An Electrochemical Measuring Apparatus Applied to Molten Salts

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1. Introduction

Electrochemical technology in the reaction media of molten salts has been considered as an important route to treat raw materials, prepare metals and alloys. Moreover, pyroprocessing employing electrolytic technology in the molten salts, adopted in spent nuclear fuel cycle, is considered as a promising method to deal with high-burn-up, short-cooled, high-plutonium-concentration spent fuels. The basic data, such as formal potential, diffusion coefficient, electrode mechanism, is of importance in developing this technology [1, 2]. A set of electrochemical measuring apparatus is designed and constructed to obtain the required data, which proves to be simply-structure and steady-performance.

Asteady reference electrode is of importance to accurate measurements. However, there is no widely accepted reference electrode in molten salts electrochemistry [3-5]. An innovative reference electrode was designed and fabricated first, with which a three-electrode measuring system was set up. Due to the sensitiveness of residue moisture in the chlorides melts electrochemical measurement, the apparatus should be able to purify the chlorides. According to the purification requirements, a combined procedureof vacuum desiccation and dry HCl chlorination was employed. On considering gas protection requirements associated with molten chlorides electrochemical experiment, a chamber sealed with a water cooled lid was designed and connected with vacuum and gas treatment [6], which is capable to fulfill the serious requirements of both the molten salts purification and the supply of gas protection to satisfy the rigid requirements of basic electrochemical data measurement in molten salts media.

2. Experiment

Asimply-structure, steady-performance Ag-AgCl reference electrode was fabricated, which uses Pyrex glass as ions conducting membrane. With hardly no inert material in molten salts, Mo, Pt andW wire sealed in quartz tube are employed as working electroderespectively. The auxiliary electrode is a graphite rode. According to the results of resistance dependence on temperature (Fig.1), Cl_2/Cl- measurement (Fig.2), and measurement of U^{3+}/U potential[7], the Ag-AgCl reference electrode is proved to be resistance suitable, potential constant, and stability satisfactory.

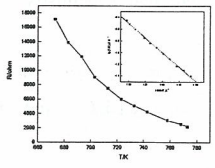

Fig. 1 Resistance of reference dependence on temperature

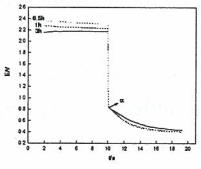

Fig.2 Electrode potential of Cl2/Cl- with the reference electrode

The molten salts electrochemical measurement system consists of a three-electrode cell and a Princeton Applied Research PAR273A potentiostat with a EG&G M273A electrochemical software (Fig.3). In order to prevent the high causticity of the molten salts, the Si_3N_4 crucible was adopted which performs satisfactorily. The heating equipment is a 30kw medium frequency induction heating oven. A K-type thermocouple sealed in an Al_2O_3 sheath was employed. The molten salts purifying system consists of a vacuum desiccation

part（working pressure<80Pa）and a reactant gas bubbling tube offering HCl in molten chlorides[8].

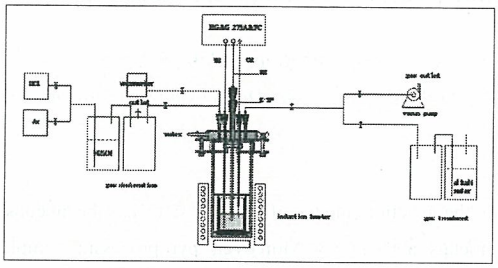

Fig.3 Schematic diagram of the apparatus

3. Results and discussion

Compared with other molten salts electrolytic apparatus, with this one satisfactory result could be obtained and no complicated and expensive glove box is needed in order to carry out electrode process study concerning non-radioactive element. The apparatus is multifunctional capable to operate both chlorides and fluorides with some parts exchanged. In order to carry out measurement in molten fluorides, SS316 should be selected as the water-cooled lid, and Si_3N_4ceramic can be adopted to build the chamber and crucible.

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