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ARTICLE

Synergism of mechanical activation and sulfurization to recover copper from waste printed circuit boards

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In the context of recycling metal to embrace the sustainability challenge, this work employs mechanochemistry to recover copper from waste printed circuit boards (WPCBs) for the first time. This work aims to recycle both copper (9.89 wt%) and resin, the two main components of WPCBs, to the largest extent. Copper and sulfur could be synthesized to copper sulfides by the aid of mechanochemistry in the model experiment, so the synergistic route of mechanical activation and sulfurization was proposed. After milling WPCB fragments and sulfur for 20 minutes and leaching as-milled sample in sulfuric acid (3M) and hydrogen peroxide (30 wt%), the yield of copper reached nearly 90% and, also, resin was conserved for further utilization. This paper highlights the microstructural assessment on synergism of mechanical activation and sulfurization. It is an alternative method of recycling metal to transform metal to its corresponding compound that exists in natural minerals, and mechanochemistry can help to fulfil this process in a green way.

Introduction

Metals or metal-bearing products are, nowadays, ubiquitous because metals are uniquely useful materials by virtue of their fracture toughness, thermal and electrical conductivity, and performance at high temperature, among other properties¹. Demand for various metals is increasing sharply, even though metals are a finite resource. It was estimated that, based on the comparison of the world mine production and the reserve base, copper in minerals would be used up in 61 years, lead in 43, zinc in 46, tin in 53, mercury in 80, nickel in 100². At the same time, metal recycling is often inefficient or essentially non-existent: end-of-life recycling rates (EOL-RRs) for the commonly used “base metal” (iron, copper, zinc, etc.) are merely above 50% (these rates are the biggest among sixty tested metallic elements)^{3, 4}. Moreover, recycling a metal is generally much more energy-efficient and environmentally-friendly than acquiring it from a mine^{2, 5-7}. So metal recycling has been identified as a key area in terms of 21st century sustainability challenge¹.

Electronic waste or e-waste has been recognized as the fastest-growing component of solid-waste stream since the mid-1990s^{8, 9}. The latest data from StEP (Solving the E-waste Problem) indicates that the production of e-waste in 2012 mounted to 48.9 metric million tons and 65.4 metric million tons in 2017 had been estimated¹⁰. Waste printed circuit boards (WPCBs) seem the most common type of e-waste as printed circuit boards are the essential part of almost all electrical and

electronic equipments (EEEs)¹¹. WPCBs contain a large amount of metals (~40%)¹¹: copper (the largest ratio), alumina, lead, zinc, nickel, iron, tin, antimony, chromium, molybdenum, aurum, platinum, silver, palladium, etc. The averaged content of copper reaches 17.6% (5.8~26.8% for different sources)¹¹ while typical copper ores contain from 0.5% Cu (open pit mines) to 1 or 2% Cu (underground pit mines)¹². More importantly, about 4 million tons of copper come from recycled end-of-use objects and manufacturing wastes in about 22 million tons of copper of coming into use per year worldwide¹². In the context of the emerging call for urban mining, copper in WPCBs should be more extensively targeted for recovery.

To recover copper from WPCBs, numerous researches related have been done, which can be roughly divided into three groups: pyrometallurgy, hydrometallurgy and physical route. Pyrometallurgical processing, a traditional technology, generates atmospheric pollution through the release of dioxins and furans¹³. In the past decade or more, attentions have been removed from pyrometallurgical process to hydrometallurgical one¹³. Hydrometallurgical methods always use strong acids or chelating agents, such as aqua regia¹⁴⁻¹⁶, sulfuric acid (>15 wt%)^{15, 17} and EDTA^{18, 19}. These processes not only generate high volumes of effluents and carbon dioxide but also do extreme damage to resin so that resin cannot be recycled. Physical methods always include crushing, screening, shape separation, magnetic separation, electric conductivity-based separation and density-based separation²⁰. Xu's research group has been the loyal supporter of the physical method in a series

of paper²¹⁻²³ about the two-step crushing and the corona electrostatic separation. However, almost all fine copper or copper products are obtained via electrodepositing copper ion in solution after dissolving copper ores in strong acids¹². So the dissolution process is unavoidable even though the physical separation of copper from resin boards seems feasible. Moreover, hardly can the physical method acquire the complete (>90%) separation of copper from resin boards because the adhesive force between copper and resin boards exists. More innovative methods are still being proposed. Recently, Zhu et al.²⁴ took use of dimethyl sulfoxide to dissolve resin boards for separating copper, but separated copper still needs to be transformed into aqueous phase if fine copper is necessary and there exists the question whether dimethyl sulfoxide is safe.

Mechanochemistry, which has once been application-oriented but is going through its current resurgence in chemistry²⁵, has been used in the extractive metallurgy for many years²⁶. Mechanical activation can influence surface and bulk properties of minerals, create a degree of disordering and break bonds in the crystalline lattice so that both a decrease in activation energy and an increase in the rate of leaching can be obtained²⁶. Also the decrease in activation energy makes thermodynamically impossible or hard reactions happen. Extracting metals from e-waste is conceptually similar to mining raw ores. Some studies have proved that mechanochemistry works in metal recovery from e-waste. Sasai et al.²⁷ utilized the planetary ball mill to extract 99% lead as a lead-EDTA species from cathode ray tube (CRT) powder. Yuan et al.²⁸ directly milled the CRT powder and high yield of 92.5% of lead were leached by dilute nitric acid. In addition, Saeki et al.²⁹ and Zhang et al.³⁰ applied mechanochemistry to lithium and cobalt recovery from waste lithium-ion batteries. Mio et al.³¹ and Zhang et al.^{32, 33} successfully recovered rare earth from waste fluorescent lamps. Indium recovery from LCD screens was carried out by the aid of mechanochemistry by Murakami et al.³⁴ and Hasegawa et al.³⁵. In these practices, mechanochemistry performs well sustainably, enabling metal recycling under environmentally friendly and essentially waste-free conditions³⁶.

This study deploys mechanochemistry to recover copper from WPCBs for the first time. Our innovated method accomplished mechanical activation and sulfurization simultaneously. Nearly 90% copper was transformed into liquid phase and resin stayed undamaged for recovery after as-milled samples were treated with weak sulfuric acid and hydrogen peroxide. We successfully avoid problems mentioned above in current treatments and achieve a green route. This route can be generalized in broadening mechanochemical application to metal recovery from other e-waste or even solid waste. This paper highlights the microstructural assessment on synergism of mechanical activation and sulfurization.

Experimental Section

WPCBs sample

The WPCBs used in this work were provided by Dongjiang Environment Co., Ltd in Shenzhen, China. The electronic components were manually dismantled from WPCBs in lab. Then the WPCBs were broken into fragments (referring to Figure 1-A) via an air cooling pulverizer (FL-150, Jiangsu Guibao Co., Ltd, China). The sample was prepared though an 8-mesh screen (particle size < 2.5mm). To ensure the homogenization of sample and reproduction of experimental results, the Carpenter left-right balancing method was utilized to pre-treat the samples. The details of this method refer to Figure S2 in supporting information.

Material characterization

The elemental compositions of WPCBs and final residues were analyzed by X-ray fluorescence (XRF), using an XRF-1800 Analyzer (Shimadzu Corp., Kyoto, Japan). The interface between copper and resin boards in WPCB fragments was determined with scanning electron microscope (SEM) (JSM-6460LV, JEOL, Japan), by the aid of energy dispersive spectrometer (EDS) (INCA, Oxford, UK). The distribution of the particle size of milled products was determined for different ball-milling time, using a laser particle size analyzer (LS13320, Beckman Coulter, Inc., FL, USA).

X-ray diffraction (XRD) analysis was performed on a SmartLab X-ray diffractometer (Rigaku Corp., Tokyo, Japan) with the following operating parameters: CuK α radiation ($\lambda=1.5418$ Å), FeK β filter, 40 kW, 200 mA power generator. An angular range of $2\theta = 5^\circ\sim 100^\circ$ was measured with a step size of 0.02° and 2 s counting time per step. The identification of all crystalline phases was conducted with X'Pert HighScore Plus (PW3212) 3.0 software (PANalytical B.V., Netherland) and the PDF-2004 database (International Center for Diffraction Data, Newton Square, PA, USA).

Ball milling experiments

In both the model (co-milling Cu with sulfur) and the practical experiments (co-milling WPCB with sulfur), the ball milling was carried out using a planetary ball mill (P-5, FRITSCHE, Germany). Two grams of copper powder and one grams of sulfur powder in the model experiment, two grams of WPCB fragments and one grams of sulfur powder in the practical experiment or three grams of sulfur powder in the verifying experiment were put into a zirconia pot of 45 mL inner volume with 7 zirconia balls of 15 mm in diameter. The mill was run for 5 min grinding and 15 min pause in turn to avoid the obvious release of heat. The rotational speed in all experiments was set at 500 rpm. Pure copper powder and sulfur powder were supplied from Beijing Modern Oriental Fine Chemistry Co., Ltd, China.

Dissolving separation experiments

One grams of milled products were mixed with 15 mL H₂SO₄ (1M, 2M, 3M and 4M, respectively) and 15 mL H₂O₂ (30 wt%). The leaching process was performed in ambient temperature and 200 rpm magnetic stirring. The solid-liquid separation after

leaching was conducted by a vacuum filter apparatus. The Cu (2) content in the leachate ($Con_{Cu-In-Each-Batch}$) was measured by Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES, IRIS Intrepid II XPS, Thermo Electron Corp., USA). The filter residues were dried in 104 °C for 2 hours before XRF analysis. Copper leaching yields were calculated as Equation 5 in which $Con_{Total-Cu}$ could be acquired by solving the milled products in aqua regia (3 thick hydrochloric acid : 1 thick nitric acid in volume) and then measuring the Cu (2) content in ICP-AES. Sulfuric acid, hydrochloric acid, nitric acid and hydrogen peroxide are supplied from Beijing Modern Oriental Fine Chemistry Co., Ltd, China.

$$Cu \text{ leaching yield (\%)} = \frac{Con_{Cu-In-Each-Batch}}{Con_{Total-Cu}} \cdot 100\% \quad (1)$$

Results and Discussion

WPCBs sample characteristics

Figure 1-A presents the pre-treated WPCB samples. XRF analysis showed that the prepared WPCBs sample contains 9.89% Cu, which falls in the range of common copper content (5.8~26.8%) of WPCBs. The elemental composition is given in Table 1. XRD analysis showed the copper in WPCBs is univalent. As is shown in Figure 1-B, copper tightly adheres to resin by adhesive force of polymer (the elemental distributions given in EDS analysis help to verify copper-resin interface in the blue rectangular and detailed data in Area-IV~VI refer to Table S1 in supporting information). If this adhesive force can be broken, it seems easy to recover copper from WPCBs. So the ensuing experiments are designed to break this adhesive force.

Determination of the specific ball-milling scheme

Copper in the earth's crust is most commonly present as copper-iron-sulfide and copper-sulfide minerals (about 80%)¹², including chalcopyrite ($CuFeS_2$), chalcocite (Cu_2S), villamaninite (Cu_5S_2), covellite (CuS), djurleite ($Cu_{1.95}S$), anilite ($Cu_{1.75}S$) etc.^{12, 37} Metallurgical techniques for copper sulfides have been well-developed to meet the need of copper. The compound CuS, as an important semiconductor material, has been found many properties, e.g. metal-like electrical conductivity, chemical sensing capabilities and ideal characteristics for solar energy adsorption^{38, 39}. So numerous CuS synthetic methods have been reported, such as the one-step solid-state reaction route³⁹ and the hydrothermal reaction³⁷. But elemental copper cannot spontaneously react with elemental sulfur in the ambient atmosphere without any external disturbance (temperature, pressure, mechanical force etc.), even though this combination reaction is thermodynamically favored, as is shown in Equation 1 (thermodynamic data source: Lange's Handbook of Chemistry, sixteenth edition, McGraw-Hill, 2005). Blachnik and Müller⁴⁰ reported that copper sulfides

could be synthesized via ball milling, and CuS, Cu_2S and a series of nonstoichiometric intermediate compounds ($Cu_{1.8}S$, $Cu_{1.95}S$, $Cu_{1.96}S$) were generated with different reaction time. In view of both the existence of available metallurgical techniques for copper sulfides and the feasible synthesis of copper sulfides via ball milling, the combination of mechanical activation and sulfurization are chosen to treat WPCBs. Furthermore, based on the redox stoichiometric calculation, the ball-milling product is targeted at CuS to save hydrogen peroxide in the later leaching process. So the determination of ball-milling time seems necessary in the first step.

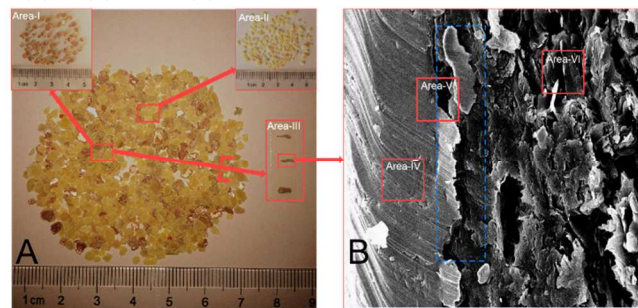
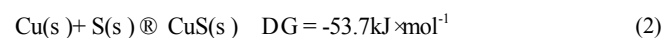


Figure 1. Pre-treated WPCB samples are presented in A, which can be separated into two groups: Area- I containing copper and Area- II containing no copper but only resin; the WPCB particles are erected in Area- III so that scanning electron microscope (SEM) can detect the interface between copper and resin, as is shown in B.

Pure copper powder is taken use of as the model sample because unitary copper-sulfur system seems clear to quantify each intermediate compound in X-ray diffraction analysis. The corresponding ball-milling time can give reference to WPCBs treatment under the same experimental condition. Figure 2 presents CuS and $Cu_{2-x}S$ ($0 \leq x < 1$) yields in different ball-milling time. As is shown in Figure 2, the desired CuS formed once the ball mill ran. Its production increased as the ball mill went on and reached its maximum at 20 minute. At the early stage of ball milling, the $Cu_{2-x}S$ formation seemed prior to the CuS generation largely because of the excessive copper at this moment. After 10 minute the $Cu_{2-x}S$ yield decreased and came to the minimum at 20 minute, just the opposite of the CuS yield. Thus 20 minute is the optimal ball milling time. Later the CuS yield decreased sharply while the $Cu_{2-x}S$ yield went through a big increase. It was notable that both CuS and $Cu_{2-x}S$ yields looked stable after 40 minute. There possibly exists a dynamic balance among CuS, $Cu_{2-x}S$ and S in the long time of ball milling, which needs further verification in the future experiment. In the XRD analysis, $Cu_{2-x}S$ included several compounds, and the specific species and the weight percentages in different ball-milling time can refer to Table S2 in supporting information. Our result does not agree with Blachnik and Müller's work⁴⁰ largely because the amount of copper and

Table 1. Elemental composition (wt%) of the pre-treated WPCB sample and the residue after final leaching.

Type	S	C	Cu	O	N	Br	Sn	Mg	Si	Ni	Ba	Pb	Ca	Fe	Zn
The raw	0.11	56.51	9.89	17.71	6.90	3.53	0.14	0.15	2.67	0.07	0.43	0.03	0.48	0.85	0.53
The residue	32.86	41.48	1.05	13.29	7.24	0.67	-	-	3.39	-	-	-	0.02	-	-

sulfur is fed in a stoichiometric ratio (1:1) into our experiment.

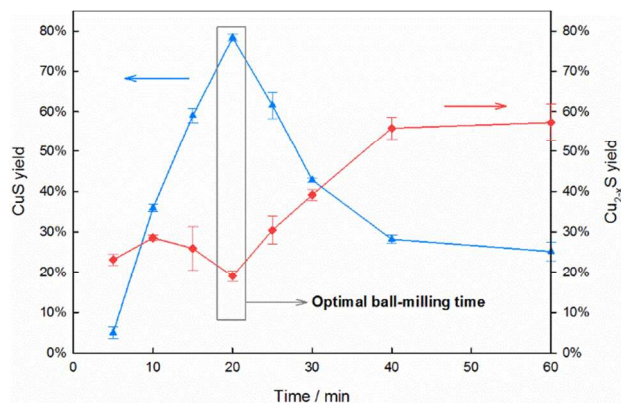


Figure 2. CuS and Cu_{2-x}S (0 ≤ x < 1) yields in different ball-milling time.

Based on the results of the model experiment above, WPCB samples were ground with sulfur for 5 minute, 10 minute, 20 minute and 30 minute, respectively. Figure 3 shows the diffractograms of products. At the beginning (5 minute and 10 minute), diffraction peaks of Cu (0) are dominant. From 5 minute to 10 minute, Cu (0) peaks obviously weaken and no Cu (0) can be detected after 20 min. This change of Cu (0) peaks indicates that Cu in WPCBs can also be mechanically activated and sulfurized via ball milling, the same to the model experiment. No CuS forms at the early stage of ball milling (5 minute), and Cu₂S is the main product with company of a small quantity of immediate compounds (Cu_{1.96}S). Next, CuS peaks appear stronger and stronger while Cu₂S and Cu_{1.96}S gradually decompose and neither can be observed after 20 min. The hypothetic dynamic balance among CuS, Cu_{2-x}S and S does not possibly exist (because no Cu_{2-x}S is left) in the practical experiment. The excessive amount of sulfur in the practical experiment can account for the difference with the model experiment (verified by co-milling copper and sulfur in 0.5:1). In addition, the diffraction peaks of sulfur also attenuate because of its consumption in sulfurization. We can conclude that ball milling can efficiently transform copper in WPCBs into CuS and the best ball-milling time is determined at 20 min.

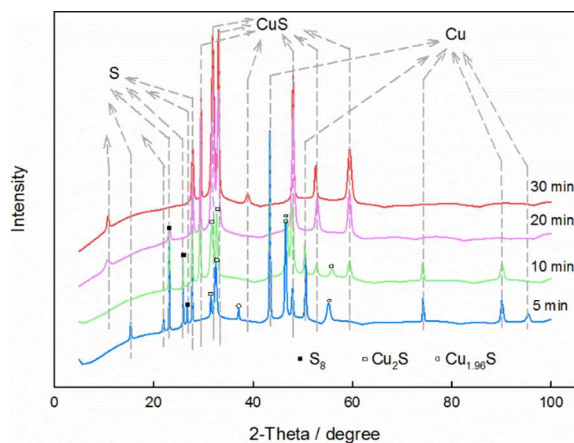


Figure 3. XRD diffractograms of products of different batches in the practical experiment.

Dissolving separation to recover copper

In traditional hydrometallurgical engineering, natural copper ores are dissolved in highly-concentrated sulfuric acid (>10 M)¹². This process not only produces large volumes of effluents and gaseous pollutants (sulfur dioxide) but also virtually leaves nothing after dissolving. Clearly, highly-concentrated acids are unsuitable for dissolving separation of copper sulfides and resin (the mixture obtained in the practical experiment above). Also dissolution of copper sulfides can be performed by the use of suitable reactants in the presence of oxidants (so-called oxidative leaching)⁴¹. Numerous studies have been conducted to achieve this. The H₂O₂/H₂SO₄ system has been successfully used to dissolve many kinds of metallic sulfides, including CuS and FeS, by its advantage of SO₂-free emission⁴¹⁻⁴⁶. Figure 4 presents copper leaching yields in different time when the mixture was leached in sulfuric acid of different concentrations (1 M, 2 M, 3 M and 4 M) and hydrogen peroxide (30 wt%).

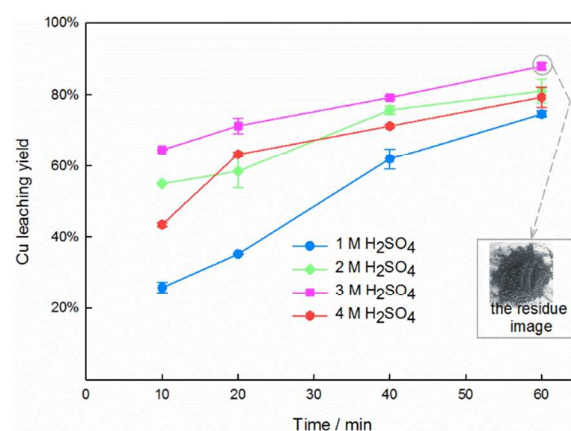
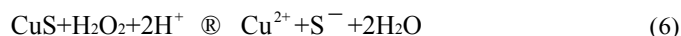


Figure 4. Cu leaching yield as a function of time in four concentrations of sulfuric acid. Conditions: 1 g samples, 15 ml H₂O₂, 15 ml H₂SO₄, 200 rpm magnetic stirring and ambient temperature.

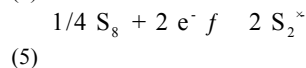
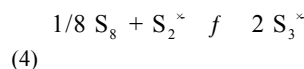
In Figure 4, Cu leaching yields of all four batches increase over time. After 60 minute, the maximum Cu leaching yield 87.97% could be obtained when the mixture were leached in 3 M H₂SO₄. The yield drops down instead when rising the concentration of sulfuric acid from 3 M to 4M. It is the rapid decomposition of H₂O₂, which is triggered by excessive H⁺ from redundant sulfuric acid. That can explain this phenomenon^{47, 48}. The residue, after filtering and drying, is shown as the image in Figure 4. XRF analysis in Table 1 indicates C and O are dominant in residue. The non-milling, pure resin was also analysed by XRF and it comprise 67.26% C and 21.47% O. The C/O ratio in the residue is almost as many as the one in the raw resin. Sulfur in residue mainly comes from two sources: the excessive sulfur fed into ball milling and sulfur generated via the oxidation of divalent sulfur in CuS⁴¹ (referring to Equation 6). It needs further investigation in our following study to recycle the residue: characterization of the residue more clearly and designing of possible recycling method of the residue (including resin and sulfur).



Microstructural assessment on synergism of mechanical activation and sulfurization

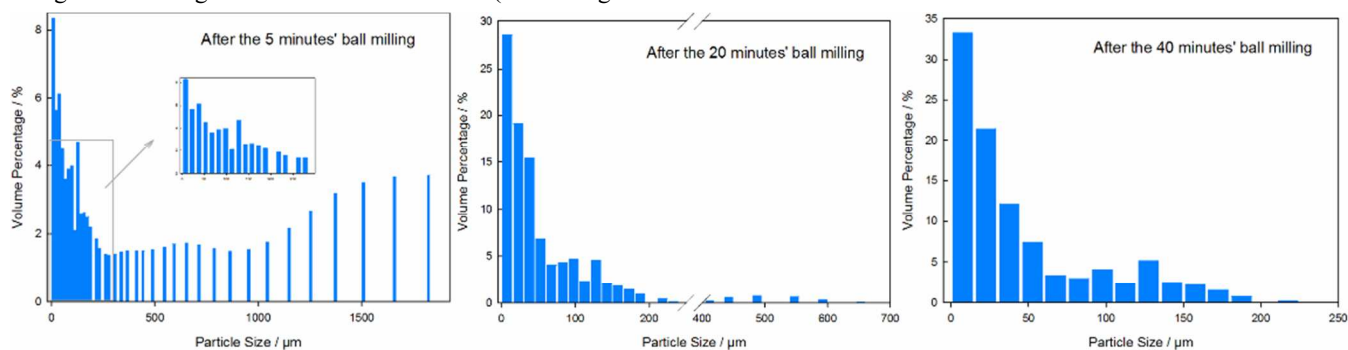
The reactions during ball milling should be attributed to the synergistic result of mechanical activation and sulfurization. Even though the totally unambiguous mechanism of reactions in the jar is hardly given because of the incapability of quantitative and in situ reaction monitoring, the limitation of microscopic understanding of mechanochemical processes²⁵ and, most importantly, the lack of related theories, access to the previous researches in mechanochemical synthesis indicates radicals formed during ball milling help to microstructurally assess these processes^{28, 49}. It is clear, too, that the generation of a univalent free radical in a chemical system will start a whole chain of reactions that will end only by collision of two radicals⁵⁰.

The only stable form of sulfur at STP conditions is orthorhombic α -S₈⁵¹ (all commercial sulfur powder is α -S₈⁵² and our sulfur sample is also unexceptional), which is a puckered eight atom ring⁵³. The distortion of the crown-shaped S₈ molecule can cause homolytic dissociation and produce a series of polysulfide anions (S₂²⁻, S₃²⁻, S₄²⁻, S₅²⁻ and S₆²⁻) and then some radical anion species. The chemistry of polysulfide radical anion S_n^{•-} (n=2-4, 6) has been characterized in detail and the most common species include S₂^{•-} and S₃^{•-}⁵¹ (two simplified reactions refer to Equation 2 and 3). Since these dissociation reactions are, of course, endothermic, it has been reported that either of heating and mechanical force can promote the radical formation. In our work, sulfur powder is ground for 5 minute to verify the radical formation. As-milled sulfur powder still looks yellow (referring to Figure 1S in supporting information). There must be, if any, the yellow disulfide radical anion (S₂^{•-}) formation in that the trisulfide radical anion and tetrasulfide radical anion are bright blue and red, respectively, and hexasulfide radical anion seems hard to form in this reaction condition⁵¹. This inference can be indirectly corroborated by the gradual weakening and disappearance of diffraction peaks of S₈ (2 θ =23.261°, 25.978° and 26.936°) in Figure 3, which indicates that S₈ decomposed during ball milling. Herein activated sulfur (containing free

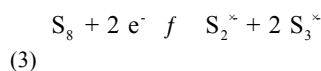


Regardless of any chemical stimulation, the fundamental action of ball milling is the repeated fracture, mixing and welding during ball-powder-ball and ball-powder-container collisions. The WPCB particles (original average particle size is 2.5 mm) are distorted, sheared, crushed, pulverized during these collisions so that the average size decreases markedly as the ball mill runs. Figure 5 presents the dramatic diminution of the average size of the mixture of WPCB particles and sulfur powder from 5 minute to 40 minute. Lateral collision can directly break the adhesive force between copper and resin. It is obvious that separated copper can more easily reacts with activated sulfur because of the increase of the possible contact area. At the meantime, the collision can also result in the rise of temperature within limited colliding area, which may contribute to the separation of copper and resin. Since high temperature can make the trend of the melting of polymer in order to break the adhesive force between. Previous related studies can give a great reference on temperature⁴⁰ and temperature should be included in the factor of our assessment. Both the above breaking effects lead to the creation of an additional surface equal to at least twice the area over which the separation has taken place⁵⁴.

Although copper sulfides can be synthesized by numerous methods, direct reactions of the elements under many conditions, such as low temperature (<150°C), do not proceed completely, but are restricted to the surface of the copper particles because CuS surface layers act as a passivating layer that prevent further reaction³⁷. Clearly, this passive layer can be efficiently removed when continuous milling goes on. This can be seen in the diffractogram of the mixture milled for 20 minutes in which no copper can be detected, see Figure 3. If continuous milling cannot efficiently remove the passive layers, there must be copper left to be detected. This inference ties in well with Blachnik and Müller's study⁴⁰. The removal of passive layers promotes the repeated creation of fresh reactive



radicals) can start the sulfurization and copper can be oxidized into copper sulfides.



surfaces and play a significant part in the complete consumption of copper.

In the early stage of reactions, the mixture of reactants is distributed heterogeneously in the container because there is a

Figure 5. Particle size histograms of the ground mixture (WPCBs particles and sulfur powder) for 5 minutes, 20 minutes and 40 minutes.

This

big gap of the average size between WPCB particles and sulfur powder, as is shown in Figure 5 (a). This gap also leads to the formation of $S_2^{\cdot-}$ -rich and $S_2^{\cdot-}$ -poor regions in the container. Further milling dramatically reduces the size of the mixed particles. And the particles become more and more homogeneous in appearance and size, as is shown in Figure 5 (b)-(c). In Figure 5 (b), the distribution range of the size of the mixed particles at 20 minute is very narrow. This narrow range of the size indicates that both reactants and products are well dispersed throughout the reaction volume. The better reactants are dispersed, the more possibly the $S_2^{\cdot-}$ and copper get touched. Naturally, the homogeneous reaction system contributes to the complete reaction. In addition, elastic deformation in metallic elements is expected because milling can be regarded as micro-rolling and micro-forging⁵⁵. So it is likely that elastically-deformed copper by mechanical activation can be added into the microstructural assessment of synergism.

Conclusions

Copper sulfide is always present in natural copper ores and there are many methods to extract copper from it in mineral engineering. It had been verified in our model experiment that copper and sulfur could form into copper sulfide by the aid of mechanochemistry. With consideration of these two points, this work proposed the synergistic route of mechanical activation and sulfurization. The model experiment, where copper and sulfur were mixed and ground, not only verified the feasibility of this route, but also determined the optimal ball milling time (20 minutes). The formation of copper sulfide was detected in XRD analysis. In the practical experiment, WPCB fragments and sulfur were mixed and ground for 20 minutes, no copper was detected but copper sulfide was left. After leaching in sulfuric acid (3M) and hydrogen peroxide (30 wt%), the yield of copper reached nearly 90% and, also, resin was conserved for further utilization.

The microstructural assessment on the synergism of mechanical activation and sulfurization is highlighted in this paper: the formation of diatomic sulfur radical ($S_2^{\cdot-}$) and the homogenization of the reaction system can account for this synergism; secondly, ball milling could help to break the adhesive force between copper and resin in order to increase the possible contact area; in addition, ball milling could effectively remove the passive layers of copper sulfides so as to promote the repeated creation of fresh reactive surfaces.

Wastes, like WPCBs, are synthetic materials, not natural minerals. It is not easy to use traditional mineral processing methods to deal with them. Mechanical activation can influence surface and bulk properties of minerals, create a degree of disordering and break bonds in the crystalline lattice in order to promote the leaching process. This work, once again, proves the effectiveness of mechanochemistry in metal recovery from second-hand resources. Additionally, it is an alternative method to transform the targeted metal into its corresponding

compound that exists in natural minerals, especially when it seems difficult to directly leach the targeted metal from scraps. Optimization of process parameters in ball milling and leaching (e.g. WPCBs-sulfur ratio, leaching temperature and H_2O_2 volume) and the potential utilization of residues after leaching will be discussed in subsequent reports. A higher recycling ratio (>95%) of copper is expected.

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Notes and references

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Electronic Supplementary Information (ESI) available: Figure S1-S2 and Table S1-S2. See DOI: 10.1039/b000000x/

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