Chemical Dissolution of Iridium Powder Using Alkali Fusion Followed by High-Temperature Leaching

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The dissolution of iridium has been investigated with an alkali fusion treatment with Na_2O_2 followed by leaching in HCl solution. Alkali fusion with Na_2O_2 allows Ir to be easily oxidized to IrO_2, which is transformed to a high oxidation state through the binding of Na-Ir-O at 600°C for 4 h. From the fused mixture, with molar ratio of 1 : 2.0 (Ir : Na_2O_2), Ir can be leached completely at 130°C using an HCl solution with a concentration above 3 M. Moreover, the leaching with 3 M HCl at 130°C can dissolve Ir from the mixture that was fused at 600°C, regardless of molar ratio of Na_2O_2. Ir can also be completely dissolved at 70°C or less when the fused mixture has a 1 : 2.0 ratio.
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1. Introduction

Iridium (Ir), one of the platinum group metals, has remarkable thermal, physical and chemical properties. It has a high melting point (2443°C) and is mechanically stable at temperatures above 1600°C. Its moduli of elasticity and rigidity are very high, and the low of Poisson's ratio indicates a high level of stiffness and resistance to deformation. This implies that severe conditions may be required to make a disorder of crystal structure, and to reduce its size by mechanical grinding or other treatments. Moreover, it is the most resistant of all metals to chemical corrosion, is insoluble in all leachates including acids and bases, and is not vulnerable to attack by other molten metals or by silicates at high temperatures. With these properties, Ir has been widely used in crucibles, thermocouples, spaceship engines, gas turbines, spark plugs and catalysts.[1,2]

Although Ir is a promising material in many ways, its application has been restricted by technical difficulties in the pyro-metallurgical and hydro-metallurgical recovery/refining processes necessary for its reuse and by its scarcity. Because the pyro-processes such as remelting and zone refining are very costly due to the high melting point, hydro-processes are the only technologically feasible method. Therefore a prerequisite for expanding its application is to convert Ir metal into a soluble state.

Many research studies were conducted related to dissolution or digestion processes for Ir metal that converted it into a chemically soluble state from ores and secondary solid materials. In these studies, several thermal treatments were adopted as pre-processing steps before the hydro-chemical Ir dissolution to enhance its solubility. These steps are summarized here:[3–14] (1) alloying with base metals (Cu, Al, Ni, Pb), (2) fusion with alkali materials (Na_2O_2, NaOH), and (3) oxidation to IrO_2 by heating to 1100°C in oxygen. Even with these thermal treatment, the recovery rate is very slow. And also the recovery was lower than 95% in the leaching procedure, and the iridium must be converted into a fine powder with particle sizes on the order of several tens of micrometers. The studies showed that it is difficult to recover Ir metal directly from secondary raw materials in a practical and efficient manner.

In this research, an experimental approach was used to determine the conditions that yield a complete Ir recovery from the acidic leaching process after an alkali fusion treatment. These results offer a new possibilities for the use of Ir-containing waste as a source in precious metal production.

2. Experimental Procedure

2.1 Alkali fusion treatment

Iridium (Ir) powder with a purity of 99.9% ($d_{50} = 22.9\,\mu m$, Furuya metals, Japan) was used as a starting material in this research, and the size distribution is shown in Fig. 1. In the alkali fusion treatment, Ir was mixed with sodium peroxide
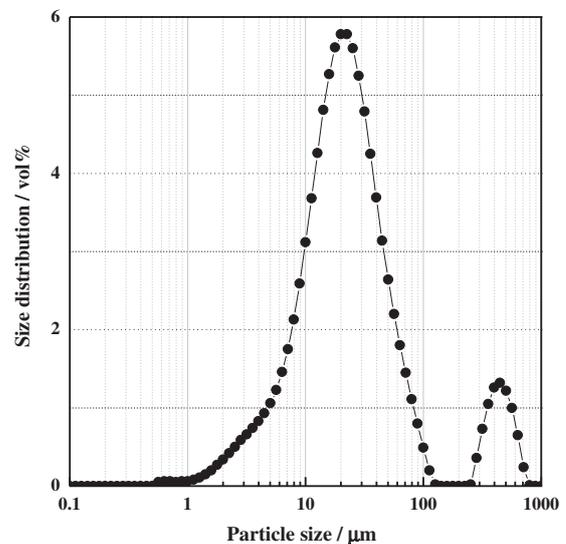

Fig. 1 Size distribution analysis of the iridium powder used as the starting material.

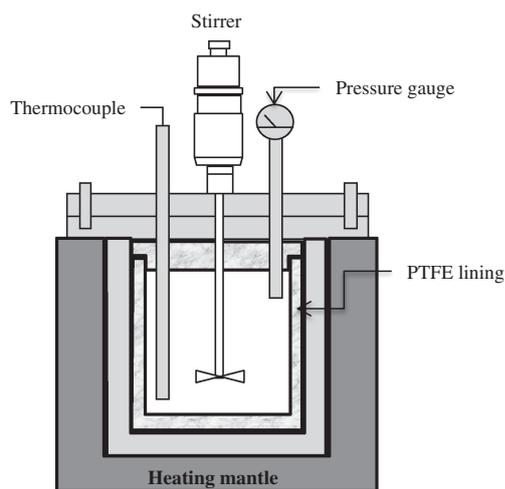*Corresponding author, E-mail: jr-lee@kangwon.ac.kr

Fig. 2   Schematic of the reactor used in leaching at high temperatures.

Fig. 3   XRD patterns for the mixtures of Ir and Na_2O_2 (molar ratio 1 : 2), treated with different thermal conditions; (a) at 500°C for 4 h, (b) at 500°C for 24 h, (c) at 600°C for 4 h, (d) at 600°C for 24 h.

(Na_2O_2) and heated. To create a uniform distribution of the two materials, a planetary ball mill (Pulverizette-7, Fritsch Gmbh, Idar-Oberstein, Germany) was used. The milling conditions were as follows: 4 g of the mixture was added to a zirconia pot (45 cm³ inner volume) with three 15 mm-diameter zirconia balls and was subjected to mixing in air at 300 rpm for 3 min. There molar ratios of Na_2O_2-to-Ir was used: 0.8, 1.4 and 2.0. For the preparation of alkali-fused Ir, 10 g of the mixture was added into nickel crucible and thermally treated thermally (500 and 600°C) in air in an electric furnace. 4 g of the fused bulk was ground at 500 rpm with seven 15 mm zirconia balls for 10 min in air. The ground samples were characterized by X-ray diffraction (XRD) (HRXRD, X'pert-pro MPD, PANalytical, Netherlands) using Cu-Kα radiation to identify the phases formed in the fusion process. X-ray/ultraviolet photoelectron spectroscopy (XPS, AXIS-NOVA, Kratos Inc., Japan) was also conducted to probe the chemical bonds presented in the mixture.

2.2   High-temperature leaching of Ir from the fused samples

For the Ir processed with the alkali fusion method, leaching tests were performed in a closed reactor, which is illustrated in Fig. 2. This reactor has an inner volume of 0.2 L and is equipped with a heating mantle, a PID temperature controller and a variable-speed stirrer. The inner surface of the reactor was lined with a 5 mm-thick layer of polytetrafluoroethylene (PTFE).

Hydrochloric acid (HCl) was used as the leachate. The HCl volume and the stirring speed were fixed to 150 mL and 100 rpm, respectively. To determine the optimum conditions for the dissolution of Ir, leaching tests were performed with various concentrations of HCl and temperatures.

At the end of the experiments, the heating system was shut down and the leached solution was cooled in air after the reactor was open. The solution was filtered using a membrane filter (cellulose acetate, pore size = 0.22 μm) to collect the solid residue. The solution was analyzed chemically using an inductively coupled plasma spectrometer (ICP, Optima 7300 DV, Perkinelmer, USA).
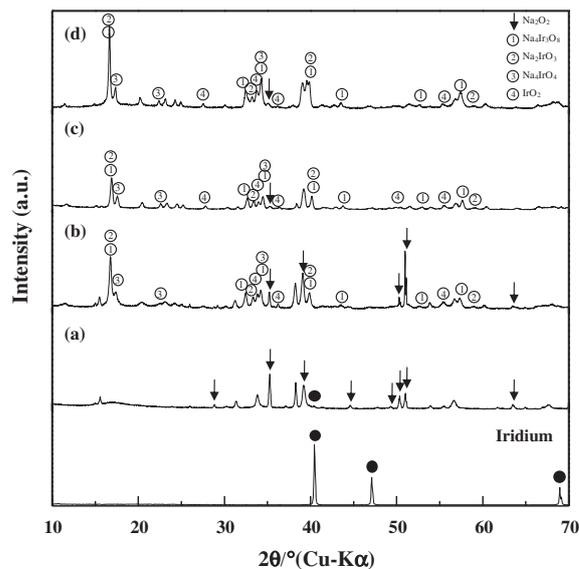
3.   Results and Discussion

3.1   Alkali fusion treatment with sodium peroxide for the leaching of iridium

To determine the optimum conditions for the fusion process, Ir was mixed with Na_2O_2 in a 1 : 2 molar ratio and was used as the test sample for the fusion experiments. The test samples were heated at two temperatures (500 and 600°C) and for two durations (4, 24 h). The XRD patterns for the treated samples are shown in Fig. 3. The strongest peak associated with Ir (Cubic, JCPDS[15] No. 46-1044) was weakly detected and the peaks for Na_2O_2 (Hexagonal, JCPDS No. 74-0111) remain in the pattern for the sample treated at 500°C for 4 h (Fig. 3(a)). The peak associated with Ir disappeared when the sample was heated for 24 h at 500°C, but Na_2O_2 was still detected in the mixture (Fig. 3(b)). Additionally, new peaks for the Ir-containing compounds appear in the pattern of this fused mixture: ① $Na_4Ir_3O_8$ (Cubic, JCPDS No. 26-1377), ② Na_2IrO_3 (Monoclinic, JCPDS No. 26-1376), ③ Na_4IrO_4 (Tetragonal, JCPDS No. 49-749), and ④ IrO_2 (Tetragonal, JCPDS No. 15-870). In the patterns for the samples treated at 600°C, most of the Na_2O_2 peaks are not present, and the new peaks for the Ir-containing compounds are observed after the fusion treatment was conducted for only 4 h (Fig. 3(c)). For the longer fusion treatment at 600°C, the intensities of the Ir-containing compounds increase significantly (Fig. 3(d)). These results imply that the fusion reaction occurs with Na_2O_2 when exposed to 600°C for 4 h and results in the formation of Na-Ir-O compounds.[16]

Based on these results, the experiments were conducted to determine the optimum ratio of Na_2O_2 to Ir. The mixtures of Na_2O_2 and Ir were treated at 600°C for 4 h, and the ratios of 0.8 and 2.0 were tested. The transformation and binding energies were examined using XPS analysis for the treated mixtures. A slow-scan XPS analysis was performed for the Ir-4f doublet (7/2 and 5/2) and oxygen O-1s peaks in
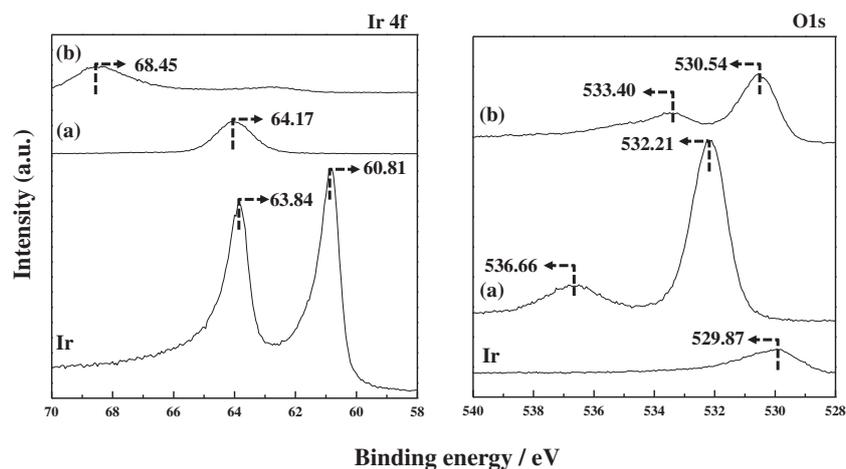
Fig. 4   XPS patterns for test mixtures treated at 600°C for 4 h with molar ratios (Ir : Na_2O_2) of (a) 1 : 0.8 and (b) 1 : 2.0.

the binding energy ranges of 58–72 and 528–540 eV, respectively.

Figure 4 shows the peak-fitted slow-scan XPS spectra of the Ir-4f and O-1s ranges obtained from unprocessed Ir powder and the treated mixtures with molar ratios of (a) 1 : 0.8 (b) 1 : 2 (Ir : Na_2O_2). In the case of Ir powder, binding energies for Ir-$4f_{7/2}$ and Ir-$4f_{5/2}$ were measured to be 60.81 and 63.84 eV, respectively, and these binding energies are in agreement with those of Ir metal.[17] The O-1s spectra for Ir powder shows only one broad peak of low intensity, which is centered near a binding energy of 529.87 eV. This peak results from the residual oxygen on the surface, not from the Ir oxide.[18,19] In the Ir-4f spectra for the fused mixture, all peaks associated with Ir metal disappear, and new peaks were detected at binding energies of 64.17 and 68.45 eV for the molar ratios of (1 : 0.8) and (1 : 2), respectively. Because XPS data for Ir are scarce in the literature, and the alkali-fused Ir compounds do not form stable crystal structures, there is considerable disagreement in the literature, and the peaks for binding energies are not symmetrical.[20–24] Based on the results of previous research studies,[25,26] the binding energy of 64.17 eV can be assigned to IrO_2 with nano-scale features. The appearance of the peak at 68.45 eV may be a result of final-state screening, such as a conduction band interaction during the photoemission process.[27] In Fig. 4(a) of the O-1s spectra, the highest energy peak at 536.66 eV is an Na KLL Auger peak.[28] The peak at 532.21 eV is the same as a single peak in O-1s in native IrO_2, and it represents the Ir-O-Ir contribution.[17] In Fig. 4(b) of the O-1s spectra, two peaks were detected at the binding energies of 533.4 and 530.54 eV. The peak at 533.4 eV indicates the existence of an impurity with a higher oxidation state in the IrO_2 matrix.[25] The peak at 530.54 eV can be explained by IrO_2 with excess oxygen, for which the ratio of O-to-Ir is larger than 2.[28] These results imply that the alkali fusion reaction occurred sufficiently with the molar ratio of 1 : 2 (Ir : Na_2O_2) when treated at 600°C for 4 h.

3.2   High-temperature leaching of iridium from the fused mixtures

Leaching tests were performed at several leachate concentrations, temperatures with the fused samples. In all leaching
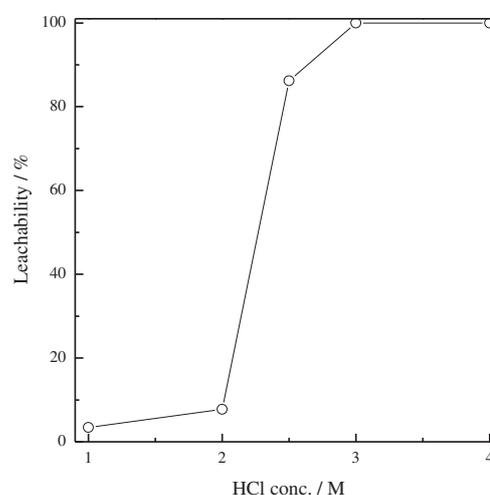

Fig. 5   Effect of HCl concentration on iridium leachability for the alkali-fused iridium mixed with Na_2O_2 (1 : 2) at 600°C for 4 h (leaching time: 1 h, temperature: 130°C, total Ir content: 1.77 mass%).

tests, leaching time, HCl volume and total Ir content were fixed at 60 min, 150 mL and 1.77 mass%, respectively.

Figure 5 shows the effect of HCl concentration on the leachability of Ir at 130°C. The fused sample (Ir-Na_2O_2 ratio: 1 : 2, fusion temperature: 600°C, fusion duration: 4 h) was used as the leaching test material. A fused sample weighing 6 g was added to HCl solution to yield a total Ir content of 1.77 mass%. As shown in Fig. 5, the leachability changed from less than 10% in the 2 M HCl solution to 86.2% in the 2.5 M HCl solution. The Ir was completely dissolved at HCl concentrations of 3 M or higher.

The influence of temperature on Ir dissolution was investigated in the range of 40 to 130°C (Fig. 6). Three fused samples with different Na_2O_2 ratios were used in this leaching study. To maintain the total Ir content at 1.77 mass%, the ratio of solid/liquid was altered for the different samples (Table 1).

The total leaching rate of Ir increased with an increase in the amount of Na_2O_2, and the leachability increased with temperature. For the 1 : 0.8 ratio, high-temperature leaching (>100°C) was required to thoroughly dissolve the iridium.
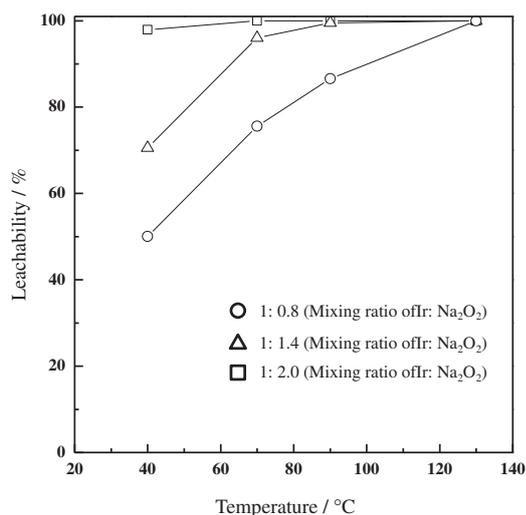
Fig. 6   Effect of the digestion temperature on Ir leachability with changes in the Na_2O_2 to Ir ratio at 600°C for 4 h (digestion time: 1 h, HCl concentration: 3 M, total Ir content: 1.77 mass%).

Table 1   Solid/liquid ratio and Ir content used in the leaching study.

Mixing ratio in fusion treatment (Ir : Na_2O_2)	1 : 0.8	1 : 1.4	1 : 2.0
Input weight of the fused sample (g)	8	10.67	16
HCl volume (mL)	150	150	150
Total Ir content (mass%)	1.77	1.77	1.77

For the ratios of 1 : 1.4 and 1 : 2.0, Ir could be dissolved entirely in the 3 M HCl solution at 90°C. Moreover for the fused sample with a 1 : 2.0 ratio, leachability was 97.9% at only 40°C and attained 100% at 70°C. This result implies that Ir can be dissolved completely at temperatures below 100°C by implementing an alkali fusion pretreatment step with Na_2O_2.

4.   Conclusions

Due to the need for new recovery processes capable of recovering iridium from Ir-containing wastes, leaching of iridium in hydrochloric acid after alkali fusion treatment with Na_2O_2 was studied as a function of fusion and leaching conditions. The results of this study allow the following conclusions to be made:

(1) For the alkali fusion process at 500°C, unreacted Na_2O_2 remained in the treated mixture after 24 h of fusion time, whereas Ir in the metal state disappeared and new Ir-containing components were detected using XRD and XPS. In the samples treated at 600°C, the fusion treatment for only 4 h enabled the starting constituents (Ir and Na_2O_2) to be converted into new Na-Ir-O compounds.

(2) Using an alkali fusion treatment step, Ir was transformed into IrO_2 with nano-scale features. With increased amounts of Na_2O_2, the structure of IrO_2 may be changed to include Na and may also form a higher oxidation state with a ratio of O-to-Ir larger than 2.

(3) After the fusion treatment, the leachability of Ir increases as the concentration of HCl increases and achieves to 100% dissolution at HCl concentrations above 3 M.

(4) When leaching at 130°C, the complete recovery of Ir can be attained from the samples fused at 600°C with Na_2O_2 ratio of 0.8 to 2.0. Additionally fused samples with the 1 : 2.0 ratio allow complete dissolution of Ir at less than 70°C.

Acknowledgement

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