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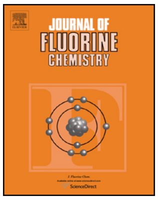

Preparation of high-purity molten FLiNaK salt by the hydrofluorination process

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ABSTRACT

The preparation conditions and purification reaction mechanism for H_2–HF treatment of molten FLiNaK salt were investigated. The optimal process conditions for preparation of high-purity molten FLiNaK salt were obtained. They are purification temperature of 650 °C, liquid height of 0.9 m, purification time of 48 h, flow ratio of H_2/HF = 10, flow volume magnitude of 800 mL/min, and reaction pressure of 0 MPa. The oxygen content of the prepared molten salt was around 80 ppm, corrosion impurity elements (Cr, Fe, and Ni) were less than 20 ppm, and the S and P contents were below 5 ppm. The quality of FLiNaK molten salt prepared by this hydrofluorination process is better than that obtained by adding NH_4HF_2 as a fluorinating reagent.

1. Introduction

Molten fluoride salts have many desirable properties, such as small neutron absorption cross-section, high temperature stability, high heat conductivity, large specific heat, high boiling point, and low saturated vapor pressure and viscosity. They are widely used in high-temperature hydrogen production, nuclear fission–fusion reactors, solar heat storage, reprocessing of nuclear fuels, and fuel cell energy as a new type of high-temperature and high-heat-flux heat storage medium. They can improve the security of production processes, conversion, and storage of energy, and greatly enhance the efficiency of energy utilization [1–6]. The LiF–NaF–KF ternary system is a simple eutectic system, which is referred to as FLiNaK salt, whose eutectic reaction will occur at a temperature of 454 °C with a molar ratio of 46.5:11.5:42 [7]. Molten FLiNaK salt is often used as the heat transfer medium in secondary circuits of molten salt reactor (MSR) and the simulative salt in the corrosion test trial because of its many desirable properties, such as low cost, low toxicity, and low volatility. Furthermore, FLiNaK is used for simulation of the primary circuit coolant molten LiF–BeF_2 (FLiBe) salt, because it has similar physical properties and the beryllium salt is often highly toxic [8–10].

Most of the thermophysical properties of LiF–NaF–KF mixtures have been adequately investigated, and a lot of work has been performed to study the corrosion behavior and corrosion mechanism of structural materials in a FLiNaK environment [11–15]. The literature suggests that the thermophysical properties and corrosivity of molten FLiNaK salt are mainly controlled by oxygen-containing impurities and water absorbed in the salt. The purity of molten salts not only influences the efficiency of the reactor, but it is also closely related to its safe operation [6]. Therefore, there are very strict requirements on the impurity content of molten salts in the reactor, which makes the preparation process and purification efficiency of molten salts difficult [16–18]. Previously, we have shown that the oxygen content in FLiNaK salt can be decreased by adding NH_4HF_2 as a fluorinating reagent [19]. However, the oxygen content in the molten salt can only be decreased to 200 ppm by extreme treatments and the oxyacid root ions in the molten salt cannot be removed.

Hydrofluorination (the H_2–HF method) has proven to be a very effective method to remove oxygen-containing impurities from fluoride salts [7,20]. In this paper, the preparation conditions and purification principle of molten FLiNaK salt were investigated and the high-purity molten salt was successfully obtained based on the H_2–HF treatment method. Metal oxide impurities can react with anhydrous hydrogen fluoride to form water and metal fluorides. The water can be expelled with the reaction off-gas at high temperature. This method can also be used to effectively remove oxyacid root ions by high-temperature hydrogen reduction, thereby greatly reducing the oxygen content. The total oxygen content in molten salts is reduced below 80 ppm and all types of neutron poisons (boron, cadmium, rare earth metals, etc.) are less

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than 5 ppm. The experimental results show that the quality of FLiNaK molten salt prepared by this hydrofluorination process is better than that produced by adding NH_4HF_2 as a fluorinating reagent. Corrosion of the molten salt is greatly reduced and can meet the requirements of secondary coolant circuits in molten salt reactors [21].

2. Experimental

2.1. Preparation of the raw material

Fluoride salts all have a hygroscopic nature. They will trigger the hydrolysis reaction and produce oxides at high temperature, which may introduce impurities into the FLiNaK molten salt. Therefore, it is necessary to remove the moisture from fluoride salts before using them. LiF (99.9%), NaF (99.9%), and KF (99.9%) were purchased and separately treated before mixing them together. To remove the moisture from the fluoride salts, they were heated at 350–400 °C in a drying oven with simultaneous vacuum pumping. H_2 (99.999%) and Ar (99.999%) were dried with P_2O_5 before use. The trace water in HF was removed by potentiostatic electrolysis. The electrolysis voltage was set as 5.5 V. With the extension of electrolysis time, the electrolysis current and the water content in HF decreased gradually, and reached a certain value. Water content of treated HF was determined by the Carle-Fischer method and the value is less than 15 ppm.

2.2. Preparation of molten FLiNaK salt

The process flow chart for preparation of molten FLiNaK salt is shown in Fig. 1. The fluoride salts were completely mixed at a specific molar ratio of LiF:NaF:KF = 46.5:11.5:42 and then added into a melting vessel and smelted at high temperature in an argon atmosphere. After melting, the mixture was transferred into a purification vessel by the differential-pressure method. A H_2–HF gas mixture was continuously bubbled through the mixture to carry out high-temperature purification reactions in the purification vessel. Finally, the molten salt product was transferred into a storage tank using a similar method to the above. The melting and purification vessels were made of industrially pure Ni (99.5 wt% purity), because pure Ni exhibits the most positive corrosion potential in molten FLiNaK salt [22]. Similarly, the gas injection pipe was made of industrially pure Ni (99.5 wt% purity). Its internal diameter was 10 mm, the thickness of pipe wall was 2.0 mm, and the angle of the cutting edge was around 45°.

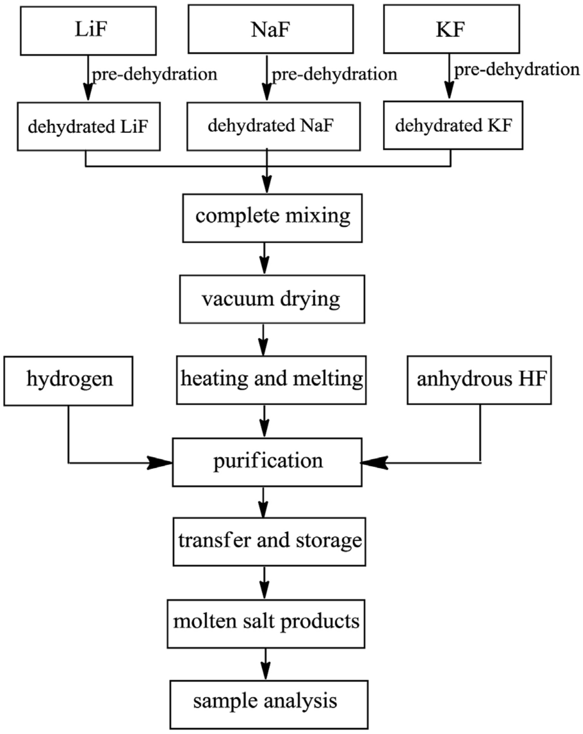

Fig. 1. Molten FLiNaK salt preparation flow chart.

All of the operations were strictly performed in an airtight, dry, and clean environment to prevent the molten salt from absorbing water moisture from the air and influencing the final oxygen content (see Fig. 2). The FLiNaK salt was ground into a fine powder in a glove box and then characterized by differential scanning calorimetry–thermogravimetric analysis (TGA–DSC), inductively coupled plasma optical emission spectrometry (ICP-OES), ion chromatography (IC), and trace oxygen determination.

2.3. Characterization

IC analysis was performed using a Thermo Scientific IC-1100 chromatograph. The anion concentrations were determined using a system fitted with a 2 mm ASRS column. The mobile phase was composed of 9 mM Na_2CO_3 gradient eluent at a 0.25 mL/min flow rate with a 25 μL injection volume. ICP analysis was performed using a Spectro Arcos spectrometer. Typically, a molten salt sample was dissolved in 2% HNO_3 solution. The operating conditions were forward power of 1.43 kW, argon gas flow rates of 12.00 L/m (plasma), 0.9 L/min (auxiliary), and 0.78 L/min (nebulizer), and spectrally pure (99.99%) argon gas. TGA measurements were performed using a TA SDT-Q600 thermogravimetric system. Samples (~10 mg) were hermetically sealed in an aluminum pan, heated to 800 °C at 20 °C min^{-1} and maintained at this temperature for 3 min, and then cooled to room temperature at the same rate. Oxygen content analysis was performed using a Leco O836 meter. Fluoride is corrosive and will easily volatilize at high temperature and damage the detection system, so a halogen trap assembly was installed after the cracking furnace to eliminate contamination by fluoride vapor [17].

Fig. 2. Smelting and purification equipment for preparation of molten FLiNaK salt.

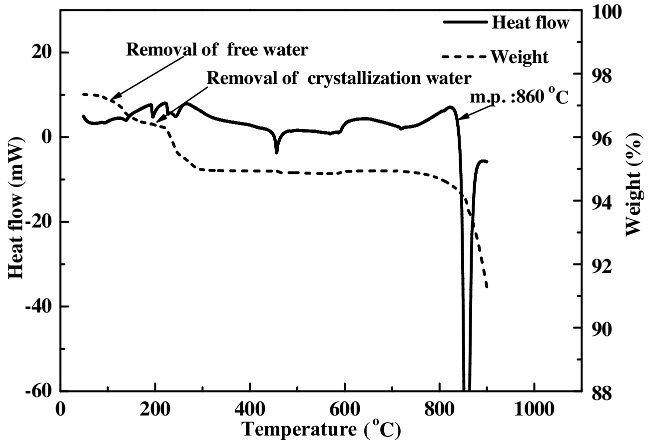

Fig. 3. Thermogravimetric analysis of KF (99.9%).

3. Results and discussion

3.1. Pretreatment of the fluoride salts

Desiccation of metal fluorides is usually performed by drying under vacuum. Nevertheless, some combined oxygen may remain in the salt. Compared with LiF and NaF salts, KF is highly deliquescent, resulting in formation of KF·2H_2O and KF·4H_2O. The TGA curves (Fig. 3) show that KF loses free water at around 100 °C. It then gradually loses crystal water at around 250 °C and tends to a constant weight. The melting point of KF is 860 °C and the large weight loss above the melting point can be associated with sublimation. The oxygen analysis result (Table 1) shows that the oxygen content in the fluoride salt can be greatly reduced by drying under vacuum. Thus, pretreatment of fluoride salts can greatly reduce their hydrolysis under high temperature melting. However, the total oxygen content of the fluoride salts was still high after drying under vacuum. This may be because a small amount of fluoride is unavoidably hydrolyzed to hydroxide and then to oxide under the drying conditions.

$$MF + H_2O \xrightarrow{HF} MOH \xrightarrow{H_2O} M_2O$$

(M = Li, Na, and K).

From the viewpoint of the thermodynamics, increasing the temperature can facilitate formation of MOH and H_2O. Therefore, it is suggested that the drying operation should be performed under both low temperature and vacuum to avoid the above-mentioned process. It is important to point out that the effect of pretreatment is negated as soon as the salt is exposed to the environment. After drying, the fluoride salt should be sealed and used as soon as possible. The anion impurities and the element contents in the fluoride salts are shown in Tables 2 and 3, respectively. Impurities not only originate from the environment (e.g., O_2, H_2O, H^+, and OH^-) but some form during the preparation process and are commonly present in fluoride salts.

3.2. Molten salt purification reaction principle

During preparation of molten FLiNaK salt by hydrofluorination, a H_2–HF gas mixture was continuously bubbled through the mixture to carry out high-temperature purification reactions. Oxygen removal is based on the principle that metal oxides react with anhydrous hydrogen fluoride and generate water and metal fluorides, and the water can be expelled with the reaction off-gas at high temperature (3-1). Because the discharge of water vapor is very convenient, continuous hydrogen fluoride can make the chemical reaction shift to the right, so the removal effect of oxygen is very effective. Under the sparging of H_2, sulfide and phosphide can be reduced to S^{2-} and P^{3-} at high temperature, and other oxides such as Fe^{3+} can also be restored to a low state. Subsequent treatment with anhydrous HF removes volatile H_2S, PH_3, and HCl. The reactions of O, S, and P removal from the molten salt are as follows [7,23]:

(3-1) $O^{2-} + 2HF(g) \leftrightarrows H_2O(g) + 2F^-$

(3-2) $SO_4^{2-} + 4H_2(g) \leftrightarrows S^{2-} + 4H_2O(g)$

(3-3) $PO_4^{3-} + 4H_2(g) \leftrightarrows P^{3-} + 4H_2O(g)$

(3-4) $S^{2-} + 2HF(g) \leftrightarrows H_2S(g) + 2F^-$

(3-5) $P^{3-} + 3HF(g) \leftrightarrows PH_3(g) + 3F^-$

HF may partially dissolve in molten FLiNaK salt and attack the equipment materials to generate NiF_2, FeF_2, and CrF_2. This type of corrosion mainly occurs by thermodynamically driven dissolution of the structural materials into the molten salt by the following reaction:

(3-6) $x\mathrm{Me} + y\mathrm{HF(l)} \rightarrow \mathrm{Me}_x\mathrm{F}_y + 0.5y\mathrm{H_2(g)}$

where Me = Ni, Fe, and Cr.

These corrosion impurities will enter the molten salt and cause impurities. However, if hydrogen can enter the molten salt, it will be able to move the chemical reaction (3–6) to the left, which can effectively inhibit corrosion of the structural materials by HF. Finally, NiF_2, FeF_2, and CrF_2 are reduced to the corresponding metals by H_2 treatment. Elemental nickel, iron, and chromium can remain in the melting vessel or be removed by filtering. Thus, hydrogen and hydrogen fluoride complement and cooperate with each other to remove the oxide impurity elements, and hydrogen can also effectively prevent impurities caused by corrosion of the elemental materials to give a high-purity molten salt.

Table 1
Oxygen content analysis of the fluoride salts before and after removing water (ppm).

Fluoride salts	Before removing water	After removing water	
		300 °C/4h	400 °C/4h
LiF	12211	9363	8852
NaF	28484	22766	1103
KF	4063	4423	520

Table 2
Anion analysis of the fluoride salts (ppm).

Fluoride salts	Cl^-	NO_2^-	NO_3^-	PO_4^{3-}	SO_4^{2-}
LiF	14.2	50.9	34.9	23.1	<5
NaF	79.6	24.3	15.6	60.5	191.7
KF	115.5	21.01	12.2	19.1	310.2

Table 3
Related element analysis of the fluoride salts (ppm).[a]

Fluoride salts	Al	B	Ca	Cd	Cr	Cu	Fe	K	Li	Mg	Na	Ni	S	P	Zr
LiF	2.0	<5	5.6	<5	<5	<5	4.5	20.5		2.5	190	14.3	<5	8.4	<5
NaF	6.5	<5	59.5	<5	<5	<5	7.5	99.1	9.6	2.3		<5	62.9	21.2	<5
KF	<5	<5	38.7	<5	<5	<5	4.0		16.2	0.6	33	<5	105	7.7	<5

[a] The rare earth element contents were below the detection limit.

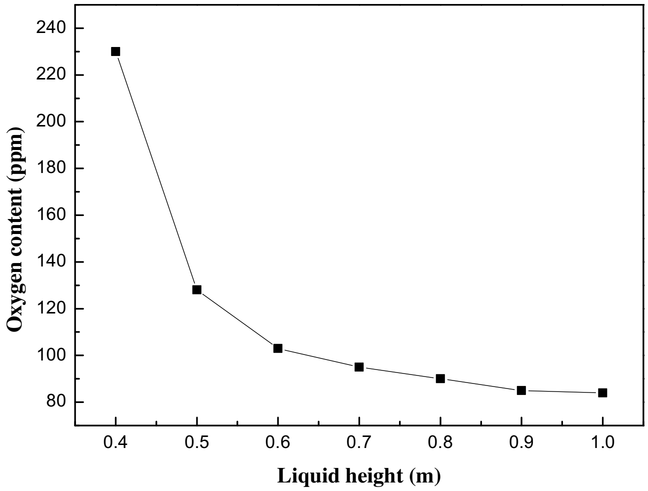

Fig. 4. Influence of the liquid height on the oxygen content in the molten salt. Experiment conditions were purification temperature of 650 °C, purification time of 48 h, flow ratio of H_2/HF = 10, flow volume magnitude of 800 mL/min, and reaction pressure of 0 MPa.

3.3. Process conditions for preparation of the molten salt

3.3.1. Effect of the liquid level

During molten salt purification, the end of the vent pipe is inserted into the bottom of the purification vessel. The molten salt liquid level is equal to the motion path of the HF–H_2 gas in the molten FLiNaK salt. It is assumed that the rising velocity of bubbles in the molten salt is a specific value, and the higher the molten salt level, the longer the retention time of the rising bubbles. Thus, the probability of the hydrofluorination reaction will increase, and the oxygen content in the molten salt will decrease. Therefore, in the case of a specific amount of FLiNaK salt, a long and narrow crucible with a large height to diameter ratio should be used as the purification vessel. Fig. 4 shows the effect of the liquid level height on the oxygen content in the molten salt (10 kg, 5.0 L) under the conditions of the same temperature and purification time. With increasing molten salt liquid level, the oxygen content gradually decreases, which is consistent with the above analysis. However, the oxygen content of the molten salt no longer dramatically decreases after the liquid level reaches 0.9 m, as shown in Fig. 4. This may be because the gas–liquid contact reaction has reached a balance, which is controlled by the hydrofluorination reaction. The effect of further increasing the height of the liquid level on the equilibrium of the reaction is very small. Therefore, a liquid height of 0.9 m is suitable for the 10 kg molten FLiNaK salt purification reaction.

3.3.2. Effect of the purification temperature

The temperature of the molten salt purification experiment needs to meet two basic requirements: ensure molten salt melting and avoid evaporation of the molten salt and strong corrosion under high temperature. Because the melting point of FLiNaK salt is 454 °C, the purification temperature of FLiNaK salt was selected in the temperature range 500 to 750 °C. The reaction temperature can affect the viscosity of the molten salt and the reaction rate, so the purification efficiency can be indirectly affected. The liquid viscosity affects the rising velocity of the H_2–HF gas in the molten salt, and it thus affects the retention time of the purifying gas in the molten salt. Generally, the viscosity of molten salts decreases as the temperature increases. Thus, the faster the H_2–HF gas rises, the shorter the gas–liquid contact time. However, the gas–liquid reaction rate increases as the temperature increases. Therefore, the effect of the reaction temperature on the efficiency of molten salt purification is contradictory from the aspects of the viscosity and

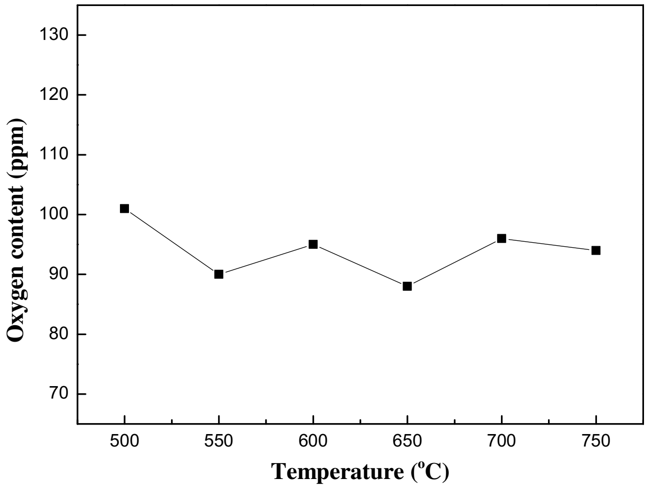

Fig. 5. Influence of the purification temperature on the oxygen content in the molten salt. Experiment conditions were liquid height of 0.9 m, purification time of 48 h, flow ratio of H_2/HF = 10, flow volume magnitude of 800 mL/min, and reaction pressure of 0 MPa.

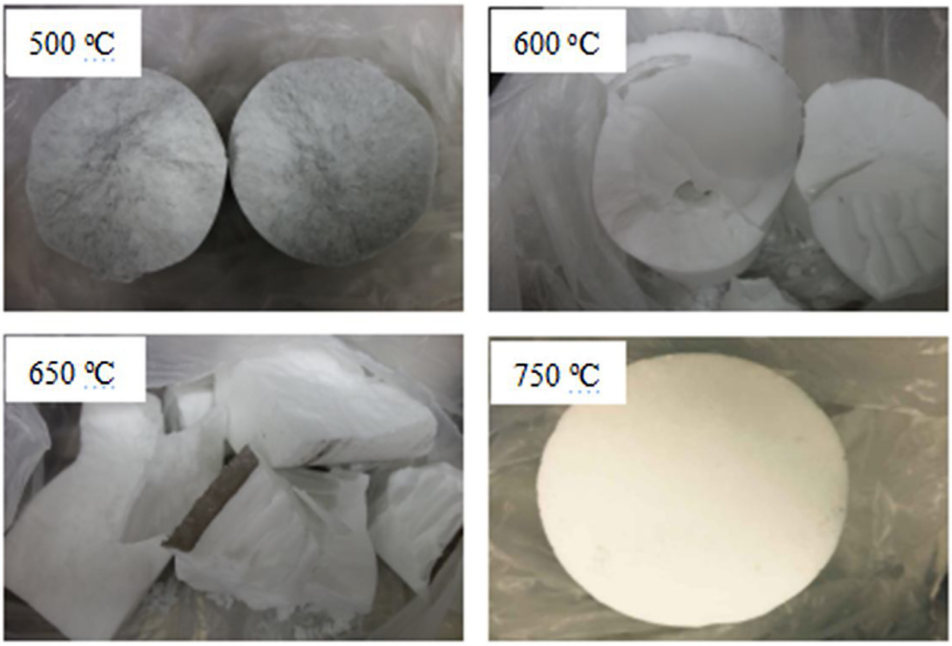

Fig. 6. Appearance of FLiNaK with different purification temperatures. Experiment conditions were liquid height of 0.9 m, purification time of 48 h, flow ratio of $H_2/HF = 10$, flow volume magnitude of 800 mL/min, and reaction pressure of 0 MPa.

the reaction rate. Fig. 5 shows the influence of the purification temperature on oxygen removal from the molten salt. From Fig. 5, the difference in the oxygen content in the molten salt is small with the different purification temperatures (88–101 ppm). This may be because the influence of the reaction temperature on the molten salt viscosity and reaction rate is not significant or they offset one another.

However, the purification temperature affects the appearance and crystallinity of the molten salt. As shown in Fig. 6, the glossy appearance of FLiNaK salt prepared with a purification temperature of 500 °C is generally darker than with purification temperatures of 600 °C and 650 °C. With a purification temperature of 750 °C, the overall appearance of the molten salt begins to become pale and a small amount of caducous white powder is attached to the surface of FLiNaK salt. Higher temperatures require harsh conditions, and an important factor to consider is that fluoride salts begin to sublime at 750 °C. The volatile powder readily causes unsteady flow and even leads to blocking of the pipe, which influences the efficiency and safety of the purification furnace. It is therefore suggested that an appropriate purification temperature is 650 °C.

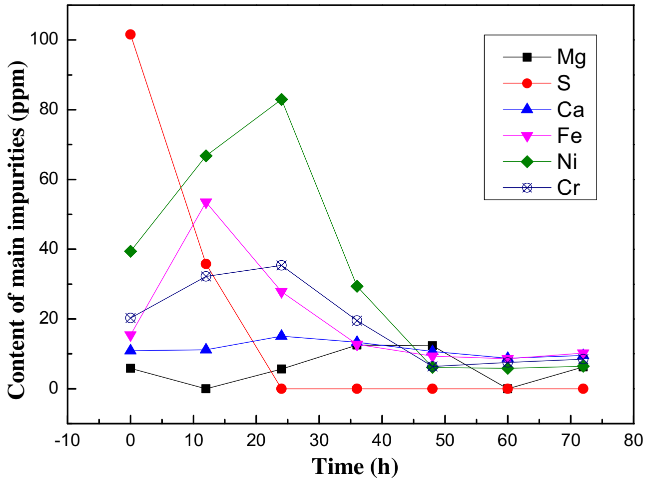

Fig. 7. Changes of the main impurity element contents in the molten salt with time using the ICP–OES determination. Experiment conditions were purification temperature of 650 °C, liquid height of 0.9 m, flow ratio of $H_2/HF = 10$, flow volume magnitude of 800 mL/min, and reaction pressure of 0 MPa.

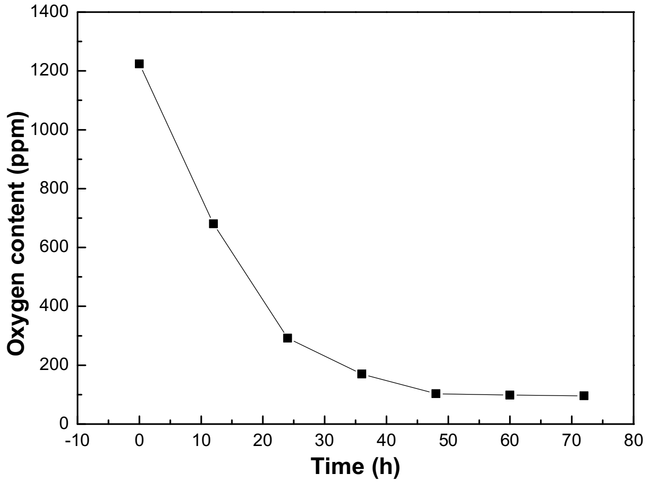

Fig. 8. Effect of the purification time on the oxygen content in the molten salt. Experiment conditions were purification temperature of 650 °C, liquid height of 0.9 m, flow ratio of $H_2/HF = 10$, flow volume magnitude of 800 mL/min, and reaction pressure of 0 MPa.

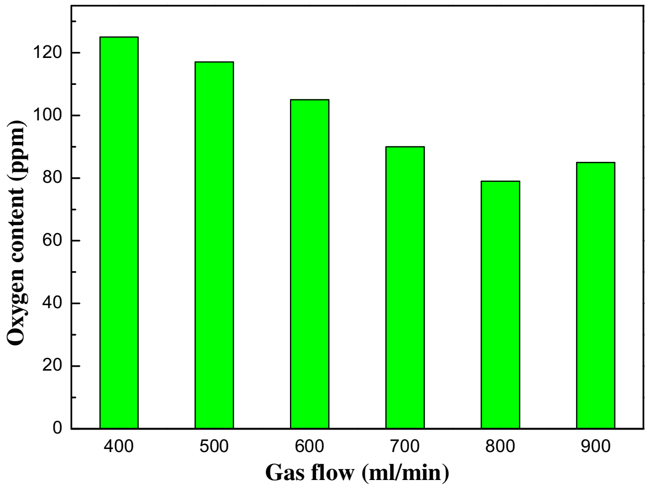

Fig. 9. Effect of the gas flow on the oxygen content in the molten salt. Experiment conditions were purification temperature of 650 °C, liquid height of 0.9 m, purification time of 48 h, flow ratio of H_2/HF = 10, and reaction pressure of 0 MPa.

3.3.3. Effect of the purification time

The impurities in the molten salt are trace elements and ions (ppm level), which determines the chemical reaction of molten salt purification. The effect of the purification time on the impurity content of the molten salt is shown in Fig. 7. The strongly corrosive element S can be removed to below the detection limit in a relatively short time (less than 24 h). Fig. 8 shows the effect of the purification time on the oxygen content in the molten salt. The oxygen content in the molten salt dramatically decreases with increasing purification time. Some oxides are thermodynamically unstable, and they are generally converted to the corresponding fluorides. The oxygen removal effect is obvious in the initial period, and the oxygen content is almost unchanged after 48 h. The Ni, Fe, and Cr impurity content initially increases and then gradually decreases. After 48 h purification time, the contents of the impurity elements show little change with further increasing purification time. Therefore, a purification time of 48 h is appropriate.

The reasons for the changes of the metal ion contents are as follows. The reaction between HF and Ni (with trace amounts of Fe and Cr) dissolves the metallic element from the purification vessel surface. Moreover, it is supposed that the oxidation reaction of vessel material by H_2O happened to increase the concentration of Ni, Cr, and Fe, as long as oxygen impurity concentration is high in the initial stage of the purification reaction. Therefore, the metal impurity contents gradually increase from the beginning of the reaction until 10 h. With increasing reaction time, the generated NiF_2, FeF_2, and CrF_2 reach saturation because they have specific solubilities in the molten salt. New metal fluorides are then unable to dissolve and they form a protective layer on the vessel surface. Subsequently, the corrosion reaction is inhibited and the reaction rate decreases. After being reduced by hydrogen, the metal fluorides (NiF_2, FeF_2, and CrF_2) gradually transform to the pure metals (Ni, Fe, and Cr) and settle on the bottom of the vessel. When the molten salt is completely purified, the purification vessel is not expected to be corroded because the free energies of the salt composition (LiF, NaF, KF, etc.) are more negative than those of the fluorides of Ni, Fe, and Cr. As a result, the impurity metal ion contents in the molten salt remain very low.

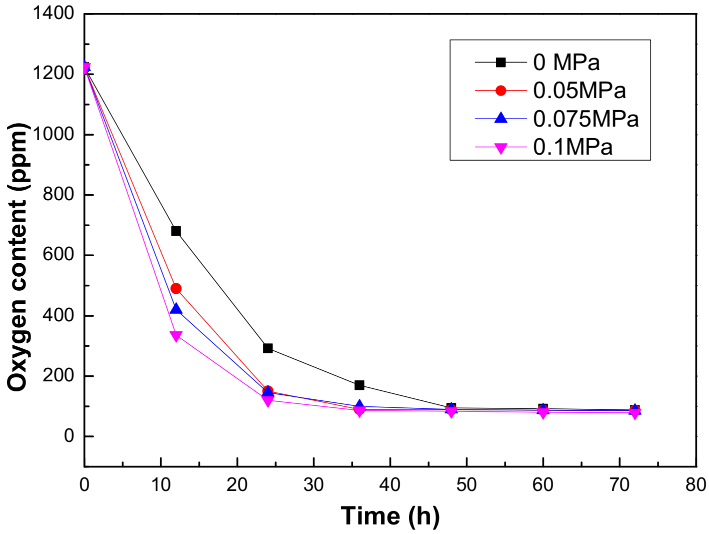

Fig. 10. Change of the oxygen content in the molten salt with time under different pressures. Experiment conditions were purification temperature of 650 °C, liquid height of 0.9 m, flow ratio of H_2/HF = 10, and flow volume magnitude of 800 mL/min.

3.3.4. Effect of the H_2/HF ratio and gas flow rate

When H_2–HF treatment is used to purify a molten salt, the balance between the impurity removal efficiency and the corrosion of the structural materials by HF needs to be considered. The interaction between H_2 and HF is complex because of the coexistence of coordination and competition. In the whole purification process, HF can corrode the metal of the vessel wall surface to generate NiF_2, FeF_2, and CrF_2, which can enter into the molten salt and cause contamination. H_2 can inhibit the corrosion process to form NiF_2, FeF_2, and CrF_2 and restore the metals, preventing contamination of the molten salt. Hence, an appropriate H_2/HF flow ratio must be used to achieve the optimal impurity removal effect. According to our experimental results, when the flow ratio is 10, Fe, Ni, and the other major impurities in the molten salt products are less than 20 ppm. If the gas flow ratio is less than 10, impurity ions in the molten salt gradually increase and other metal ions can occur in minor or trace amounts. When the gas flow ratio is greater than 10, the oxygen content in the molten salt gradually increases, leading to extension of the purification time. Thus, the gas flow ratio should be set to 10:1 in the purification process.

The overall purification efficiency of the system depends on the gas–fluid contact area between H_2–HF and the molten salt at a certain temperature. As the gas enters the vessel by spraying and

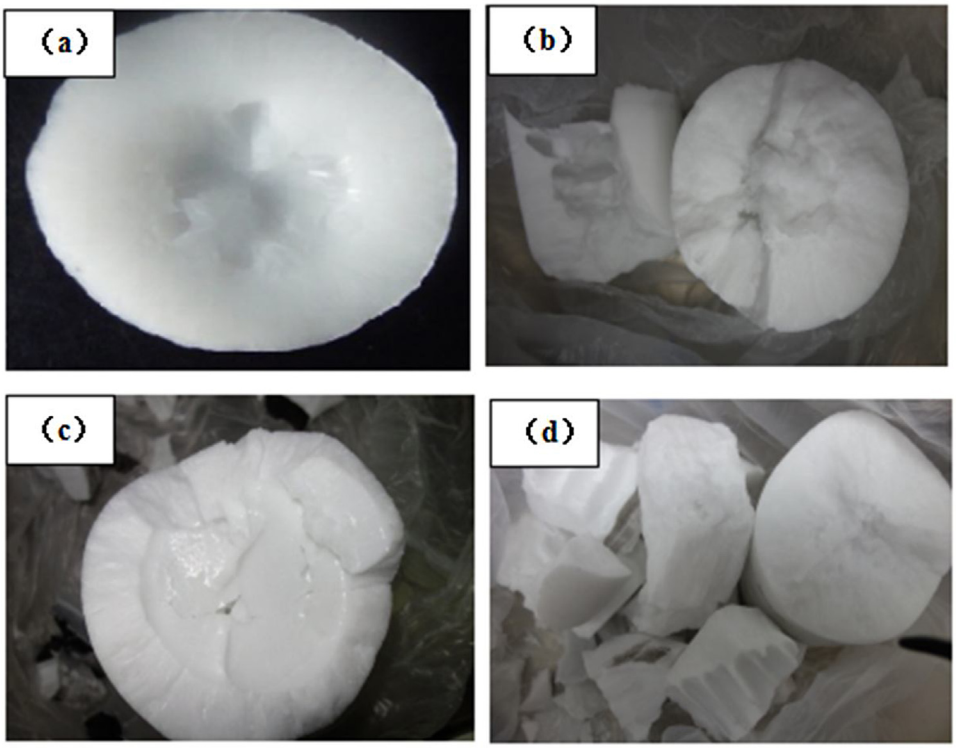

Fig. 11. Appearance of FLiNaK molten salt prepared under the optimized conditions. Experiment conditions were purification temperature of 650 °C, liquid height of 0.9 m, purification time of 48 h, flow ratio of $H_2/HF = 10$, flow volume magnitude of 800 mL/min, and reaction pressure of 0 MPa.

Table 4
Melting points and oxygen contents of the molten FLiNaK salt samples.

Entries	1	2	3	4	5	6	7	8
Melting point (°C)	454	457	453	454	458	454	453	456
Oxygen content (ppm)	79	82	88	76	85	80	84	78

Table 5
Impurities in the molten FLiNaK salt samples.

Entry	B	Mg	Al	P	S	Ca	Cr	Fe	Ni	Cu	Cd	Pb	Mn	Co	Zn	Cl-	NO_2^-	NO_3^-	PO_4^{3-}	SO_4^{2-}
1	<5	<5	5.5	<5	<5	<5	<5	5.7	10.4	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5
3	<5	<5	5.1	<5	<5	<5	<5	5.6	7.9	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5
4	<5	5.9	<5	<5	<5	<5	<5	<5	6.8	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5
5	<5	<5	<5	<5	<5	<5	<5	9.4	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5
6	<5	<5	6.3	<5	<5	7.4	<5	<5	6.5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5
7	<5	<5	<5	<5	<5	<5	<5	6.9	12.1	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5

bubbling, it will play the stirring action, which helps to mix the gas and liquid. Consequently, increasing the gas flow can improve the purification efficiency. The effect of the H_2–HF flow rate on the purification efficiency is shown in Fig. 9. The purification efficiency is lower and the oxygen content is higher when the gas flow rate is lower. With increasing gas flow rate, the oxygen content significantly decreases, and it then reaches a plateau. However, as the gas flow rate further increases, the purification efficiency decreases. This may be because the molten salt will undergo a serious “boiling” phenomenon when the gas flow rate reaches a certain level (> 800 mL). Although stirring is more intense, a considerable part of the gas cannot completely react and rapidly escape from the liquid level, resulting in a decrease in gas utilization. Thus, a gas flow of 800 mL/min is appropriate.

3.3.5. Effect of the gas pressure

The pressure is one of the most important factors in gas–liquid chemical reactions, and the pressure is often used to strengthen chemical reactions in industry. The higher the purification pressure, the less likely it is that bubbles will escape. Thus, the longer the bubble stays in the molten salt solution, the greater the chance that the gas molecules can completely react with impurities to improve the utilization ratio of the purifying gas. Fig. 10 shows the change of the oxygen content in the molten salt with time under different pressures. The purification time is 48 h under normal pressure (0 MPa), and the oxygen content in the molten salt is about 80 ppm, which is maintained at a constant value. From this figure, in the purification stage, maintaining an appropriate pressure can shorten the purification time of the molten salt. At a purification pressure of 0.05 MPa, the oxygen content decreases to 80 ppm after 36 h. However, the pressure seems to have no obvious effect on oxygen removal with extension of the reaction time. This may be because the removal of the impurity elements, such as oxygen, sulfur and phosphorus, mainly produces volatile substances (H_2O, H_2S, etc.). If the pressure is too high at the late stage of the purification reaction, it is difficult for the trace volatiles to escape from the molten salt, resulting in O, S, and other impurities not being able to be removed. Although increasing the pressure can shorten the reaction time, it is difficult to ensure personnel safety at a high temperature for a long reaction time because HF is extremely corrosive and H_2 is flammable and explosive. Therefore, an atmospheric pressure purification reaction is suggested.

4. Conclusions

Various conditions that affect the quality of molten FLiNaK salt were investigated by the hydrofluorination process. The optimal conditions are purification temperature of 650 °C, liquid height of 0.9 m, purification time of 48 h, flow ratio $H_2/HF = 10$, flow volume magnitude of 800 mL/min, and purification pressure of 0 MPa. Dozens of batches of FLiNaK molten salt (10 kg batches) were successfully prepared. The appearance of the molten salt is a white crystalline solid (see Fig. 11). The melting point is 454–458 °C. The contents of S and P are below 5 ppm, and the oxygen content is around 80 ppm (see Table 4), which is lower than that achieved by adding NH_4HF_2 as a fluorinating reagent. Furthermore, the contents of the corrosion impurity elements (Ni, Fe, and Cr) are less than 20 ppm and neutron poisons (boron, cadmium, and rare earth metals) are less than 5 ppm (see Table 5). The corrosion study revealed that corrosion of the reactor materials by the resultant FLiNaK salt is relatively small and meets the requirements as a suitable coolant in molten salt reactor [21,24,25].

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