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# 論文内容要旨

Not only crude oil and natural gas, metal resources will be exhausted in future. The number of year available for such mineral resources has been estimated to be less than 30 years for lead, zinc and tin. On the other hand, metal is different from oil and the natural gas and does not disappear when it is recycled. There exist possibility and necessity to recycle the metal from wastes not only to avoid the exhaustion of the metal resources but also to prevent environmental pollution.

Every year Japan consumes a large amount of nonferrous metals. However, the supply depends almost completely on the overseas mines (For examples: Copper: 99.9%, zinc: 92.0% at 2001). A simple and reliable method to sulfidize the metal oxides in a waste is quite reasonable for recycling these nonferrous metals compared to the difficulties in the specific development of new recycling process for each specific kind of waste. The use of sulfides in the reported sulfidization generally results in secondary contamination. On the other hand, little attention has been paid to the use of elemental sulfur. This sulfur has been emitted as byproducts from oil refineries and the mining industry, in addition to the natural occurrence, so that an inexpensive supply exists.

Once sulfur would be used for sulfidizing metal oxide by a simple method, it would be very useful to recover it from waste such as fly ash. The simple method would be a milling operation, due to non-thermal operation, leading to mechanochemical reaction. That is, it is known that milling operation induces mechanochemical changes including mechanochemical effects such as activation, amorphization and phase transformation and mechanochemical solid state reactions. There are increasing reports about mechanochemical phenomena involving almost every branch of chemistry, of which mechanochemical treatment of sulfide minerals to raise leaching kinetics and synthesis of some sulfides as functional materials are the examples.

A systematic investigation of sulfidization including complete sulfidization, surface sulfidization and minor sulfidization/sulfur doping by means of mechanochemical treatment using element sulfur as starting sample has been tried in this thesis. As the applications of mechanochemical sulfidization, development of a new metal-recycling process is attempted. Further development of minor sulfidization, namely doping sulfur, has been also tested for the synthesis of doped photocatalyst.

This thesis consists of six chapters, and followings are brief contents.

Chapter 1 has surveyed the importance and necessity about metal recycling and development of a new method for sulphidizing metals and metal oxides. Then, an introduction is made toward the understanding of mechanochemical effects and mechanochemical reactions.

Chapter 2 has dealt with the sulphidization reaction of nonferrous metal oxides such as CuO, ZnO by cogrinding with sulfur and iron powders as a reducer. The merit of this process is the use of elemental sulfur and there is no much concern over the release of secondary toxic wastes related to the sulfides. The mechanically induced solid-state reaction results in the formation of nonferrous metal sulfides without observable emission of other hazardous gases. As a reference, other oxides such as $TiO_2$ and $SnO_2$ are also examined. The necessary conditions to achieve such sulfidization are clarified by thermodynamic discussions on both successful reaction and unsuccessful one. Fe powder plays a significant role to reduce the oxides during the grinding, forming magnetite. There exists the tendency for the formation of iron sulfide during the grinding. The negative change in $\Delta G_{298}$ is not sufficient to cause the reaction to occur. Successful sulfidizing reactions exhibit a larger standard Gibbs free energy change in absolute value than the corresponding formation reaction of iron sulfide.

Chapter 3 has studied the surface coating of sulphur on nonferrous metal oxide under mild milling conditions. The improvement in the floatability of the oxide suspended in liquid under gaseous condition is achieved and discussed by analyzing the surface compositions of the coated oxide. Direct sulfidization reaction results in the sulfide product of heavy agglomerate. It is not easy to disperse and disaggregate these agglomerates. When grinding conditions are controlled so as to prevent the reaction, no agglomeration takes place. As show in Figure 1, the XPS analysis has indicated the difference between CuO sample and $SiO_2$ sample when ground with sulphur separately. The only observable S-S bonding means that sulphur is just in a physically mixed state with $SiO_2$ sample. The existence of S-O and S-Cu bonding confirms the chemically absorption of sulphur sample on the surface of CuO sample. As a result, the surface properties of CuO and $SiO_2$ sample ground with sulphur have changed in a different way. When the sulfur is coated on the surfaces of the oxides and the coated degree of sulphur on the oxides is found to be dependent on kind of oxide. This

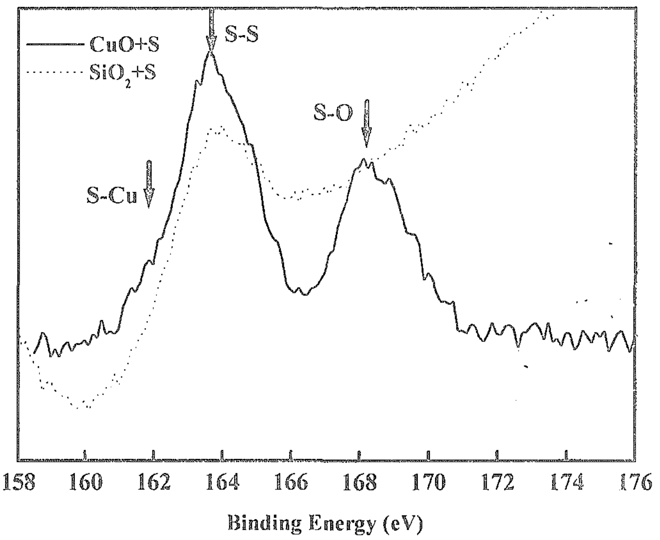

**Figure 1: The XPS analysis shows significant results**

phenomenon can be used to separate them.

Chapter 4 has introduced the synthesis of visible-light active photocatalyst by means of mechanochemical doping. It is well known that $TiO_2$ is generally a stable compound, and not easily doped by a nonmetal element. It is particularly difficult for $TiO_2$ to dope atom of big size such as sulfur. In order to dope nonmetal elements into $TiO_2$, one can heat $TiO_2$ at high temperature under gaseous environment such as $NH_3$, $H_2S$. However, the calcination of $TiO_2$ under $H_2S$ gas flow does not give always satisfactory results. Heating $TiS_2$ in air has been proposed to prepare S-doped $TiO_2$. The preparation of $TiS_2$ itself is not easy, not to say the enormous emission of $SO_2$ gas. Mechanochemical method allows the use of solid sulfur as the dopant and easy doping has been achieved. A visible-light active $TiO_{2-x}S_x$ photocatalyst can be synthesized by cogrinding $TiO_2$ with sulphur and subsequent heating at low temperature. As show in Figure 2, it is clearly observed that the reference sample (a) exhibits low photocatalytic activity by the irradiation of light with wavelength over 510 nm. On the contrary, about 20% NO has been removed in the range of the wavelength over 510 nm for sample (b), while nearly 40% NO is decomposed for sample (c). This means that sample (c) has a high photo-reactivity under visible-light irradiation. The photocatalytic ability of the prepared samples is found to be almost the same as that of the reference sample under ultraviolet light. Similarly sulfur doping to other oxides such as ZnO has been applied.

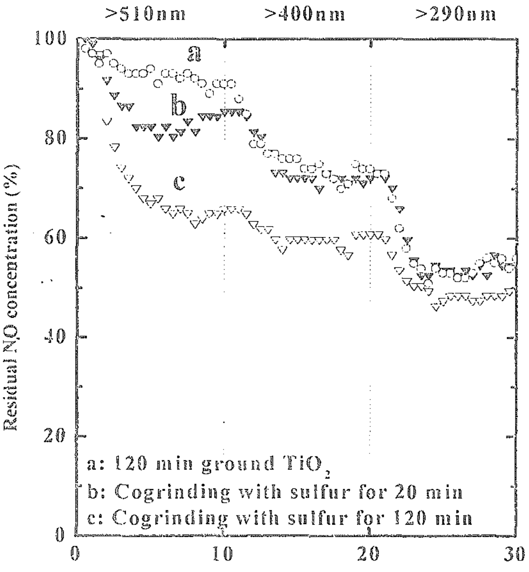

Figure 2: The relationship between light wavelength and the photocatalytic ability for the oxidation of NO of the prepared samples

Chapter 5 has discussed the doping of $TiO_2$ by cogrinding with $TiS_2$ and Raman spectroscopy has been done for the doped oxide. The solid state reaction between two compounds offers an easy doping operation without further heating treatment. This chapter introduces the basic information on the solid state reaction between $TiS_2$ and $TiO_2$ by means of mechanochemical method and evaluates the feasibility of Raman spectroscopic analysis for the doped oxide. When $TiO_2$ is doped with nonmetal elements, the oxygen stoichiometry will vary correspondingly. The line positions due to the Raman active Eg mode in $TiO_2$ have been reported to be sensitive to this oxygen deficiency. As show in Figure 3, it is interesting to note that, with an increase

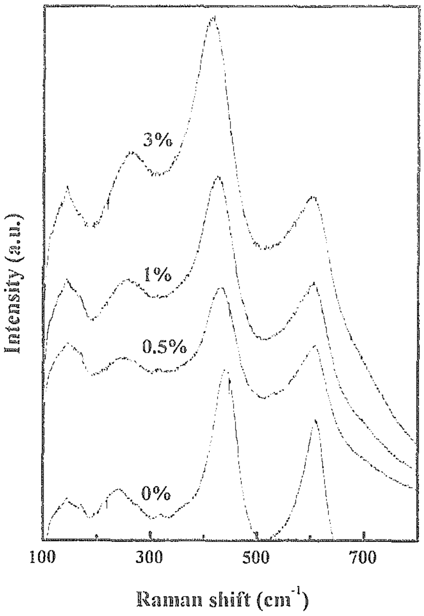

Figure 3: Raman spectra of the samples ground for 120 minutes with different added molar ratio of $TiS_2$

in added molar ratio of $TiS_2$, the peak 438 $cm^{-1}$ (Eg) mode has demonstrated a further clear shifting to a lower mode based on the ground sample without $TiS_2$ addition while the peak 609 $cm^{-1}$ related to Ti-O stretch mode shows little shifting compared with the peak 438 $cm^{-1}$. Because both samples with and without $TiS_2$ additions were ground under the exactly same conditions, effects of defects, strains and impurity doping resulting from the grinding treatment may be considered to be equal.

Chapter 6 has summarized the experimental results and conclusions drawn from the works done in each chapter. It is concluded that the investigated mechanochemical sulfidization is applicable for recycling metals from wastes and preparing sulfur-doped photocatalyst.

# 論文審査結果の要旨

非鉄金属鉱石の国内自給率は、極めて少なく、多くは海外に大きく依存している。一方、非鉄金属は種々の形態で一般ならびに産業廃棄物焼却飛煤に含まれている。わが国における一般ならびに産業廃棄物の排出量は約5000万t/年で、内，産業廃棄物は約4億t/年と膨大な量であり，含有する有価物のリサイクルが資源の有効利用の観点から極めて重要である。焼却飛灰に含まれる金属は，通常，酸化物の形態にあり，したがって，非鉄金属も同様である。焼却飛灰に含まれる非鉄金属酸化物は有望な資源であり、その簡便な回収法の確立は，未利用資源の有効利用と環境保全の立場からも急務である。一方，$TiO_2$は，紫外光応答型光触媒として最近注目されているが，これに窒素（N）や硫黄（S）をドーピングすれば，バンドギャップが低下し，可視光にも応答可能な光触媒となり，環境保全に貢献する。特にSはわが国には余剰にあり，その有効活用が望まれている。

本論文では，焼却飛灰中の非鉄金属酸化物を簡便に回収する手法として，メカノケミカル法による非鉄金属酸化物の硫化についての基礎研究を行い，その結果を踏まえて，浮選法によって簡便に回収するプロセス開発を行った。次いで，チタニア（$TiO_2$）粉末にSを添加して乾式粉砕（メカノケミカル処理）し，酸化物を部分硫化する処理を行い，その可視光応答性をNOガス分解能によって評価する実験を行った内容を纏めたものであり，全編6章よりなる。第1章は，緒論であり，本研究の背景，過去の研究をレビューし，その上で，本研究の目的を述べている。

第2章は，メカノケミカル法により，非鉄金属酸化物の硫化の機構を実験と熱力学的検討を行い，硫化する上での必要条件と十分条件を明確にした。

第3章は，微粒子凝集を防止したマイルドなメカノケミカル処理条件で非鉄金属酸化物にSを添加して処理し，前者を部分硫化し，浮選法によってそれを回収する手法を提案し，実際の焼却飛灰にも適用し，含有する非鉄金属酸化物の回収について実証している。

第4章は，$TiO_2$へのS添加によるメカノケミカル硫化による光触媒調整についての検証し，部分硫化によるNOガスの酸化性評価を行い，処理効果を明確に示した。

第5章は，$TiO_2$と$TiS_2$とのメカノケミカル硫化について検討し，第4章と同様の触媒能を示す物質を合成し，そのNOガスの酸化性評価を行った。

第6章は，結論である。

これらの結果は，環境科学と素材工学の分野に寄与するところ少なくない。

よって，本論文は博士(学術)の学位論文として合格と認める。