A NEW ELECTROLYTIC PRODUCTION OF NITROGEN TRIFLUORIDE IN A MOLTEN CsF-HF-NH_4F SYSTEM

A. Tasaka, K. Mizuno and K. Miki
Department of Applied Chemistry, Doshisha University
Imadegawa, Karasuma, Kamigyo-ku, Kyoto 602, JAPAN

In order to decrease the vapor pressure of hydrogen fluoride and the anodic dissolution of the nickel anode for the electrolytic production of nitrogen trifluoride, the electrochemical behavior of nickel and some nickel-based alloys were investigated at 50 °C or 100 °C in a molten CsF-HF-NH_4F system. A platinum wire was used as the reference electrode, and a part of potential was reduced to a standard of the hydrogen electrode. Anode gas was analyzed by both infrared spectroscopy and gas chromatography.

In the potentiostatic electrolysis at 6 V vs. Pt and 50 °C, the ratio of the anodic dissolution of nickel to total amount of passing electricity (Q_a/Q_t) was only 1.32 % in calculation from the electron number in the discharge of 2. In the case of nickel-based alloys, only monel consisted of nickel and copper was available for the anode material and its ratio of Q_a/Q_t was almost similar to that of nickel. The anodic polarization curve on monel was also similar to that on nickel, but the current density was smaller than that of nickel. In the galvanostatic electrolysis at the current density of 25 $mA \cdot cm^{-2}$ and 100 °C, the anode gas was composed of N_2, O_2, N_2O, NF_3, N_2F_2 and so on. The current efficiency of NF_3 increased with decreasing the concentration of NH_4F and reached the value of about 60 % in the molten $0.3NH_4F \cdot CsF \cdot 2.6HF$. In contrast, the ratio of Q_a/Q_t of nickel decreased with decreasing the concentration of NH_4F and its value in the same electrolyte was 2.78 %.