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Chemical Reactions between Aluminum Dross and Various Aqueous Solutions

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Chemical reactions between aluminum dross with water, various basic and acid solutions were investigated. The NH_3 gas was evolved owing to the hydrolysis of AlN, resulting in the increment of pH of the solutions. The change behavior in pH of the water with AlN powder was quite different from that with aluminum dross. The pH value of AlN powder solution increased by one step, on the other hand, that of the dross solution increased by two steps. The pH increment in the 1st stage was due to the magnesium ions eluted from MgO and that in the 2nd stage was due to the hydrolysis of AlN. Basic solutions such as NaOH and KOH promoted the hydrolysis of AlN included in aluminum dross.

Key words: aluminum dross, recycle, aluminum nitride, hydrolysis, ammonia

1. INTRODUCTION

Environmental problems such as greenhouse effect, saving energy and resources will be more serious in the 21th century. So the recycle of materials is very important. In particular, aluminum and its alloys are suitable for the recycle due to the following reasons. It is generally known that too much electric energy is necessary to make them from bauxite. On the contrary, only 3% of the electric energy in the case of making aluminum from bauxite is necessary to reproduce aluminum alloys from aluminum scraps. In addition, the amount of CO_2 gas that is evolved during reproducing of aluminum alloys is just 3%, compared with producing them from bauxite [1]. Therefore, aluminum and its alloys are typical recyclable materials, and so the establishment of an aluminum recycle process is quite urgent.

We have a lot of serious technical and economical problems for the establishment of aluminum recycle process. The environmental problem due to aluminum dross is one of the significant problems. Aluminum dross are kinds of scum formed on the surface of molten aluminum in the furnace. They are mainly composed of aluminum, aluminum oxide (Al_2O_3) and aluminum nitride (AlN) and they, moreover, contain a lot of other compounds such as KCl, NaCl, Fe_3O_4, MgO, Al_4C_3, SiO_2, CaO and Al_2S_3 [2-4]. Their compositions are not constant and are depended on the kind of scraps, flux, the ways of collecting scraps and so on. Approximately 50% of aluminum dross is now used as a fluxing agent for steel-making and the rest is treated as industrial waste. When they are disposed, some compounds such as AlN, Al_4C_3 and Al_2S_3 included in aluminum dross react with water, that is rain, and harmful gases are evolved by following reactions [2].

$$2AlN + 3H_2O \rightarrow Al_2O_3 + 2NH_3 \quad (1)$$
$$Al_4C_3 + 6H_2O \rightarrow 2Al_2O_3 + 3CH_4 \quad (2)$$
$$Al_2S_3 + 3H_2O \rightarrow Al_2O_3 + 3H_2S \quad (3)$$

Besides these gases, H_2, PH_3 and the other harmful gases are evolved [5]. Moreover, since these hydrolysis reactions are exothermic, aluminum dross will be ignited during transportation or at open dump areas. In particular, the hydrolysis of aluminum nitride is main reaction (eq.(1)). So AlN in aluminum dross must be hydrolyzed to neutralize its harmful factor before the disposal.

In this study, the chemical reactions of AlN and aluminum dross with water, in which some basic and acid aqueous solutions were also investigated. A few effective water treatment methods were proposed.

2. EXPERIMENTAL PROCEDURES

Aluminum dross which was extracted from type 5000 aluminum (Al-Mg system) scraps and commercial AlN powder of *c.a.* 0.5 μm in particle size were used in this work. For example, the chemical composition of A5052 alloy is shown in Table I. Temperature of the molten aluminum was approximately 1023 K. The aluminum dross has been squeezed by the MADOC one time to recover aluminum alloy. The major chemical compositions of the aluminum dross are shown in Table II. The other chemical compositions were not detected. The constituents of dross before and after the immersion tests were detected by X-ray diffraction (XRD) analysis.

Table I Chemical composition of A5052 alloy (mass%)

Si	Fe	Cu	Mn	Mg	Cr	Zn	Al
<0.25	<0.40	<0.10	<0.10	2.2-2.8	0.15-0.35	<0.10	bal.

They were immersed in deionized water and some basic and acid solutions such as NaOH, KOH, H_2SO_4, HCl, $CuSO_4$ and $FeSO_4$ at 318 K. The concentration of those solutions was 0.1 N. The temperature was kept constant using a water bath and the solutions were stirred during the immersion tests. The pH and the ammonia (NH_3) concentration in the solutions against the immersion time were measured by using the glass electrodes. The solutions were extracted and filtered, and the eluted ions in the solutions were identified by an inductively coupled plasma (ICP) spectroscopy.

Table II Chemical composition of dross (mass%).

m-Al	Al_2O_3	AlN
56.1	21.5	7.6

3. RESULTS AND DISCUSSION

Figure 1 shows the X-ray diffraction patterns of the aluminum dross before and after the immersion treatments. Aluminum nitride (AlN), Al_2O_3, Fe_3O_4, KCl, MgO, SiO_2 and aluminum were identified before the immersion test as shown in Fig.1(a) although some peaks could not be identified. Commercial aluminum alloys often contain small quantities of Fe and Si, which are present either as impurities or deliberate alloy additions. KCl was mixed as flux and Mg was originally contained in the type 5000 aluminum alloy. Since the standard Gibbs energy of Al_2O_3, Fe_3O_4, MgO and SiO_2 are negative at temperatures of aluminum melting condition, the formation of those oxides is reasonable. Since the Gibbs energy of reaction between molten aluminum and nitrogen is also negative below 2836 K [6], the AlN was produced during melting aluminum scraps.

The peaks of aluminum, AlN and MgO decreased remarkably with increasing the immersion time. After the immersion test, $Al(OH)_3$ was also detected although most of the peaks overlapped with the other peaks. Present authors reported that when AlN powders and general drosses were immersed in deionized water, the pH of the solution increased with increasing in the immersion time and the reaction was more quickly at higher temperatures, and the change behavior in pH value of AlN powder solution was different from that of dross solution [3-4].

In this study, the aluminum dross extracted from type 5000 aluminum scraps and AlN powder were immersed in the deionized water at 318 K, and pH of the solutions were measured. Figure 2 shows the pH of the solutions against the immersion time. The pH of the AlN powder solution was not changed until 6000 s, and then increased abruptly. On the other hand, the pH of the dross solution gradually increased immediately after the immersion, and increased moreover again; i.e., the behavior of pH change could be divided into two stages. The pH increment behavior of aluminum dross solution was quite different from that of AlN powder solution.

So the pH and NH_3 concentration were measured together in order to identify the pH increment in the first stage.

The changes of pH and NH_3 concentration in dross solution are shown in Fig.3 and those of AlN powder solution are shown in Fig.4. The NH_3 concentration of the AlN powder solution increased after the incubation time, which were corresponded to the pH change. After the immersion test, not AlN but $Al(OH)_3$ was detected by XRD analysis. So the pH change depends on the AlN hydrolysis as expressed by the following reaction.

$$AlN + 3H_2O \rightarrow Al(OH)_3 + NH_3 \qquad (4)$$

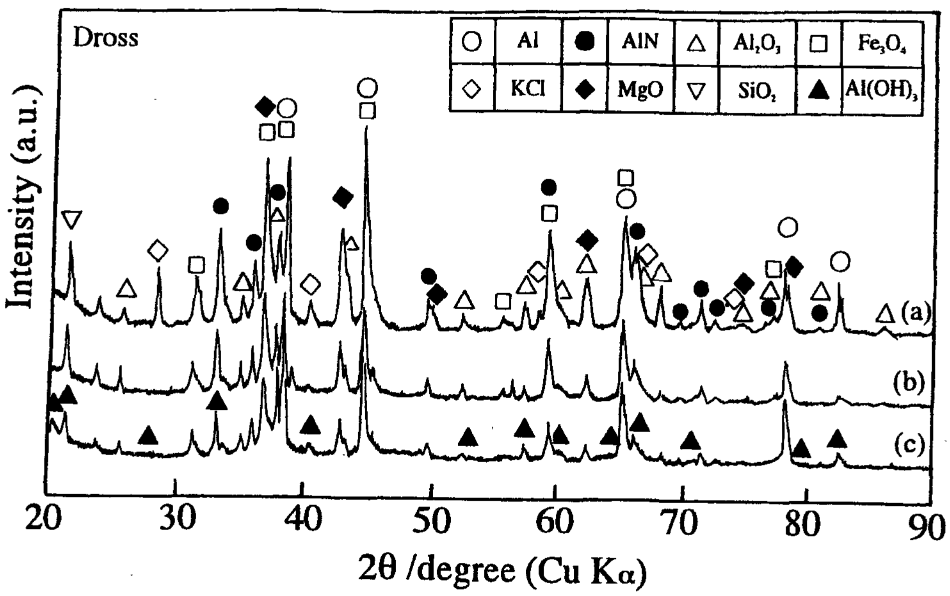

Fig.1 XRD patterns of aluminum dross before and after immersion.
(a) Before immersion (b) 18 ks (c) 36 ks

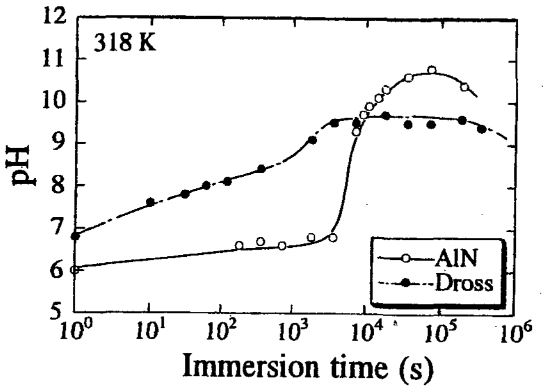

Fig.2 Changes in pH of solutions with AlN powder and dross.

On the other hand, although NH_3 was evolved after the incubation time in the case of Al dross solution, pH increment behavior did not have the incubation time. The NH_3 evolution might cause the second increment of pH. Since the AlN in aluminum dross transferred to $Al(OH)_3$ during the immersion test as shown in Fig.1(c), AlN in dross was also hydrolyzed. Moreover, the peaks of aluminum and MgO decreased after the immersion test as shown in Fig.1(b) and (c). So the eluted ions in the solution were identified by ICP spectroscopy.

Magnesium and aluminum ions were detected in the solution. Magnesium ions were probably eluted from MgO in aluminum dross. So AlN and MgO powders were immersed in deionized water together. In this case, two steps change in pH was also identified. NH_3 evolved after the incubation time and the concentration increased with increasing immersion time.

The behaviors of pH and NH_3 concentration changes were almost the same to that of the aluminum dross immersion as shown in Fig.3. The elution behavior of magnesium ions in the solution of aluminum dross was also investigated. Magnesium ion eluted into the solution immediately after the immersion and its concentration reached to the maximum value of 30 ppm at the immersion time of 100 s. The increment of pH at the first stage corresponded to the elution of magnesium ion. The second increment of pH corresponded to the NH_3 evolution that was due to the hydrolysis of AlN in aluminum dross. Therefore, each increment of pH of the dross solution was due to the following reactions, respectively.

$$MgO + H_2O \rightarrow Mg^{2+} + 2OH^- \quad \text{(1st stage)} \quad (5)$$
$$AlN + 3H_2O \rightarrow Al(OH)_3 + NH_3 \quad \text{(2nd stage)} \quad (6)$$

As a result, since the hydrolysis of AlN depended on pH of the solution, AlN powder was immersed in various basic and acid solutions such as NaOH, KOH, H_2SO_4, HCl, $CuSO_4$ and $FeSO_4$ at 318 K. The relation between NH_3 concentration and immersion time is shown in Fig.5. The hydrolysis rates of AlN powder were higher in every basic and acid solutions than those of the deionized water. The NH_3 gas was evolved immediately after the immersion except for in deionized water. The NH_3 evolution rates were higher in basic solutions (NaOH and KOH) than those in acid solutions (H_2SO_4, HCl, $CuSO_4$ and $FeSO_4$). It has been reported that NaOH played an important role as catalytic agent to accelerate the hydrolysis of AlN as following reactions [7].

$$2AlN + 2NaOH + 8H_2O \rightarrow Na_2Al_2O_4{\cdot}6H_2O + 2NH_3 \quad (7)$$
$$Na_2Al_2O_4{\cdot}6H_2O \rightarrow 2NaOH + 2Al(OH)_3 + 2H_2O \quad (8)$$

$$AlN + 4H_2O \rightarrow Al(OH)_3 + NH_4OH \quad (9)$$

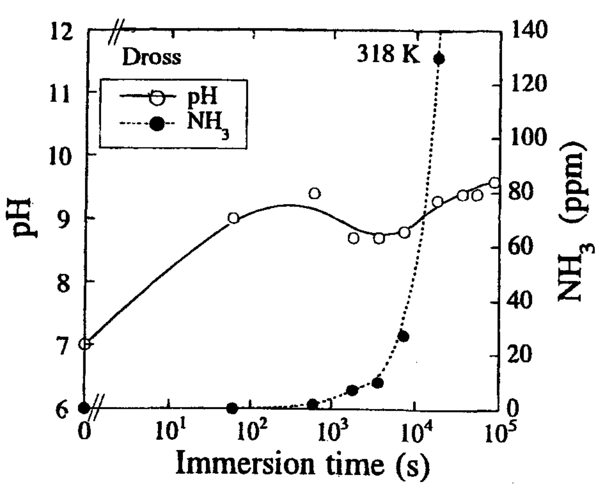

Fig.3 Changes in pH and NH_3 concentration of dross solution.

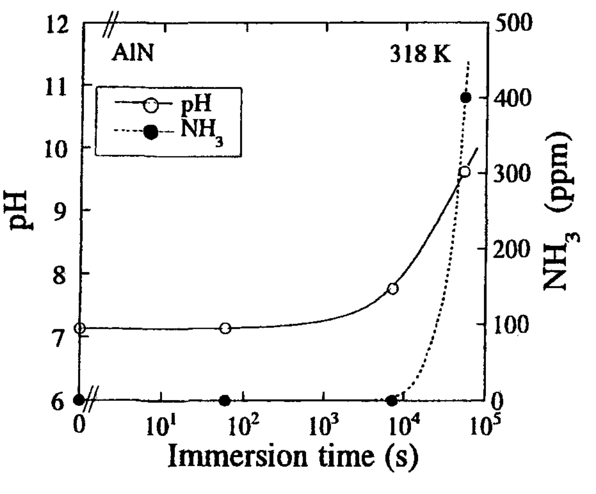

Fig.4 Changes in pH and NH_3 concentration of AlN powder solution.

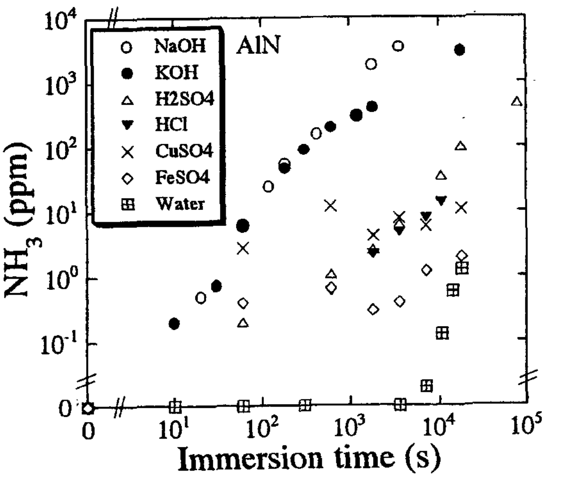

Fig.5 Changes in NH_3 concentration in various basic and acid solutions with AlN powder.

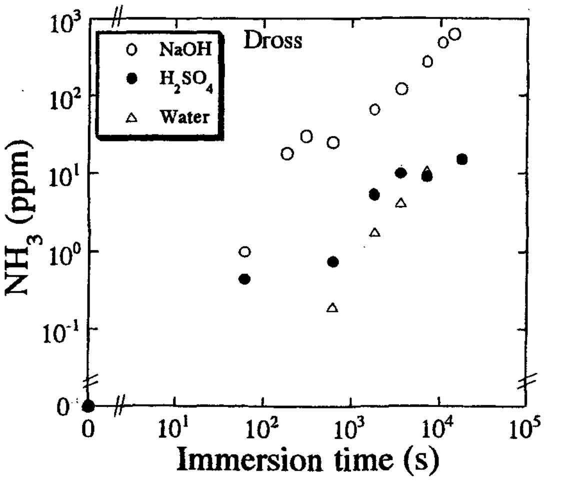

Fig.6 Changes in NH_3 concentration in NaOH and H_2SO_4 aq. with dross.

The almost same reaction probably occurred between AlN and KOH.

On the other hand, when SO_4^{2-} was contained in the solutions, the complex ion was formed between SO_4^{2-} and NH_3. So the harmful NH_3 gas was trapped in the solution. Thus harmful smell due to the NH_3 gas could not be detected. Next aluminum dross was immersed in NaOH and H_2SO_4. NH_3 concentration against immersion time is shown in Fig.6. NH_3 evolved immediately after the immersion, and so AlN included in aluminum dross was also hydrolyzed in NaOH and H_2SO_4. Similar to the immersion of AlN powder in those solutions, the hydrolysis was more promoted in acid and basic solutions than in deionized water. Moreover, the hydrolysis rates of AlN in dross in NaOH was higher than that in H_2SO_4. The basic solutions was very effective on the hydrolysis of AlN in aluminum dross.

A few proposals for the effective method for aluminum dross treatment are described as follows: basic solution should be used to promote the hydrolysis of AlN included in aluminum dross, H_2SO_4 is effective to suppress the NH_3 smell, the hydrolysis rate of AlN powder is faster at the higher temperature [3-4] and furthermore, when particle size of dross will be small by crashing them, the reaction will be promoted owing to the extending surface area.

4. CONCLUSIONS

Aluminum dross and AlN powder were immersed in deionized water, basic and acid solutions. The chemical behavior between dross and AlN powder and those solutions were investigated by monitoring pH, NH_3 concentration and ions in the solutions. The main results are as follows:

1) Aluminum dross was composed of aluminum, Al_2O_3, AlN, MgO, Fe_3O_4, SiO_2 and KCl.

2) The change in pH of the AlN powder solution was just due to the hydrolysis of AlN powder.

3) The change in pH of aluminum dross solution could be divided into two stages. Each stage depended on eluted Mg ion from dross and hydrolysis of AlN in dross, respectively.

4) The hydrolysis rate of AlN was faster in basic solutions.

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