena.

#### 1.4.1 Phase equilibria diagrams

Phase equilibria diagrams, also referred to as phase diagrams, are graphic representations of the ranges of stability for the phases of metals and alloys. Stability regions (phase fields) are represented as a function of the chemical composition, temperature, pressure, or in case of electrochemical systems - pH and Eh. A phase may determine the physical state - gaseous, liquid, or solid, and, as is the case in metals and other solid substances - homogeneous or crystallographically-distinct structure. Phase diagrams are a very useful tool for understanding the composition of the alloy as well as heat treatments.

Metallic systems of copper. Out of the several types of phase diagrams that can be made for metallic systems, the most common are those, which define the areas of phase stability in terms of chemical composition and temperature. These usually consist of two components. Ternary phase systems, which are three-dimensional, are usually presented as isothermal or isocompositional. Quaternary and higher phase systems cannot be visualized, and phase stability in such cases may be represented in terms of constant temperatures and chemical composition.

In case of compounds that at least meet the Hume-Rothery rule stating the electron-atom relationship (the type of structure of intermetallic phase depends on the density of valence electrons, i.e. the ratio of the number of valence electrons to the number of atoms), general observations were made, leading to the following conclusions:

- the first stable phase appears in double Cu-X alloys, after (X) solubility limit exceeds the volume ratio between electrons and atoms of 3/2. As stated earlier, 3/2 phases seeks to form β body-centered structure (provided there is disorder or β’ if there is order); hexagonal structure is usually marked ζ or ζ’; as well as β-magnesium μ structure,
- increasing the valence of the solute favors the formation of structures ζ and μ at the expense of structures β or β’, whereas increased temperature accelerates the diffusion and favors disordered structures β at the expense of β’ or ζ,
- increased atom size of the solvent favors the formation of β structures, whereas the range of chemical composition decreases by 3/2 components. The range of stability of such compound may also change in order to reduce electron concentration,
- large differences in electronegativity favor the formation of compound valence, e.g. Cu₃P. Such compounds differ from true intermetallic compounds by the nature of their bonds.
even higher concentration of solute supports the formation of 21/13 electron compounds, which have a complex cubic structure γ-brass (also known as structure β-manganese with 52 atoms per unit cell). These compounds are characterized by 87 or 88 electrons per unit cell. Increasing the size of atoms in a solute moves the concentration of electrons to lower numbers, but phases γ are not formed beyond the size difference of 20%. Increasing the electrochemical difference between the solute (Cu) and the solvent moves electron concentration to higher numbers.

We may list several copper alloys that are very important from the commercial point of view, where second phases play a key role. The metallic system copper - zinc is the most important; it has been illustrated in figure 1.9. Here the area of solid solution expands to 32,5% Zn at 903 °C (1657 °F) and around 39% Zn at lower temperatures (chemical compositions are provided in percentages by weight, unless specified otherwise). This area includes alpha brass, whose structure and properties are similar to pure copper. An increase in zinc content beyond α phase leads to the formation of body-centered cubic β phase (CuZn) with an electron concentration of 3/2. Other intermetallic phases in the system include γ - compound 21/13 with complex cubic structure Cu₃Zn₈ and compound 7/4 ε, nominally called CuZn₃, which has a hexagonal structure.

![Fig. 1.9. Cu-Zn phase equilibrium system](image)

The phase equilibrium system for copper-tin, illustrated in figure 1.10 is common for tin bronze, which is also called phosphor bronze. Tin makes an alpha solid solution with copper, with the content of up to 15,8% Sn at temperatures between 520 °C and 586 °C (968 to 1087 °F). One of the major practical differences between phase systems Cu-Sn and Cu-Zn is that in the former, the range of temperatures between liquid and solid states is quite large. This expanded range results in tin bronze go into semi-solid state while solidifying. Castings must therefore be designed taking into account their weak structure. The expanded range between the liquidus and solidus is also responsible for the dendritic segregation or microsegregation in the tin bronze in question.

The Cu-Sn system includes several electron compounds. Phase β with the electron concentration of 3/2 is a compound located in the vicinity of Cu₃Sn. Therefore, it has a body-centered cubic structure. The ratio 21/13 is formed by a complex cubic phase δ (Cu₃Sn₈) and 7/4 is made by the rhombohedral phase ε with a content of approximately 38% Sn (Cu₃Sn). Phase β, much like another γ (which is not an electron compound) is only stable at high temperatures and cannot be maintained by strengthening. Due to microsegregation, the metal may be held in all α compounds that may undergo periodic
reactions to β, which dissociates to the γ phase when cooled down, and finally the brittle δ phase, which may be maintained at room temperature. However, low-temperature dissociation of the α phase to α + ε occurs rarely due to the slow reaction of the formation of ε in this temperature range. Therefore, for practical purposes the phase equilibrium system can be treated as one that includes a vertical line stretching downward from the content of 15.8% Sn.

![Cu-Sn phase equilibrium system](image)

**Fig. 1.10. Cu-Sn phase equilibrium system**

Copper-aluminum phase equilibrium system (fig. 1.11) contains numerous intermetallic phases. Copper is characterized by the area of solid solution, which extends to the content of 9.5% Al at 565 °C (1050 °F), and an alloy with content lower than 8.5% Al belongs to single-phase alpha .aluminum bronzes. Due to segregation and non-equilibrium solidification and cooling, casting alloys containing between 8.5 and 9.5% Al are characterized by high concentration of the β phase, which is stable in aluminum content from around 8.5 % to 15% at increased temperatures. The phase includes Cu₃Al with electron concentration of 3/2. The β phase is characterized by body-centered cubic structure. Following the cooling process, it dissociates eutectoidally to α + γ₂. Whereas the χ phase includes Cu₉Al₄ with electron concentration of 21/13, which is a stable compound at temperatures over 963 °C (1765 °F). Regular structure characteristic of compounds with electron concentration of 21/13 is presented as the γ₂ phase, and one of χ phases is the final product of degradation. The γ₂ phase contains slightly more aluminum than required for electron concentration of 21/13.

Eutectoidal degradation of the β phase may avoid quick cooling, during which another phase is marked β'. The β' phase transforms martensitically at lower temperatures to gain hexagonal structure β' and γ', individual phases depend on aluminum concentration.
1.4.2 State of thermodynamic disequilibrium

It is important to realize that phase diagrams described above represent conditions that exist in thermodynamic equilibrium. Such conditions may require taking very long times for slow or kinetically inhibited reactions, due to which they are not always obtainable in practice. However, when that is the case, they become very useful for creating disequilibrium diagrams, for instance describing phase changes that occur in variable temperature and time. The so-called time-temperature-transformation charts (TTT) and continuous cooling diagrams, which describe specific values are of limited use in case of copper alloys.

1.4.3 Segregation

For many practical thermal processes, the phase surface interface may be more important than the metal's physical properties in its entire volume. Several examples of such phenomenon are related to the chemical heterogeneity caused by segregation. Segregation occurs when the first metal of a multiple-metal alloy solidifies differently than the one that solidifies after it. For instance, solutes in castings are enriched in a cooled down surface that solidifies first. Hot plastic processing and annealing allow for the segregation of structures to homogenous through diffusion processes in solid state. Effect of segregation on properties. Segregation also occurs inside grains and dendrites, where it may also lead to fragility and corrosion. Furthermore, changes in electrical and thermal resistivity may be observed. Segregation may affect the phase changes, which creates bubbles on the boundaries of grains, thus affecting the alloy's structure and properties. Moreover, it has the ability to affect surface diffusion, which occurs in grain boundaries, thus deciding on the degree of sintering during the processes of powder metallurgy.

Fig. 1.11. Cu-Al phase equilibrium system
2.0 Strengthening mechanisms of metallic materials

The level of mechanical properties of a material, represented by yield stress increases in polycrystalline materials along with limited mobility of linear defects present in the material in the form of dislocations, which are responsible for plastic flow of the material. The freedom of movement of dislocations may be limited by various kinds of “obstacles” that may occur in the material individually or in combinations. The most common obstacles for dislocation movement in material are: grain boundaries, atoms of solute in solution, second-phase particles, and other dislocations generated due to deformation. The above mechanisms that strengthen semi-crystalline materials, including copper-based materials, have been discussed below. The first of these methods - strengthening metal through grain boundaries, i.e. through reducing the size of grains in metal, is a very efficient way to increase mechanic properties. When considering this issue from geometry point of view, grain boundaries are much greater obstacles for a moving dislocation than other linear defects (dislocations) or point defects (solute atoms), since the intersection of slip surfaces of a dislocation with the boundary surface is a line, not a point as in the case of linear defects. Grain boundaries are therefore effective obstacles for the movement of dislocations that, due to crystallographic factors do not allow dislocations to move from one grain to another through grain boundary. Literature provides several models describing how grain boundaries strengthen material, one of which has been discussed below. Before the plasticity of material in macroscopic scale can be achieved, microplasticity first occurs within grains that have a slip system with privileged orientation (grain No. 1 in fig. 2.1.) relative to the axis of application of force to the material. This results in multiplication of dislocations and their looping in grain boundaries, which separates such a grain from adjacent grains with less preferred crystal orientations (grain No. 2 in fig. 2.1.).

![Fig. 2.1. Microplasticity in a grain (grain No. nr1) with preferred crystallographic orientation precedes plasticity of material in macro scale. However, macroscopic flow of material requires dislocation movement in all grains (including grain No. 2), which may be caused by internal stress caused by dislocation loops in the No. 1 grain boundary. Such stress may cause the emission of dislocations from grain boundary, or activate the source of dislocation in grain No. 2 (point in distance r from boundary). The size of stress concentration depends on the number of dislocations in dislocation loops, and increases together with the grain's diameter [Ref: 21]](image)

However, in order for plasticizing to take place in macroscopic scale, the slip systems must be triggered in all grains, including those with undesired crystallographic orientation. The movement of dislocations in grains with undesired orientation may be
caused by generating dislocations from grain boundary, or alternatively, dislocation loops located in the grain boundary may generate a concentration of stress strong enough to activate slip in grains with undesired orientation.

Let us assume that $\tau^*$ is a stress required to activate dislocation movement within the grain with undesired orientation, and that the source of these dislocations is located in distance $r$ from the grain boundary (as shown in fig. 2.1.). Concentration of stress, resulting from loop dislocations, increases together with the number of dislocations that hit the impassable grain boundary. Whereas the number of dislocations generated inside the deforming grain increases together with the length of the slip surface, which is identical to the grain’s diameter $d$. Analyses show that activation in grains with undesired orientation takes place when the following condition is met [Ref: 21]:

$$\left( \tau_{app} - \tau_0 \right) \left( \frac{d}{4r} \right)^{1/2} = \tau^* \quad [21]$$

where:

$\tau_{app}$ - is the applied shear stress, at which activation takes place,

$\tau_0$ - is the internal stress that resists the motion of dislocations in a deforming grain, the $(d/4r)^{1/2}$ parameter - represents the concentration of stress coming from dislocation loops.

It is worth noting that this parameter increases along with the number of dislocation in dislocation loops, i.e. together with the diameter of the grain. Rearranging the above equation allows expressing the shear stress as a function of the diameter of the grain [Ref: 21]:

$$\tau_{app} = \tau_0 + 2\tau^* r^{1/2} d^{-1/2} = \tau_0 + k'_y d^{-1/2} \quad [21]$$

With respect to yield, the above equation is equivalent to the well-known Hall-Petch relation, which determines the linear growth of yield in polycrystalline material together with $d^{-1/2}$

where:

$\sigma_y$ - yield stress,

$\sigma_0$ - material constant expressing the resistance of the lattice against dislocation movement,

$k'_y$ - strengthening coefficient characteristic of the material,

d - average grain size.

It should be noted that the physics of the phenomenon of material strengthening through grain boundaries has been included in equation 2.1. That is, if the size of the grain is large, stress concentration takes place in the adjacent grain, hence the applied stress required to activate the slip in that grain is relatively low, and vice versa. The smaller the grain, the smaller the stress concentration within the adjacent grain, which requires applying greater force to generate a slip. The degree to which you can effectively strengthen the material by reducing the size of grains depends on the possibility to reduce grains in that specific material as well as on the $k_y$ coefficient, which in case of copper is 0,112 [MN/m$^{3/2}$]. Strengthening material through reducing the size of grains is effective with small or medium plastic deformations. In the case of large deformations, the effect of grain boundaries on yield stress is smaller compared to other physical phenomena that take place during deformation.
2.1 Solution strengthening

The second of the strengthening mechanisms mentioned in the introduction occurs with the participation of solute atoms in the solution that increase the yield of crystalline materials, which results from the effect between them and the dislocations moving during the deformation. The impact of the stress fields caused by the dislocation is classified as a long range effect, hence atoms on both sides, both above and below the slip surface, interact with dislocations. However, considering that the maximum effect concerns atoms in the immediate vicinity of the slip surface, only these should be considered in terms of impact on yield increase resulting from the presence of atoms in the solution.

The presence of solute atoms in the lattice causes deformation within the lattice, which results in a spherical stress field around the solute atom. If an addition atom is smaller than that of a solvent, the deformation is negative and vice versa. The resulting stress field interacts with the stress field generated by dislocations, which gives rise to the energy of interaction between the atom and the dislocation. For instance, the edge dislocation moving along the slip surface hits a small solute atom located directly above that surface (fig. 2.2)

Fig. 2.2. Edge dislocation moving along the slip surface, where an atom of solute is located, with a diameter smaller than that of a solvent atom [Ref: 21]

In this case, the energy of interaction will be negative, since the small atom reduces the energy of dislocation, which results from the reduced volume above the line of dislocation. Dislocation is therefore attracted towards the atom of the solute. In the reverse situation, when a small atom is below the slip surface, the energy of interaction would be positive and the dislocation would be repelled by such atom. Of course, in such case one should expect the dislocation to encounter the same number of repelling and attracting atoms. However due to the fact that the edge dislocation is flexible, it takes more time, or rather much of the length of the dislocation is located in areas negative interaction energy. Therefore, the energy of interaction between the dislocation and small atoms is negative in general, and as shown by similar analyses, this is also true in case of atoms larger than the solvent atoms. Generally, the strengthening of material with atoms in solution can also be caused by other kinds of interaction between the dislocation and atoms. Both the kind of dislocation (linear, helical) as well as the type of stress field generated by a specific atom of addition in the lattice (stress field with a spherical or tetragonal character). Compared to other methods, strengthening material with single atoms of solute in a solution is considered weak and independent of the material's history of deformations.

2.2 Strengthening with second phase particles
The third method of strengthening polycrystalline materials through solute atoms located in precipitations may greatly enhance the plasticity of the material, even with little amounts of solute (< 10 %). Clusters of solute atoms pose a much greater resistance to the moving dislocations than single atoms of this substance. The degree, in which particles strengthen the material depend on many factors, e.g. the size of particles, their volume fraction, the shape of particles and the nature of phase boundary between the particle and its surroundings. The type of inter-phase depends on many factors as well, including the size of the particle and the way it has been formed inside warp. Small particles that were formed as a result of precipitation from a supersaturated solid solution are mostly coherent with the lattice. Such precipitations interact with the moving dislocations by means of coherent strengthening (fig. 2.3) (when precipitations are very small, order of a few nanometers) and through chemical strengthening (fig. 2.4), which regards coherent, or semi-coherent particles of larger sizes (order of several dozen to several hundred nanometers). Chemical strengthening is the name of an increase in the force required to cross the dislocation of a coherent ore semi-coherent particle. Larger particles formed e.g. during crystallization have incoherent interphase boundaries, hence dislocations cannot cross them. In the case of precipitations with incoherent interphase boundaries, the main mechanism of interaction with the moving dislocations are the so-called dispersion mechanisms, such as: Orowan mechanism, cross slip, or climbing dislocation mechanism. Figures 3 - 5 below present the basic mechanisms of interaction between dislocations and second phase particles.

Fig. 2.3. Diagram of precipitation coherent with lattice structure. In the presented case precipitation has smaller parameters than the structure, which causes deformation in the lattice and the resulting stress field, which then interacts with the moving dislocation [Ref: 21]

Fig. 2.4. Edge dislocation crossing coherent precipitation. During this process, a new interphase boundary is formed, with determined interphase energy, hence work must be done [Ref: 21]

Fig. 2.5. Methods of interaction between dislocation and precipitations with relatively large size and small coherence with lattice structure [Ref: 22]
2.4 Strain strengthening

Another highly effective method to strengthen materials is the cold plastic deformation, which leads to an increase in the density of dislocations responsible for the phenomenon referred to as strain strengthening, since dislocations themselves are obstacles in their movement. The stress field around the dislocation within the lattice may be large enough to inhibit the movement of other dislocations at intersecting slip surfaces. This results in an increase of force required to move the dislocation, which in that case has to overcome the stress field around another dislocation as well as the resistances within the lattice (see fig. 6.). Intersecting dislocations lead to the formation of dislocation jogs in one or both dislocations, increasing the length of the dislocation line. Furthermore, dislocation jogs formed by the intersection of dislocations are often less mobile than other parts of dislocation. This effect may lead to strain strengthening. Immobilization of part of dislocation line may lead to the multiplication of dislocations e.g. by means of Frank-Read mechanism - a phenomenon commonly observed during plastic flow. The density of dislocations in an annealed material remains at the level of $10^{10}$ m/m$^3$, whereas in a strongly deformed metal, the density of dislocations is $10^{15}$ - $10^{16}$ m/m$^3$. Strengthening through mutual blocking of dislocations is considered the most powerful obstacle in the movement of dislocations and plays a major role in strongly deformed materials.

![Fig. 2.6. The stress field around a dislocation may be large enough to create resistance during the intersection of dislocations moving along the intersecting slip surfaces [Ref: 21]](image)

3.0 Characteristic of copper alloy intended for electrical purposes - applications, standardization, performance properties

Copper conductive material should meet a set of electrical properties (high electrical conductivity), mechanical properties (tensile strength, yield strength, creep strength), thermal properties (high thermal conductivity, high melting point, high operating temperature range), technological properties (formability, solderability, weldability), chemical properties (low chemical activity, corrosion resistance) and economical properties (low cost). The typical applications of this group of materials include cables
Characterization of conductive copper alloys has been included in table 3.1. The criterion for material selection covers the values of electrical conductivity between 50 %IACS and 102 %IACS. Application possibilities for alloys have been presented as well as their plastic processing capacities, corrosion resistance, and physical, mechanical, electrical and thermal properties.

Table 3.1. Characterization of conductivity copper alloys. 

4.0 Impact of alloying additions on selected properties of copper alloys

Based on information provided in the previous subsection of this paper, it has been noted that copper-based conductive materials, whose electrical conductivity covers the range of 50 - 102 % IACS largely consist of high-purity copper (Cu-OFE, Cu-OFHC, Cu-ETP), copper containing admixtures of silver (CuAg; CuAg0,04OF; CuAg0,1OF; Cu-FRTP) and phosphorus (Cu-HCP, Cu-DLP, Cu-Ag-P) and alloys Cu-Cd, Cu-Te-P, Cu-S, Cu-Zr, CuZHC, Cu-Mg-P, Cu-Al2O3, Cu-Cr, Cu-Co-Be, Cu-Cr-Zr-Mg, Cu-Pb, Cu-Fe-P, Cu-Fe-P-Zn, Cu-Fe-P-Co-Sn, Cu-Fe-P-Mg, Cu-Zn, Cu-Al.-Si-Co, Cu-Ag-P-Si, Cu-Cr-Be. While discussing the effect of admixtures on some properties of copper alloys, it should be noted that whether the admixture present in the material is considered an impurity or a desirable alloy component largely depends on its origin and physical nature (positive, negative, mild) and its effect on the set of performance properties of copper. It is a generally known fact that alloy components include materials added to copper specifically in order to obtain certain - desirable properties. Impurities is also responsible for a kind of characteristic effects, but differs from true alloy admixtures by the random nature of its occurrence. Impurities in copper come from the ore, which is then refined and/or accumulates them during subsequent stages of processing.

In case of high-purity copper, such impurities as phosphorus, tin, tellurium, selenium and arsenic have a negative impact on crucial (from the economical point of view) properties such as electrical conductivity and recrystallization temperature. Whereas, when their content is controlled, these elements provide a number of benefits. For instance, phosphorus as a deoxidizer improves weldability, tin provides solution strengthening and improves corrosion resistance, tellurium has a positive effect on machinability, and arsenic (together with phosphorus, tin and antimony) inhibits corrosion of brass to alpha brass.

It must be noted that alloy components have the greatest impact on the following performance properties of copper:

- thermal and electrical conductivity,
- mechanical properties, including processing capacity,
- chemical properties, mainly in reference to corrosion resistance,
- magnetic properties,
- susceptibility to processing and processing capacity.

The rest of this subsection shall discuss the abovementioned groups of properties.

4.1 Electrical conductivity. Resistivity

Metals such as copper conduct electricity due to electron movement in the lattice. Conductivity is reduced (along with the improved resistivity) due to thermal vibrations.
within atoms in network nodes and as a result of present disturbances (lattice defects or solute atoms). Both these components scatter the movement of conduction electrons. In case of temperatures close to absolute zero, the effect of the thermal component on conductivity decreases, and the presence of impurities and structural defects becomes the dominant factor. This effect (e.g. solute substances, grain boundaries) is reduced with the increasing temperature, although technically it is still very significant. The phenomenon in question is set by the Matthiessen principle.

It should be noted that all alloy components present in copper intended for electrical purposes decrease its conductivity. They are therefore seen as impurities. Silver, which is present in some copper ores and may still be found in the material during refining processes, is tolerated or omitted, since it has a relatively small impact on conductivity in concentrations that are typical. The effect - small or more noticeable, of other impurities on the conductivity of copper has been illustrated in figures 4.1 - 4.3. Figures 4.1 and 4.2 point out the impurities that are easily oxidized or not in molten copper in types Cu-ETP and Cu-OFE.

Whereas figure 4.3 illustrates the principle stating that changes in resistivity are proportional to the concentration of the solute, when they are small. In general the rule states that electrical conductivity of copper is reduced most by alloy components, which create solid solutions with the material, while those that are in a separate phase, like bismuth and lead, have the weakest effect. The results of many impurities accumulate in single-phase alloys.

Fig. 4.1. Decrease in electrical conductivity of copper Cu-ETP in the function of impurity content [Ref: 24, 25, 26, 27]
4.2 Thermal properties

Solute atoms reduce thermal conductivity by disturbing the distribution and the interaction of phonons within the lattice. In general, the reduction of thermal conductivity of copper is a similar effect to electrical conductivity. Solutes also increase the metal's specific heat, and thus its enthalpy and free energy. When the content of solute increases, the propellant force of the system, aiming at minimizing free energy, may lead to the generation of a new phase, which has different thermal properties than copper.

4.3 Magnetic properties
While pure copper is diamagnetic, numerous copper alloys may exhibit paramagnetic or even ferromagnetic behavior by generating magnetic phases. Iron is the most common source of ferromagnetism in copper and its alloys. The susceptibility of copper becomes positive (e.g., paramagnetic) when Fe reaches just 0.1% by weight, even if copper had been annealed, and it decreases in order to preserve more iron in the solution. Other examples of magnetic phenomena include copper alloys with cobalt, which generate magnetic structures through spinodal decomposition; phases of Cu-Ni-Co that are generated in the reaction of precipitation strengthening; Haussler phases, such as MnCu$_2$Al (this is the name for the σ phases, which are ferromagnetic through the distribution of manganese atoms in the lattice) and Hume-Rothery electron compounds.

### 4.4 Mechanical properties

Strength, toughness and resistance largely result from the presence of alloy components. Impurities may have a major impact on mechanical properties and these effects may, although or may not be harmful. This is the main task while designing alloys - to skillfully balance the mentioned effects and obtain an optimal combination of the required material properties. Mechanisms (discussed in detail in the previous subsection of this paper), due to which solutes affect the mechanical properties of copper include:

- solution strengthening,
- creation of hard phases,
- precipitation strengthening,
- grain fragmentation,
- order-disorder transformations,
- dislocation transformations during martensitic conversion,
- dispersion strengthening.

Solution strengthening is definitely the most common strengthening mechanism in commonly applied copper alloys. It is the dominant source of strength in alpha brasses, high-alloyed copper alloys (with the exclusion of precipitation strengthening), tin bronze, Cu-Ni alloys and Cu-Ag alloys as well as alpha-aluminum bronze. Mechanical strength usually increases together with the increasing solute content, and toughness is reduced.

Hard phases are most of all responsible for high mechanical properties - i.e. high tensile strength of yellow brass, which is also called manganese bronze, as well as silicon bronze and brass. The main component of these alloys is the δ - regular body-centered phase, although other structures contribute as well. Strengthening through the formation of secondary phases is a very effective way of increasing the strength of material, but it may entail the risk of reduced corrosion resistance in case of some alloys.

Precipitation strengthening - already discussed earlier, it occurs in case of alloys with a high copper content, with such elements as chromium, zirconium and beryllium. Phases strengthened by precipitation, coming from supersaturated solid solutions are also used to improve the properties in copper alloys with nickel and aluminum bronze containing iron, nickel, chromium, or cobalt.

Tensile strength increases along with the decrease in grain size (Hall-Petch rule). This is particularly useful, since unlike most other strengthening mechanisms, increasing strength by reducing the size of grains does not affect the plasticity of the material. Castings with small grain sizes and small amounts of iron are known as refining grains, are often included in casting copper alloys. It is worth noting that nickel has a similar effect.

Order-disorder transformation and spinodal decomposition both occur in copper-based alloys and some of them are commonly used for improving properties. Spinodal
decomposition in Cu-Ni-Sn alloys, such as C71900, C96800 and C96900 is responsible for strength comparable to that, which is typical of Cu-Be alloys. Dislocation transformation during martensitic conversion occurs in some aluminum bronzes, which may be improved thermally, much like steel for heat treatment. Martensitic conversion is also responsible for the shape memory effect (SME), presented in alloys Cu-Zn-Al and Cu-Al-Ni.

Dispersion strengthening (DS), also discussed in the previous stage of the study, is based on incorporation of insoluble secondary phases in copper. Dispersion phases are not necessarily metallic, but they may be oxides, carbonates, or other compounds. DS materials are called alloys, but they are more precisely characterized as composites, since their secondary structure is insoluble in the warp. The most recognized commercial examples of DS copper-based alloys are aluminum bearing oxides - C15715 to C15760. These materials are mainly used for high-performance resistance welding (RWMA class III). In powder metallurgy, Cu-W alloys have been used for welding electrodes and other abrasion-resistant electrical products. Cu-Nb composites, which combine high thermal conductivity and good mechanical properties at high temperatures are used in liquid-cooled rocket engines. Composites based on Cu + (Zr or Ti) B2 offer similar combinations of mechanical and thermal properties.

4.5 Susceptibility to processing and processing capacity

Solute additions may modify the performance properties of copper and its alloys, even if they are present at the level typical of impurities. For instance, copper is usually deoxidized with the use of phosphorus, which has little detrimental effect at around 0.04%, but is also responsible for increasing strength, while reducing plasticity. Manganese, magnesium and boron are also used as deoxidizers, but these may be harmful if used improperly. For example, more than 0.5% of manganese causes harmful inclusions in the castings.

Annealing. Plastic treatment is the most common, most effective and - in terms of the usefulness of materials for specific applications - the most important way to improve the strength of copper alloys. Cables and pipes are products made with the draw method applied as a cold process; sheets and tapes are also cold rolled and shaped as products used on a wide scale. Such processes are classified as cold methods, since they are performed at temperatures below the point of recrystallization. Cold plastic processing makes the material stronger, harder and less ductile than before deformation. In case of copper, the degree of material deformation generally describes the state of the material. Since the material in its hard state does not exhibit satisfying properties for most applications (e.g. cables), the material is annealed partly or completely prior to its direct use.

Recovery and recrystallization reduce residual stress left after the treatment. The energy provided by annealing accelerates the processes. First of all, metal recovers, at which point more mobile dislocations are generated upon deformation change and destroy one another to some extent, thus forming a subgrain unit or structure. Internal stress is partly relaxed, and the deformed structures start aligning to the state of lower internal energy. Upon that, no change in the phase accompanies these reactions.

Recrystallization, nucleation of new grains, may occur together with the recovery, or commence as soon as the recovery has ended. The final size of grains largely depends on cold deformation and, to a lesser degree, from annealing temperature. The temperature of recrystallization, in turn, depends on the size of the cold deformation. It is particularly vulnerable to even small concentrations of solute that convert the activation energy and affect the kinetics of grain boundary migrations, which are the nucleation locations. The activation energy for recrystallized copper is 29.900 kcal/mol (Cu-OFE after cold rolling with the degree of deformation of 99.7%); 22,400 kcal/mol (spectrographically pure copper after cold rolling with a deformation of 98%) and 28,800 kcal/mol.
Recrystallization may lead to the development of preferred orientations in crystals, called textures. Rolled products have textures oriented in such a way so that the surfaces (110) and directions tend to align parallel to the direction of rolling. This is the so-called brass fracture. Whereas drawn products have double fiber structures with directions of both and in parallel to the axis of the wire. Compressed products have the surface (110), and the direction is created by twisting the deformation.

Impurities increase both the point of recrystallization and the temperature threshold, at which recrystallization stabilizes after a set period of time. The effects increase together with the number of impurities. Comparing with the material previously subjected to plastic cold processing, annealing at a given temperature takes longer in the presence of impurities. Therefore, their presence increases the cost of treatment.

On the other hand, recrystallization annealing of bearing copper alloys is suitable for soldered products, such as springs and electric car heaters. Phosphor is yet another admixture, which may increase the point of recrystallization in copper, provided it is present in sufficient quantities. Deoxidizer - phosphorus; copper with high phosphorus content, C12200 used for the manufacture of hydraulic pipes, which is normally subjected to soldering. Other admixtures, which may limit softening the deoxidized copper, include cadmium, iron, cobalt and zirconium.

Oxygen is present as Cu2O in copper grade Cu-ETP, it limits grain growth at high temperatures during annealing. Grain size in case of bearing alloys (containing oxygen) is therefore more homogeneous than in case of high-purity oxygen-free copper.

**Susceptibility to processing:**

Copper is very susceptible to hot and cold plastic processing, allowing over 99% deformation rate (annealing required). Susceptibility to processing is usually reduced by impurities and alloy components. The results are particularly strong when impurities segregate along grain boundaries, which may cause fragility, as well as when the alloy creates fragile phases, such as β in Cu-Zn alloys.

Impurities that dissolve in the solution - such as silver, gold, nickel and arsenic have no effect on susceptibility to processing. Since these admixtures do not create strong copper oxides, they are mild in the case of oxidized copper, deoxidized copper, and oxygen-free copper. Cadmium and antimony, which are also soluble in copper, but create stable oxides, are harmless as well, since their concentration is usually too low to cause adverse effects. Oxides of iron, tin, zinc, phosphorus, silicon and aluminum are not harmful, since they are rarely "taken" during crystallization. Selenium and tellurium create fragile sulfides and oxides, and the presence of these compounds in copper drastically reduces both hot and cold plastic processing capacity.

Zinc improves cold formability, which reaches its optimal level in the known alloy 70Cu-30Zn - brass used for bullets, C26000. The presence of the δ phase in alloys with a higher content of zinc makes cold plastic processing difficult, but facilitates hot treatments. Forged brass, C37700, is one of the examples of a material using this effect. This alloy’s susceptibility to hot processing (forging) is high enough to overcome the negative effect of small amounts of lead added to improve machinability.

Bismuth and lead are nearly insoluble in copper in solid state, and their melting points are within or below the hot working range for copper and its alloys. These impurities seriously impair susceptibility to hot plastic processing, causing brittleness. Cold plastic processing is limited as well, particularly due to the presence of bismuth, which easily precipitates in grain boundaries.

**Weldability:**

Oxygen bearing alloys of copper become fragile under the influence of hydrogen, or hydrocarbon gases at higher temperatures. Hydrogen diffuses in metal, where it combines with oxygen to form water. Vapor accumulates in naturally available hollows and bay build up pressure sufficient to deform or crack copper. This phenomenon causes cracking when oxygen bearing alloys are welded with oxy-acetylene flame. Other welding
conditions that favor the presence of hydrogen in metal are high humidity and using jet drives as cellulosic electrodes.

The degree of sensitivity to impurities depends on the composition of the alloy. Bismuth, sulfur and phosphorus are particularly harmful to Cu-Ni alloys. Lead content in this alloy should not exceed 0.01%. Bismuth, selenium, antimony and boron are harmful as well. Only a maximum of 0.01% of phosphorus is acceptable in aluminum bronze, which are welded, since phosphorus causes brittleness during hot treatment of this material. As little as 0.01% Mg has a negative effect on the ductility of aluminum bronze.

Castability:

Since they do not have to endure mechanical stress of work, casting copper alloys tolerate a higher level of admixtures than their forged equivalents. For instance, lead is very harmful to hot processing and high-lead forged brass rarely contains over 3.5 to 4% of this admixture. Casting lead brass usually contains as much as 6 to 8% Pb, and the content of lead may even reach 25% in some bearing bronze types and copper alloys with lead.

Lead improves the liquidity of casting alloys, due to which it becomes easier to reproduce fine detail. Lead also seals microscopic pores produced during the solidification of some alloys. On the other hand, even small amounts of lead are very harmful to the strength and ductility of high-strength casting yellow brass. Phosphorus also improves liquidity, but acceptable concentrations are much more limited, especially if there is aluminum in the material.

![Copper Properties Chart](image_url)

**COPPER**

- Improvement on strength: 
  - Al, Mn, Ni, P, Si, Sn, Zn, Zr

- Improvement on corrosion resistance: 
  - Al, As, Mn, Ni, Si, Zn

- Improvement on strength without decreasing of electrical conductivity: 
  - Bem Cr, Fe, Ni+Si+Cr, Ti

- Improvement on wear resistance: 
  - Al, Ag, Cd, Si, Sn

- Improvement on machinability: 
  - Pb, S, Zn

- Improvement on heat resistance: 
  - Cr, Mg, Zr

*Fig. 4.4. Influence of addition elements on the copper properties*

Machinability:

Lead, tellurium, sulfur and bismuth are added to copper alloys in order to break them down into smaller fragments, making alloys for automatics. Lead is spread across cut surfaces, and its content in alloys for automatics is limited to around 3.5%, since reduced plasticity of alloys with more lead has made such operations as thread rolling or knurling
particularly difficult. Similar limits apply to other admixtures used in case of alloys intended for automatics.

A summary of the previously discussed effect of alloy components on the performance properties of copper has been illustrated in figure 4.4.

Whereas table 4.1 provides a diagram of the interaction of alloy components on the properties of various copper alloy groups, including low-alloy ones.

Table 4.1. Schematic effects of alloying additions on properties of copper alloys

In low-alloy copper alloys, arsenic improves heat resistance, but greatly impairs electrical conductivity to 35 - 45% IACS. Adding silver improves heat resistance of low-alloy copper alloys, but does not degrade their electrical conductivity. Resistance to cold and heat in this group of alloys is increased by added cadmium, which only slightly decreases the electrical conductivity of the alloy to 80 - 95% IACS. Chromium and zirconium have a similar effect; they increase resistance to cold and heat of low-alloy copper alloys. Therefore, alloys containing chromium may be used at temperatures up to 350 °C. Added chromium and zirconium only slightly reduce electrical conductivity by 80 - 85% IACS and 85 - 90% IACS respectively. Both these elements generate intermetallic phases, which participate in perspiration strengthening of low-alloy copper alloys. Whereas added selenium, tellurium and sulfur increase the machinability of these alloys without reducing their strength and electrical conductivity, which is 90 - 98% IACS. Out of these three, a particularly preferred addition is sulfur.

In copper alloys with zinc, the increasing concentration of zinc within the range 0 - 30% increases strength properties (see table 4.1). Elongation is reduced upon the emergence of the β phase. In the case of alloys containing 30% zinc, adding arsenic inhibits dezincification, as well as improves the manufacturability of pipes used in heat exchangers. Adding aluminum favors the formation of the β phase and the creation of the double-phase α+β structure. Cu-Zn alloys with the 30-40% zinc, adding tin, manganese and nickel improve strength properties. Adding 10% Ni stabilizes the structure of the mixture α+β, since it essentially has a negative equivalent of zinc, and with the highest of the concentrations mentioned, alloys with this addition have a single-phase α structure. Added arsenic interacts analogously to alloys with less zinc. Introducing aluminum to these alloys improves mechanical properties and corrosion resistance. Adding iron increases mechanical properties, mainly due to significant fragmentation of grains, whereas lead only slightly increases strength. Whereas adding silicon increases the corrosion resistance of the alloy group in question.

Double-phase alloys Cu-Al, containing 7-11% aluminum, particularly at concentrations around 11% aluminum, differ perfectly from double-phase alloys Cu-Sn and Cu-Zn, mainly due to the possibility to shape their structure and properties through strengthening and tempering. Strength may thus be improved by 25%, while enhancing elongation by 70%. Double-phase Cu-Al alloys are used in as-cast or after hot plastic processing. Adding iron to double-phase Cu-Al alloys inhibits grain growth, although it does not prevent the eutectoidal decomposition of the β phase. Adding nickel, usually introduced together with iron, causes an increase in corrosion and oxidation resistance, strength, abrasion resistance and fatigue strength, thus preventing adverse eutectoidal decomposition of the β phase into a mixture of α+y2(δ), which causes a reduction in corrosion resistance and an increase in the alloy's brittleness.

Cu-Ni alloys with nickel concentration over 15% have a reddish color; however, if nickel concentration is lower than 15%, the alloy is white. These alloys have a better corrosion resistance than low-alloy copper alloys and the comparable constant properties.

Apart from high corrosion resistance, nickel concentration above 30% also provides high mechanical properties (see table 4.1). Low-alloy Cu-Sn alloys, at tin concentration lower than 5%, are intended for plastic forming, whereas if the concentration of this element fits between 5-10%, it mainly strengthens the alloy, despite making it harder to deform in cold processes. A concentration of tin greater than 8% makes it impossible to perform cold processing, due to the generation of fragile phases in the warp. Nevertheless, long-
term annealing at around 700°C affects the dissolution of these phases in a solid solution, which allows for pulling wires or rolling sheets and tapes.

Copper alloys containing more than 10% tin are used as-cast with special purpose; if they contain 12-18% Sn - to make wear-resistant elements burdened with large compressive forces, at 20-30% Sn - bells, and if they contain 30-40% Sn - mirrors, optical and decorative elements, due to their reflexivity and high hardness that favors resistance to scratching. Phosphorus is added to these alloys in order to improve resistance to oxidation, preventing the precipitation of SnO₂ during casting: first of all, however, it increases their elastic modulus and stabilizes their structure, which makes them an appropriate material for springs. Added lead, usually at 0.5-1.0% improves the machinability of Cu-Sn alloys. Although lead improves the spreading properties of these alloys, it also reduces their strength, elongation and impact toughness. Alloys containing above 10% lead may be used for plain bearings, whereas those with 20% lead may be used to manufacture self-lubricating bearings, or in case when a significant degree of surface self-smoothing is required. Adding above 1 % of nickel to these alloys favors homogenization of the distribution of lead particles in the matrix.

Adding less than 5% nickel in Cu-Sn alloys improves their strength, but reduces their castability (see table 4.1). Nickel at 5-10% provides alloy strengthening as a result of heat treatment, particularly if these alloys contain zinc. Alloys with the same chemical composition have been applied to manufacture guns and have performed better than Cu-Ni. Cu-Sn-Ni alloys are precipitation strengthened and are characterized by very good tightness and high tensile strength. These alloys show increased thermal stability, related to the presence of nickel. If nickel concentration exceeds 10%, these alloys are characterized by increased corrosion resistance; hardness and strength can be improved by adding 1-5% silicon. Such alloys are used for valve seats and other equipment working in corroding environment in water or vapor, as well as elements of plain bearings, such as e.g. rolls and sleeves.

Cu-Al alloys can have a single-phase structure, provided they contain up to 7% aluminum. Single-phase Cu-Al alloys are in many respects similar to Cu-Sn and Cu-Zn, although their properties differ from each other. Adding aluminum determines the increase in resistance to corrosion, particularly in marine environment. Adding arsenic introduced to alloys with aluminum concentration below 7% improves corrosion resistance and strength, although at 0.4%, arsenic increases the alloy's brittleness. Hot deformability and weldability of double-phase Cu-Al alloys are improved after adding manganese as a result of increasing the lowest temperature required for the occurrence of a single-phase structure, required for forming. Strength and ductile properties are then improved as a result of favorable changes in the structure obtained after cooling the temperature at the end of hot forming. Adding manganese also reduces eutectoidal temperature. Adding silicon to single-phase Cu-Al alloys improves strength, machinability, hot formability and corrosion resistance (see table 4.1). Lead is also added in order to improve machinability.

Alloys containing 40-45% nickel are used as resistor alloys in light of their low electrical conductivity and very low temperature coefficient of resistance. Adding iron to alloys with around 30% nickel improves corrosion resistance, particularly in seawater. Cu-Ni alloys containing 60% Cu and 20% Mn are heat treated, have properties similar to Cu-Be and are used to make springs. Ni-Cu alloys containing over 50% nickel are characterized by very good mechanical properties combined with a very good resistance to corrosion and oxidation.

While summing up the effect of alloy components on some properties of copper alloys, one must remember that electrical conductivity decreases significantly at even the slightest concentration of admixtures, mainly phosphorus, iron, cobalt, arsenic, which dissolve in copper and - due to the major difference in atomic diameters - which cause substantial lattice deformation in copper as a result of contraction or expansion. Cadmium, silver and zinc, whose atoms differ slightly in size from copper atoms, have a small effect on reducing electrical conductivity. Bismuth and lead - which do not dissolve in copper - act likewise. However, these elements, which create low-melting eutectics,
have a particularly negative impact on mechanical and technological properties and favor hot brittleness, which prevents copper forming. Such processing is also impaired by sulfur, which forms a low-melting eutectic with the sulphide Cu₂S and oxygen, which forms a eutectic with Cu₂O, reducing the ductility of copper.

As a result of the reduction of the resulting copper oxide with hydrogen, water is formed, whose vapor causes cracks and tears at high temperatures, thus preventing further forming, which is referred to as hydrogen embrittlement, and occurs after annealing copper in an atmosphere containing hydrogen. Cold working is made particularly difficult by arsenic.

4.5.1 Hydrogen embrittlement

When tough pitch copper is heated in reducing atmospheres containing hydrogen, the gas can dissolve in the metal, where it combines with the grain boundary oxides in form water vapor. Molecular water is unable to diffuse into the metal. Instead, it form microscopic voids in which extremely high pressures develop. The voids eventually lead to a brittle fracture phenomenon known as hydrogen embrittlement. Hydrogen embrittlement of copper used for electric purposes prevents the conduction of current by the copper wire [Ref: 586, 587]. Examples of the effects of annealing Cu-ETP wire in hydrogen atmosphere are presented in figure 4.5 [Ref: 567]. It was noted that the material is completely brittle.

Fig. 4.5 Cross-section of Cu-ETP wires after the annealing process in a hydrogen atmosphere [Ref: 567]
The mechanism behind the hydrogen embrittlement of copper is the penetration of a hydrogen atom which forms as a result of molecular hydrogen dissociation at high temperature and a reduction of copper oxide. Water vapours are released as a result of the redox reaction, thus increasing its capacity at high temperatures and leading to the cracking of copper on the grains limits.

Atomic hydrogen is more active than molecular hydrogen. Moreover, the intensity of hydrogen penetration of copper rises with the increase in temperature and duration of the annealing process. Figure 4.6 shows the experimental dependence of annealing time of a grade Cu-ETP copper sample in relation to the depth of hydrogen penetration to its interior.

![Graph showing correlation between annealing time and hydrogen penetration depth](image)

Fig. 4.6. The impact of annealing a Cu-ETP grade copper sample at a temperature of 600°C on the depth of hydrogen penetration [Ref: 28]

The relationship shown in figure 4.6 indicates that several minutes of annealing copper at a temperature of 600°C causes the depth of hydrogen penetration to be up to 0.05 mm. This shows the importance of hydrogen embrittlement in relation to copper wires of diameters ranging from 1-0.1mm.

Figure 4.7 shows a scanned image of Cu-ETP copper, where concentrations of Cu₂0 are found on the grain surface. Figure 4.8 shows a scanned image of Cu-ETP copper after the annealing process in a hydrogen atmosphere. An analysis of this pictures shows that after annealing in a hydrogen atmosphere, the structure of Cu-ETP grade copper is free from copper oxides and is characterised by the occurrence of numerous cracks at the grain limits.
Fig. 4.7. Fracture of Cu-ETP ingot. Magnification: x 100 [Ref: 567]
Fig. 4.8. Image of the surface of Cu-ETP grade copper grain limits after hydrogen disease taken from a scanning microscope. Magnification: x 1000 [Ref: 567]

It can be observe that the danger of the occurrence of hydrogen disease in copper can be delayed by the application of oxygen-free copper. The diagram shown in figure 4.9 indicates that approximately 8 ppm of oxygen dissolves at a temperature of 850°C, while the data shown in [Ref: 588], indicates only 2 ppm at a temperature of 700°C.
According to the world standardisation, oxygen-free copper is copper with oxygen contents lower than 10 ppm [Ref: 587]. Regarding copper for electrical purposes, the oxygen content is much lower and is typically accepted to be on a level lower than 5ppm [Ref: 589].

Another positive effect of the lack of CuO and Cu$_2$O oxides in copper is the possibility of drawing wire to diameters less than 0.1 mm [Ref: 327].

References:


8. **Understanding copper alloys** - Mendenhall J. H., Olin Brass, East Alton, IL, 1977, p 87

9. **Kupfer** - Deutsches Kupfer - Institut E.V., Berlin, Germany, 1982


15. **Copper rod alloys for machined products** - Copper Development Association Inc., 1993


17. **Magnetic properties of copper and copper alloys** - B u t t s A., Copper, Reinhold Publishing Co., 1954


22. **Phase transformations in metals and alloys** - Porter D. A., Easterling K. E., Sh er if M. Y., CRC Press, 2009


27. **Effect of certain fifth - period elements on some properties of high - purity copper** - Smart J. S., Smith A. A., Trans. AIME, Vol 152,1943, p 103


1995

567. AGH-UST - own research - contact person: tknych@agh.edu.pl

582. The physical chemistry of copper, Chapter 20, Copper - Wakeman D. W., Butts A., Reinhold Publishing 1954


586. Cables in fire - Kornowska K., Szota B, Brochure V of the International Conference and Intelligent Building Exhibition

587. PN-EN 1977:1998 Product for drawing from copper (wire rod) -


589. ASTM B49-08a Standard specification for copper rod drawing stock for electrical purposes -