

Research paper

Oxidative fluorination of iridium metal for urban mining: Kinetic studies

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Abstract

The process of oxidative fluorination of a compact iridium metal has been studied. For this purpose, tetrafluoridobromates(III) of alkali and alkaline-earth metals were chosen as oxidizing agents with numerous advantages. The main results of this work include the kinetic dependencies for the two following processes: 1) interaction of iridium with molten potassium tetrafluoridobromate; and 2) interaction of iridium with a solution of potassium tetrafluoridobromate in liquid bromine trifluoride. In both cases it has been found out that iridium can be transformed into its soluble fluorinated derivative; the reaction with molten potassium tetrafluoridobromate proceeds almost 50 times faster (in comparison to the interaction in BrF₃ solution) and can be potentially applied for the practical purposes.

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Keywords: Iridium; Urban mining; Oxidative fluorination; Tetrafluoridobromates; Kinetics

1. Introduction

In a general case, “urban mining” is a complex process of extraction and separation of valuable components (such as precious, rare, and rare-earth metals) from industrial and/or solid urban wastes: used electronics, batteries, magnets, and catalysts. Search for effective methods of recovery of such expensive components as noble, rare, and rare earth metals is a top priority task for modern industry. This fact can be figured out from the recent trends in patent and innovation activities on waste processing, recycling and recovery of materials from consumer products, which grow rapidly in such countries as India, USA, Germany, Japan, etc. [1,2]. Re-obtaining the valuable metals from electronic scrap is extremely important for both economic and environmental reasons, e.g. it improves resource efficiency of production, decreases expenses for raw materials and prevents environmental and health issues of inappropriate landfilling in open dumps [2–5].

Nowadays, numerous technologies for the extraction of a wide range of metals exist [6]. However, an optimal solution has not yet been found because of technological and organization issues. As suggested in Ref. [3], the main challenge in waste processing is to deal with the impurities that are present in waste along with the target metals. Common technologies imply homogenization of an initial scrap material, separation or/and chemical treatment with acids (e.g. hydrofluoric acid or aqua regia). These agents have technological disadvantages such as big amounts of liquid acidic waste formed during the first stage of treatment and long duration of the process. As far as the organization aspects are concerned, the level of recycling of rare, rare earth and noble metals is very limited, and there are only a few companies in Europe that are actively involved in recovery processes while the major part of them deal only with the initial collection, dismantling and pre-processing of scrap [3,7].

In the present work we focused on such prospective oxidizing agents as tetrafluoridobromates(III) of alkali and alkaline-earth metals. This is a substance class with a general formula of MBrF₄ (where M = Na, K, Rb, Cs) or M(BrF₄)₂, where M = Ba [8–10]. As reported previously in Ref. [11], they demonstrate significant advantages when compared to the above-mentioned traditional techniques, both groups being strong fluorinating agents. This is primarily because these substances are solid and relatively stable under normal conditions. It was previously shown that their extreme oxidative and fluorinating capacity

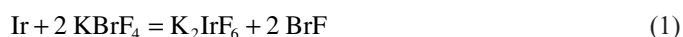
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reveals during their thermal decomposition [11]. These two facts provide a basis for their convenient usage in such important procedures as decomposition of the most inert samples and treatment of individual noble metals with further conversion into a liquid form and their recovery as solid metals and/or alloys. Numerous experiments were done to confirm successful oxidative activity of tetrafluoridobromates in case of noble metals where a complete transformation into soluble forms was achieved without significant losses [12,13].

In our previous work [11] the detailed studies on oxidative fluorination have involved a series of interactions of iridium metal with potassium tetrafluoridobromate in different ratios: a high excess of fluorinating agent with Ir:KBrF₄ = 1:12 by mass/1:11.8 (molar), as well as in stoichiometric, and under-stoichiometric ratios (Ir:KBrF₄ = 1:1 by mass, 1:1.02 by moles) in terms of the following reaction:



The experiments on interactions between iridium and tetrafluoridobromates of Rb, Cs, and Ba in stoichiometric ratios were also carried out [11]. All the principal results including the phase analysis by means of X-ray powder diffraction as well as simultaneous thermogravimetric and differential thermal analyses of reaction mixtures were obtained and interpreted. In summary, it was shown that in all cases it was possible to obtain the corresponding hexafluoridoiridates(IV).

However, for the practical application in analytical chemistry and industry, a deeper insight into the above-mentioned oxidative fluorination process is crucial. In the present work we report the results of our detailed investigations on the kinetics of the oxidative fluorination of iridium metal. Iridium has been chosen for the study because this metal has special importance for industry. It is commonly used as a hardening agent in thermo-resistive alloys and as a component of several catalysts in oil refinery and in automobile industry for reduction of nitrogen oxide emissions. In a compact form, this metal exhibits strong chemical resistance to aggressive media of organic and mineral acids that significantly complicates its transformation into a soluble form for further recovery [13].

2. Materials and methods

For the described kinetic studies, BrF₃ was used as a solvent for KBrF₄ in the temperature range up to 130 °C (403 K, close to the boiling point of pure BrF₃). At the temperature of 400 °C (673 K) pure KBrF₄ was used as a fluorinating agent.

All experiments were carried out in isothermal conditions; the temperature measurements were recorded using a chrome–aluminum thermocouple and the device for data acquisition “cFP–2100” (National Instruments). The accuracy of temperature control was ±0.25 K. Iridium metal was used in a form of small cylinders with the diameter of 2.5 mm and the length exceeding the diameter no more than 1.8 times, with a total mass of ~0.5 g and purity of 99.9%.

2.1. Synthesis of BrF₃

Bromine trifluoride was synthesized in a nickel reactor using liquid bromine (JSC Vekton, chemically pure) and elemental

fluorine obtained directly in the laboratory using a fluorine cell with consequent purification on sodium fluoride. The obtained product was distilled using the technique described in Ref. [14], and stored in tightly closed PTFE containers. It was distilled again immediately before the synthesis of KBrF₄.

2.2. Synthesis of KBrF₄

KBrF₄ was synthesized in three-component heterogeneous system containing solid potassium fluoride (JSC Vekton, analytical grade) and two non-mixing liquids: bromine trifluoride and Freon-113 (Roskholoda Ltd., technical grade). The technique is described in our previous studies [9,10].

2.3. Interaction between iridium metal and molten KBrF₄

The reaction was carried out in a glass–carbon crucible at the temperature of 673 K under argon atmosphere. The average mass of KBrF₄ in the mixture was 5 g so that the mass ratio of Ir:KBrF₄ was close to 1:10 (1:9.85 by moles).

After the interaction the crucible was cooled, the product was hydrolyzed in water, and the surface area of the clean iridium sample was measured using a vernier caliper.

2.4. Interaction between iridium metal and KBrF₄ dissolved in BrF₃

This series of experiments was performed in PTFE crucibles in isothermal conditions at 373, 388 and 403 K at various times of the process (up to 6 hours). KBrF₄ was formed *in situ*. The fivefold excess of bromine trifluoride was used to prevent the formation of bromine monofluoride as well as to maintain the enough amount of liquid medium for dissolving the reaction products.

A sample of iridium was put into a crucible; KF and BrF₃ were added in a mass ratio of Ir:KF:BrF₃ = 1:1.21:5 (1:4.01:7.02 by moles). The pre-distillation of possible volatile impurities was performed by evacuation until the pressure was close to the vapor pressure of bromine trifluoride at 298 K (~0.01 bar). The crucible with the initial mixture was tightly closed with a PTFE stopper and inserted into a furnace at a fixed temperature. After 6 hours, the crucible was rapidly cooled, and the amount of dissolved iridium as well as its surface area was measured after sample cleaning according to the procedure described above.

3. Results and discussion

In this research we have studied kinetic dependencies for the two following processes: interaction of iridium metal with molten potassium tetrafluoridobromate, and with the solution of potassium tetrafluoridobromate in liquid bromine. The formal rate of transformation of iridium into its fluorinated derivative is accounted as a main quantitative characteristic for both experiments.

3.1. Interaction of molten potassium tetrafluoridobromate with iridium metal

In this series of experiments with different interaction times, the initial substances were mixed in a mass ratio of

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