

Application of atmospheric-pressure non-thermal plasma to chlorination of hardly soluble materials



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ABSTRACT

The chlorination reaction in which hardly soluble materials are chemically converted into soluble chlorides by atmospheric-pressure non-thermal plasma (APNTP) and the effect of the plasma-irradiation conditions on the chlorination reaction were investigated. The CeO₂ specimens, which have the same crystallographic structure (CaF₂ type, cubic) and valence fluctuation behavior as ThO₂, were used to simulate hardly soluble nuclear materials. CCl₄ and He mixed gas were used as the plasma discharge. The emission and electrical properties of APNTP and dissolution behaviors of chloride generated by plasma irradiation were evaluated. The results of the emission spectroscopic analysis and electrical property measurements showed that chlorine and carbon were generated from the decomposition of CCl₄ caused by the excited atmospheric components and He. Moreover, the production of CeCl₃ from CeO₂ and a logarithmic progression of the chlorination reaction were indicated with increasing plasma-irradiation time.

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1. Introduction

In the various wet analysis or treatment processes for hardly soluble materials such as ThO₂ fuel and fuel debris generated by severe nuclear accidents, the dissolution of materials is a major problem. Although irradiated ThO₂ fuel can be dissolved by HNO₃–HF, F[−] ions affect the material corrosion. Therefore, corrosion-resistant materials are required (Suzuki et al., 1987). Additionally, the fuel debris generated by the TMI-2 accident did not completely dissolve in acid; therefore, pyrosulfate fusion, which has potential explosive properties, had to be used for the analysis (Akers et al., 1986). Also, conversion of an oxide to a chloride makes the material more easily soluble. However, the existing chlorination method is a high-temperature reaction with chemically active chlorine; therefore, special considerations for the safe control of the gas and corrosion of reactor material are required.

In recent years, atmospheric-pressure non-thermal plasma (APNTP) technology, which can be used at room temperature and atmospheric pressure, has been developed. It does not require a vacuum device and generates high-density plasma, and,

therefore, it is expected to provide a low-cost alternative to traditional processes, which use low-pressure plasma, and to have applications for processes that do not use plasma. For example, for surface modification, polyethyleneterephthalate films were irradiated by APNTP with He and CF₄ mixed gases, and a change in the surface energy due to fluorination was indicated (Kanazawa et al., 1987).

Here, we suggest a new application of APNTP for surface modification, an innovative dissolution method for the analysis or treatment of hardly soluble materials. This method would chemically convert the materials into a soluble chloride using APNTP, allowing for dissolution in water. This method does not use strong acids or chemically active chlorine; therefore, a decrease in the material corrosion and safety improvements is expected. Applications of arc-plasma for metal chlorination have been reported (Takeuch et al., 2002). Because the chloride generated by the plasma is vaporized, the reactor would be contaminated if nuclear material were to be irradiated and nuclear material accounting would be difficult. Chlorination with APNTP at low temperatures and atmospheric pressure minimizes vaporization and retains most of the material. In the present study, the chlorination reactions and solubility changes upon the irradiation of APNTP were investigated using CeO₂, a hardly soluble material that has the same crystallographic structure (CaF₂ type, cubic) and valence fluctuation behavior as ThO₂.

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2. Experimental method

Fig. 1 shows an overview of the APNTP test equipment used in this study. Capacitively coupled plasma-type electrodes, which consisted of a copper electrode covered with 3-mm-thick glass (SiO_2), were used. The electrode was 40-mm long in the gas-flow direction and 20-mm long in the perpendicular direction. The gap between the electrodes is 2.5 mm, and both sides of the gas flow are sealed to prevent gas diffusion. The discharge part was set in a sealed chamber made of an acrylic polymer with a small exhaust system. In this experiment, Helium was used as a working gas, because it has a high-energy metastable excited state that can easily decompose mixed gases (Massines and Gouda, 1998). CCl_4 gas was used as the chlorination source. The use of CCl_4 decreases the secondary waste, because only UCl_4 and CO_2 were generated when CCl_4 was used as the chlorinating agent to convert UO_2 into UCl_4 (Katz and Rabinowitch, 1951). CCl_4 liquid was heated above the boiling point, 76.8 °C, and mixed with He. The He gas was fed to the gas flow at 500 or 1000 mL/min. CCl_4 liquid was fed at the rate of 10 mL/h, and the CCl_4 gas-flow rate was ~40 mL/min at this time. The mixed gas flowed between the electrodes under atmospheric pressure. The gas temperature was measured using a thermocouple and was 3 °C higher than room temperature. Although the plasma under this condition was mixed with a small amount of air, we simply refer to it as the He/ CCl_4 plasma or He plasma, which did not include CCl_4 . The plasma was discharged by a radio-frequency power source with an applied frequency of 7 kHz, and the electrical source was supplied from an adjustable transformer. The current value of the plasma was adjusted by voltage from an adjustable transformer. The range of the applied voltage ranged from 70 to 90 V. At this time, the discharge was switched from the “on” to the “off” state every 0.5 s using the thyristor to prevent any breakage of the glass electrodes by the increase in temperature. The plasma-gas temperature was measured using the insulated thermocouple. When the plasma concentrates around the thermocouple, the plasma-gas temperature was 114 °C. This shows that this plasma is non-thermal plasma. The temperature of the specimen during plasma irradiation was lower than that caused by plasma broadening. In fact, the temperature of the specimen soon after plasma irradiation was 57 °C, as measured using a radiation thermometer.

The disc-shaped or powder form of CeO_2 specimens were used as the hardly soluble materials. Rare-earth elements were used as the substitutes for nuclear materials. CeO_2 is hardly soluble in nitric acid such as ThO_2 and PuO_2 , and the only stable tetravalent rare-earth ion is Ce^{4+} . The disc-shaped specimens were made by casting CeO_2 powder and sintering for 2.5 h at 1100 °C. After sintering, the dimensions of the pellets were $\phi 9.5 \times 1$ mm, the weight of the specimens was 0.37 g on average, and the bulk density was ~72%. The specimen was set on the earth electrode.

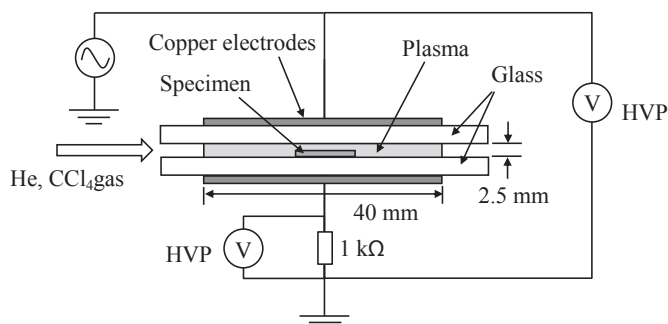


Fig. 1. Schematic diagram of discharge electrode structure.

In this study, emission spectrometric analysis, measurements of the current value and voltage of the APNTP, and quantitative analysis of Ce ions dissolved in ultrapure water were performed. A grating spectrograph (JASCO, CT-50C) with a monochromator scanner (JASCO, MS-50C) was used for emission spectrometric analysis, and an oscilloscope (Tektronix, DPO2014) with a high-voltage probe (Tektronix, P6016A) was used to measure the current and voltage waveforms. CeO_2 irradiated by plasma was dropped in 50 mL of stirred ultrapure water, and the Ce ion concentration in the water was measured using inductively coupled plasma mass spectrometry (ICP-MS, Agilent Technology, 7700). Because CeO_2 does not dissolve in water, the Ce ion measured in the ultrapure water must be from the dissolution of a soluble chemical form such as a hydroxide or a chloride.

3. Result and discussion

3.1. Emission spectrometric analysis

To investigate the decomposition reaction of CCl_4 in He/ CCl_4 plasma, emission spectrometric analyses of He and He/ CCl_4 plasmas were carried out. At this time, the flow rate of He was 500 mL/min and CCl_4 gas in He/ CCl_4 plasma was ~40 mL/min. Fig. 2 shows the results from the emission spectrum. In this figure, the main light-emitting sources are the atmospheric components such as O and N_2 ; the emission of He was also confirmed. In the case of a flowing mixed gas of He and CCl_4 , the peaks identified were small. Instead, the peaks for Cl, Cl^+ , C, and C^+ were observed. This indicates the decomposition of the CCl_4 gas. It was considered that the excited species of He, O, or N_2 can cause the degradation of CCl_4 , and the following reactions might occur (Kogoma, 2003).

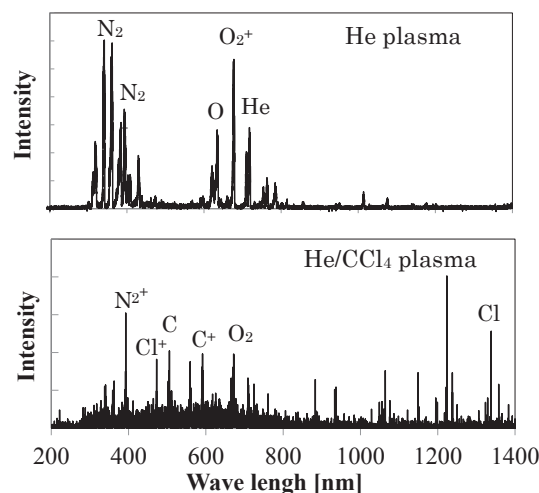
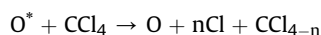
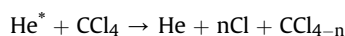
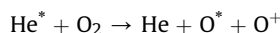
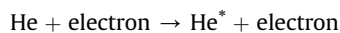


Fig. 2. Emission spectra of He plasma and He/ CCl_4 plasma. Frequency: 7 kHz, He gas-flow rate: 500 mL/min, CCl_4 gas-flow rate: ~40 mL/min.

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