The use of concentrated solar energy for the reduction of CuO in H₂

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Abstract

The reduction of copper (II) oxide was carried out under concentrated solar radiation in a stream of gaseous mixture 5/95 v/v H₂/N₂ in a 1.5 kW thermal power vertical axis parabolic concentrator at the PROMES-CNRS solar facility (Odeillo-Font Romeu, France). Experiments were performed using a commercial oxide in two different forms, powdered and compacted specimens. The reduction of CuO to elemental Cu was more effective for compacted specimen yielding a dendrite microstructured metallic copper with an electrochemical behavior similar to that exhibited by the commercial metal. In the case of powdered specimen, a composite metal/oxide (Cu/Cu₂O) block was obtained as a macroporous material. The reduction process of CuO under concentrated solar energy tracks through the formation of Cu₂O as the only intermediate phase, which was evidenced by X-ray diffraction and scanning electron microscopy.

1. Introduction

According to the World Meteorological Organization, since the Industrial Revolution, humankind has emitted 375 billion of tonnes of CO₂ into the atmosphere, producing a level of concentration of this gas in excess of 400 ppm (Ballantyne et al., 2012). Last August 2018, such high concentration of global CO₂ of 407 ppm was recorded by the American National Oceanic and Atmospheric Administration (www.esrl.noaa.gov/gmd/ccgg/trends/global.html). This growth is a direct consequence of the emissions produced by the use of fossil fuels. In this respect, the metallurgical

activities are responsible for a significant percentage of these emissions. In the case of Spain, the CO₂ emissions from the metallurgical sector, consists of the 11% of the total greenhouse gas emissions in the industrial processes (Moreno et al., 2017; Spanish Ministry of Agriculture Food Environment, 2015). The primary metal industry is considered one of the most energy intensive sector (Boulamanti and Moya, 2016), and accordingly one of the major sources of climate altering gases (Murray, 1999; Yadav and Purkait, 2016). In this line, primary copper production is ranking third in specific energy consumption among the five major basic metals (aluminum, copper, iron, lead and zinc) and presents important environmental hazard (Alvarado et al., 1999). The copper ores mined can broadly be categorized as being either sulfide or oxide ores. There are two methods to produce primary copper depending on ore types: hydrometallurgical for oxide ores and low-iron sulfide ores, and pyrometallurgical for sulfide ores. About 80 % of primary copper worldwide is produced by the latter process (Boulamanti and Moya, 2016; Northey et al., 2013) which involves smelting; the 20 % remaining is produced by hydrometallurgical process, which includes leaching, and is commonly used for copper oxide ores. (Boulamanti and Moya, 2016; Northey et al., 2013 (Moreno-Leiva et al., 2017).

During the last decades, studies are being carried out to reduce the high level of CO₂ emissions (Gattrell et al., 2006) and the dependence upon electricity by developing high-temperature solar processes which allow direct thermal route from the ore to metal (Lee et al., 2013; Murray, 1999). In this sense, solar energy is one of the most promising renewable energies for its application to highly heat-demanding processes because it allows reaching sufficiently high temperature when solar energy is properly concentrated. According to Flamant et al. (Flamant et al., 1999) concentrated solar energy (CSE) allows performing high temperature material synthesis on the basis of efficient energy transformation and competitive cost in relation to conventional processes, among others, laser and plasma. When high power density or high temperature, and high purity are needed, solar concentrating systems appear to offer some unique opportunities for high temperature transformation and synthesis of materials from both technical and economical points of view. Different applications in materials science and metallurgy are being developed nowadays (Ceballos-Mendivil et al., 2015; García et al., 2016; Romero et al., 2013; Vázquez-Vaamonde et al., 2016; Vishnevetsky and Epstein, 2015). In a recently published review (Fernández-González et al., 2018), solar energy applications regarding to different metallurgical processes

(Al, Fe, Mn, Ti, Zn, etc.) are described; the authors stated that the couple concentrated solar energy-materials is still an immature technology.

In relation to the application of concentrated solar energy to copper oxides, several studies have been performed related to the usage of the CuO/Cu₂O system for thermochemical energy storage (Alonso et al., 2015; Block and Schmücker, 2016). CuO is used as a catalyst or catalyst precursor in many chemical reactions that involve hydrogen as a reactant or product (Rodriguez et al., 2003). Reduction of copper oxide under hydrogen atmosphere has been widely reported due to the interest of the process from the point of view of the mechanism of the reaction and especially for the design and manufacture of products for catalysis and electronic devices (Ahmed et al., 2016; Antrekowitsch, 2007; Ardestani et al., 2009; Champion et al., 2003; Jelić et al., 2011; Kim et al., 2005; Li et al., 1989; Yamukyan et al., 2009).

This paper is focused on studying the feasibility of using concentrated solar energy to the reduction of copper oxide to metallic copper, in hydrogen atmosphere. Hydrogen was used because it presents several advantages as a reductant, such as to enable the production of pure metals and to short the reaction time (Antrekowitsch, 2007). Besides, from the environmental point of view, its impact in the carbon foot print is null, especially if it is obtained via solar energy (Fernández-González et al., 2018). The use of concentrated solar energy and hydrogen, for the synthesis of metals, would highly contribute to the diminishing of the greenhouse gases, and also it can be profitable for mining areas with high solar irradiation (Vázquez-Vaamonde et al., 2016). A good example would be Chile, which hosts several places with the highest level of solar irradiance and sunniest sites (Molina et al., 2017), and is also the major copper producer (Boulamanti and Moya, 2016). In relation to copper oxide ores, mining deposits of cuprite and tenorite are also found in sites with high solar irradiation such as: USA (Arizona, New Mexico), Spain (Zaragoza, Huelva, Almeria), and even Chile (Antofagasta) (<https://www.mindat.org>).

2. Experimental

2.1. Materials and methods

Commercial CuO (dark-grey tiny-needle sample, Carlo Erba, ACS reagent, purity >99.7%) was milled in a planetary balls mill (FRISTSCH mod Pulverisette 6) for 5 min at 400 rpm, in order to obtain a fine powder sample. Two types of experiments were performed using both the powdered as-obtained sample and compacted sample, in order to study the effect of sample form on the efficiency of the reduction process. Compacted sample was obtained as a 13 mm diameter disc in an 8 t press. For reduction experiment on powdered sample, an 80 mm long and 10 mm wide alumina crucible (boat) was used, and for compacted sample a 22 mm diameter and 25 mm high cylindrical crucible was used. In the first case, for the measurement of temperature a K-type thermocouple was positioned into a hole made in the middle of the bottom of the crucible, just below the powdered sample. In the cylindrical crucible, the thermocouple was placed in a hole made in the bottom of the crucible.

Reduction experiments were performed in an atmosphere composed of a mixture of gases H_2/N_2 in a ratio of 5/95 v/v at a pressure of 8 bar.

Concentrated solar energy was provided by 1.5 kW vertical axis parabolic concentrator in the PROMES–CNRS Solar Furnace installation, Font Romeu-Odeillo, France (<http://www.promes.cnrs.fr>). A heliostat (Fig. 1) redirects solar beam vertically up to the bottom of a balcony on the sixth floor where the equipment is installed. A 2 m diameter parabolic reflector concentrates solar beams in a focal spot, ca. 15 mm diameter placed at 85 cm from the concentrator (focal distance), where a power intensity up to 16 MW m^{-2} with a Gaussian distribution can be achieved. The maximum angle of incidence is 60° and the concentration ratio is 15000 (Flamant et al., 1999; <http://www.promes.cnrs.fr>). Total incident radiation was controlled by a shutter on the bottom of the balcony (Romero et al., 2013). Fig. 1 also shows the parabolic reflector which concentrates the solar radiation over the sample chamber. This one consists of a hemispherical quartz chamber of 35 cm diameter which is positioned at the focus of the solar concentrator system. The quartz chamber is water-cooled on its bottom, during reduction process to prevent overheating (García et al., 2016; Romero et al., 2013). The

chamber is positioned on a XYZ axis table with an automatic motor device allowing a horizontal movement (right to left and vice versa) of 71 mm. The movement along Z axis is only used to place the sample on the focus. The horizontal displacement rate of the boat during reduction was maintained at 1 mm s^{-1} . The purpose of this displacement is to heat the entire sample surface homogeneously. The scheme of the chamber and the position of the crucible in its inner are shown in Fig. 2.

Solar normal direct irradiation during the experiments was quasi-steady, and values between $843\text{--}898 \text{ W m}^{-2}$ were registered. The shutter was partially opened (30 %) at the beginning of the experiments to avoid an abrupt increase of temperature on the sample; immediately after, the shutter was progressively opened until temperature was around $1100 \text{ }^{\circ}\text{C}$.

Fig. 1. Parabolic solar concentrator medium size solar furnace at Odeillo (1.5 kW foreground) installation, and quartz chamber during the test placed on a XYZ axis table.

Fig. 2. Scheme of the experimental device.

2.2. Characterization

Samples, before and after the experiments, were characterized by X-ray diffraction (XRD). Measurements were carried out on compacted and powdered specimens in a Bruker AXS D8 Advance diffractometer equipped with central Euler ring and scanner in X-Y with monochromatic Co K α radiation ($\lambda = 1.789010 \text{ \AA}$). Diffraction data were collected in the angular range 20° to 125° 2θ with a step-size of 0.02° and 2 s of counting time. Once the specimens were processed, they were mounted in a cold epoxy resin and mechanically polished to mirror-finished using a wet grinding on SiC papers down to 1200 grit and final polishing with colloidal silica suspension ($0.04 \text{ \mu m}$). The microstructure of both samples (compacted and powdered specimen) was examined by field emission gun scanning electron microscopy (FEG-SEM) utilizing a Hitachi S 4800 J instrument equipped with energy dispersive X-ray (EDX) detector. The microstructural characterization of the specimens was also conducted using an Olympus GX 5 optical microscope.

Potentiodynamics curves were carried out in order to evaluate the electrochemical behaviour of Cu compacted specimens obtained by solar treatment. For comparison purposes, commercial copper specimens were also studied. The electrochemical measurements were carried out using a three-electrode cell connected to a Gamry Reference 600 Potentiostat. The Cu specimens were used as a working electrode; a platinum wire as an auxiliary electrode, and a Silver-Silver chloride electrode (Ag-AgCl, 3 M KCl) was the reference electrode. All the tests were carried out in a naturally aerated NaCl 0.6 M solution at room temperature. Before the polarization curves start, the evolution of the open circuit potential (OCP) was recorded for an immersion period of 900 seconds. Subsequently, a potential step of -0.3 V with respect to the corrosion

potential was applied, starting the sweep in an anodic direction at a scan rate of 0.16 mV s^{-1} until reaching a potential of 1.5 V vs. Ag-AgCl (3 M KCl); or a limit current density value of 0.75 mA cm^{-2} .

3. Results and discussion

The temperature measurements recorded during the experiments are shown in Fig. 3, along with the corresponding approximation curves. The sinuous profile of temperature curve recorded for powdered sample is due to the right-left movement of the XYZ axis table. The solar focus moves along the sample surface. Because of the position of the thermocouple, (as described above) the registered temperature value only corresponds to that under the focus (about $1100 \text{ }^{\circ}\text{C}$) when the center of the boat is in the middle position of the quartz chamber. By the contrary, the compacted sample is positioned in a fix position just under the radiation focus. The approximation curves for both experiments follows similar three-grade polynomial curve. Experiments were finished when melting of sample was observed. The time required for compacted sample, about 500 seconds, was half of that corresponding to powdered sample. As shown in the figure, the heating rate is higher for the compacted sample than for the powdered sample, as expected, because the compacted sample has a higher conductivity and also due to the fixed/variable position of samples during the solar radiation exposure. Nevertheless, when the steady stage is reached both approximation curves are similar.

Fig. 3. Temperature plots during the experiment (compacted sample: red; powdered sample: blue)

The macroscopic appearance of the specimens is shown in Fig. 4. The characteristic metallic copper color is much better observed for the compacted specimen than for the powdered specimen. This would indicate that the total reduction of CuO to Cu was not completely attained for powdered sample.

Fig. 4. Macroscopic appearance of powdered (a) and compacted (b) specimens

The optical microscopy images are shown in Fig. 5. The powdered specimen after the solar radiation exposure is presented as a compacted block in which two different phases randomly distributed can be observed (Fig. 5a). The optical micrograph (Fig. 5b) shows like-reddish zones corresponding to metallic copper mixture with blue phases (Cu_2O) in a highly porous structure. The metallic copper phase is mostly predominant in the surface of the sample (Fig. 5c) because in this area the interaction of hydrogen with CuO powder is more favored than in the bottom of the sample.

For compacted specimen, a major area of metallic copper is observed which spreads over the surface of the sample (Fig. 4b), but it is not totally developed in the bottom. Thus in the bottom of the specimen two well-differenced zones (1 and 2 in Fig. 5d) are observed. The micrograph (Fig 5e) of this bottom surface shows that the zone 1 is composed of metallic copper with a typical dendrite microstructure and the zone 2 consists of grains of Cu_2O . The image corresponding to the surface of the specimen (Fig. 5f) clearly shows the dendrite microstructure of metallic copper which spreads over with extremely low porosity. No other phases are observed on the surface of the compacted specimen. Results indicate that the reduction of copper oxide with CSE is favored by compacting initial CuO sample.

Fig. 5. Optical microscopy images of powdered (a-c) and compacted (d-f) specimens

The XRD patterns of specimens are collected in Fig. 6. Initial sample (right corner) exhibits the profile corresponding to CuO according to the reference file (ICDD PDF 01-089-5898). The powdered specimen consists principally of Cu₂O (ICDD PDF 01-078-2076) and Cu^o (ICDD PDF 01-070-3038). For compacted specimen, the XRD pattern recorded on zone 2, indicate the presence of both Cu₂O and Cu^o, and in the corresponding pattern to zone 1, only Cu^o is observed. It is noticeable the flat background of the pattern indicating the high purity and crystallinity of the sample in agreement with the optical microscopy observations.

Fig. 6. XRD patterns of initial sample (right corner, blue), and solar treated samples: powdered sample (dark blue) and compacted sample (green- zone 2 and red- zone 1)

Back-scattered SEM images of the powdered specimen are shown in Fig. 7. The random distribution of metallic copper (clear grey) and Cu_2O (dark grey) is clearly distinguished in the image. In the magnified zone pointed out in this figure, EDX mapping was recorded. As can be seen, the oxygen content drastically falls down in the grain bordering between Cu^{1+} and Cu^0 phases. This corroborates the reduction process of copper oxide by H_2 under concentrated solar radiation, as a two stage process according to the follow reactions:

Kinetics of the reaction 2 is specially favored by a major contact between grains in the initial CuO sample, i.e, by compacting, because it allows higher heat diffusion. Thus a shorter time of solar radiation exposure on compacted sample, produces a major level of reduction to metallic copper than on powdered sample. Although the sequential reduction of copper oxide with H_2 is reported in the literature as $\text{CuO} \rightarrow \text{Cu}_4\text{O}_3 \rightarrow \text{Cu}_2\text{O} \rightarrow \text{Cu}$, there is a certain controversial on this point and several experiments

reported that the reduction can occur in one, two or three steps (Bhattacharyya et al., 2015; Günter et al., 2001; Jelić et al., 2011; Kim et al., 2003; Rodriguez et al., 2003). According to Kim et al. (Kim et al., 2003) the mechanism of the CuO reduction is complex, involving an induction period and the embedding of hydrogen into the bulk of the oxide. These authors also stated that the reduction of CuO is easier than the reduction of Cu₂O, so during the reduction of CuO the system can reach metastable states and react with hydrogen instead of forming Cu₂O. In our experiments the formation of Cu₄O₃ was not observed, by the contrary the formation of Cu₂O was extensive. This means that the Cu¹⁺ is a very stable intermediate in the reduction process employing CSE, probably due to the temperature gradient between surface and bottom of sample, and also to the rapid cooling of sample when the solar radiation is cut off. The cooling rate is variable as a function of the temperature ranges; thus the maximum cooling rate (30 °C s⁻¹) was obtained between 1200-1000 °C. This finding could be very useful for the application of the material to catalysis because the kinetics of reduction is connected to the stability of catalytic activity of copper oxides (Jelić et al., 2011).

Fig. 7. Back-scattered SEM micrographs of powdered specimen (left) with the EDX mapping of O (blue) and Cu (orange), recorded on the magnified zone (Right)

The back-scattered SEM micrograph of compacted specimen is shown in Fig. 8a), the dendrite microstructure of metallic copper is clearly observed. An area in the bottom surface of the sample is shown in Fig. 8b). The EDX spectra confirmed the presence of two phases, one of them (zone 1), composed principally of Cu. The microanalysis results indicate that this phase corresponds to metallic copper of 98.5 % w/w. The

spectrum of zone 2 shows a higher content of oxygen with a copper content of 89 % w/w, quite similar to the theoretical value for Cu₂O (88 % w/w).

Fig. 8. Back-scattered SEM micrographs of the surface of the compacted specimen (left) and an area from the bottom of the specimen with partial reduction (right), with EDX spectra of the marked zones. The atomic composition of these zones is also included.

A study of the porosity of the powdered specimen was performed by optical image analysis using IMAGEJ software. The results can be seen in Fig. 9. The total porosity is 14% and most of the pores exhibits an area < 200 µm². Although the aim of this work was not to prepare samples for catalysis and/or microelectronic components, the high power supplied on the sample surface and the temperature gradient between the directly irradiated surface and the bottom of sample which is heating by heat diffusion could produce interesting metal/oxide composite to be used in such applications.

Fig. 9. Porosity of the powdered specimen

In order to characterize the electrochemical behavior of the Cu obtained by reduction of CuO with H₂ under CSE, a corrosion study was carried out. Figure 10 compares the polarization curves in 0.6 M NaCl solution of the compacted specimen and a commercial Cu sample. As it can be seen both materials show a similar behavior. This test provides information of corrosion kinetics. The curves reveal that the system is under activation control. Nevertheless, it is important to note that the cathodic branch of the Cu commercial sample exhibits an activation control at potentials closer to E_{corr} and a concentration limited cathodic behavior (diffusion) at lower potentials.

Figure 10. Polarization curves of compacted Cu obtained by CSE and commercial Cu in 0.6 M NaCl solution.

The anodic branch for both samples showed an activation control (charge transfer controlled metal anodic dissolution). The determination of the corrosion current density, i_{corr} , of both samples has been done by Tafel extrapolation method (The Tafel regions of the polarization curves extrapolated to the corrosion potential E_{corr} , intersect there to give the value of the corrosion current density i_{corr} .)

Table I summarizes the electrochemical parameters obtained from the polarization curves. The value of the corrosion potential for the commercial Cu specimen was about -202 mV vs. Ag-AgCl (3M KCl) while for the compacted copper specimen obtained by CSE was -192 mV vs. Ag-AgCl (3M KCl). The corrosion current density was 2.8 $\mu\text{A cm}^{-2}$ for commercial Cu specimen and 1.3 $\mu\text{A cm}^{-2}$ for the compacted Cu specimen.

Similar corrosion current density has been reported in literature for Cu in aerated NaCl solution (Rhattas et al., 2011). Therefore, compacted copper specimens obtained by CSE present similar corrosion behavior than Cu processed by conventional metallurgical process.

Table I. Electrochemical parameters calculated from polarization curves.

Specimens	E_{corr} (mV vs. Ag-AgCl, 3M KCl)	Cathodic Tafel slope β_{cat} (mV dec ⁻¹)	Cathodic Intercept O_{cat} (mV)	Anodic Tafel slope β_{anod} (mV dec ⁻¹)	Anodic Intercept O_{anod} (mV)	i_{corr} (μA cm ⁻²)
Commercial Cu	-202	-63	-545	44	49	2.8
Compacted Cu (CSE)	-192	-161	-1124	33	18	1.3

In relation to determine the applicability of the CSE for copper production some considerations could be taking into account:

- The use of CSE for the treatment of copper oxide ores, would allow processing these ores by a pyrometallurgical route (smelting) instead of the traditional hydrometallurgical one, with the corresponding savings in energy, acid, water and effluents.
- Most of the copper mining is placed in sites with high solar irradiance. Indeed, about 20 % of the metallurgical plants for smelter production are located in zones with that characteristic (Cruz-Robles et al., 2018).

A first approach to integrate solar energy in the process to copper oxide ores reduction in hydrogen atmosphere is shown in Fig. 11. Two solar technologies could be considered. A concentrated solar reactor in a tower plant to supply the heat required for smelting and a photovoltaic installation (PV) for the H₂ generation from water electrolysis. This new approach would provide very important savings in both energy and greenhouse gas emissions. Thus, Northey et al. (Northey et al., 2013) reported that typical figures of energy intensity for copper production range between 10-70 GJ/t Cu

with an average of 22.2 GJ/t Cu, and greenhouse gas emissions between 1-9 t CO₂-e/t Cu, with an average of 2.6 t CO₂-e/t Cu. According to Cruz-Robles et al. (Cruz-Robles et al., 2018), the energy consumption in the smelting stage is about 8.17 MJ/Kg Cu with operating temperature around 1250 °C. This temperature can be reached by the solar reactor proposed, and in this way the use of fossil fuels would be eliminated and therefore, the greenhouse gas emissions, which reach values about 1.9 t CO₂-e/t Cu (Moreno-Leiva et al., 2017) during the smelting process.

Fig. 11. Conceptual design of the integration of solar technologies on copper production.

The copper oxide reduction process is schemed in Fig. 12. The proposal route includes the production of hydrogen by means of hydrolysis of water and consequently, with the generation of oxygen as an added-value product of the process.

Fig. 12. Scheme of copper oxide reduction by hydrogen using solar technologies (CSE = concentrated solar energy, PV = photovoltaic energy).

Therefore, the development of a more sustainable process for the production of copper will face the global warming challenge.

Conclusion

Metallic copper was obtained from CuO by reduction in H₂/N₂ atmosphere and direct application of concentrated solar energy. The reduction process occurs in two stages (Cu²⁺ → Cu¹⁺ → Cu⁰) and is favored when the initial sample is compacted. The characteristics (microstructure and corrosion behavior) of the as-obtained metal are similar to those of the commercial product. Intermediate product consisted of a solid composite material Cu₂O/Cu exhibits interesting porosity characteristic. The application of CSE to conventional metallurgical process, highly energy consuming, would produce a high decreasing in the power cost and also in the environmental impact as a result of the use of both energetic vectors: a "green energy" such as the concentrated solar power, and "hydrogen" as a reducing agent, which does not produce greenhouse gasses. Thus, the proposed method could be a best alternative route for the hydrometallurgical processes conventionally used for the copper production from oxide ores.

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