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Formation of cyanide compounds in aluminium dross

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Although cyanide compounds are not used during the casting of aluminium alloys, cyanide ions have often been detected in the aluminium dross. This paper describes the formation of cyanide ions in the aluminium dross and suggests a possible formation mechanism. Cyanide ions were detected in all the samples obtained by extraction from the aluminium drosses. In particular, a large amount of cyanide ions are formed in aluminium drosses treated with nitrogen gas. Metal cyanamide is formed by a reaction between metal carbide in the dross and nitrogen gas. When water is added to the metal cyanamide, cyanide ion is formed by hydrolysis.

Previously, one of the authors has reported that cyanide ions have been detected in factories not using cyanide compounds[1]). Furthermore, this author has made it clear that hydrogen cyanide is formed from various organic compounds and some nitrogen-containing compounds during the distillation process for total cyanide determination[2]). Burkhalter et al.[3]) reported cyanide contamination from an aluminium smelter. Cyanide has also been formed during aluminium electrolytic melting.

When aluminium melting waste (dross) is discarded, a test for harmful materials in the dross is performed. Although, cyanide compounds are not used during the casting of aluminium alloys, cyanide ions have often been detected in the aluminium dross. This paper investigates the formation of cyanide ions in the aluminium dross and suggests a possible formation mechanism.

Experimental

The apparatus and reagents used have been described previously[2)4]), except for the following: Emission spectroscopy of drosses and fluxes. A Nippon Jarrell-Ash M-2W emission spectroscopic analyzer was used. Calcium cyanamide of extra pure grade was obtained from Tokyo Kasei Co. Ltd.

Eleven samples of aluminium dross from five companies were examined. A typical aluminium melting apparatus is shown in fig. 1. The samples were separated with a sieve (mesh No 14, 1.19 mm). A 30 g sample was put into a 500 ml separating funnel with 300 ml of water and shaken for 1 hour. The solution was filtered, and the cyanide ion in the filtrate was determined by a pyridine-pyrazolone method or by ion chromatography[4]).

Results and discussion

Detection of cyanide ions in aluminium dross

The amounts of cyanide ions found in the aluminium drosses are shown in table 1, together with the type of aluminium alloy and processing conditions in the factories. The dross floats on the aluminium alloy during melting.

The results showed that cyanide ions were detected in all of the samples obtained by extraction from the aluminium drosses. The amounts of cyanide ions ranged from 0.3 to 6.3 μg/g. In Japan, the permitted limit of cyanide ion concentration in industrial waste is 1 ppm. Thus, some types of aluminium drosses in table 1 exceeded the limit.

Large amounts of hydrogen and small amounts of nitrogen, methane, carbon dioxide gases etc. in the aluminium alloy have also been detected by mass spectrometry[5]).

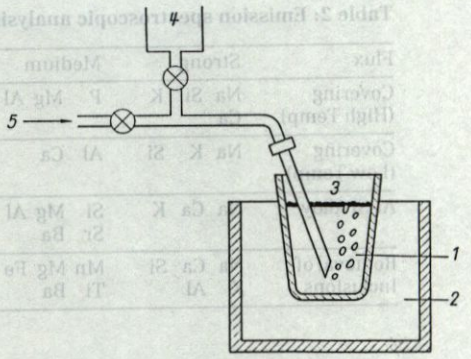

Fig. 1: Aluminium melting equipment; 1 aluminium alloy, 2 furnace, 3 aluminium melting waste (Dross), 4 fluxes, 5 nitrogen gas

Since recently, nitrogen gas processing is carried out for degassing and to prevent fluorine and chlorine gas formation from the flux during aluminium alloy casting[6]). However, as far as the cyanide ion is concerned, a larger amount of cyanide is formed in the aluminium drosses when nitrogen gas is used.

Emission spectroscopic analysis of flux and dross

Various fluxes such as NaCl, KCl, $CaCl_2$, NaF, hexachloroethane, etc. are used to exclude gases and eliminate inclusions during aluminium alloy casting[6]). Emission spectroscopic analyses of fluxes and drosses were performed. The results are shown in tables 2 and 3. As shown in table 2, the major components of the fluxes are sodium, potassium, calcium and silica. Table 3 shows that the major components of the drosses are aluminium, sodium, magnesium, silica, potassium, iron, copper, etc. It is considered that aluminium, magnesium, silica, iron, etc. originate from the aluminium alloy and sodium, potassium, calcium, etc. originate from the fluxes.

Table 1: Concentration of cyanide ions in aluminium drosses

Sample no	Aluminium alloy	Melted temp. in °C	N_2 gas processing	CN^-/Dross in μg/g
1	Al-Si-Mg	710	Yes	0.4
2	Al-Si-Cu	650 to 670	Yes	2.3
3	Al-Si-Cu	780	Yes	2.0
4	Al-Cu-Si	700 to 720	None	0.4
5	Al-Cu-Si	700 to 720	Yes	2.1
6	Al-Si-Mg	700 to 720	None	0.7
7	Al-Si-Mg	700 to 720	Yes	0.3
8	Al-Mg	700 to 730	None	0.7
9	Al-Si-Mg	700 to 750	Yes	4.5
10	Al-Si-Cu-Mg	740 to 770	Yes	6.3
11	Al-Si-Cu-Mg	740 to 770	None	0.9

Table 2: Emission spectroscopic analysis of various fluxes

Flux	Strong	Medium	Weak	Very Weak	Trace
Covering (High Temp)	Na Si K Ca	P Mg Al	Mn Fe	B Pb Cr V	Cu Ti
Covering (Low Temp)	Na K Si	Al Ca	Mn Mg Fe Cr V	Cd Pb Cu	
Al-Si Alloy	Na Ca K	Si Mg Al Sr Ba	Mn Fe	Pb	Ti
Removal of Inclusions	Na Ca Si K Al	Mn Mg Fe Ti Ba	Pb	B Cr Zr	Cu

Table 3: Emission spectroscopic analysis of aluminium drosses

Sample No.	Strong	Medium	Weak	Very Weak	Trace
2	Al Na Mg Si K Fe Cu	Mn Cr Ni Ca Ti Zn	B Pb Sn Ga Bi	Cd Be V	Ag
5	Al Na Mg Si K Ca Fe Cu Ba	Mn Cr Ti	B Pb Sn Ga Bi Ni Zn Sr	Be V	Ag
9	Al Na Mg Si K Fe	B Mn Ca Ti	Ga Cr Cu Zr	Be Pb Ni V	Sn
10	Al Na Mg Si K Fe	Ca Cu Mn Cr Bi	B Pb Sn Ga Ni Ti Zn	Cd Be V	

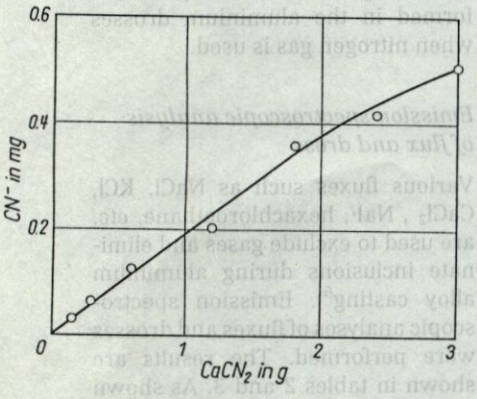

Fig. 2: Relation between $CaCN_2$ content and measured CN^-

Detection of cyanide ion from calcium cyanamide

Bredig[7]) and Aono[8]) have reported that a small amount of cyanide ion is present in cyanamide. To a separating funnel containing 300 ml of water, a fixed quantity (0.15 to 3.0 g) of calcium cyanamide was added. The solution was shaken for 1 hour, then filtered. The cyanide concentration in the filtrate was then determined. The results are shown in fig. 2. The concentration of cyanide ions increased as the amount of calcium cyanamide increased, the relationship being almost linear. The content of cyanide ions in the calcium cyanamide was 0.017 to 0.022%.

Scheme of cyanide formation in aluminium dross

Grjotheim et al.[9]) have reported that aluminium carbide is produced on the surface of carbon and cryolite. When water is added to calcium carbide and aluminium carbide, acetylene and methane are the products[10]).

When water was added to the aluminium dross, it smelled the same as when water is added to calcium carbide (CaC_2). The gas formed when water was added to the aluminium dross was analyzed by GC-MS. Methane, ethane, ethylene, acetylene etc. were detected[11]). Thus, it is thought that the carbides of calcium and aluminium are present in aluminium dross.

Possibly, calcium cyanamide is formed when nitrogen gas is used during aluminium alloy casting. Typical reactions between metal carbides and nitrogen are as follows:

$$CaC_2 + N_2 \rightarrow Ca(CN)_2 \rightarrow CaCN_2 + C \quad (1)$$

$$Al_4C_3 + 6N_2 + 9C \rightarrow 4Al(CN)_3 \quad (2)$$

Reaction (1) is the reaction used for the manufacture of calcium cyanamide from calcium carbide and nitrogen[8])[12]). In addition, Krase et al. have reported that calcium nitride reacts with carbon and nitrogen to give calcium cyanamide[12]).

$$Ca_3N_2 + 6C + 2N_2 \rightarrow 3CaCN_2 + 3C \quad (3)$$

In reaction (1), calcium chloride and calcium fluoride are added as catalysts[13]). In the process of aluminium smelting, fluxes such as NaCl, KCl, $CaCl_2$ and NaF are added to the smelter. Thus, it is thought that these fluxes enhance the reaction which produce calcium cyanamide.

Hence, the following scheme for cyanide ion formation in the aluminium dross may be considered.

1. The metals in the aluminium alloy or fluxes react with carbon to form metal carbides.
2. Metal carbides react with nitrogen in air or with the nitrogen used in the degassing process, to form metal cyanamides.
3. When water is added to metal cyanamides, the cyanide ion is formed by hydrolysis.

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