Reclaim of Rare Earth Metals from Bond Magnets by Means of Thermally Activated Semiconductors (TASC)

Y. Tsukada, H. Takahashi, M. Kaneko and J. Mizuguchi

Fiber Innovation Incubator, Faculty of Textile Science and Technology, Shinshu University, Ueda 386-8567, Japan

Recovery of rare earth metals from bond magnets has been investigated by means of thermally activated semiconductors (abbreviated to TASC). TASC is a novel technology developed recently by us, allowing to decompose any organic materials including polymers in an instant into H2O and CO2. This technology has been utilized in the present investigation to reclaim rare earth metals from bond magnets by removing only polymer binders while retaining mostly the original composition of magnets. The TASC technology is based on our accidental finding that the semiconductor exhibits significant oxidative catalytic effects when heated at about 350-500°C. The initial process of the polymer decomposition is the capture of bonded electrons to create cation radicles in polymers. Then, the unstable radicles propagate throughout the polymer chains to make the whole polymer unstable, resulting in the fragmentation of the polymer into tiny molecules such as ethylene, propane etc. These fragmented molecules end up with reaction with oxygen in air to give rise to H2O and CO2. In this way, rare earth metals are successfully reclaimed from bond magnets in about one-two hours in the form of powders.

(Received November 19, 2013; Accepted December 27, 2013; Published February 15, 2014)

Keywords: rare earth metal, thermally activated semiconductors, recovery of metals

1. Introduction

As is well known, rare earth metals are nowadays widely used as materials for permanent magnets,1,2) polishers of optical glasses,3) catalysts,4) phosphors,5) magnet-optic storage system,6) etc. Rare earth metals are no more scarce resources as their name once implied. The amount of the reserve is said to be about 130 million tons, of which about 48.3% is held by China. In addition, the production of rare earths is centered on China and its market share is about 97% in 2009. The present situation really reflects the state of oligopoly (i.e., a state of seller’s market). Because of this, the supply of rare earth metals can easily be influenced by political situations and thus unstable at times. In addition, the price has constantly and drastically been rising every year. In order to obviate the present situation, it is urgently necessary to break up the rare-earth suppliers into several countries other than China. At the same time, we need to accelerate the reclaim and reuse of rare earth metals from the disposals.

Bond magnets are made of magnetic powders together with a minute amount of polymers used as the binder and prepared by means of injection molding in combination with thermoplastic polymers, or compression molding together with thermosetting polymers. Bond magnets are especially preferred because the magnets of desired shapes can easily be prepared with low costs. In addition, bond magnets are also appropriate for those magnetic powders (for example, Sm–Fe–N, Nd–Fe–B etc.) whose composition can be deviated from the original one during the conventional sintering process at high temperatures. The filling factor (or packing density) of magnetic powders is about 97 mass% when thermosetting polymers (for example, epoxy or phenol resins) are used as the binder; whereas about 93 mass% for thermoplastic resins (for example, polyamides).

In the present investigation, we aim at reclaiming rare earth metals from bond magnets by decomposing only polymer matrix alone, utilizing thermally activated semiconductors (TASC).7–10)

2. Outline of the TASC Technology and an Example of Complete Decomposition of Polycarbonate (PC) by TASC

The TASC technology is characterized by the use of highly oxidative holes generated by thermal excitation of semiconductors. Since the decomposition is carried out in air (i.e., in an oxygen atmosphere) at high temperatures, oxide semiconductors such as TiO2, ZnO, Cr2O3, Fe2O3 etc. are the semiconductor of choice. Among these, we are particularly interested in Cr2O3 because of its high stability (melting point: about 2200°C). In addition, its safety is ensured as shown by the fact that Cr2O3 is widely used in our daily life as the green colorant for glass dyeing of whisky or wine bottles etc.

At first, we describe the optical excitation of semiconductors together with its subsequent photoconducting phenomenon [Fig. 1(a)] and then discuss the oxidative property of holes. When the semiconductor is excited by a photon whose energy is larger than the band gap, then an electron in the valence band is excited to the conduction band, leaving behind a positively-charged defect electron called hole in the valence band. Both electrons and holes are mobile and thus contribute to the increase in electrical conductivity. This is known as the photoconducting phenomenon. We focus here on the property of holes. The hole is known to strongly attract an electron from the conduction band or from organic compounds adsorbed on the surface in order to bring back the semiconductor to the original stable state. In other words, the hole has strong oxidation ability. These oxidative holes are utilized in photocatalysts for decomposition of organic compounds adsorbed on the surface. However, the decomposition performance is known to be quite poor. Then, an important question arises how we can construct a strong oxidation system with semiconductors. Then, we simply believed that we could achieve it by creating a vast number of holes in the valence band by exciting the semiconductor with higher light intensity. However, this is
not the case. The electrons and holes are immediately recombined after excitation, because the light excitation occurs only on the surface of semiconductors where there are a number of carrier recombination centers due to lattice defects. Therefore, the increase in electrical conductivity is limited to, at most, one order of magnitude. Then, we considered instead the thermal excitation [Fig. 1(b)] which is the bulk excitation rather than the surface one. The number of electrons and holes increases in accordance with an exponential function of temperature according to the semiconductor theory. 11) In fact, our experiment using a single crystal of TiO₂ showed that the resistivity is about 10¹¹ Ω cm at RT. However, the resistivity is remarkably reduced to only 15 Ω cm at 500°C. 9) That is, the resistivity is reduced by ten orders magnitude! This clearly indicates the formation of a vast number of charge carriers. This is actually the effect of the TASC that we found which leads to the appearance of significant catalytic effects. 7–10) In this way, we finally achieved a very strong oxidation system with thermal activation of semiconductors.

We will show below an example of the instantaneous, complete decomposition of polycarbonate (PC used as the substrate for compact discs) by means of TASC. 8,9) We carried out an experiment using two glass tubes, each of which contains PC chips in the presence or absence of TiO₂ used as a semiconductor. These were heated at 500°C for 30 min in air. The PC in the absence of TiO₂ melted at about 200°C and then boiled, ending up with the carbonization. This is a typical result when a plastic is roasted in air. On the other hand, no trace of PC was recognized in the presence of TiO₂. Here remain just white powders of TiO₂. Gas analysis of the decomposition product was made by mass spectrometer and the result is shown in Fig. 2(a). 8) Since the experiment was performed in air, we see peaks of N₂ (28) and O₂ (32) that are components of air, as well as peaks of H₂O (18) and CO₂ (44). Furthermore, we observe a peak of Ca (40). This is due to a metallic soap of Ca used as a lubricant in optical discs. The present result indicates that PC (molecular weight: about 25,000) has entirely been decomposed into H₂O and CO₂ in an instance. This is an amazing effect! On the other hand, when the experiment was carried out under vacuum, we see a number of small fragments as shown in Fig. 2(b). However, these peaks disappear in an oxygen atmosphere, leaving only two peaks of H₂O and CO₂. This clearly indicates that oxygen is absolutely necessary for the disappearance of fragment peaks.

On the basis of the above experiments as well as those by electron spin resonance (ESR) for radicals, we proposed the destruction mechanism as shown schematically in Fig. 3. 8,9) The first process of the decomposition reaction is the capture of bonded electrons from polymers by defect electrons,
leaving behind cation free radicals. The free radical is unstable and can propagate throughout the polymer chain at 350–500°C. This makes the whole polymer chain unstable and induces a “radical splitting”. This results in the fragmentation of the giant molecule, in a fashion, just “the reverse of radical polymerization”. The fragmented molecules then react with oxygen in air to give just H2O and CO2. To summarize the destruction mechanism, the process is composed of the three steps: 1. oxidation, i.e., creation of radicals, 2. radical splitting, i.e., fragmentation of the giant molecule, and 3. reaction with oxygen, i.e., complete combustion.

Up to now, we have achieved complete elimination of various volatile organic compounds by TASC: toluene & benzene,10) chloro-based organic solvents,12) formaldehyde.13) The TASC technology has also been applied to the recycling of reinforcing fibers from FRPs (fiber-reinforced plastics).14,15) Furthermore, metals have also been recovered from mold motors in about 20 min at about 400°C.15)

3. Experiment

3.1 Materials and equipment

Cr2O3 powders (purity: 99%; specific surface: 3 m2/g) were purchased from Junsei Chemical Co., Ltd. α-Fe2O3 powder (specific surface: 4.1 m2/g) was obtained from Toda Kogyo Corporation.

Two kinds of bond magnets J16 and K12, based upon the composition of Nd–Fe–B/Sm–Fe–N, were obtained from Nichia Corporation. These are tablet magnets (size: 10 mm in diameter and 7 mm in height). The magnets are prepared by injection molding using polyamide 12 (PA12) as the binder for J16, or using polyphenylene sulfide (PPS) for K12. According to the WEB information, fine particles of Sm2Fe17N3 (about 3 µm in diameter) are added to the coarse particles of Nd5Fe14B (about 30–200 µm in diameter) so as to fill the void of Nd–Fe–B in an attempt to minimize the stress concentration and thus to suppress the mechanical destruction. Therefore, the bond magnets are a mixture of the two components: Sm2Fe17N3 and Nd5Fe14B.

Bond magnets of Wellmax S3A (Composition: Sm–Fe–N) were purchased from Sumitomo Metal Mining Co. These are also tablets prepared by injection molding using PA as the binder: 20 mm in diameter and 13 mm in height.

An energy dispersive micro X-ray fluorescence spectrometer (Shimadzu: µEDX-1300) was used for measurements of metal contents. The X-ray beam diameter is about 50 µm. A scanning electron microscope (SEM) of VE-8800 from Keyence Corporation was used for SEM pictures.

3.2 Procedure for the removal of polymer matrix in bond magnets

First, the bond magnets were coated with a dispersion layer of Cr2O3 or α-Fe2O3 (thickness: about 5 µm) by dipping the magnets into an acetone suspension containing powders of Cr2O3 or α-Fe2O3, as well as a minute amount of polymers as the binder. Next, the bond magnets were heated at 500°C for 20 min in air in a muffle furnace in order to decompose the polymer binder into H2O and CO2 with our TASC technology. This process is called hereafter TASC-treatment.

4. Result and Discussion

4.1 Removal of polymer matrix in bond magnets

TASC-treatment was carried out on the bond magnets as described above. However, even after TASC-treatment, the magnets of J16, K12, and Wellmax S3A remained still rigid retaining the original form and could not be pulverized by grinding in a mortar with a pestle. The present situation was obviously different from the conventional recovery of reinforcing fibers from FRPs13) or coils from mold motors15) that revealed the fibers or the coils immediately after TASC-treatment. Although the TASC-treated magnets remained rigid, we were confident that all polymer must have surely been decomposed into H2O and CO2 according to our experience up to now, and thus believed that there must be another cause which governs the rigidity of the bond magnets. Then, we noticed that there is a huge difference in filling factor, or packing density, between bond magnets [i.e., extremely high about 93–97 mass% (see 1. Introduction) and FRPs or mold motors (about 70 mass%)]. This prompted us to assume that the magnetic particles must have been slightly sintered during the injection molding and that the present sintering might be responsible for the stiffness of TASC-treated samples.

4.2 Sintered magnetic particles and their separation

Figure 4 shows the assumed schematic representation for the lightly-sintered grain boundaries between magnetic particles with a minute amount of polymer binder. Our assumption is that the magnetic particles are held together by a binder before injection molding and then become slightly sintered during the injection molding. As a result, all polymers are supposed to decompose into H2O and CO2, giving rise to narrow channels between the grain boundaries as caused by the vanishment (i.e., decomposition) of binders. As is well known, the grain boundary possesses a relatively high energy and serves as a barrier for the charge transport of free carriers in semiconductors. For this reason, we often etch the high-energy grain boundary with an acid in order to distinctly study the topology of grain boundaries. This trick motivated us to dissolve the lightly-sintered area with a diluted acid such as hydrochloric acid so as to dissolve and separate sintered particles (i.e., pulverization). We also assumed that infusion or penetration of an acid into the grain boundaries proceeds efficiently as assisted by the capillary effect.

![Magnetic particle](image-url)
4.3 Pulverization of lightly-sintered bond magnets that possess channels created by decomposition of polymer binders

In accordance with the above trial, we prepared a diluted hydrochloric acid of about 10% in order to etch the grain boundaries. Experiments were carried out in a beaker of 100 ml in a N₂ box. As soon as a TASC-treated tablet was immersed into the diluted HCl, small bubbles began to appear on the surface of the tablet, but quite slowly. After one min, the diluted acid penetrates well into the channels between grain boundaries and a great deal of bubbles were evolved from the tablet. Then, the Cr₂O₃ or α-Fe₂O₃-layer on the surface of the tablet was easily detached from the tablet. The evolved gas was found to be H₂ resulting from the following reactions: 2Sm + 6HCl → 2SmCl₃ + 3H₂; 2Nd + 6HCl → 2NdCl₃ + H₂; Fe + 2HCl → FeCl₂ + H₂. After 3 min, the tablet was taken from the beaker and washed with de-ionized water, and dried at about 80°C for one hour in an N₂ atmosphere. Then, the tablet was placed in a mortar and ground easily into powders with a pestle. In this way, we have succeeded in reclaiming rare earth metals from bond magnets. We believe that our assumption (i.e., slight sintering of the magnetic particles) was right and that the dissolution of the sintered layer led to the successful pulverization of the lightly-sintered particles. It should also be noted that the use of a diluted acid is crucially important for the dissolution of metals, because concentrated acids often lead to the passivation of the metals.

Diluted sulfuric acid or nitric acid can be used in place of hydrochloric acid.

4.4 Characterization of the reclaimed rare earth powders

The recovered powders from J16, K12, and wellmax S3A are well attracted to a magnet. This shows that the metals are mostly unoxidized in view of the fact that the oxide of rare earth metals exhibit no ferromagnetism.

Figure 5 shows the pictures for the tablets and reclaimed powders: J16 and K12 treated with Cr₂O₃, and wellmax S3A treated with Cr₂O₃ or α-Fe₂O₃. The powders of J16 and K12 bear slightly reddish color; whereas the wellmax S3A powders look pure black. Figure 6 shows the SEM pictures for J16 and K12 as well as wellmax S3A before and after TASC-treatment: (a) J16 before treatment, and after treatment with Cr₂O₃, (b) K12 before treatment, and after treatment with Cr₂O₃, (c) wellmax S3A before treatment, and after treatment with Cr₂O₃ or α-Fe₂O₃.

X-ray fluorescence analysis was also carried out on reclaimed powders. Figures 7(a) and 7(b) show the intensity ratio of Sm/Fe and Nd/Fe for J16 before TASC-treatment; whereas Fig. 7(c) illustrates those for J16 after treatment. Likewise, Figs. 7(d) and 7(e) show the result for K12 before treatment, while Fig. 7(f) for K12 after treatment. In these samples, measurements were made for 10 sampling spots for each ten samples. The analytical values are, however,
extraordinarily scattered. This is attributed to the X-ray beam size as well as to the two component system based on Nd–Fe–B/Sm–Fe–N. In addition, the particle size plays a decisive role, as described in Section 3.1: Nd$_2$Fe$_{14}$B (about 30–200 µm in diameter) and Sm$_2$Fe$_{17}$N$_3$ (about 3 µm in diameter). Therefore, the analytical values measured with an X-ray beam diameter of about 50 µm can basically vary from one sampling spot to another, depending on the sampling area of the two-component system. As judged from the present situation, it scarcely makes sense to discuss the component ratio of the two-component system before and after TASC-treatment.

On the other hand, wellmax S3A is composed of one single component of Sm–Fe–N, and thus the analytical result is expected to be reproducible. Figures 8(a) and 8(b) show the intensity ratio of Sm/Fe measured for ten points in each ten samples, and those of reclaimed powders, respectively. No significant difference in composition is recognized before and after TASC-treatment. This provides us with a high potential for the use of the TASC-technology for the recycling of bond magnets.

5. Conclusion

TASC technology has been applied to the reclaim of rare earth metals from bond magnets. The result of the present investigation can be summarized as follows:

1. TASC is characterized by the use of oxidative holes in semiconductors heated at high temperatures.
2. Magnetic powders can be reclaimed in about one-two hours from bond magnets by TASC-treatment and the original composition appears to be well retained in reclaimed powders.
3. The key to the successful reclaim of metal powders is the dissolution of the lightly-sintered layers in grain boundaries by means of a diluted acid.
4. The present TASC technology opens up a new horizon for the reuse of the bond magnet disposals.

REFERENCES

Reclaim of Rare Earth Metals from Bond Magnets by Means of Thermally Activated Semiconductors (TASC)