

Review

# Phase Equilibrium Study of Rare Earth Oxide–Fluoride Salt System: A Review

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**Abstract:** The applications of rare earth metals and alloys are becoming increasingly widespread and there is a strong market demand. Currently, most of the production enterprises adopt the fluoride–oxide system for electrolytic preparation of rare earth metals and alloys. The solubility of rare earth oxides in molten salt directly affects the selection of operational parameters in the electrolysis process. When the added amount of  $\text{RE}_2\text{O}_3$  is less than its solubility, it leads to a decreased electrolytic efficiency. Conversely, an excessive amount of oxide is prone to settle at the bottom of the electrolytic cell, impeding smooth production. The  $\text{RE}_2\text{O}_3$  solubility in the fluoride salt can be represented by the phase equilibrium of the  $\text{RE}_2\text{O}_3$ – $\text{REF}_3$ – $\text{LiF}$  system. The isothermal lines in the primary phase field of rare earth oxide represent the solubility of the oxide in the fluoride salt at the corresponding temperature. This paper outlines the research methods and experimental results on the phase equilibria of the  $\text{RE}_2\text{O}_3$ – $\text{REF}_3$ – $\text{LiF}$  system. The characteristics and existing problems in the current phase equilibrium study are analyzed. The solubility data of  $\text{RE}_2\text{O}_3$  are expressed in the forms of ternary and pseudo-binary phase diagrams of the  $\text{RE}_2\text{O}_3$ – $\text{REF}_3$ – $\text{LiF}$  system, providing theoretical guidance for the establishment of an accurate and reliable rare earth electrolysis system database and the optimization of electrolytic processes.

**Keywords:** rare earth; molten salt electrolysis; phase equilibrium; solubility



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## 1. Introduction

Rare earth metals and alloys are increasingly used in the field of new materials, and there is a strong market demand. Rare earth elements have unique physical and chemical properties due to their special electronic structures, such as excellent optical and electrical properties, magnetic properties, and active chemical properties. With the development of modern science and technology, REEs have become indispensable key materials for high-tech and novel functional materials [1,2].

In recent years, with the momentum of technological innovation and the ongoing revolution in global manufacturing, there have been significant changes in the consumption structure of REEs, with an increasing production of rare earth metals such as La, Ce, Nd, Pr, and Y [3–5]. The production of rare earth metals and alloys is an important component of the rare earth industry. Rare earth metals, being highly reactive, are usually produced from chloride or oxide raw materials using two major methods: metallothermic reduction and molten salt electrolysis. Compared with thermal reduction, molten salt electrolysis is a relatively economical method as it allows continuous production and easy control of product quality. It is currently widely used in the production of single rare earth metals, such as La, Ce, Pr, and Nd, and mixed rare earth metal alloys [6–9].

The production of rare earth metals and alloys by molten salt electrolysis can be divided into two categories: a chloride melt system and an oxide–fluoride melt system. The

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