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Morphology of uranium electrodeposits on cathode in electrorefining process: A phase-field simulation

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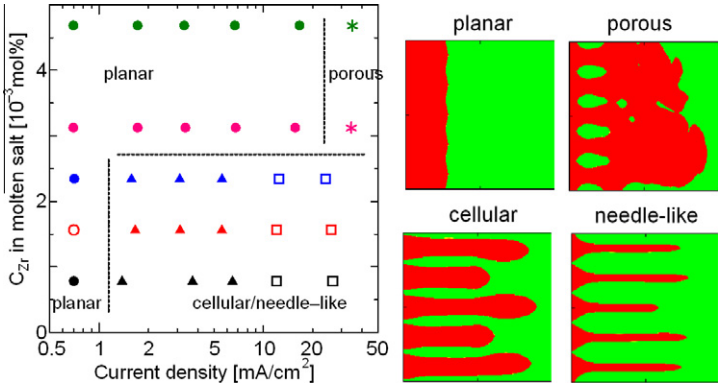
GRAPHICAL ABSTRACT



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ABSTRACT

Morphology of uranium electrodeposits on cathode with respect to applied voltage, zirconium concentration in the molten salt and the size of primary deposit during pyroprocessing is systematically investigated by the phase-field simulation. It is found that there is a threshold zirconium concentration in the molten salt demarcating planar and cellular/needle-like electrodeposits, which agrees with experimental results. In addition, the effect of size of primary deposits on the morphology of electrodeposits is examined. It is then confirmed that cellular/needle-like electrodeposits are formed from large primary deposits at all applied voltages considered, whereas both the planar and cellular/needle-like electrodeposits are formed from the primary deposits of 10 μm and less.

1. Introduction

Molten salt electrorefining is a main process of pyro-metallurgical reprocessing for spent metal fuels [1–9]. By electrolysis, a spent metal fuel is dissolved from an anode and simultaneously a uranium product and an uranium/trans-uranium product are recovered on a solid cathode and in a liquid cadmium cathode, respectively, as illustrated in Fig. 1a [8]. At the solid cathode, the uranium product has a variety of shapes such as cellular, dendritic and planar structures depending on the experimental condition [3,4,8,9]. In particular, current density, electrode potential and zirconium impurity strongly affect the morphology of uranium electrodeposits as shown in Fig. 1b, which are quoted from Ref. [8]. The control of morphology is an essential issue to design the industrial apparatus since the uranium dendrite is recovered mechanically after electrolysis. Therefore, it is very significant to understand the effect of such controllable parameters on the morphology of electrodeposits. Under such a situation, we have performed the controlled-current electrolyses of uranium from

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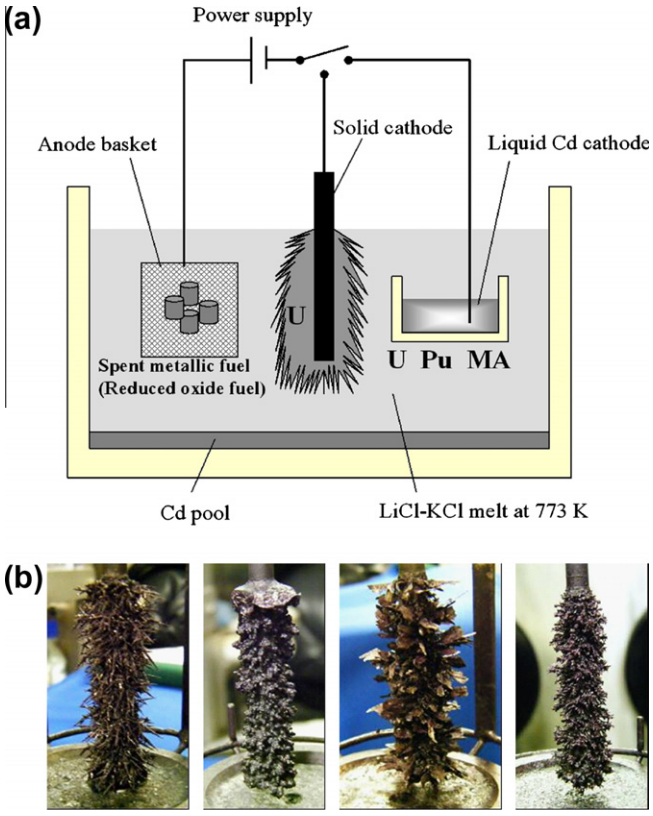

Fig. 1. (a) Schematic image of electrorefining step. (b) Typical pictures of uranium dendrite under various conditions: (from left to right) high current density, high zirconium impurity, high current density and zirconium impurity, and a reference condition. Reprinted from Ref. [8], with permission from Elsevier.

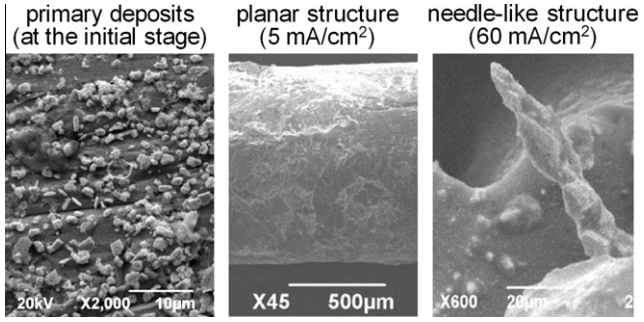

Fig. 2. SEM images of the primary deposits, the planar-shape deposit and the needle-like shape deposit of uranium obtained by the controlled-current electrolyses of uranium from 1.53 wt.% UCl_3–LiCl–KCl at 773 K, which are quoted from Ref. [9] with modification in layout.

LiCl–KCl eutectic salt and examined the morphology of uranium dendrites as a function of current density [9]. Fig. 2 shows scanning electron microscope (SEM) images of uranium deposits obtained by the electrolyses, which are quote from Ref. [9] with modification in layout. From the SEM images, it is confirmed that the primary deposits are formed at the initial stage, and then some of them evolve to the needle-like uranium deposits at the higher current density whereas the planar-shape deposits are formed at the lower current density. The threshold current density is estimated to be between 5 and 10 mA/cm^2 from the morphology diagram. Detail of the experimental condition is reported in another paper [9].

Parallel to a lot of effort from the experimental approach, computational studies have also contributed to understand various properties of uranium, uranium oxide and other nuclear fuels. Now, mainstream of computational studies on nuclear fuels is the atomic simulation such as classical [10–16] and quantum [17] molecular dynamics (MD) simulations and a static *ab initio* calculation [18] since their methodologies have been established over the years. For example, structure of molten uranium chloride [10], diffusion of oxygen and uranium in uranium dioxide [11], thermal conductivity in uranium oxide [12–14] and uranium–plutonium oxide [13], defects formation in uranium dioxide [15] and fracture behavior in crystal uranium oxide [16] have been investigated by classical MD simulation using the Born–Mayer–Huggins (BMH) and Morse potentials. Although the MD simulation is powerful tool to understand various properties of nuclear fuels including its dynamics, the temporal–spatial scale of MD simulation is limited in the order of nanoseconds and nanometers. Therefore, it is not straightforward to compare the results from MD simulations directly with experimental results in meso- and macro-scales at present, although acceleration techniques of MD simulation have been extensively developed and employed in the field of material science [19,20]. Therefore, meso- and macro-scale simulations are essential to examine complex phenomena at electrodes during electrorefining as describe above.

On the other hand, meso- and macro-scale techniques such as the fractal dimension analysis [21], the diffusion-limited aggregation (DLA) model [22], the mean-field model [23,24] and phase-field model [25–32] have been employed to understand a complex morphology of various materials in process, although these techniques are not widely-applied to the nuclear fuels yet. Among them, the phase-field model is suited for the calculation of morphological evolution of various materials in process since it can treat a free boundary problem in the biphasic system explicitly [33,34]. Under such circumstances, we have taken the lead in the development of a phase-field model for the electrochemical process, in which the uranium and zirconium in molten-salt are taken into account, and examined the uranium dendrite growth on the planar cathode [8]. Since then, the SEM observation of the cathode after the uranium electrodeposition in LiCl–KCl eutectic salt [9] revealed that the primary deposits are formed at the initial stage and some of them evolve to uranium dendrites as shown in Fig. 2, which is not taken into account in our previous work [8]. Therefore, the growth of uranium electrodeposits from primary deposits is focused on in this study. In particular, a variety of morphologies with respect to the applied voltage, concentration of zirconium in molten salt and the size of primary deposits is discussed. After summarizing the phase-field model for electrochemical process following our previous paper [8] in Section 2, the effect of controllable parameters such as applied voltage and zirconium concentration in the molten salt on the morphology of uranium electrodeposits is examined in Section 3.1. Then, the phase diagram of morphology of uranium electrodeposits with respect to the zirconium concentration in the molten salt and the current density, which is estimated on the basis of Faraday's laws of electrolysis, is summarized in Section 3.2. Moreover, the size effect of primary deposits on the morphology of uranium electrodeposits is examined in Section 3.3.

2. Simulation methodology

2.1. Phase-field model for electrochemical process

A phase-field model is employed to study the morphology of uranium electrodeposits on cathode during pyroprocessing. In general, a state of the phase is represented by the value of the phase