Sulphidization of Metal Oxides by Means of Mechanochemical Solid Reaction

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Co-grinding nonferrous metal oxides and sulphur together with iron/aluminium metal stimulates a solid-state reaction to form the nonferrous metal sulphides and iron/aluminium oxide, allowing the use of the current mineral processing technologies to recover metals from various kinds of wastes.

Metals are the key materials to support material civilization. They have been widely used and a vast amount of waste arises after the use of the materials. In the cases of nonferrous metal such as Cu, Pb, Zn in Japan, for example, amount as high as 10–30% of their outputs annually has been discarded in various types of waste. Recycling these metals from the wastes are highly required from the points of environmental resource preservation and sustainable development. These metals are mainly obtained by processing sulphide minerals such as sphalerite (ZnS), ganela (PbS), and charcopyrite ($CuFeS_2$). There have been existing efficient technological systems to process these sulphide minerals. However, the states of metals in the wastes are rare in sulphide but oxide and oxidized compounds besides metals. When a simple and reliable method to sulphidize the metals in the waste is developed, the existing mineral processing and metallurgical technologies can be applied to treat these synthetic sulphides, making the metal recycling system feasible technologically and economically, compared to the difficulty in the specific development of a new recycling processes for each specific kind of wastes.[1–5] Efforts have been reported for the sulphidization, such as high temperature reaction and precipitation from solution using H_2S and other sulphides.[6,7] As the sulphides are used as sulphidizer, it is difficult to avoid the secondary emission of wastes as well as the release of toxic gases by these methods. In addition, it entails the acid leaching of the wastes to extract metals into solutions before the precipitation operation. On the other hand, little attention has been paid on the use of element sulphur,[8] of which such a great deal has been emitted as byproducts from oil refinery, besides the natural occurrence, that an overabundance state of supply has to be resolved.

Our research work has shown that a mechanochemical solid-state reaction induced by a simple grinding allows the use of sulphur sample to sulphidize both the metals and their oxides easily. The basic information is reported in this paper. A dry grinding of the starting samples was conducted to stimulate the solid-state reactions, using a planetary ball mill in air. Nonferrous metals of Cu, Pb, and Zn were chosen as the targets. The ground samples were mainly characterized by X-ray diffraction analysis to determine the phases. The reaction was also evaluated quantitatively by measuring the remaining sulphur in the ground sample through the CS_2 washing.

Each metal of Zn, Pb, and Cu was mixed with sulphur at equimolar ratio and ground for 60 min. The results are shown in Figure. 1. The results confirm that the following reaction occurs during grinding.

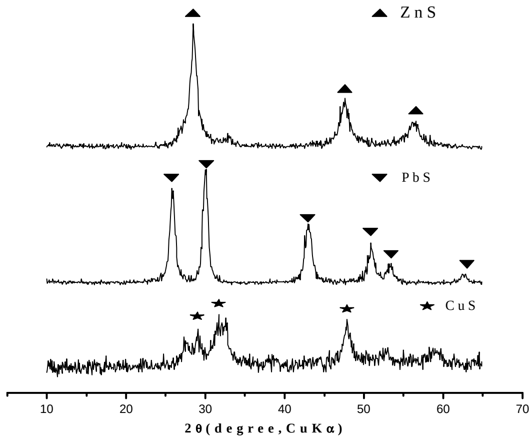

Figure 1. XRD patterns of the nonferrous metal (Zn, Pb, or Cu) and sulphur mixtures ground for 60 min.

$$M + S = MS \quad (M = Zn, Pb, Cu) \qquad (1)$$

In other words, the nonferrous metals can be simply sulphidized by just grinding with sulphur sample. In fact, the changes in the standard Gibbs free energy (ΔG_{298})[9] of the Eq. (1) are -200.4(Zn), -97.0(Pb), and -53.5 kJ/mol(Cu), respectively. The negative changes also suggest a thermodynamically feasible occurrence of the reactions. Similarly the mechanochemical reactions offer a easy method to synthesize sulphide materials.[10,11]

As for grinding the oxides with sulphur, the reaction given by Eq. (2) was not confirmed by XRD analysis because only the starting oxides and sulphur were detected after grinding.

$$MO + S = MS + 1/2O_2 \qquad (2)$$

In fact the oxides are more stable than the sulfides thermodynamically, and the reactions have positive ΔG_{298}: 120.1(Zn), 91.7(Pb), and 74.8 kJ/mol(Cu), respectively. How to transform these oxides into sulphides is vital in the sulphidizing treatment of wastes. Our further research has shown that it needs the use of additives, functioning as a reductant to the oxides. Additives such as iron and aluminium metals are found to be effective to induce the transformation. Using ZnO as a sample and iron powder as an additive, the occurrence of reaction (3) was confirmed by the results shown in Figure. 2.

$$4ZnO + 4S + 3Fe = 4ZnS + Fe_3O_4 \qquad (3)$$

With an increase in the grinding time, the peak intensity of the starting samples decreases and becomes unobservable in the pattern of the sample ground for 60 min. Only the peaks of reaction products are observed in the patterns of the sample ground for over 120 min. In addition, the ground samples were

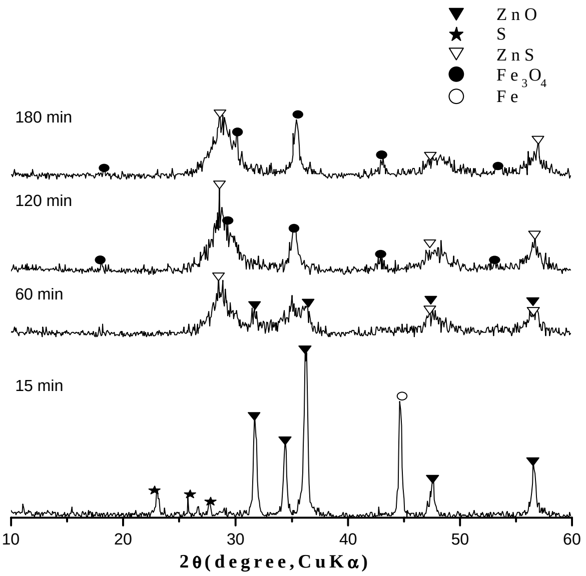

Figure 2. XRD patterns of the ZnO, S, and Fe mixture ground for different times.

washed with CS_2 solvent and the unreacted elemental sulphur was measured. Only 1.8% sulphur is remaining in the ground sample after 180 min grinding, indicating that the reaction (3) is almost completed by the time. The ΔG_{298} of reaction (3) is -534.9 kJ/mol (-133.7 kJ/mol of ZnO), confirming that the addition of iron converts a thermodynamically improbable reaction into a feasible one. Similar reactions occurred with other oxides such as PbO and CuO and even the mixtures of the oxides when iron was added, although the grinding time needed to complete the reactions varied. The iron oxide formed in the ground products is magnetite so that it may be separated by the magnetic separation. The formed sulphides can be recovered and separated by the traditional flotation separation.

When a pure sample of iron is used, there exists a concern about the cost. Fortunately, wastes containing iron metal at high concentration are released from various processes[12,13] and it is advisable to use these wastes as additives for a practical application. For example, tens of millions of used vehicles destroyed per year offers a vast amount of scrap iron. Besides, many recycling processes are also providing iron metal byproducts from various industrial and domestic wastes. However, the purity of the scrap iron or other byproducts is generally not so high and the presence of other metals such as copper prevents their direct application as raw material for steel-making. The byproducts offer an ideal additive for our sulphidizing process, where the heavy metals in the scrap iron may be sulphidized as well.

Similar to iron, the use of aluminium powders also brings about the transformation of the oxides into the corresponding sulphides, being accompanied by the formation of alumina, as shown in Eq. (4):

$$3ZnO + 3S + 2Al = 3ZnS + Al_2O_3 \quad (4)$$

And the ΔG_{298} of reaction 4 is -1223.6 kJ/mol (-407.9 kJ/mol of ZnO). Although it is economically impossible to use pure aluminium as additive to treat waste, this method offers a new approach to treat aluminium dross waste, which remains as an environmental problem for aluminium industry and needs proper treatment.[14,15]

In a general word, a novel metal recycling process is developed: two kinds of waste containing nonferrous metals (in oxide or metal) and iron/aluminium metals, respectively, are ground with sulphur sample to induce solid-state reaction to form nonferrous metal sulphides and iron/aluminium oxides. The existing mineral processing methods such as magnetic and flotation separation can be applied to the ground sample to recover the metals. The process also exhibits an environment-friendly merit because most heavy metals are sulphidized and recovered to leave the waste a non-hazardous residue that can be stored without problem or can be used in proper fields, besides the no emission of hazardous substance from the process itself.

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