# Annex I to the CLH report

## Proposal for Harmonised Classification and Labelling

**Based on Regulation (EC) No 1272/2008 (CLP Regulation), Annex VI, Part 2**

## International Chemical Identification:

**EC Number: 231-159-6**

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## ”Section 2, Information on copper in massive and powder forms"of ECI (2021) European Copper Institute Report “The Environmental Hazard Classification of Copper”, Version 2.2.

The document ECI (2021) European Copper Institute Report “The Environmental Hazard Classification of Copper”, Version 2.2, is also attached to the Copper Chemical Safety Report (CSR). Other sections (than section 2) of this document is not included in this Annex

European Copper Institute
Copper Alliance

# The environmental hazard classification of copper

Attachment to the copper Chemical Safety Report (CSR)

Version tracker:

| | | |
|---|---|---|
| Version 1.0 | January 2017 | |
| Version 1.1 | January 2018 | Adjustment of chronic ERVs; Addition of TD data on copper massive at pH 7 and 8 |
| Version 1.2 | February 2019 | Addition of new studies on Rapid Removal; Consideration of recent RAC opinion |
| Version 2.1 | June 2020 | New TD data on copper powder, added argumentation to support the differentiation between powder and massive forms, and further information to support the ERV derivation. Revision of copper powder classification. |
| Version 2.2 | February 2021 | New information added to support differentiation between powder and massive forms: description of malleability, ductility and brittleness of copper; description of copper chips. |

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## 2. INFORMATION ON COPPER IN MASSIVE AND POWDER FORMS

The copper REACH dossier considers two forms of copper: copper massive and copper powder, defined based on their composition and specific surface area. Copper massive is defined as copper with specific surface area below 0.67 $mm^2/mg$. This cut-off value is equivalent to 1-mm spherical copper particles. Copper powder is defined as copper with specific surface area above 0.67 $mm^2/mg$.

The form of a metal can be considered when deriving the environmental hazard classification under the CLP Regulation. This recognition is based on previous discussions which originate from a 1995 debate on zinc. The concept of different classification entries for different forms of the same substance was then accepted, based on the recognition that the metal released per surface in transformation-dissolution test is specific for each metal and therefore an intrinsic property that could be used for classification. The policy debate at EU and at UN level indicated that separate classification entries for metals substances were justified. A default value of 1 mm was assumed to distinguish between two forms (powders and massive). The 1 mm was defined as the lower limit for massive, and was adopted by the UN (Annex 9, section A9.7.5.4.3 of the GHS Rev.6).

Based on this debate, the CLP Guidance (version 5.0, Annex IV, section IV.5.5) describes how particle size can be considered for the purposes of deriving the environmental hazard classification of metals:

> "Normally, the classification data generated would have used the smallest particle size marketed to determine the extent of transformation. There may be cases where data generated for a particular metal powder are not considered as suitable for classification of the massive forms. For example, where it can be shown that the tested powder is structurally a different material (e.g. different crystallographic structure) and/or it has been produced by a special process and is not generally generated from the massive metal, classification of the massive can be based on testing of a more representative particle size or surface area, if such data are available. (…) Massives will usually be tested as 1 mm particles. (…)[This] default value may be altered if sufficient justification."

In line with these agreements, the Copper Voluntary Risk Assessment (Appendix K1) indeed already considered a different classification for copper in powder and massive form. To further support this differentiation, this section provides further information on copper in massive and powder forms.

## 2.1. Production of copper massive

The massive form of copper is traded worldwide under the name "copper cathode". Copper cathodesare square sheets of the metal of typically 1000 x 1000 mm with thickness between 3 and 16 mm (Figure 2). Copper cathodes are listed and traded publicly on the London Metals Exchange (LME). An overview of copper cathode properties from the key EU producers, including the calculated specific surface area, is listed in Table 1. The specific surface area of copper cathodes is more than an order ofmagnitude below the cut-off value between copper powder and copper massive. The global market of copper is about 23 million tonnes annually, and the EU market approximately 4 million tonnes.

The production process of copper has been described in detail in the copper REACH dossier, the Copper Voluntary Risk Assessment, section 2.1.1 (European Copper Institute, 2008), and in the NFM- BREF (Best Available Techniques Reference Document for the Non-Ferrous Metals Industries) developed in the context of the Industrial Emissions Directive (European Commission, 2017). Additionally, more information on the production process of copper can be found in Schlesinger et al.(2011) and from the International Copper Study Group (ICSG, 2019).

Copper may be produced from either copper ore concentrate or from recycled copper-containing scrap. The pyrometallurgical route is by far the most common production process (Figure 3), and is described in the REACH Copper Chemical Safety Report. The copper ore concentrate is smelted in a furnace to produce copper matte. In that process, iron and sulphur contained in copper concentratesare partially oxidised and removed. The matte is treated in a converter to eliminate the rest of the iron and sulphur by oxidation, i.e. by blowing oxygen enriched air into the melt, producing blister copper. The blister copper is refined in an anode furnace to produce copper anode. The final step in the production of copper cathode involves the transformation of copper anode (EC 918-168-7) into the copper cathode in the tankhouse, through a process called "electrorefining" (Figure 4). In the presence of an electrical current, the copper anode is dissolved into a sulphuric acid solution, and the highly pure copper is deposited as "copper cathode". The electrorefining process has been visualized in a video available at https://www.youtube.com/watch?v=Kc7mhsUlJok. The information from these various resources is only briefly summarized below. A less common process is the hydrometallurgicalroute. In this case, the final step is called "electrowinning" and the copper is deposited directly from solution as the copper cathode.

Figure 2: Copper cathodes, the main form in which copper is produced and traded worldwide.

Table 1: Properties of copper cathodes from selected EU copper producers.

| **Company** | **Brand** | **Length x width** *mm* | **Thickness** *Mm* | **Weight** *kg* | **Calculated specific surface area** *$mm^2/mg$* |
|---|---|---|---|---|---|
| Atlantic Copper | FMS | 985 x 930 | 5—7 | 45—50 | 0.032—0.045 |
| Aurubis | NA-ESN | 975 x 965 | 5—10 | 50—70 | 0.023—0.045 |
| | HK | 1060 x 906 | 5—10 | 50—70 | 0.023—0.045 |
| | OLEN | 1005 x 995 | 5—10 | 50—70 | 0.023—0.045 |
| | PIRDOP | 1020 x 1000 | 5—10 | 50—80 | 0.023—0.045 |
| Boliden | BK | 1000 x 1000 | 7 | 50 | 0.032 |
| | BCH | 1000 x 1000 | 12 | 80—130 | 0.019 |
| KGHM | HMG-S | 910 x 910 | 14 | 80—145 | 0.016 |
| | HMG-B | 1030 x 1030 | 16 | 80—130 | 0.014 |
| | HML | 910 x 780 | 15 | 90—110 | 0.015 |
| Metallo | | 1004 x 1000 | 3.3—6.8 | 30—55 | 0.033—0.068 |

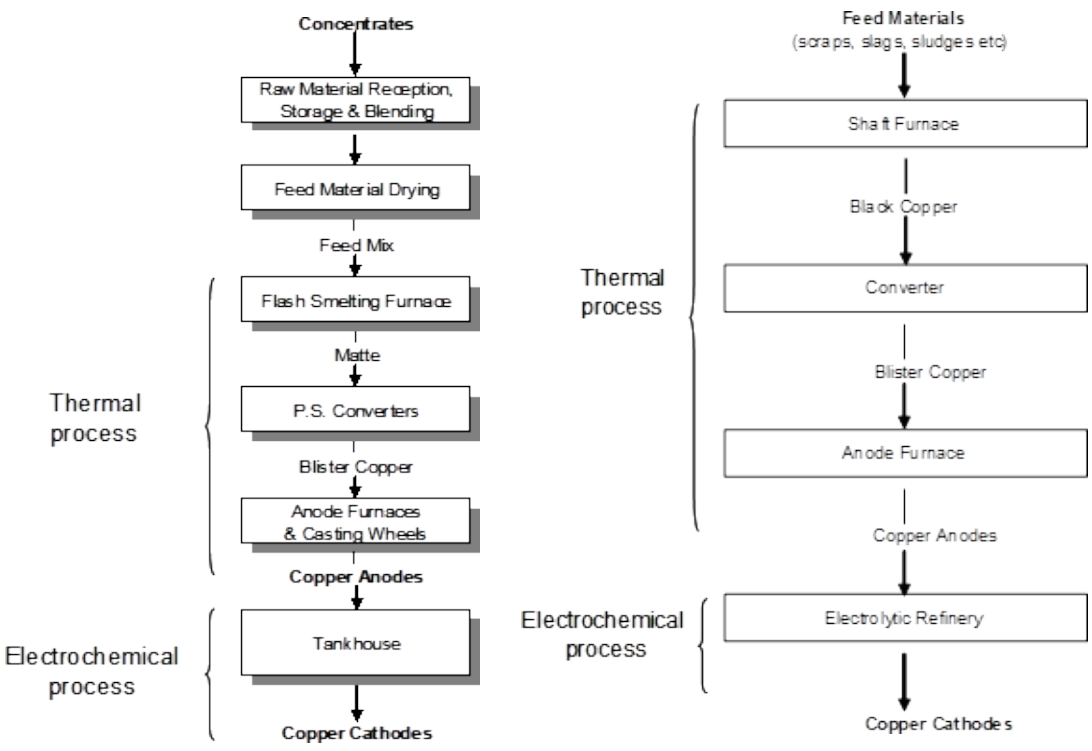


Figure 3: The production of copper cathode, from ore concentrates or from recycled scrap, via thepyrometallurgical route (from: Copper Voluntary Risk Assessment, section 2.1.1).

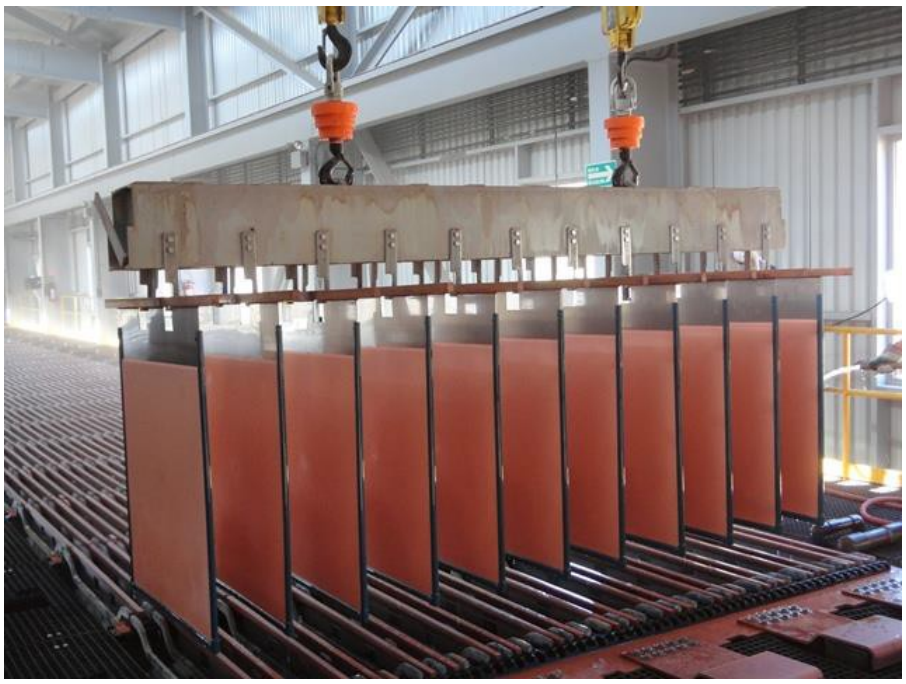

Figure 4: Production of copper cathode through electrorefining in the tankhouse.

## 2.2. Production of copper powder through a special process

Copper powders are produced by special, dedicated methods. These methods are tailored specifically to the intentional production of copper powder. Approximately 25 000 tonnes of copper powder are produced annually in Europe, and atomization is by far the most common production technique for commercial copper powder (Figure 5). First, copper is melted in a furnace. The melt is transferred to a holding furnace; the molten metal is poured in a thin stream and atomized by an air, inert gas (nitrogen or argon), or water jet. The atomized droplets are solidifying while falling down in a container where they are stored temporarily before going into further processing such as drying or sieving. Air or gas atomization produces spherical powder particles, whereas water atomization produces powder particles with an irregular shape. The atomisation process generates a powder with particles mainly between 10 and up to 1000 µm. This powder must subsequently be sieved to yield various subfractions with defined particle size distributions. The median diameters ($D_{50}$) of typical product types (e.g. "< 45 µm" or "25 - 75 µm" or "100 - 200 µm") vary between 20 µm and 400 µm.

Production of copper powder through other techniques, such as chemical precipitation, oxide reduction, or electrochemical deposition are less common in Europe.

More information on copper powder production techniques is available from Pelletiers and Daye (2015).

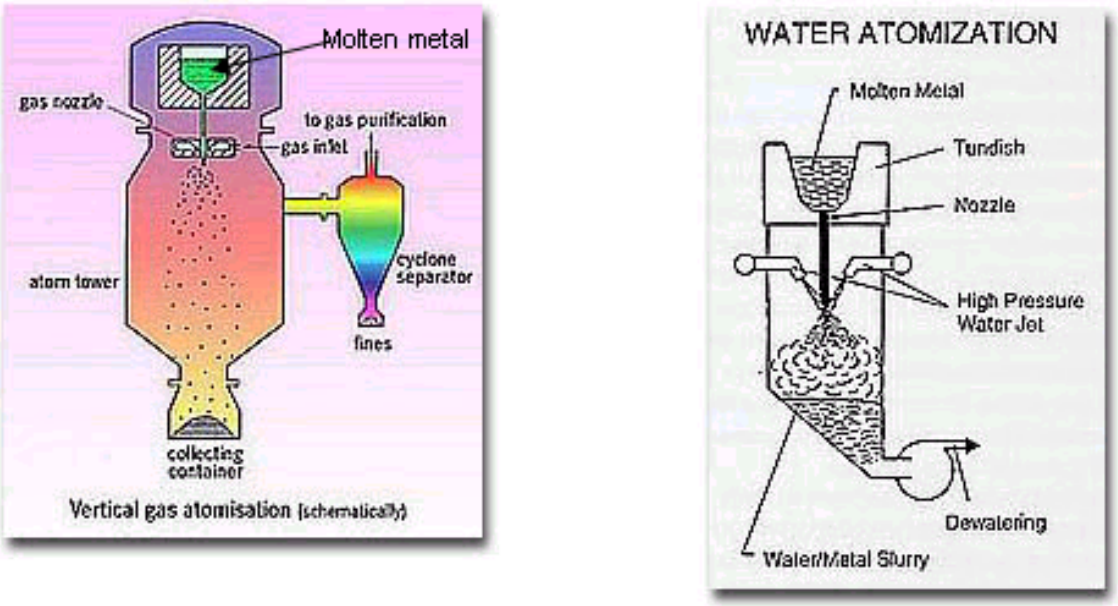


Figure 5: Schematic view of the production of copper powder: gas atomisation (left) and water atomisation (right). From the Copper Voluntary Risk Assessment, section 2.1.6 (European Copper Institute, 2008).

## 2.3. Copper powder is not generated during production and use of coppermassive

Copper is a malleable and ductile metal. These properties allow copper to be formed and stretched into various complex and intricate shapes and surfaces without breaking. This can be seen in many copper and copper alloy articles encountered in everyday life, for example in instruments, faucets, valves, bells, and statues. In addition, copper is resistant to fracture, and it is a relatively soft metal, meaning that it can be easily scratched by other materials. Below, the meaning of these properties is illustrated and quantitative data are provided. Together, these properties can support that there is no potential for the generation of powder from massive copper.

Ductility is the ability of a material to undergo significant plastic deformation before rupture or breaking (Callister & Rethwisch, 2014, sections 1.4 and 8.4). A ductile material like copper can therefore easily be stretched into a wire without breaking. Malleability, a similar property, is a material's ability to deform under compressive stress. A malleable material like copper can therefore be hammered or rolled into a thin sheet. Malleable and ductile metals have been described as follows(Anderson, 1869):

> *"It will be convenient to think of the malleable or ductile metals, such as lead, tin, copper, wrought iron, and steel, (are) substances that can be moved about like dough, that can be spread out as with a roller, that can be elongated by drawing out with the hands, that can be squirted through a hole by pressure like macaroni, or even that the dough can be pushed or gathered back again into its original mass of dough."*

The opposite of ductility is brittleness. A material is brittle if, when subjected to stress, it breaks into smaller pieces with little plastic deformation. Very brittle metals can break into pieces during normal handling and use, e.g. when falling to the ground or when moved inside a container.

Elongation, or elongation to failure, is a common measure of the ductility of a material (Callister & Rethwisch, 2014). It is the amount of strain a material can experience before it beaks (fails) – or, in other words, it is the extent to which it can be stretched before it breaks. Empirical observation shows that most metals have high elongation and therefore are ductile materials (Figure 6 and Figure 7). The ductile behaviour of most metals is opposite to that of brittle materials, e.g. glass and most other ceramic materials, which do not bend but rather break into pieces when subject to mechanical stress. With an elongation at fracture of approximately 0.5 (equal to 50%), copper is among the more ductile materials and metals, as opposed to e.g. cast iron which is relatively brittle (University of Cambridge, 2002; Callister & Rethwisch, 2014). Brittle materials are approximately considered to be those having an elongation of less than about 0.05, equal to 5% (Callister & Rethwisch, 2014).

The ductility of most metals can be explained on the basis of their specific atomic structure, i.e. the metallic bond between atoms which is unique to metals (Callister & Rethwisch, 2014, section 2.6 and section 9). Metals consist of atomic nuclei surrounded by a large "cloud" of nonlocalized electrons, meaning that these electrons are not bound to particular atoms. The negatively charged electrons exert an electrostatic attraction to the positively charged metal ions, thereby holding the entire atomic structure together. The shape of metallic objects can be changed without breaking: the cloud of electrons allows the metal atoms to move or "slip" past one another without breaking the metallic bond. There are however a few notable exceptions to the rule that most metals are ductile, the most notable one being beryllium: pure beryllium metal is brittle, likely due to its low atomic number (Christensen, 2012 and 2014).

The ductility of materials can be further illustrated through the concept of "resistance to fracture" or "fracture toughness". It refers to the ability of a material to absorb energy and plastically deform before fracturing or breaking. The fracture toughness of a wide variety of materials is shown in Figure 8 and Figure 9 (Callister & Rethwisch, 2014; Ashby, 2011).

Hardness is another property that illustrates the likelihood of a material to break into smaller particles and generate powder. Hardness is defined as a material's resistance to local plastic deformation (Callister & Rethwisch, 2014). A soft material can be scratched by a harder one, i.e. the softer material absorbs energy and is compressed locally. Because hard materials strongly resist such local deformation, they have less ability to absorb energy and they are more likely to break up into smaller pieces when subject to local mechanical stress. The simplest and most straightforward way to measure hardness is the Mohs scale. The Mohs hardness of some pure metals is presented in Table 2. It can be inferred that copper is a relatively soft metal. It should be noted that hardness can be defined in a number of ways, and other scales are in use for measuring the hardness of metals and other materials (Callister & Rethwisch, 2014).

The characterization of mechanical properties of metals is complex. When considered in in isolation, none of the above measurements may be sufficient to fully characterize the potential for generating powder from a massive metal. However, when considered together, the ductility, elongation, malleability, resistance to fracture, and softness of copper illustrate a consistent picture: there is no potential for forming powder from massive copper. These properties all confirm that copper metal does not break apart into smaller pieces under mechanical stress. Rather, when exerting mechanical forces on copper, the material is bent and deformed to yield a different shape. As a consequence of these properties, copper does not break apart during mechanical processes, handling, storage, transport, processing and use. Copper powder is not produced or generated as a by-product during the production of copper massive, or during the processing of copper massive into articles. This is corroborated by the observation that none of the copper cathode producers in Europe produce or market any copper powder. Instead, copper powder is produced by different companies, at different sites, and through a special, dedicated process (see section 2.2).

To further provide context, the main uses of copper in massive form to produce copper articles are briefly described. In an industrial setting, the use of copper in massive form employs several processes, as described in the copper REACH dossier. These processes transform copper into shapes, and further into articles such as wire rod, wire, strip, sheet, rod, and tube. An overview of the relative importance of these products in EU is provided in Figure

10. The dominant industrial processes to produce copperarticles are described in Table 3. The size of the copper chips from cutting, sawing, and milling processes in two different factories is illustrated in Figure 11 and Figure 12. Clearly, the dimensions ofthese chips are well above the 1-mm default cut-off between powder and massive forms referenced in the CLP guidance. Overall, this analysis shows that in this wide variety of physical, thermal, and chemical processes, no copper powder is generated when producing copper articles from copper massive. Finally, it must be noted that all the scrap produced by these manufacturing processes is fully collected and immediately recycled to produce new copper cathodes, shapes, or articles.

In conclusion, copper powder is not produced or generated as a by-product during the production of copper massive, or during the processing of copper massive into articles. This is a logical consequence of the inherent properties of copper, i.e. its malleability and ductility. Copper powder is exclusively produced through a special, dedicated process.

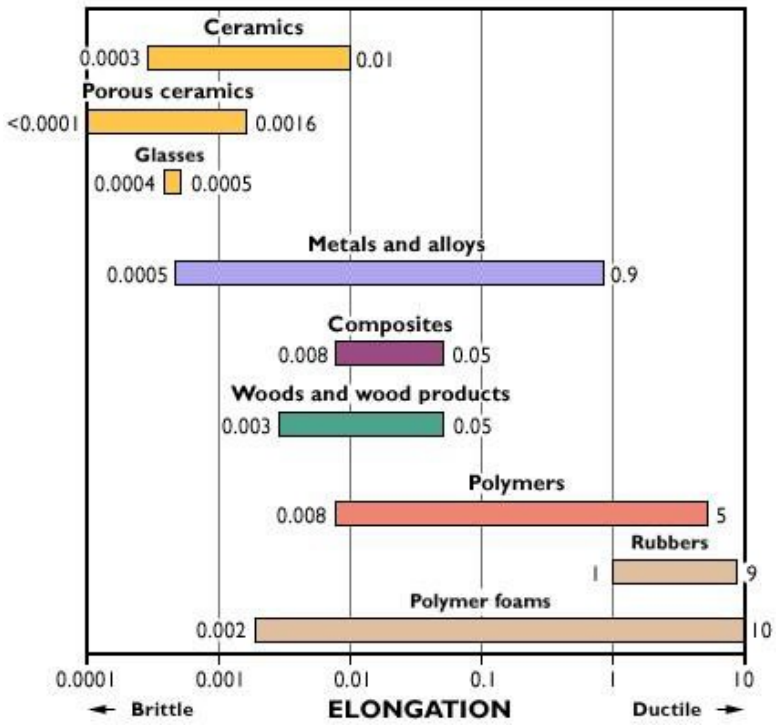


Figure 6: The elongation of materials, a measure of their ductility. It corresponds to the degree ofplastic deformation that has been sustained when a material fractures (University of Cambridge, 2002).

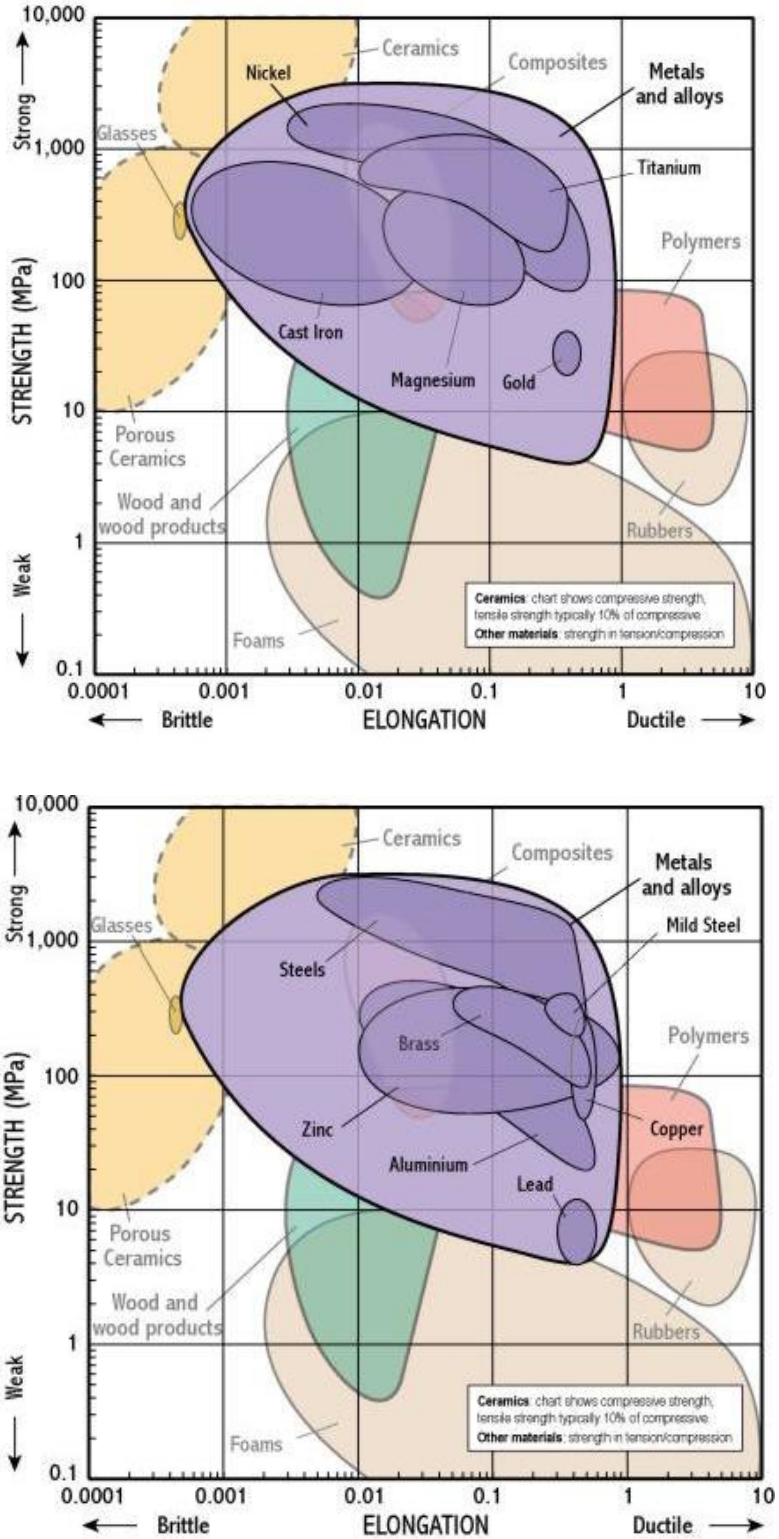


Figure 7: The elongation of materials, a measure of their ductility (University of Cambridge, 2002). Copper has an elongation of approximately 0.5, and therefore has high ductility compared to most other metals and materials. The elongation is plotted here against the strength of the materials, which is the maximum stress a material can sustain before breaking. Two separate plots were drawnto allow a clear visualization of the position of a wide variety of metals.

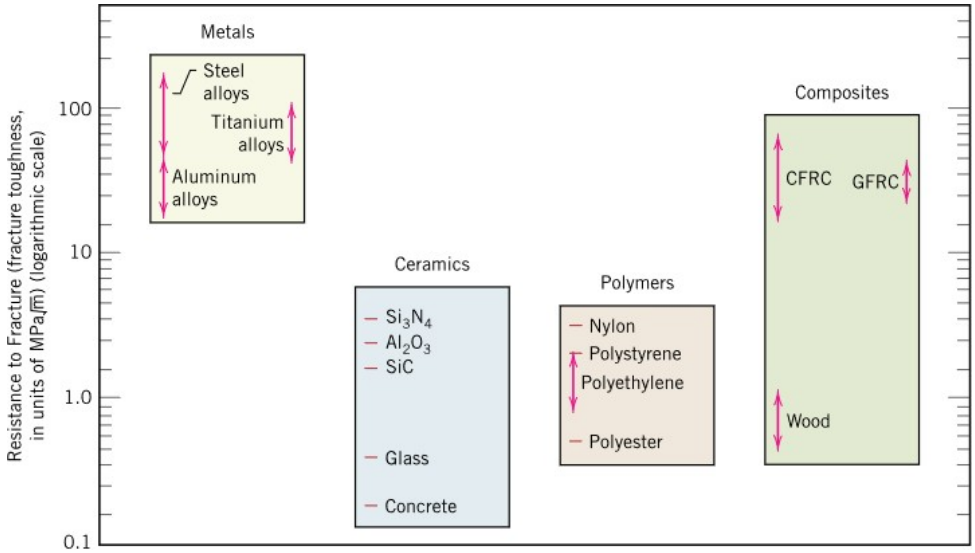


Figure 8: Room-temperature resistance to fracture for various materials (Callister & Rethwisch, 2014). The fracture toughness of copper and copper alloys is between 30—90 MPa·m$^{1/2}$ (Ashby,2011), which is within the range for metals shown in this chart.

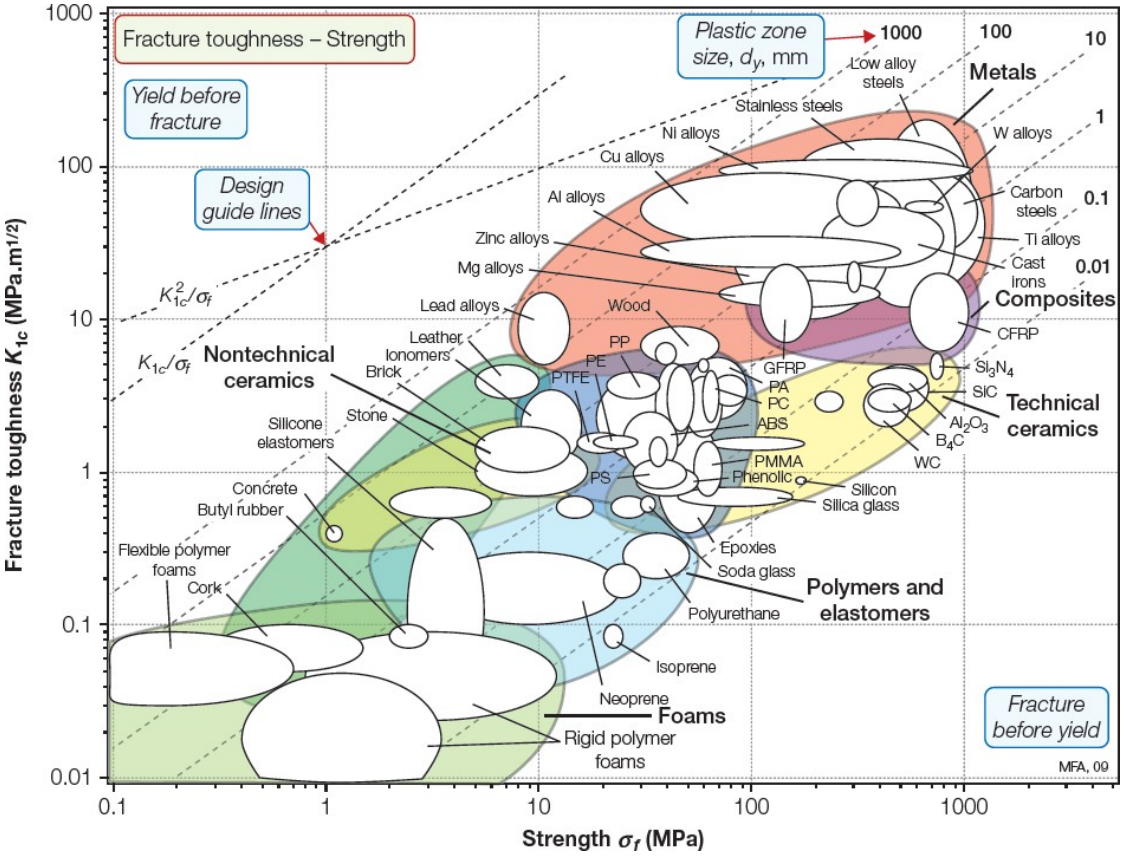


Figure 9: The fracture toughness (or resistance to fracture) for various engineering materials, plottedagainst the strength. The fracture toughness of materials, an indication of their ductility, can be red on the vertical axis. The strength is the maximum stress a material can sustain before breaking. FromAshby (2011).

Table 2: Mohs hardness of some pure metals and other materials (Samsonov, 1968). Low numberscorrespond to soft materials, high numbers indicate hard materials.

| | **Mohs hardness** |
|---|---|
| Sodium | 0.5 |
| Lead | 1.5 |
| Tin | 1.5 |
| Zinc | 2.5 |
| Aluminium | 2.75 |
| Copper | 3 |
| Nickel | 4 |
| Iron | 4 |
| Steel | 4—4.5 |
| Cobalt | 5 |
| Beryllium | 5.5 |
| Titanium | 6 |
| Manganese | 6 |
| Silicon | 6.5 |
| Tungsten | 7.5 |
| Chromium | 8.5 |
| Diamond | 10 |

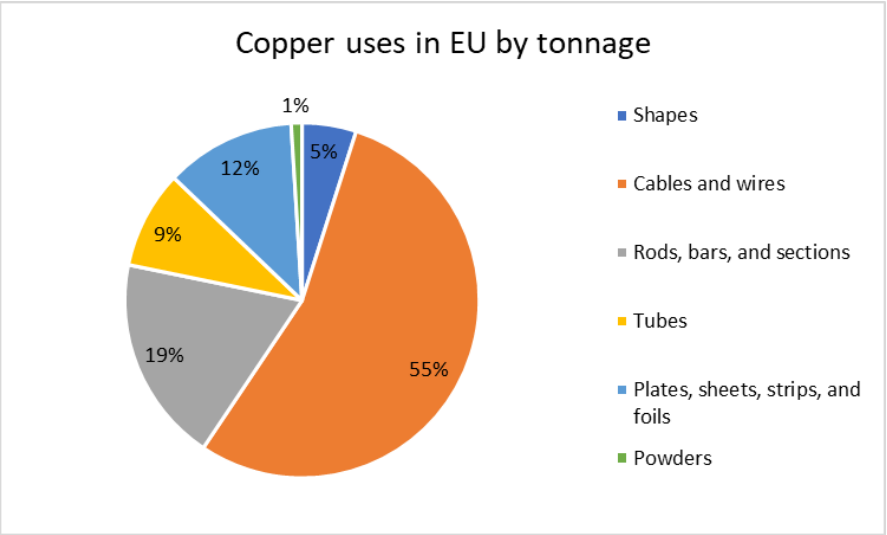


Figure 10: Overview of copper uses in the EU. Data for 2018 from the International Wrought CopperCouncil.

Table 3: Overview of dominant industrial processes for the production of copper articles from copper massive, and an assessment whether copper powdercan be generated or produced during these processes.

| Process | Description | Use in manufacture of copper articles | Potential for generating copper powder |
|---|---|---|---|
| Melting and casting | Solid metal is heated in a furnace to produce molten metal. Molten metal is poured into a mould, which contains a cavity of the desired shape, and is then allowed to solidify. This produces shapes, e.g. billets or slabs, which are then processed further. | All | None. In all metal smelting and melting operations, minor amounts of metal evaporate as fumes. These oxidise and form dust with a complex composition, which is collected and recycled. |
| Cutting and sawing | Cutting and sawing of castings is performed to obtain the appropriate size for the subsequent process | All | None. Some large chips may be generated. Typical copper chips are well above 1 mm. They are collected and recycled as scrap. |
| Extrusion | Heated metal is pushed through a die of the desired cross-section. Extrusion is often done in water. It can create metal products with a fixed, complex cross-sectional profile. | Tube, rod, wire | None. The material is heated and subject to physical forces. As copper is malleable and ductile, no powder is generated. |
| Rolling | Cold or heated metal is passed through one or more pairs of rolls to reduce the thickness and to make the thickness uniform. | Sheet, strip, foil, wire rod | None. The material is heated and subject to physical forces. As copper is malleable and ductile, no powder is generated. During hot rolling, some copper oxide scale particles may form on the surface due to oxidation, which are collected and recycled. |
| Milling | A mechanical process to remove impurities on the surface. During the milling, the surface layer is scraped off. | Sheet, strip | None. Some large chips may be generated. Typical copper chips are well above 1 mm. They are collected and recycled as scrap. |
| Drawing | A metalworking process which uses tensile forces to stretch metal. As metal is drawn (pulled), it stretches thinner, into a desired shape and thickness. For wire, bar, and tube drawing, the starting stock is drawn through a die to reduce its diameter and increase its length. | Wire, cable, rod, tube, profiles | None. The material is heated and subject to physical forces. As copper is malleable and ductile, no powder is generated. |

| Process | Description | Use in manufacture of copper articles | Potential for generating copper powder |
|---|---|---|---|
| Annealing | A treatment which involves heating a material above its recrystallization temperature, maintaining a suitable temperature for an appropriate amount of time, and then cooling. The aim is to make a material more workable. | Tube, rod, sheet | None. Annealing is in most cases done under a protective gas. If done under oxidizing conditions, some copper oxide scale particles may form on the surface due to oxidation, which are collected and recycled. |
| Pickling (or etching) | A surface treatment consisting of immersing a material in a bath with sulphuric acid, followed by rinsing in water. | Rod, wire | None. The process is a chemical reaction which is performed in aqueous solution. |
| Finishing | E.g. straightening, cutting, bevelling or chamfering of ends and edges | All | None. |

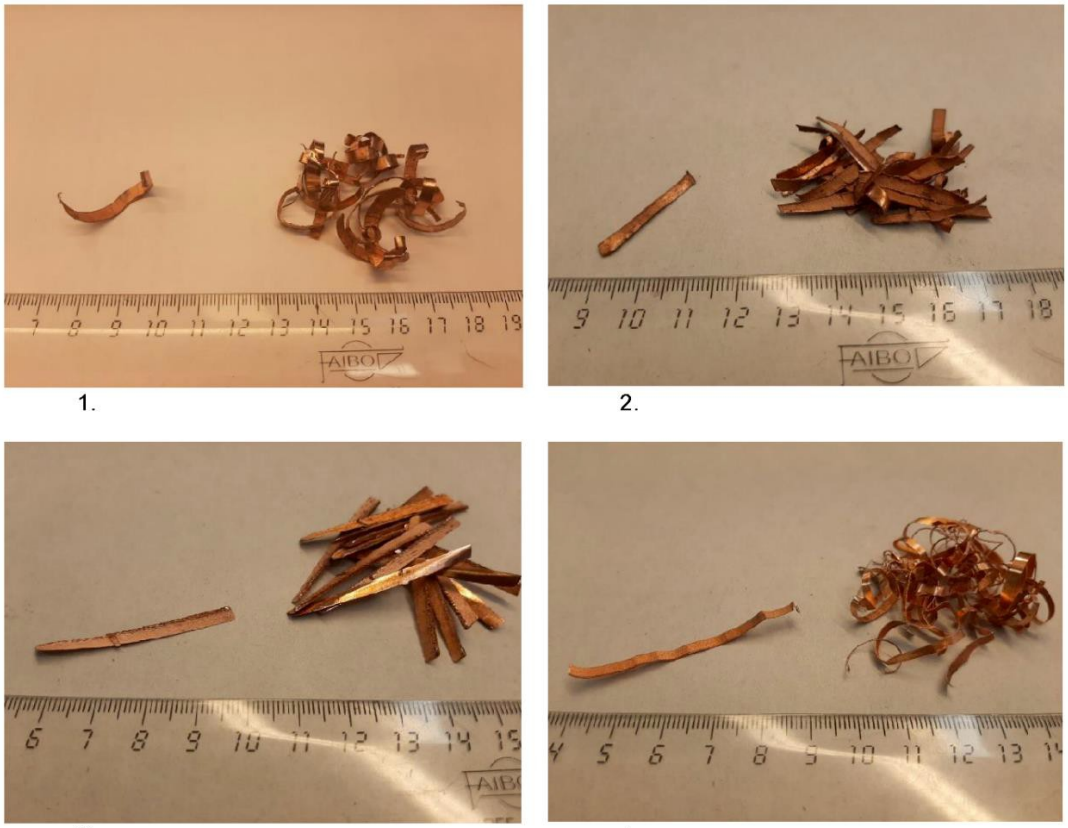


Figure 11: Four types of chips originating from the cutting, sawing and milling of copper in factory A.

1) Chips from the sawing of copper castings. 2) Chips from the one-sided milling of copper, for the production of copper sheet. 3) Chips from the two-sided milling of copper, for the production of copper strip. 4) Chips from the cutting of copper sheet. All chips are collected and recycled within the factory. The ruler acts as a scale bar; numbers are in centimetres.

Figure 12: Chips from the sawing of copper castings in factory B. All chips are collected and recycledwithin the factory. The ruler acts as a scale bar; numbers are in centimetres.

## 2.4. Conclusion

From the above information, it is concluded that copper powder is produced by specific processes, clearly different from the production of copper massive. The production of copper powder and copper massive in Europe occurs at different sites and by different companies. This is the only way in which copper powder is produced. Copper powder is never produced as a by-product during the production or use of copper massive. Therefore, the conditions are fulfilled for deriving separate environmental classifications for copper in powder and massive forms.

Copper in massive and powder forms are defined as noted below in the REACH registration dossier. Environmental hazard classifications are derived separately for each form according to the CLP Regulation.

**Copper massive** is defined as copper with a specific surface area (SSA) below 0.67 $mm^2/mg$. This corresponds to the default 1 mm cut-off in the CLP Guidance, if assuming spherical copper particles of 1 mm in diameter (density 8.96 $mg/mm^3$). The environmental classification of copper massive is derived assuming a SSA of 0.67 $mm^2/mg$. This includes a large degree of conservatism: the specific surface area of copper cathode, the form in which copper is produced and traded globally, is more than an order of magnitude below this default cut-off.

**Copper powder** may span a wide range of SSA and particle sizes as indicated previously. In line with the CLP Guidance Annex IV (section IV.5.5), transformation-dissolution data of the finest representative powder are used to derive the environmental hazard classification. To this end, initial transformation-dissolution data were generated for 3 representative copper powders. The finest powder was subsequently subject to a full transformation-dissolution test covering all test durations and pH bands (see section 4.5), and this dataset was used to derive the environmental classification.