

A soft-solution process for recovering rare metals from metal/alloy-wastes by grinding and washing with water

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Abstract

We have developed a novel process for recovering metals from alloy-wastes by using a mechanochemical (MC) reaction. The process consists of co-grinding both alloy and polyvinyl chloride (PVC) samples, followed by washing with water and filtration. The co-grinding of the wastes causes a solid-state MC reaction to form metal chlorides and hydrocarbon in the product. The former products are soluble in water, so they can be recovered from the wastes by washing with water, followed by filtration. The PVC waste plays a significant role as a chlorine source in the MC reaction. After filtration, the solid residue can be used as a fuel, due to the absence of chlorine in the product, and the filtrate is subjected to hydrometallurgical process to extract metals from the solution.

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1. Introduction

Some of functional metal and alloy products such as permanent magnets and electric parts contain precious metals such as Co, La, Ni. These products are fate to dispose after usage, but they should be recovered from the point of sustainable development. Similarly, polyvinyl chloride (PVC) is a popular plastic and has been widely used in various fields. After the usage, it is also fate to dispose. When the PVC is burned out in a furnace without any temperature control, a great amount of toxic substances such as HCl and dioxins would be formed [1]. This implies that dechlorination of PVC wastes would be crucial in their waste treatment. Several methods have been proposed to recycle PVC waste; one is material recycling, second is chemical recycling [2] and the last the thermal one [3]. Especially, dechlorination of PVC waste is very important chemical recycle operation. Zhang et al. [4–6] have proposed a new process for dechlorination of PVC wastes and other chlorinated compounds. However, little attention has been paid on the process for recovering metals from alloy-wastes by reaction with PVC waste. An attempt is made to develop a process for recovering metals from a waste by its co-grinding with PVC in air, followed by washing with water and filtration [7]. The co-grinding

causes mechanochemical (MC) reaction, to form chlorides in the product. The PVC plays a big role as a chloride source in the formation of chloride during co-grinding of both materials. After the co-grinding, the ground product is subjected to washing with water to separate from the product, so that it comes into the filtrate after filtration. The metal chloride in the filtrate can be recovered by hydrometallurgical operation.

The main purpose of this paper is to introduce a new process for recovering metals from alloys and oxides by co-grinding with PVC waste.

2. Experimental

2.1. Samples

Three kinds of waste samples were mainly used in this work; one was misch metal ($\text{MmNi}_{3.55}\text{Co}_{0.75}\text{Al}_{0.40}\text{Mn}_{0.30}$, $\text{Mm} = \text{La}_{0.34}\text{Ce}_{0.47}\text{Pr}_{0.04}\text{Nd}_{0.14}$), the second one was lithium cobalt oxide (LiCoO_2) powder (Aldrich Chemical Co., Ltd., USA), and the third one was polyvinyl chloride (PVC) reagent (Wako Chemical Co., Ltd., Japan). Their mean particle sizes were about $30\ \mu\text{m}$ for $\text{MmNi}_{3.55}\text{Co}_{0.75}\text{Al}_{0.40}\text{Mn}_{0.30}$, $11\ \mu\text{m}$ for the LiCoO_2 sample and about $133\ \mu\text{m}$ for the PVC sample. Polymerization degree of the PVC sample is about 1100. These alloy and oxide samples were ground individually and ground with the PVC sample at different mixing ratios.

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2.2. Procedure

Grinding device used in this work was a planetary ball mill (Pulverisette-7, Fritsch, Germany). The mill consists of pair of pots made of stainless steel, each having 50 ml in inner volume and a rotational disk. The pots are installed on the disk and rotated at counter direction to the disk revolution. The ratio of the rotational-to-revolution speed was fixed at 1. The grinding media (steel balls) were mono-size spheres having 16 mm diameter. A 3.0 g of the starting mixture (alloy-PVC and LiCoO₂-PVC) were charged in the pot and ground by the mill in air for different periods of time. After grinding, the mill was stopped and the product was removed for characterization as well as water leaching.

As for the leaching with water, 1.0 g of the ground product was dispersed in 250 ml water for 1 h, subsequently the slurry was filtered to separate a powder from the filtrate. The powder on the filter paper was dried in an oven.

2.3. Characterization

The X-ray diffraction (XRD) analysis (Rigaku, RAD-B system, Cu K α) was conducted for the ground and the washed samples to determine the phases and compositions. Chemical analysis of the filtrate was made by an inductively coupled plasma-atomic emission spectroscopy (ICP-AES) (Optima 3300SYS, Perkin-Elmer, USA). The concentration of chlorine ion in the filtrate was measured by an ion chromatograph (IC) (LC10 series, Shimadzu Co., Ltd., Japan) and the degree of dechlorination of PVC was calculated from both values of the Cl-concentration in the filtrate and the amount of PVC in the starting mixture.

3. Results and discussion

3.1. Recovery of metals from $MmNi_{3.55}Co_{0.75}Al_{0.40}Mn_{0.30}$

Fig. 1 shows XRD patterns of the mixture of PVC (1.99 g) + alloy (1.01 g) samples ground for different periods of time. As expected, peaks of chlorides appear in the pattern of the mixture ground for 12 h or more, and their intensity tends to increase with an increase in the grinding time. Accordingly, peaks of $MmNi_{3.55}Co_{0.75}Al_{0.40}Mn_{0.30}$ in the ground product decreases gradually with an increase in grinding time, and finally the peaks disappear after 24 h. The formation of chlorides means the occurrence of the MC reaction between the two kinds of wastes. The chlorides formed in the product tend to adsorb moisture from the air, to be in hydrated states. In any case, these chlorides can be separated by the water leaching because of their high solubility in water. Fig. 2 shows photos of the mixtures ground for 6 and 12 h, respectively. As for the 6 h ground mixture, the colour looks light gray, whereas it looks dark gray for the 12 h ground mixture. The light gray colour of the mixture implies the insufficient MC reaction between the alloy and the PVC waste samples, but the dark colour means further progress in the MC reaction between the two. Fig. 3 shows yield of metals extracted from the mixture as a function of grinding time. The

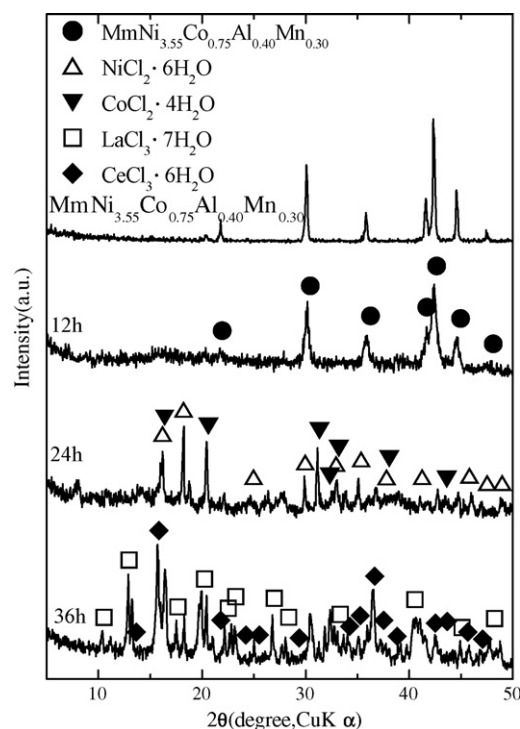


Fig. 1. XRD patterns of the mixtures of PVC (1.99 g) + alloy (1.01 g) ground for different times.

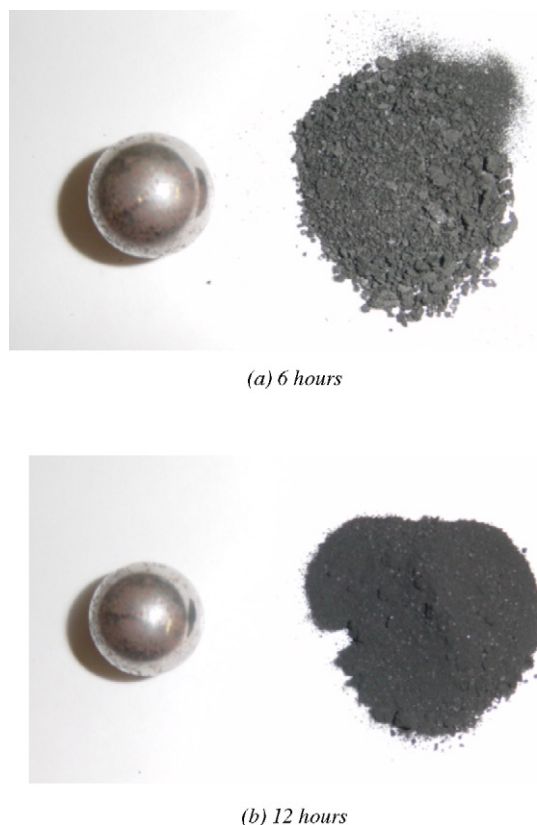


Fig. 2. Photos of the ground products after 6 and 12 h.

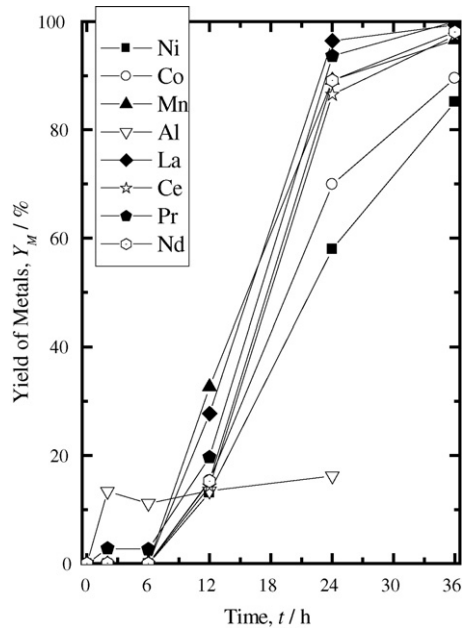


Fig. 3. Yield of metals extracted from the mixtures.

yield of all of the metals except Al increases with an increase in milling time, and it reaches over 80% at 36 h.

Fig. 4 shows dechlorination of PVC in the ground mixture as a function of grinding time. The data have been determined from the concentration of chloride ion in the filtrate after the water leaching. The dechlorination is confirmed to be improved as the grinding progresses, and it reaches almost 95% within 36 h grinding. This is well consistent with the results shown in Fig. 1.

Fig. 5 shows XRD patterns of a mixture prepared by mixing PVC (1.15 g) with alloy (1.85 g), ground for different grinding time. The mixing ratio between the two samples was different

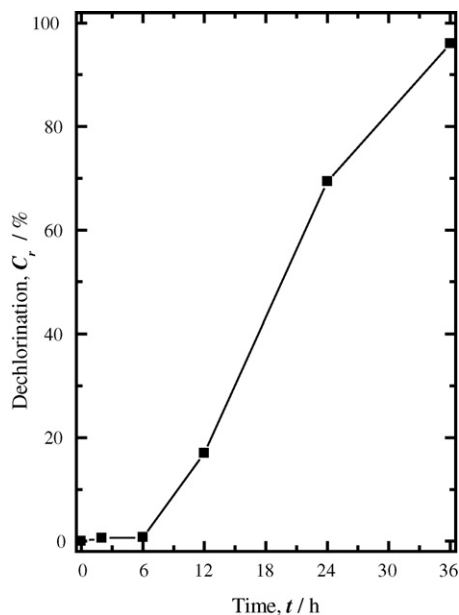


Fig. 4. Dechlorination of PVC by its grinding with alloy.

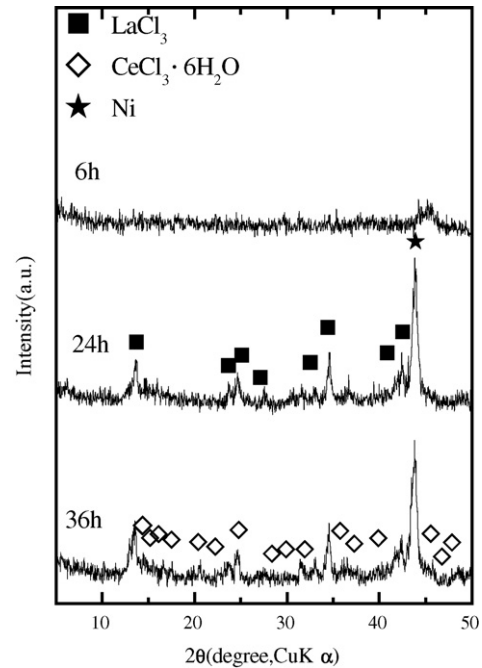


Fig. 5. XRD patterns of ground mixtures of PVC (1.15 g) and $MmNi_{3.55}Co_{0.75}Al_{0.40}Mn_{0.30}$ (1.85 g).

from that in the previous one, where the Cl in PVC is sufficient for the formation of all metal chlorides. In this case, the chlorine amount is reduced just for the chloride formation of rare earth group. It can be seen that La and Ce chlorides are formed in the product, as has been expected. In contrast to the results shown in Fig. 1, no chloride formation of nickel and cobalt has been observed. The peaks of metal nickel have been observed. It is very interesting to note that rare earth group shows higher reactivity with PVC than nickel and cobalt. This difference offers the possibility to separate the two groups. Yields of metals extracted from the ground mixture as a function of grinding period of time are shown in Fig. 6.

Consistent with the results shown in Fig. 5, rare earth group exhibit high yields due to the formation of chlorides. On the other hand, quite low yields of nickel and cobalt are obtained.

3.2. Recovery of metals from $LiCoO_2$

Fig. 7 shows XRD patterns of the mixture $LiCoO_2$ and PVC ground for different periods of time. The patterns of the ground mixtures show the formation of chloride of cobalt in the products. This suggests that these chlorides can be recovered by water leaching, due to their high solubility in water. Fig. 8 shows yields of Co extracted with water as a function of grinding time: one was the $LiCoO_2$ sample and the other was the mixture of $LiCoO_2$ and PVC. As for the ground mixture, the yield increases as the grinding progresses and reaches about 90% at 36 h grinding. On the contrary, the Co-yield is almost zero when the $LiCoO_2$ sample was ground, implying that Co is hardly extracted from the ground $LiCoO_2$ by water leaching even the crystal structure has been disordered. Fig. 9 shows Li-yield extracted with water from the both samples as a function of grinding time. In

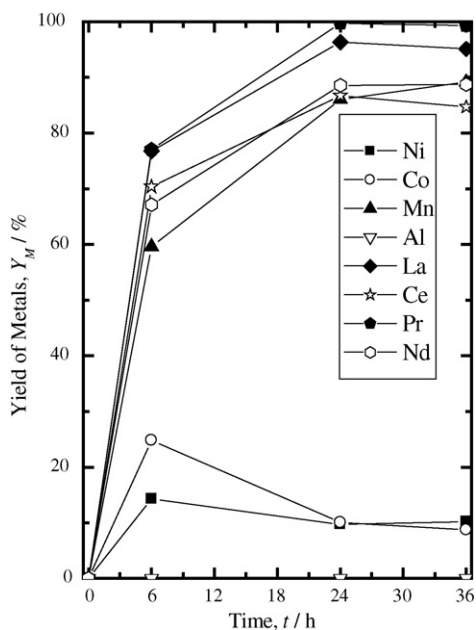


Fig. 6. Yield of metals extracted from the ground mixture of PVC (1.15 g) and $MnNi_{3.55}Co_{0.75}Al_{0.30}Mn_{0.40}$ (1.85 g) as a function of grinding time.

contrast to the case of cobalt, Li-yields in both cases increase as the grinding progresses regardless of the presence of PVC in the grinding stage. However, the yield from the ground mixture is much higher than that from the ground $LiCoO_2$ sample. Thus, the co-grinding $LiCoO_2$ with PVC enables us to form Li-compound in the product. The formed compound in the former mixture is $LiCl$, while in latter case, Li compound might be lithium oxide from the amorphous $LiCoO_2$ due to the decomposition induced by grinding. The solution of lithium oxide into water may be

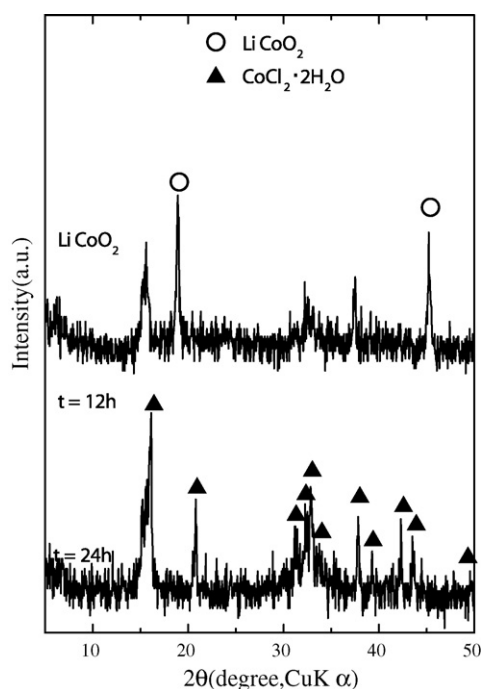


Fig. 7. XRD patterns of the mixtures of PVC and $LiCoO_2$ ground for different periods of times.

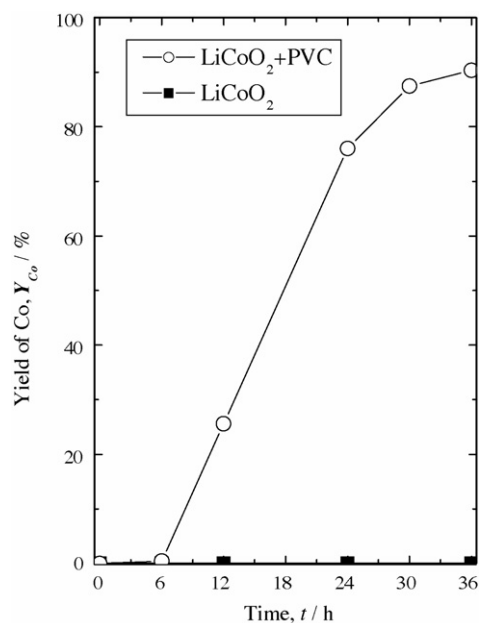


Fig. 8. Yield of Co extracted by water from the ground samples as a function of grinding times.

the main reason why lithium can be leached from the ground sample without PVC during water washing.

Fig. 10 shows pH change in the filtrate in the two different samples as a function of grinding time; one is the $LiCoO_2$ sample and the other is the mixture. As for the pH curve of the ground $LiCoO_2$ sample, it increases from 7 to the alkaline region ($pH > 7$) and levels off after showing pH 11 at 6 h of grinding. This result confirms the formation of lithium oxide in the product and it is transformed into lithium hydroxide ($LiOH$) in the washing operation. On the contrary, the pH decreases gradually from 7 to the acid region ($pH < 7$) as the grinding progresses when the

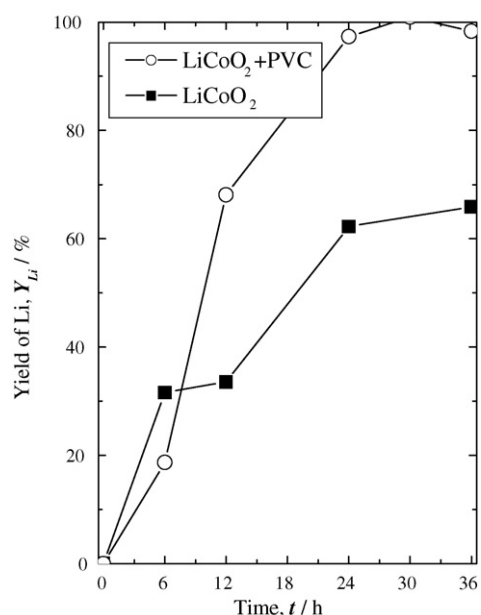


Fig. 9. Yield of Li extracted by water from the ground samples as a function of grinding times.

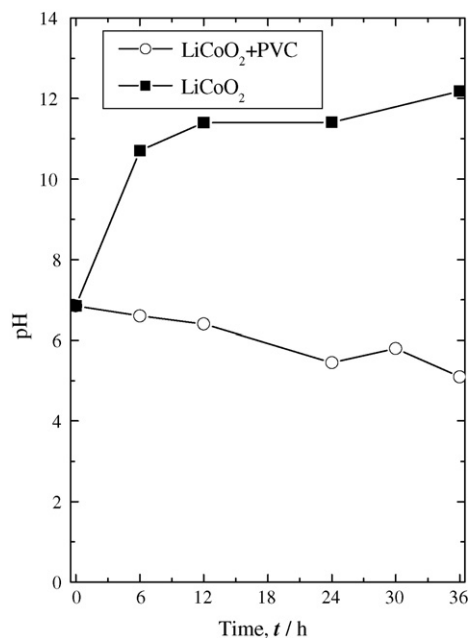


Fig. 10. pH of the filtrates from the samples ground for different periods of time.

mixture has been ground and reaches 5 at 36 h of grinding. This implies that LiCl has formed in the ground product and this is completely different from the case in the grinding the LiCoO₂ sample.

4. Conclusion

A waste sample, i.e., $\text{MmNi}_{3.55}\text{Co}_{0.75}\text{Al}_{0.40}\text{Mn}_{0.30}$ and LiCoO₂ powder was subjected to grinding with PVC powder in air using the planetary ball mill. The ground products were dispersed in water to extract metals at room temperature. The experimental results are summarized as follows:

- (1) The co-grinding the mixture causes the mechanochemical reaction to form soluble chlorides in the ground product. These chlorides can be extracted by water leaching.
- (2) When the mixture is ground, the metal yield increases with an increase in the grinding time and it reaches about 90% at around 36 h of grinding. The yield for the ground mixture is higher than that for the ground product of LiCoO₂ sample itself.
- (3) When the LiCoO₂ sample itself is ground, followed by water leaching, the yield of Li extracted increases as the grinding progresses, but no significant extraction for Co from the ground LiCoO₂ sample has been detected. As for the ground mixture of LiCoO₂ and PVC samples, the yield is also increased as the grinding progresses. Accordingly, the dechlorination of PVC is improved by the co-grinding with these wastes.

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