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Study on the Solubility of RE_2O_3 (RE=La and Nd) in Light Rare Earth Fluoride Molten Salts

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Abstract: The chemical reaction and dissolution processes of RE_2O_3 in REF_3-LiF (RE=La and Nd) molten salts were studied by X-ray diffraction, differential thermal analysis and chemical analysis. Firstly, RE_2O_3 disperses in molten salts and reacts with REF_3 and LiF, which lead to the generation of a new phase REOF, resulting in the dissociatation or form of complex ions by part of REOF, and the sedimentation of excessive REOF at the bottom. The RE contents in molten salts were used to determine the solubility of RE_2O_3. The results show that with the 20%~40% of REF_3, the solubility ranges 1.79~3.05 g RE_2O_3 per 100 g electrolyte and the corresponding mole concentration is 0.33%~0.87%. RE_2O_3 solubility increases with increasing temperature and REF_3 concentration. The natural logarithm of the RE_2O_3 solubility is plotted against 1/*T* and can be interpreted by linear relationship. The fitting parameters can be used to estimate the solubility of RE_2O_3 with minimized experimental efforts and difficult experiment conditions.

Keywords: REF_3-LiF; RE_2O_3; rare earth; molten salts; solubility; electrolyte

1 Introduction

In modern industry, rare earth metals play an increasingly important role in the field of metal materials [1-3] and the most important method for the preparation of rare earth metals and its alloys is electrolyzing in REF_3-LiF-RE_2O_3 molten salts system. Chen et al [4-5] have researched the preparation processes of Nd by submerged liquid cathod. Wang et al [6-8] have simulated electric, flow and temperature field in a 10 kA bottom-cathode-structure rare earth electrolytic cell. Those above researches indicate that the foundation and development of novel electrolysis technology and equipment are also based on the REF_3-LiF-RE_2O_3 molten salts system. Moreover, the REF_3-LiF molten salts attract increasing use interests in extracting valuable lanthanum elements from the reprocess of nuclear wastes [9-11].

However, for achieving better application of this molten salts system, the detailed physicochemical properties of electrolytes containing liquidus temperature [12], solubility limit of RE_2O_3 [13, 14], surface tension [15], ionic structure [16], density [17] need to be studied. The knowledge of physicochemical properties contained and so on. Those were useful for understanding well the mechanism and process of electrolysis. Especially the dissolution behavior and solubility of RE_2O_3 in REF_3-LiF molten salts are pivotal for establishing reasonable RE_2O_3 addition system in the practical production. The solubility of RE_2O_3 was widely researched in the previous reports: the solubility of RE_2O_3 (RE=La, Ce, Nd, Pr, Y, Sm, Yb and Eu) in molten chlorides [18, 19], the solubility of RE_2O_3 (RE=La, Nd, Y, Sm, and Ho) in molten fluorides [20-23], and review research on the solubility of RE_2O_3 in molten salts [24-26]. However, the large data variation in solubility values in the previous researches indicates the inconsistency of different investigations. So the accurate determinations of RE_2O_3 solubility in REF_3-LiF molten salts will have theoretical and practical meanings.

RE_2O_3 need to be added continuously for supplementing the consumption in the practical production. It was found that the current efficiency increases and then reaches the highest value with the increasing feeding speed of RE_2O_3 [27]. However, due to the complex chemical reaction and limited solubility of RE_2O_3 in the RE_3-LiF molten salts, excessively increasing feeding speed will lead to the precipitation and slag, which terribly effects to the electrolysis process. And the analysis showes that REOF is the main chemical composition of the precipitation [28].

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