Facile Remediation Method of Copper Sulfide by Nitrogen Pre-Treatment

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Abstract. The deactivation and destabilization of copper sulfide when exposed to an oxidizing environment has led to the economical concerns as this sulfidic material can be easily destroyed by a series of oxidation processes. A promising and effective remediation technique in limiting the contact between covellite (CuS) and oxygen has been developed using a simple, hassle-free, non-corrosive, and eco-friendly pre-treatment of nitrogen approach. This remediation technique is remarkably effective as various techniques such as powder XRD, EDX, elemental mapping, and TGA-MS analyses have confirmed that covellite prepared with the pre-treatment of nitrogen does not oxidize to any mixed phase compound. Meanwhile, the study also shows that covellite stored without the pre-treatment of nitrogen has transformed to a mixed phase of pentahydrate copper sulfate and covellite. Hence, this method can be practically exercised not only on covellite, but possibly on other metal sulfides which are prone to be attacked by oxygen and water molecules in oxidizing environment.

Introduction

Copper sulfides have been prospectively applied as p-type semiconductor in solar cell [1-2], photovoltaic and photodetector [3], nonlinear optical material [4], cathode material in lithium rechargeable batteries [5], thermoelectric cooling material [6], catalyst [7-8], and chemical sensor [9]. Consequently, the fabrication of this material has been of intense attention from both industries and academics. Since most of the sulfide compounds are prone to be oxidized to their respective sulfates and oxides [10], the degradation of sulfide materials might lead to the loss of active surface area and more importantly, the loss of functionality with respect to their useful applications. From the past, vast literatures have been extensively studied for the methods to produce phase pure copper sulfides. Nevertheless, the appropriate storage and effective handling of the prepared phase pure copper sulfides to sustain the phase purity of this material have always been neglected. For other metal sulfide such as pyrrhotite (Fe1-xS), there are ideas of employing different types of dry and organic covers, such as clay, soil, peat, hay, straw, sawdust, sludge or compost which could help to prevent or limit the contact between pyrrhotite and oxygen [11-13]. It was also reported that pyrrhotite can be stabilized in combination with a binder, neutralizers, bactericides or surfactants [14-15]. These methods are commonly exploited to prevent the oxidation of iron sulfide. However, the suggested methods might impose additional predicaments with regards to higher cost, more time, and hassle-leading procedures during the preparation of the oxygen inhibiting agents. Herein, we investigate the effectiveness of N₂ pre-treatment remediation technique to prevent the oxidation of covellite (CuS) in comparison to the storage of covellite without the pre-treatment after a selected time intervals.
Materials Synthesis. The reagents used in this study are of analytically pure and used without further purification. In a typical synthesis, the preparation of covellite was carried out by reacting 0.025 mol of copper nitrate (Cu(NO₃)₂·2½H₂O, Sigma Aldrich) with 0.050 mol of sodium thiosulfate (Na₂S₂O₃·5H₂O, Merck) in 40.00mL of deionized water. The solution was mixed thoroughly under constant stirring for 15 minutes; homogeneous solution was formed, which was then transferred into a sealed 100mL Teflon-lined stainless steel tube in a rotating furnace. The rotating furnace was maintained at 155.0°C for 12 hours and cooled to ambient temperature. After the reaction has completed, the Teflon-lined stainless steel tube was allowed to cool at ambient temperature. The obtained product was washed with batches of deionized water until the final filtrate showed conductivity of less than 10µS/cm. The collected product was then dried overnight in a vacuum desiccator which consisted of silica gel as drying agent at ambient temperature. To study the phase transformation of covellite (CuS) towards mixed phase of covellite and copper sulfate (CuSO₄), 2 batches of similar products were generated. The first batch of sample was subjected to pre-treatment of nitrogen by allowing the flow of purified nitrogen gas for 3 minutes through a tube connecting into a sample holder which consisted of sample; while the other one was done without the pre-treatment. Both of these samples were then capped in a separate sample bottle and stored in a cool and dark place for selected time intervals. The powder X-ray Diffraction (XRD) patterns of the stored products were taken after 1 week, 4 weeks, and 12 weeks of synthesis time to determine their crystal phase transformation. In addition, the stored products from these two approaches after time interval of 12 weeks were also analyzed by different techniques such as, Field Emission Scanning Electron Microscopy (FESEM), Energy Dispersive X-ray (EDX), elemental map, and Thermogravimetric Analysis coupled to Mass Spectroscopy (TGA-MS) analyses to investigate the surface and structural changes occur on these 2 samples.

Materials Characterizations. The synthesized products were characterized by X-ray powder Diffraction (XRD) using a Bruker X-ray Diffraction Model D-8 equipped with a Cu Kα monochromatized radiation source (λ=1.5406 Å) in the range of 4°≤ 2θ ≤ 80°. Field Emission Scanning Electron Microscopy (FESEM) images were taken with a FEI Quanta 200 FESEM. The surface elemental compositions of the formed products were done by using Energy Dispersive X-Ray Spectrometer (EDX) on INCA Energy 400 software from Oxford. The TGA results were acquired using NETZSCH STA 449C device. The thermal analyses were conducted in 100% Ar gas with heating rate of 5 K min⁻¹ and flow rate of 70cm³min⁻¹. The NETZSCH STA 449 C TG-DSC unit is coupled with Quadrupole Mass Spectrometer (Thermostat, Balzers) in order to characterize the evolved gas products.

Results and Discussion.

Phase Stability of Covellite with and without Pre-Treatment. The powder XRD patterns of the products prepared with pre-treatment of N₂ gas are illustrated in Fig. 1. It can be observed that all the salient peaks arose from the diffractogram correspond well to hexagonal covellite (CuS) which can be indexed to PDF 06-0464. It can be noted that the phase pure covellite has not transformed to any other mixed phase compound after 12 weeks of storage. The time interval was then further extended to 24 weeks. To our surprise, the sample exhibits similar XRD pattern which signifies that the sample is stable and does not transform to its sulfate or oxide even after 24 weeks of storage under N₂ environment. In contrast, the sample which was prepared without the pre-treatment of N₂ gas was found to be a phase pure covellite initially was transformed to a mixed phase of covellite and pentahydrate copper sulfate (PDF 77-1900) after 12 weeks of storage (Fig. 2c). This shows that covellite without the pre-treatment of N₂ gas has been oxidized where the presence of oxygen and moisture in the air might induce the diffusion of oxygen and moisture molecules into the crystal framework of covellite. Therefore, we believe that the pre-treatment of N₂ gas prior storage is able to chemically stabilize the crystal structure of covellite from oxidation process.
Fig. 1. XRD profiles of products with pre-treatment after (a) 1 week (b) 12 weeks (c) 24 weeks.

Fig. 2. XRD profiles of products without pre-treatment after (a) 1 week (b) 4 weeks (c) 12 weeks.

**Surface and Structural Properties of Phase Transformed Covellite.** A number of characterization tools have been applied to ascertain the phase stability of covellite under pre-treatment of \( \text{N}_2 \) gas besides to identify the differences in structural, surface and thermal features of the phase pure and mixed phase covellite powder. The morphology of the covellite prepared with pre-treatment was studied by FESEM as shown in Fig. 3. It can be observed that highly agglomerated structure which is built by many hexagonal nanoplates was formed. The FESEM images were also captured on sample prepared without pre-treatment of \( \text{N}_2 \) gas and no significant change on the morphology of the phase transformed covellite can be observed as the distinguished hexagonal nanoplates could still be detected.

Fig. 3. FESEM image of phase pure covellite.

Fig. 4. FESEM images of phase transformed covellite.
In order to verify the atomic composition on the surface of covellite nanoplate, several spots and areas of phase pure covellite have been selected to undergo EDX analysis (Fig. 3). The results of EDX analysis of phase pure covellite are tabulated in Table 1. The detailed examination of covellite prepared with pre-treatment of N₂ gas suggests that the relative atomic composition of Cu: S is quite closed to each other, approaching percentages of almost 50: 50. Furthermore, the elemental map (Fig. 5a.) reveals that the distribution of Cu and S are homogeneous on the surface of covellite. The EDX and elemental map analyses point out that the results strongly agree well with the nominal stoichiometric of covellite, which is of 1: 1 of Cu: S. In comparison, EDX analysis on the covellite prepared without pre-treatment of N₂ gas has recorded high percentages of O element on its surface (Table 2). This is further supported by the elemental mapping analysis where the sample is found to rich in O element apart from Cu and S elements on its surface as depicted in Fig. 5b. Thus, it can be deduced that the O element detected on the surface of covellite might be resulted from the pentahydrate copper sulphate which was discovered from powder XRD analysis. The surface degradation encountered by the phase transformed covellite reveals that pre-treatment of nitrogen is important to act as a shield to protect this air-sensitive material from the intrusion of oxygen or moisture onto the surface layer of covellite.

<table>
<thead>
<tr>
<th>Area/ Spot</th>
<th>Cu Atomic %</th>
<th>S Atomic %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Area A</td>
<td>51.53</td>
<td>48.47</td>
</tr>
<tr>
<td>Area B</td>
<td>50.23</td>
<td>49.77</td>
</tr>
<tr>
<td>Spot C</td>
<td>48.28</td>
<td>51.72</td>
</tr>
<tr>
<td>Spot D</td>
<td>51.40</td>
<td>48.60</td>
</tr>
<tr>
<td>Area E</td>
<td>50.52</td>
<td>49.48</td>
</tr>
<tr>
<td>Spot F</td>
<td>50.55</td>
<td>49.45</td>
</tr>
<tr>
<td>Spot G</td>
<td>50.24</td>
<td>49.76</td>
</tr>
</tbody>
</table>

*Area or spot taken with reference to Fig. 3.

Table 2. EDX analysis of phase transformed covellite.

<table>
<thead>
<tr>
<th>Area/ Spot</th>
<th>Cu Atomic %</th>
<th>S Atomic %</th>
<th>O Atomic %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spot A</td>
<td>41.12</td>
<td>40.10</td>
<td>18.78</td>
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<td>Spot B</td>
<td>25.00</td>
<td>27.65</td>
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<td>Area C</td>
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<td>45.37</td>
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<tr>
<td>Area D</td>
<td>36.29</td>
<td>37.42</td>
<td>26.29</td>
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<tr>
<td>Area E</td>
<td>36.97</td>
<td>46.13</td>
<td>16.90</td>
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</tbody>
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*Area or spot taken with reference to Fig. 4.

Fig. 5. Elemental map of (a) phase pure covellite (b) phase transformed covellite.

**Thermal Properties of Phase Transformed Covellite.** The thermal property of both the phase pure and phase transformed covellite was studied by TGA-MS under inert atmosphere. For the sample prepared with pre-treatment of N₂ gas, three significant weight losses can be recognized from the TG curve as displayed in Fig. 6. A slight weight loss happened from 311-621 K can be attributed to the...
loss of moisture and crystallization water which is evidenced by the MS result where 2 intense peaks at m/z of 18 analogous to water were detected at 338 and 571 K. This is followed by the weight loss at 618-743 K which can be related to the decomposition of covellite with the formation of sulfur deficient compounds, i.e. anilite (490-621K) and chalcocite (622-743 K) [16-17]. In the entire heating process, no peak arising from the evolution of SO₃ products (such as m/z of 48 or 64) is detected from the MS technique. This has strengthened the phase pure identity of the covellite preserved under nitrogen pre-treatment coupled with the different analytical results discussed previously. On the other hand, it can be noticed that the phase transformed covellite undergoes a quite similar thermal decomposition as compared to phase pure covellite. Nevertheless, the MS results of the transformed material (Fig. 7) confirm that 2 defined peaks (m/z of 48 and 64) identified at 591 K are corresponded to the gaseous products of SO and SO₂ respectively. From these thermal analyses, it is obvious that the presence of crystallization water alone in the framework of covellite is not sufficient to oxidize covellite to its sulfate. The oxidation of covellite, in this case can only happen if it is in contact with air or most probably in the presence of oxygen. Therefore, this analysis has again implied that the pre-treatment of N₂ gas provides a protective layer to copper sulfide which chemically stabilizes its crystal structure that prone to oxidation.

Conclusions

In a nutshell, a promising and effective storage method in preserving covellite from further oxidation has been demonstrated by an easy, hassle-free, non-corrosive, and environmental-friendly pre-treatment of N₂ approach. This treatment can be broadly applied to preserve covellite or even other metal sulphides from further deactivation and oxidation.
Acknowledgements

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References


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