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RECOVERY OF NICKEL FROM SPENT NICKEL-CADMIUM BATTERIES USING A DIRECT REDUCTION PROCESS

ODZYSK NIKLU Z ZUŻYTYCH BATERII NIKŁOWO-KADMOWYCH ZA POMOCĄ BEZPOŚREDNIEJ REDUKCJI

Most nickel is produced as Ferro-Nickel through a smelting process from Ni-bearing ore. However, these days, there have been some problems in nickel production due to exhaustion and the low-grade of Ni-bearing ore. Moreover, the smelting process results in a large amount of wastewater, slag and environmental risk. Therefore, in this research, spent Ni-Cd batteries were used as a base material instead of Ni-bearing ore for the recovery of Fe-Ni alloy through a direct reduction process. Spent Ni-Cd batteries contain 24wt% Ni, 18.5wt% Cd, 12.1% C and 27.5wt% polymers such as KOH. For pre-treatment, Cd was vaporized at 1024K. In order to evaluate the reduction conditions of nickel oxide and iron oxide, pre-treated spent Ni-Cd batteries were experimented on under various temperatures, gas-atmospheres and crucible materials. By a series of process, alloys containing 75 wt% Ni and 20 wt% Fe were produced. From the results, the reduction mechanism of nickel oxide and iron oxide were investigated.

Keywords: Spent nickel-cadmium batteries, Direct reduction, Recycling, Heat treatment

1. Introduction

Nickel is one of the valuable metals which have applications in various fields. Approximately 65% of Nickel is generally used for manufacturing stainless steel. About 22% of that is used to create super alloys such as nichrome wire, monel and inconel. Besides that, it is also used in nickel plating (8%) and nickel catalysts. According to the USGS(United State Geological Survey) [1], the world production of nickel in 2013 was about 2,490 thousand tons, and is steadily increasing. Nowadays, the demand for nickel continues to increase; however, there is reduced raw material containing nickel minerals. In recent years, the demand of nickel has been rapidly increasing since expansion of the stainless steel market in China.

Many researches with respect to nickel recovery have been studied. At first, Won et al. and Jung et al. obtained nickel powder through hydrothermal process and combustion synthesis process, respectively. [2, 3] As mentioned above, however, nickel is mainly produced from nickel ore. From that, nickel concentrates are made by a separation process, after which ferro nickel or nickel metal is manufactured through a smelting process. Many studies on the reduction process of nickel ore have become active. Sharma *et al.* studied the reduction kinetics of pure nickel oxide by using a CO-CO₂ mixture. [4] H. Purwanto *et al.* researched iron and nickel reduction behavior of a laterite briquette in a CO-CO₂ mixture.

[5] E.N. Zevgolis *et al.* used Greek laterite dust and pellets for reduction in CO gas. [6] However, the reduction rates were quite low because of other gangue. Anotola *et al.* studied the reduction of nickel-iron concentrates in H₂ gas. [7] Like this, almost all nickel reduction studies started from nickel ore. However, high grade ore is continuously becoming exhausted, so an alternative material needs to be found.

This study focused on nickel scrap, especially nickel-cadmium batteries, although the total production was reduced due to cadmium. However, nickel-cadmium batteries are regarded as good nickel suppliers for manufacturing ferro nickel, since the iron content is a little bit high. The contents of spent nickel-cadmium batteries are indicated in Table 1.

TABLE 1
Composition of spent nickel cadmium batteries (%)

Element	Ni	Cd	Fe	C	Polymer et al.
Composition	24	18.5	17.9	12.1	27.5

Some recycling facilities have tried to recover the nickel from nickel-cadmium batteries by using a smelting method at high temperature. [8, 9] In this study, however, a direct reduction method was considered, to provide economic processing without smelting to Fe-Ni alloy.

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2. Experimental

In this study, two samples were prepared. First, Sample A was prepared after distilling the cadmium in the spent nickel-cadmium batteries in a vacuum at 700°C. In the case of sample A, however, a large amount of carbon was also present. Metal and metal oxide components also coexisted in sample A, making it difficult to determine the reduction behavior. Therefore, sample A was oxidized in an air atmosphere at 800°C to obtain a new sample (sample B). The ingredients and XRD(X-ray Diffraction) peaks for each sample are indicated in Table 2 and Fig. 1, respectively. Nickel and iron were the main components in both sample A and B. In sample A, carbon and potassium made up about 5% and 12%, respectively. In sample B, all of the carbon was oxidized, but there was high oxygen content. Potassium was present in the samples since it is come from the electrolyte KOH used in nickel-cadmium batteries. The XRD results of samples A and B provided different forms, which will be discussed in detail later.

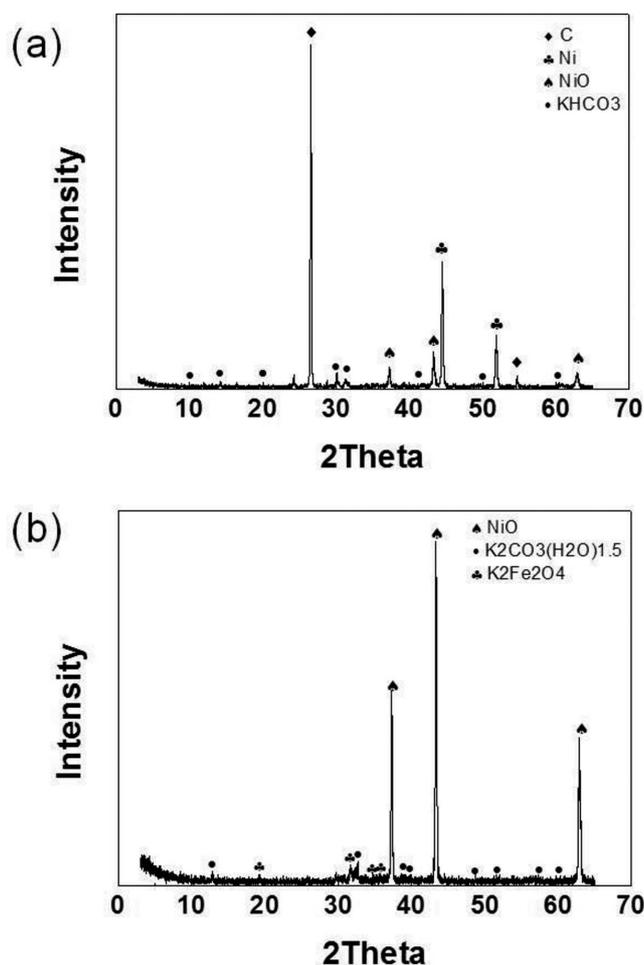


Fig. 1. (a) XRD results of sample A. (b) XRD results of sample B

TABLE 2
Composition of Sample A and Sample B (%)

Component	Ni	Fe	O	C	K	Co	Cd	Mg	Mn
Sample A	44.85	14.56	15.4	12.8	8.1	0.91	0	0.04	0.03
Sample B	43.55	14.78	25.3	0	6.9	0.95	0	0.04	0.03

Reduction experiments were carried out in a Kanthal super resistance vertical furnace. The temperature was between 1000°C and 1200°C, below the melting point of nickel. The atmosphere in the system was a reducing atmosphere controlled by Argon (Ar) and carbon monoxide (CO) gas. Samples (3~4 gram) were placed in an alumina crucible and carbon crucible then retained in the hot zone for 5 hours. After the experiment, samples were taken out and quenched with 6N Ar gas (99.9999%). The samples were then ground, and the elements were analyzed using an Atomic Absorption Spectrometer (AAS), Inductively Coupled Plasma (ICP), a Carbon/Sulfur Determinator, and a Nitrogen/Oxygen Determinator.

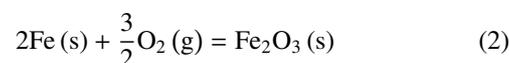
3. Results and discussion

3.1. Heat treatment of samples

In sample A, nickel oxide, iron oxide and potassium compounds with nickel metal were detected by XRD. As mentioned above, when nickel metal and nickel oxide coexist, it is complicated to confirm the reduction behavior. Therefore, the nickel metal in sample A was oxidized to the oxide form at 800°C in air atmosphere. Oxygen partial pressure, $P_{O_2} = 0.2 \text{ atm}$, provided a very strong oxidation atmosphere, enough to oxidize the nickel. While nickel changed to nickel oxide, the carbon was also oxidized. In the XRD results (Fig. 1a), nickel oxide was present, and the $KHCO_3$ in sample A changed to $K_2CO_3(H_2O)_{1.5}$. The case of potassium will be discussed later. During the air heat treatment, the following oxidation reaction occurred:



Iron was not found in the XRD results, but it was observed during AAS analysis. Iron may exist as iron metal, which adhered to the nickel metal in sample A. After air heat treatment, iron became oxidized to iron oxide as follows:



The oxidized sample was sample B.

3.2. Stable state of nickel and iron according to oxygen partial pressure and temperature

Fig. 2 shows the stable state of nickel and iron according to the oxygen partial pressure and temperature. The graph was drawn by calculating from a thermodynamic equation. It was confirmed that oxygen partial pressure or temperature started reduction. For example, nickel oxide could be reduced at 1000°C and below about 10^{-10} atm of oxygen partial pressure. In the case of iron oxide, the reduction reaction can theoretically occur at 1000°C below 10^{-15} atm of oxygen partial pressure. For calculation of the thermodynamic equation, appropriate reactions were used [10].

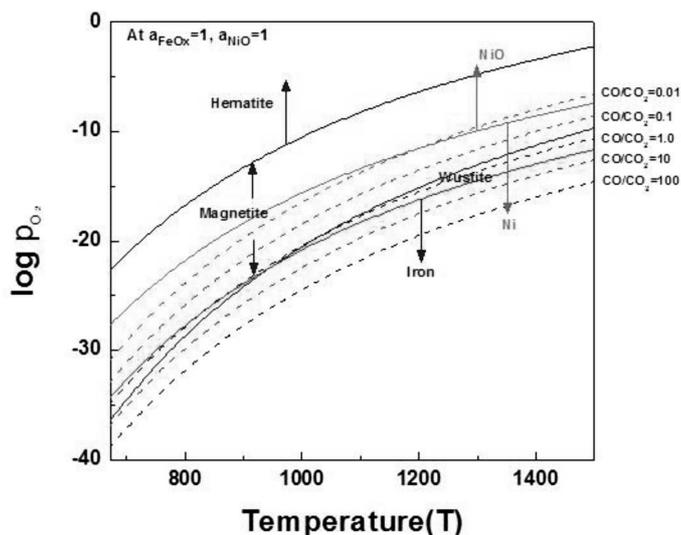


Fig. 2. Nickel and iron stable state according to temperature and oxygen partial pressure

In this study, the experimental condition was retained in an area where nickel and iron metal were present in a stable state, in Fig. 2, above 1000°C.

3.3. Effect of temperature on reduction in Ar atmosphere

Sample B, which was already pre-oxidized, was put into a carbon crucible and reduction experiments were carried out in an Ar atmosphere at 1000, 1100 and 1200°C. After the experiments, the reduced mass of the sample and components were analyzed. Fig. 3 shows the percentage of weight loss according to temperature. The dotted line indicates the theoretical weight loss of sample B after assuming that all oxide forms were reduced, and potassium compounds decomposed completely.

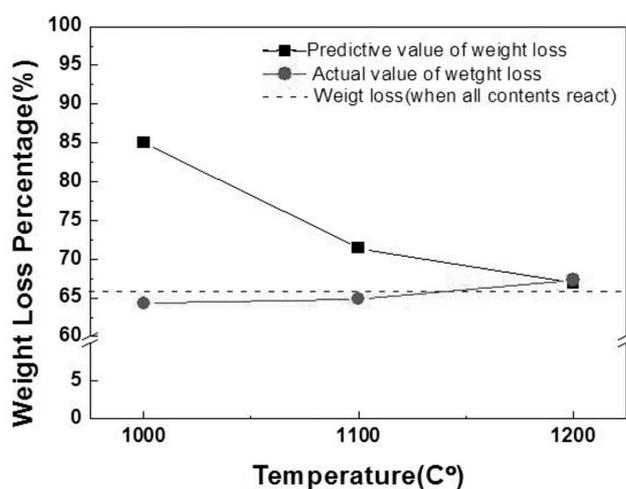
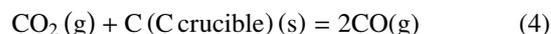
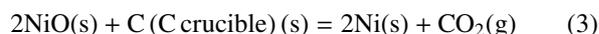


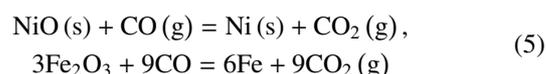
Fig. 3. Weight loss of sample B after experimentation at various temperatures, Ar gas, carbon crucible

This is not dependent on temperature. The square line shows the predictive value of weight loss after considering the possible reactions at each temperature. The real weight loss was closer to the dotted line than the square line. This means that the reduction reaction of oxides and potassium decompo-

sition all progressed during the experiment, even at 1000°C. The same results were observed for the experiment at 1100°C. In this experiment, no CO was supplied artificially. However, CO gas was produced naturally through the following reaction:



↑↓



During the experiments at 1000 and 1100°C, CO gas was produced, so a strong reducing atmosphere was created in the system.

At 1200°C, the weight loss of the sample was less than at other temperatures. That is, the weight of the product at 1200°C was heavier than that of products at 1000 and 1100°C. This phenomenon can be explained by the Boudouard equilibrium, which is indicated in Fig. 4. The Boudouard reaction shows the reduction behavior of iron oxide according to temperature and CO partial pressure.

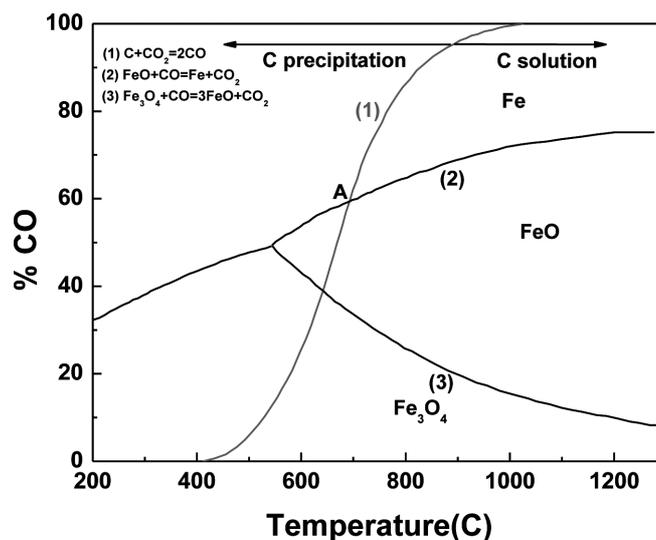


Fig. 4. Boudouard Equilibrium

At 1000 and 1100°C, iron oxide is reduced to produce CO naturally. At 1200°C, all of the iron oxide is reduced at first. However, the arrow in Fig. 4 indicates that iron becomes iron oxide (FeO) with increasing temperature at the same CO partial pressure. Some part of the iron is oxidized partially at 1200°C. Therefore, the difference of weight loss between 1200°C and other temperatures is caused by reoxidation.

Fig. 5 and Table 3 show the XRD peaks and results of component analysis of the products of each experiment, respectively. In the XRD peaks, no difference was observed. Nickel oxide peaks and potassium compound peaks disappeared and Ni₃Fe peaks were observed at all temperatures. Ni₃Fe is in the metal alloy form, providing evidence of reduction. In Table 3, the oxygen content at 1200°C was a little bit higher than for the other temperatures because of the reoxidation of iron.

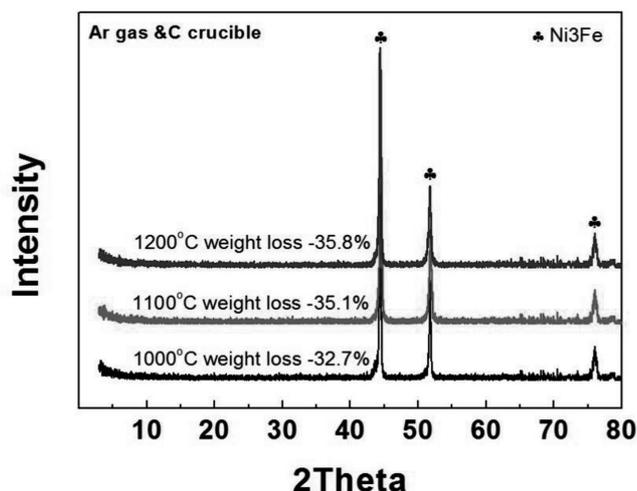


Fig. 5. XRD results of sample B after reaction at various temperatures, Ar gas, carbon crucible with weight loss data

TABLE 3

Elemental composition of sample B after reaction at various temperatures, Ar gas and carbon crucible (%)

Composition	Ni	Fe	O	C	K	Co	Cd	Mg	Mn
Sample B	43.55	14.78	25.3	0	6.9	0.95	0	0.04	0.03
1000°C	68.33	20.07	0.92	0.139	0.4	1.55	0	0.05	0.07
1100°C	75.08	12.89	0.5	0.079	0.25	1.43	0	0.07	0.09
1200°C	74.28	17.34	1.15	0.167	0.31	1.40	0	0.08	0.09

3.4. Effect of temperature on reduction in CO atmosphere

Sample B was put into a carbon crucible and reduction experiments were carried out in a CO atmosphere at 1000, 1100 and 1200°C. After the experiments, the reduced mass of the sample and components was analyzed. The weight loss percentage according to temperature was shown in Fig. 6. The lines indicate the things explained above for Fig. 3.

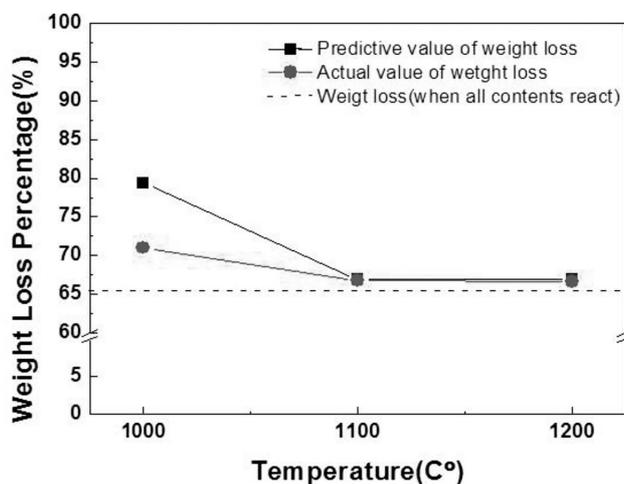
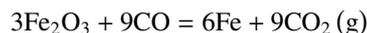
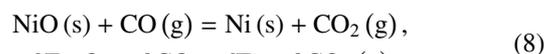
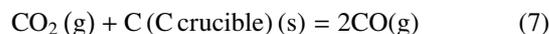
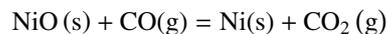
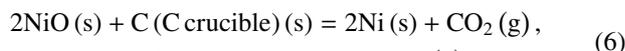


Fig. 6. Weight loss of sample B after reaction at various temperatures, CO gas, carbon crucible

In this experiment, CO gas was added artificially, which was expected to accelerate the reduction reaction compared to the Ar gas experiment. In this case, reduction occurred through the following reactions:



In Fig. 6, the weight loss of the product at 1000°C was less than that observed in the Ar atmosphere. It seems that the reduction was incomplete; however, the conditions of this experiment made a very strong reduction atmosphere. It is certain that the reduction reaction of iron oxide and nickel oxide was fully completed. That is, the weight of the sample increased at the end of the experiment. This phenomenon can be explained by using the Boudouard equilibrium. In this experiment, CO gas was quite sufficient to reduce the oxides in the sample. After the reduction reaction finished, no sources of oxide were present to react with the exceeded CO gas. Therefore, the CO partial pressure increased, resulting in thermodynamic activation of the backward reaction, $\text{CO}_2(\text{g}) + \text{C}(\text{s}) = 2\text{CO}(\text{g})$. This reaction is the carbonization reaction, causing curve (1) to be shifted to the right in Fig. 4, which means that carbonization can be activated at lower temperatures. The reason that the sample had a higher weight at 1000°C was that carbon formed in the sample due to the carbonization reaction. At other temperatures, the weight loss of the sample matched well with the theoretical calculations, and the effects of carburization were not strong.

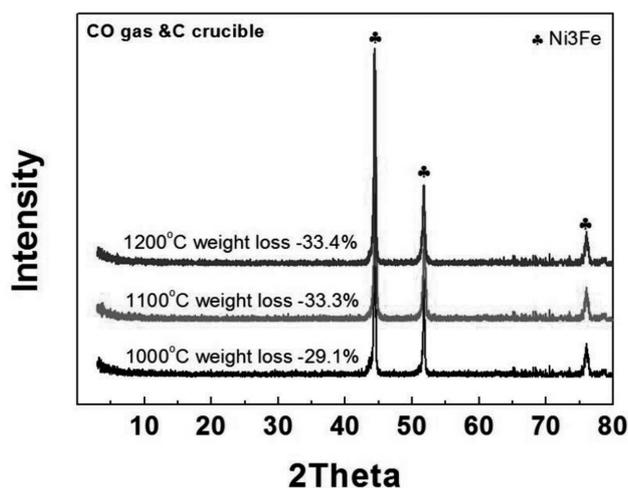


Fig. 7. XRD results of sample B after reaction at various temperatures, CO gas, carbon crucible with weight loss data

Fig. 7 and Table 4 show the XRD peaks and results of component analysis of the products at each experimental condition, respectively. In the XRD peaks, no differences were observed. Nickel oxide peaks and potassium compound peaks disappeared, and Ni_3Fe peaks were observed at all temperatures. Ni_3Fe was in the metal alloy form, providing evidence of reduction. In Table 4, the carbon content at 1000°C was a

little bit higher than at other temperatures due to carbonization of the sample.

TABLE 4
Elemental composition of sample B after reaction at various temperatures, CO gas and carbon crucible (%)

Composition	Ni	Fe	O	C	K	Co	Cd	Mg	Mn
Sample B	43.55	14.78	25.3	0	6.9	0.95	0	0.04	0.03
1000°C	68.91	19.34	0.87	0.789	1.91	1.37	0	0.07	0.08
1100°C	76.94	19.42	0.88	0.362	0.28	1.40	0	0.07	0.09
1200°C	77.43	17.2	0.94	0.545	0.26	1.43	0	0.07	0.09

3.5. Spent nickel-cadmium reduction

So far, sample B, which was pre-oxidized, was used with reducing agents such as a carbon crucible and CO gas. Finally, sample A was utilized for reduction without supplying a reductant. Instead, the utilization of the carbon in sample A as a reductant was attempted. Sample A was put into an alumina crucible, and the experiment was carried out at 1000°C in an Ar atmosphere. Table 5 shows results of the analysis of sample A and the products, while the XRD peaks can be seen in Fig. 8. In the XRD spectrum, C still remained while Ni₃Fe was formed after reduction by carbon in sample A. In conclusion, it was possible to use the carbon in sample A as a reductant. However, there was remaining carbon in the product. It is necessary to look for another method to utilize all of the carbon in sample A.

TABLE 5
Elemental composition of sample A after reaction, Ar gas and alumina crucible (%)

Composition	Ni	Fe	O	C	K	Co	Cd	Mg	Mn
Sample A	44.85	14.56	15.4	12.8	8.1	0.91	0	0.04	0.03
1000°C	66.36	21.03	1.65	8.59	0.12	1.41	0	0.06	0.05

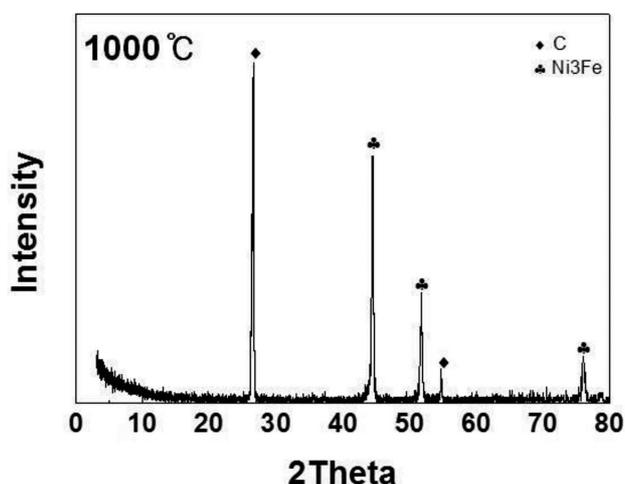
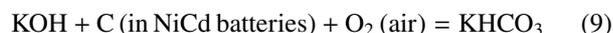


Fig. 8. XRD results of sample A after reaction at 1000°C, Ar gas, alumina crucible

3.6. Behavior of potassium compounds

As mentioned above, there was also a potassium component in the samples. This came from the electrolyte KOH in the spent nickel-cadmium batteries. Since the boiling point of KOH is about 1327°C, it did not distill or decompose during the cadmium evaporation process. However, KOH became KHCO₃ during the process, as follows:



The presence of KHCO₃ could be confirmed in sample A. While the temperature increased, the potassium compounds went through a series of reactions [11, 12, 13].

Thermodynamically, K₂CO₃ decomposes above 1100°C. However, K₂CO₃ was expected to decompose at 1000°C in this study. More research is needed in this area.

4. Conclusions

In this study, nickel and iron could be recovered as Ni₃Fe by direct reduction from spent nickel-cadmium batteries. Nickel oxide and iron oxide could be reduced at 1273K, since the reduction atmosphere is strong as provided by CO gas due to the Boudouard equilibrium. Reoxidation phenomenon occurred at 1200°C when using Ar gas and a carbon crucible. Carbonization phenomenon was observed at 1000°C for CO gas and a carbon crucible. The carbon in spent nickel-cadmium batteries can be used as a reductant, but the carbon still remains in the product. Potassium from the electrolyte decomposes at 1000°C, but more research with respect to this mechanism will be needed. Consequently, spent nickel-cadmium batteries can be used for the recovery of Ni-Fe in the form of an alloy by using direct reduction.

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