Study on the mechanism of deoxidization and purification for

Li_2BeF_4 molten salt via graphite nanoparticles

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Abstract

Graphite nanoparticles originated from high purity graphite crucible were used for deoxidization and purification of Li_2BeF_4 molten salt containing a bit of $(\text{NH}_4)_2\text{BeF}_4$ under high temperature vacuum condition. And the mechanism of deoxidization and purification via graphite nanoparticles was put forward based on analysis of sample characterization and chemical reaction Gibbs free energy calculation. The morphology, particle size, chemical composition and crystal structure of graphite nanoparticles in Li_2BeF_4 molten salt were characterized by High Resolution Transmission Electron Microscopy (HRTEM, SAED and EDS). Phase analysis, total oxygen content, full elemental and anion concentration for as-prepared Li_2BeF_4 products were studied by X-Ray Diffraction (XRD), LECO nitrogen-oxygen analyzer, Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) and Ion Chromatography (IC), respectively. The results of sample characterization showed that graphite nanoparticles in Li_2BeF_4 molten salt were the poly-crystal round sheet shape with an average diameter of $< 100\text{nm}$. The concentration of total oxygen, sulfur and nickel in as-prepared Li_2BeF_4 molten salt after treatment were 548 ppm, < 0.6 ppm and $< 0.4\text{ppm}$, respectively. Experiment and calculation all showed that SO_4^{2-} and NO_3^- could react with carbon at 700°C . And vacuum degassing play an excellent role in deoxidization and purification for Li_2BeF_4 molten salt via graphite nanoparticles.

Keywords: Mechanism; Li_2BeF_4 molten salt; Deoxidization and purification;

Graphite nanoparticles; Vacuum degassing

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1. Introduction

As a new type of high heat flux heat transfer medium, molten salt is widely used in various industrial applications, which include high temperature hydrogen production, nuclear fission / fusion reactors, storage of solar energy, nuclear fuel reprocessing and fuel cell energy field [1-3]. For example, LiF-NaF-KF (46.5-11.5-52 mol%, abbreviated FLINAK), ${}^7\text{LiF-BeF}_2$ (66-34mol%, abbreviated FLiBe), and so on. They have such many remarkable physical and chemical properties as high specific heat, high boiling points, good radiation stability, high density at low pressures, and high-temperature stability [4, 5].

In view of neutron economy, due to element of ${}^7\text{Li}$ ($\sigma_{\text{thermal}}=0.045$ barn), Be ($\sigma_{\text{thermal}}=0.0088$ barn) and F ($\sigma_{\text{thermal}}=0.0098$ barn) having low neutron absorption cross section, ${}^7\text{Li}$, Be and F are main elements of a primary cooling salt [6, 7]. And then, ${}^7\text{LiF-BeF}_2$ mixture is of significance because of its potential applications as a solvent for primary circuit loop in molten-salt reactor [8].

According to ratio of ${}^7\text{LiF-BeF}_2$ (66-34 mol%), its molecular formula should be ${}^7\text{Li}_2\text{BeF}_4$, which is synthesized by high purity ${}^7\text{LiF}$ and high purity $(\text{NH}_4)_2\text{BeF}_4$ [9]. Furthermore, the content of impurities in Li_2BeF_4 molten salt should be at a very low limit value attributed to the stability of physical & chemical properties and corrosion resistance of structure materials [10]. Usually, the oxidizing impurities in fluoride salts have been considered as the main oxidizing driving forces to result in corrosion, such as H_2O , metal oxides, oxyacid, and so on [11]. H_2O among these impurities is extremely hard to be removed completely, and it may react with molten fluorides to generate HF, which then attacks metals to form metal fluorides [12]. For the oxyanions, they have a decrease in the corrosion rate in the order: $\text{P}_2\text{O}_7^{4-} < \text{PO}_4^{3-} < \text{SO}_3^{2-} < \text{SO}_4^{2-} < \text{O}_2^{2-} < \text{CO}_3^{2-}$ which runs parallel to the order of increasing ability of O^{2-} ion donation [13]. Thus, total oxygen content of these oxidizing impurities become one of the most important measure indicators of deoxidization and purification effect for molten salt.

In addition, Sulfur is quite destructive to nickel-based alloys at temperatures above 350°C, because a nickel-nickel sulfide eutectic which melts at about 645°C penetrates the grain boundaries and leads to intergranular attack of the metal [14]. And Chromium in nickel-based alloys can also be attacked by Cr^{3+} , Fe^{3+} , and Ni^{2+} so as to result in corrosion of alloy [15]. Therefore, the other elements besides oxygen also have to be controlled below the limit value in the molten salt, especially for the element of S, Cr, Ni and Fe. [16, 17].

There are several reported methods on deoxidization and purification for Li_2BeF_4 molten salt. For example, NH_4HF_2 reaction [18], re-crystallization [9], HF-H_2 bubbling method [19], electrochemistry [20], etc. Among them, HF-H_2 bubbling method is widely used for deoxidization and purification, which begins at the Oak Ridge National Laboratory (ORNL) in the 1960s [19]. But, this method isn't suitable for industrial production owing to adoption of danger HF-H_2 gas with properties of explosive, corrosive, flammability, highly toxic and high gas pressure. And the HF-H_2 bubbling time is very long [21]. In recent years, the electrochemical method is also employed to remove and monitor the oxygen ions concentration in the molten salt [22]. This technique can only be used to remove oxygen ions, and there is little effect on the oxyanion, such as SO_4^{2-} 、 OH^- 、 NO_3^- 、 PO_4^{3-} , etc. [23]

As we all know, the reduction property of carbon is stronger than hydrogen at high temperatures, and HF can dissolved into fluoride to form HF_2^- [24, 25]. Thence, graphite nanoparticles as reducing agent cooperated with HF_2^- maybe play an excellent role on deoxidization and purification for molten salt, similar to the role of HF-H_2 bubbling method.

In this work, graphite nanoparticles derived from high purity graphite crucible were dispersed in Li_2BeF_4 molten salt containing a bit of $(\text{NH}_4)_2\text{BeF}_4$ under high temperature vacuum condition, and its effect and mechanism of deoxidization and purification was studied.

2. Experiment

2.1 Raw materials and experiment equipment

Li_2BeF_4 molten salt was purchased from Shanghai Feixing special ceramics factory. High-purity graphite crucible with lid were purchased from Shanghai Chemical Reagents Co. Ltd.

High temperature autoclave was not only filled inert gas but also evacuated. (Rated temperature: 1000°C)

2.2 Experiment of deoxidization and purification in the Li_2BeF_4 molten salt

The Li_2BeF_4 molten salt in the high-purity graphite crucible was put into sealing high temperature autoclave which could be vacuumed. First step, the autoclave with atmospheric pressure was heated up to 500°C at a rate of 5°C min^{-1} under argon atmosphere and maintained for 2h. Second step, the autoclave with atmospheric pressure was heated up to 700°C at a rate of 5°C min^{-1} and maintained for 1h. Third step, the gas pressure of autoclave was vacuumed to 1×10^{-3} mmHg and maintained for 3h. At last, the autoclave was naturally cooled to room temperature under vacuum.

2.3 Characterization of sample and Gibbs free energy calculation

1) Graphite nanoparticles in Li_2BeF_4 separated by vacuum filtration were put on the copper mesh, the morphology and size of which were observed by High Resolution Transmission Electron Microscopy with an accelerating voltage of 200kV (HRTEM, Hitachi, H-800, Japan). And the electron diffraction pattern of the graphite nanoparticles was obtained by SAED (Selected-Area Electron Diffraction) of HRTEM. Element qualitative analysis of sample was characterized by EDS (Energy Disperse Spectroscopy) of HRTEM.

2) The Phase compositions were carried out by a standard powder X-ray diffraction with the CuK α radiation (XRD, PANalytical, DY3614, Netherlands). The content of $(\text{NH}_4)_2\text{BeF}_4$ in the Li_2BeF_4 was also determined by XRD.

3) The concentration of main impurities in the samples was analyzed by Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES, ThermoFisher, America).

4) The total oxygen content in the Li_2BeF_4 molten salt was measured using LOD (LECO RO600, LECO Co., Ltd.). The other oxygenated anions in molten salt were determined by ICE ion chromatography (IC, ThermoFisher, America).

5) Chemical reaction Gibbs free energy calculations were carried out by HSC chemistry 6.0 software.

3 Results and discussion

3.1 Characterization of graphite nanoparticles in Li_2BeF_4 molten salt

The photograph of Li_2BeF_4 before and after treatment could be seen from Fig. 1 A and B. The color of raw Li_2BeF_4 was white in Fig. 1 A. Li_2BeF_4 after treatment was homogeneous grey-black glossy crystals in Fig.1 B. The results showed that the graphite nanoparticles were dispersed into the Li_2BeF_4 molten salt as a result of the raw Li_2BeF_4 salt's color turning from white to grey-black.

The electron diffraction ring of the SAED pattern in Fig. 1 C showed that the graphite nanoparticles had polycrystalline structure. The spacing distance corresponding to electron diffraction ring were 3.3756 Å, 2.0390 Å and 1.1604 Å from the center to the outer ring, and the miller indices were (002), (101) and (112), respectively. And the measuring lattice distance was approximately 3.37 Å corresponding to crystal planes of (002), in Fig. 1 D. These values could correspond better to the JCPDS card No. 41-1487 of graphite whose measured density was 2.16 g/cm³. Due to the graphite having flakes-like structures, TEM image showed that the morphology of the graphite nanoparticles in the Li_2BeF_4 was mainly round-sheet shape and with an average diameter of < 100nm according to the image contrast of TEM.

EDS pattern in Fig. 1 E indicated the main element of nanoparticles was carbon, and the copper element was originated from the sample holder of TEM. There were no other impurities found in the nanoparticles.

Fig. 1 Photograph of Li_2BeF_4 molten salt before (A) and after treatment (B); TEM & SAED (C), HRTEM (D) and EDS pattern (E) of graphite nanoparticles

3.2 Content analysis of impurity element in Li_2BeF_4 molten salt

In Tab. 1, before and after the raw Li_2BeF_4 molten salt treatment, the concentration of S and Ni were reduced from 30.7 ppm to < 0.6 ppm and from 60.6 ppm to < 0.4 ppm, respectively. And they were near to the detection limit of the ICP-OES instrument. S and Ni could be removed in the Li_2BeF_4 molten salt. However, the most of impurities' element concentration were increased, such as Mg, Ca, Si, P, Cr and Fe, and so on. Because this experiment just involved in high pure graphite crucible except for Li_2BeF_4 molten salt. Therefore, these impurities were originated from high pure graphite crucible. Especially, Cr and Fe in high pure graphite crucible should be controlled to a certain limit value.

The EDS pattern (in Fig. 1 E) showed that there were no other peaks of impurities' element in graphite nanoparticles. It confirmed indirectly that the impurities' element of graphite nanoparticles derived from graphite crucible was almost dissolved in Li_2BeF_4 molten salt.

Tab. 1 content of impurities' elements in Li_2BeF_4 molten salt

Impurities' elements	Unit	Concentration	
		Raw Li_2BeF_4	Treated Li_2BeF_4
Ti	ppm	0.8	3.0
Mg	ppm	13.5	67.2

Ca	ppm	23.1	56.4
Ba	ppm	34.8	39.0
Ni	ppm	60.6	< 0.4
Mo	ppm	0.6	< 0.2
Cr	ppm	1.6	18.3
Fe	ppm	40.0	120.1
Cu	ppm	<0.3	< 0.3
Pb	ppm	<0.8	< 0.8
Cd	ppm	< 0.05	< 0.05
Zn	ppm	1.1	0.6
Co	ppm	< 0.2	< 0.2
P	ppm	35.1	88.6
Si	ppm	16.5	29.7
S	ppm	30.7	< 0.6
B	ppm	< 0.5	0.7
W	ppm	< 0.5	3.5
Mn	ppm	5.7	3.4
Zr	ppm	0.9	1.9

3.3 Content analysis of oxyacid and total oxygen

Based on the IC results (in Tab. 2), NO_3^- and SO_4^{2-} were not found in the Li_2BeF_4 molten salt after treatment. This indicated that NO_3^- and SO_4^{2-} were removed by graphite nanoparticles efficiently. However, the anions concentration of PO_4^{3-} was increased from 98.0ppm to 232.1ppm. It also proved indirectly that PO_4^{3-} was not react with graphite nanoparticles. The increment of PO_4^{3-} anion was 134.1 ppm. And P concentration converted by PO_4^{3-} anion was 43.76 ppm. According to Tab. 1, P concentration increased 53.5 ppm. As a result, there was P element of 9.74 ppm existed by non PO_4^{3-} forms in the molten salt. In addition, although the concentration of oxyacid containing Si element was not given owing to the reason of ICE ion chromatography test in this work, it was not involved in the reaction similar to P element. And then parts of oxygen which could not react with carbon were remained in the Li_2BeF_4 molten salt. The concentration of total oxygen in the Li_2BeF_4 molten salt was greatly reduced from 1978 ppm to 548 ppm.

By the way, due to HF_2^- having corrosive property as a result of damage to ICE ion chromatography instrument, there was no test for concentration of HF_2^- anion.

Tab. 2 Content of oxyacid and total oxygen in Li_2BeF_4 molten salt

Kinds		unit	Li_2BeF_4	Li_2BeF_4 Treatment
Oxyacid	PO_4^{3-}	ppm	98.0	232.1
	SO_4^{2-}	ppm	89.5	---
	NO_3^-	ppm	26.8	---
total oxygen		ppm	1978	548

3.4 Phase analysis

The XRD pattern (Fig. 2 A) and partial XRD (Fig. 2 B) patterns of Li_2BeF_4 molten salt before (I) and after treatment (II) was shown in Fig. 2. The Li_2BeF_4 phase with a rhombohedral system was in good agreement with the JCPDS card No. 00-20-0116. And there was no change on the Li_2BeF_4 crystalline phase before and after treatment. Based on Fig. 2 A, 2θ angle interval of $36^\circ \sim 37^\circ$ was selected for further analyzing the residual $(\text{NH}_4)_2\text{BeF}_4$ phase of Li_2BeF_4 molten salt in Fig. 2 B. Compared with Fig. 2 B (II), there were two obvious diffraction peaks located at $2\theta=36.4^\circ$ and $2\theta=36.5^\circ$ corresponding to $d=2.4682 \text{ \AA}$ and $d=2.4616 \text{ \AA}$ in Fig. 2 B (I). According to JCPDS card No. 01-083-2335 of $(\text{NH}_4)_2\text{BeF}_4$, there were two diffraction peaks located at $2\theta=36.31^\circ$ ($d=2.47 \text{ \AA}$) and $2\theta=36.59^\circ$ ($d=2.45 \text{ \AA}$), which corresponded to the crystal plane of (140) and (310). In view of raw material's components in this experiment, it could prove that these two diffraction peaks belonged to the residual $(\text{NH}_4)_2\text{BeF}_4$. At the same time, the proportion of residual $(\text{NH}_4)_2\text{BeF}_4$ was about three percent in the Li_2BeF_4 via XRD quantitative analysis. Furthermore, these two diffraction peaks were disappeared in Fig. 2 B (II). Therefore, it was concluded that the residual $(\text{NH}_4)_2\text{BeF}_4$ could be decomposed after treatment. In addition, the broadening peak located at $2\theta=21.89^\circ$ was originated from sealing film of sample preparation.

Fig. 2. XRD patterns (A) and Partial XRD patterns (B) of Li_2BeF_4 molten salt before (I) and after treatment (II).

3.5 Gibbs free energy calculation and analysis of chemical reaction

Chemical reaction in Li_2BeF_4 molten salt needed to be considered together, containing hydrolysis, carbon reduction, displacement reaction, and so forth. The results of Gibbs free energy calculation on several main reactions were following in Tab. 3. In this work, 700 °C was selected as reaction temperature. According to above-mentioned analysis result of ICP-OES and IC, it could explain that Ni metal produced by reaction of hydrolysis and carbon reduction in succession was separated from molten salt by precipitation owing to its high density (8.902 g/cm³), compared with Li_2BeF_4 's low density (1.805 g/cm³, 700°C[26]), in Tab. 3 (1, 2). Therefore, the content of Ni decreased to < 0.4 ppm in Li_2BeF_4 molten salt.

Representative chemical reaction of substances containing oxygen were also listed in Tab. 3 (2~6). For example, NO_3^- and SO_4^{2-} could react with carbon at 700°C in Tab. 3 (3, 4). Carbon could also react with H_2O , hydroxide and part of oxide in Tab. 3 (2, 5, 6). But some substances could not react with carbon below 700°C via calculation, such as SiO_3^{2-} , PO_4^{3-} , Fe_2O_3 , and so on. Correspondingly, carbon could just reduce the amount of total oxygen in Li_2BeF_4 molten salt. Compared with Tab. 2, the conclusion of calculation was corresponded to the result of this experiment.

In addition, according to XRD analysis, the residual $(\text{NH}_4)_2\text{BeF}_4$ in Li_2BeF_4 molten salt was decomposed during the process of experiment. As already mentioned in the

introduction, HF which was generated by $(\text{NH}_4)_2\text{BeF}_4$ decomposition can dissolve in fluoride molten salt to form HF_2^- . Therefore, HF_2^- in the molten salt could react with S^{2-} and O^{2-} in Li_2BeF_4 molten salt. To calculate by LiHF_2 as an example in Tab. 3 (7, 8).

Tab. 3 Gibbs free energy calculation of chemical reaction

Reaction equation	ΔG (kcal)			
	Temperature			
	400°C	500°C	600°C	700°C
(1) $\text{NiF}_2 + \text{H}_2\text{O}(\text{g}) \rightarrow \text{NiO} + 2\text{HF}(\text{g})$	6.907	3.842	0.783	-2.265
(2) $\text{C} + \text{NiO} \rightarrow \text{CO}(\text{g}) + \text{Ni}$	1.487	-2.785	-7.025	-11.236
(3) $\text{C} + 4\text{LiNO}_3 \rightarrow \text{CO}_2(\text{g}) + 2\text{Li}_2\text{O} + 4\text{NO}_2(\text{g})$	-8.994	-21.253	-32.873	-43.968
(4) $4\text{C} + \text{Li}_2\text{SO}_4 \rightarrow 4\text{CO}(\text{g}) + \text{Li}_2\text{S}$	18.066	1.686	-14.309	-29.511
(5) $\text{C} + \text{H}_2\text{O}(\text{g}) \rightarrow \text{CO}(\text{g}) + \text{H}_2(\text{g})$	9.359	5.953	2.536	-0.887
(6) $\text{C} + \text{Be}(\text{OH})_2 \rightarrow \text{BeO} + \text{CO} + \text{H}_2(\text{g})$	-1.685	-8.303	-14.862	-21.366
(7) $2\text{LiHF}_2 + \text{Li}_2\text{S} \rightarrow 4\text{LiF} + \text{H}_2\text{S}(\text{g})$	-65.678	-69.989	-74.463	-79.087
(8) $2\text{LiHF}_2 + \text{Li}_2\text{O} \rightarrow 4\text{LiF} + \text{H}_2\text{O}(\text{g})$	-81.391	-85.464	-89.660	-93.977

3.6 Analysis of mechanism

As already mentioned in characterization of graphite nanoparticles, the density of graphite nanoparticles and Li_2BeF_4 molten salt at 700 °C were 2.16 g/cm³ and 1.805 g/cm³. These two data of density were very close. Besides, both the viscosity & thermal diffusivity of Li_2BeF_4 molten salt and molten salt wettability of graphite nanoparticles also had an effect on diffusion of graphite nanoparticles in Li_2BeF_4 molten salt except for factor of density. Not described here. Experiment showed that graphite nanoparticles with an average diameter of < 100 nm could diffuse easily in Li_2BeF_4 molten salt. Further work will focus on the relationship of property between graphite nanoparticles and Li_2BeF_4 molten salt.

Fig. 3 was the schematic diagram of deoxidization and purification in Li_2BeF_4 molten salt. Based on analysis of sample characterization and chemical reaction Gibbs free energy calculation, the mechanism of deoxidization and purification for Li_2BeF_4 molten salt via graphite nanoparticles was following. There were three main stages for

deoxidization and purification. The first stage was to make Li_2BeF_4 molten salt have HF_2^- anion; the second stage was graphite nanoparticles diffusion, carbon reduction and hydrolysis of Ni^{2+} ion; the third stage was vacuum degassing and metal precipitation.

First of all, to control gas pressure and temperature of autoclave achieved the purpose of maintaining the certain content of HF_2^- originated from above-mentioned residual $(\text{NH}_4)_2\text{BeF}_4$ decomposition in molten salt. Furthermore, the system of Li_2BeF_4 molten salt containing HF_2^- and other impurities was formed in Fig. 3 A.

Secondly, part of Li_2BeF_4 molten salt's impurities reacted with graphite crucible wall so as to graphite scraps peeling off the graphite crucible. Because viscosity of Li_2BeF_4 molten salt reduced when temperature arose [26], it benefited for graphite scraps diffusing into the molten salt. However, particle size of graphite also determined its diffusibility in Li_2BeF_4 molten salt. The experiment proved that particle size of graphite better diffusibility in molten salt was below 100 nm. In this stage, the impurities of ion or molecular would react with graphite nanoparticles, and the reaction equations were shown in Fig. 3 D. And hydrolysis of Ni^{2+} took place to form NiO due to residual traces water existed in molten salt, in Fig. 3 B.

Finally, chamber was vacuumed in order to make such gas formed by carbon or HF_2^- chemical reaction as SO_2 , NO , CO , H_2S and H_2O escape from the Li_2BeF_4 molten salt. And NiO could be reduced to Ni metal by carbon reduction so as to Ni metal precipitating to the bottom of graphite crucible, in Fig. 3 C.

Fig. 3. Schematic diagram of deoxidization and purification in Li₂BeF₄ molten salt

4. Conclusions

In this work, the mechanism of deoxidization and purification for Li₂BeF₄ molten salt via graphite nanoparticles were discussed based on sample characterization and Gibbs free energy calculation. That is, vacuum carbon reduction cooperated with HF₂⁻ could realize the deoxidization and purification in Li₂BeF₄ molten salt.

- ① Graphite nanoparticles with only average diameter of < 100 nm diffused into the Li₂BeF₄ molten salt, played the role of carbon reduction at high temperature.
- ② HF₂⁻ derived from decomposition of residual (NH₄)₂BeF₄ in Li₂BeF₄ molten salt could react with S²⁻ and O²⁻ in the molten salt.
- ③ That vacuum degassing executed in the airtight container could make such gas formed by carbon or HF₂⁻ chemical reaction as SO₂, NO, CO, H₂S and H₂O escape from the Li₂BeF₄ molten salt efficiently.
- ④ The mechanism of deoxidization and purification for Li₂BeF₄ molten salt via graphite nanoparticles had effect on the reduction of total oxygen, S and Ni. There were no effect on the PO₄³⁻, Cr and Fe, as well as the other oxyanions involved in element of Si and P.

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