Electrical conductivity of NaF−AlF$_3$−CaF$_2$−Al$_2$O$_3$−ZrO$_2$ molten salts

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Abstract: The electrical conductivity of NaF−AlF$_3$−CaF$_2$−Al$_2$O$_3$−ZrO$_2$ system was studied by a tube-type cell with fixed cell constant. The results show that the electrical conductivity of NaF−AlF$_3$−3%Al$_2$O$_3$−3%CaF$_2$−ZrO$_2$ molten salt system decreases with increase of ZrO$_2$ content in an interval of 0−5%. The increase of 1% ZrO$_2$ results in a corresponding electrical conductivity decrease of 0.02 S/cm, and the equivalent conductivity increases with the increase of molar ratio of NaF to AlF$_3$. When the temperature increases by 1 °C, the electrical conductivity increases by 0.004 S/cm. At last, the regression equations of electrical conductivity relative to temperature and ZrO$_2$ are obtained by quadratic regression analysis.
Key words: ZrO$_2$; molten salt electrolysis; electrical conductivity; NaF; AlF$_3$; Al−Zr alloy

1 Introduction

Al−Zr alloys as one of the new structural materials are used in various fields, such as aerospace, military, nuclear reactions and atomic energy [1−4]. Cryolite-zirconia can be used as electrolyte for producing Al−Zr alloy by molten salt electrolysis. Compared with the common methods of preparing Al−Zr master alloys, such as ingot metallurgy, mechanical alloying method and aluminum thermal reduction method [5−7], molten salt electrolysis exhibits many excellent advantages, such as no contamination, homogeneous dispersion in the high productivity of aluminum matrix and low fabrication costs.

It is important to study the physicochemical properties of cryolite−zirconia molten system from theoretical and technological aspects [8,9]. STERTEN and SKAR [10] investigated the Na$_3$AlF$_6$−ZrO$_2$ phase diagram. But data on conductivities of the cryolite−zirconia melt are quite restricted. Conductivity directly affects the energy consumption of the molten salt electrolysis.

In this study, electrical conductivities of NaF−AlF$_3$−CaF$_2$−Al$_2$O$_3$−ZrO$_2$ molten salts are measured by improved fixed conductivity cell. The aim of the present

work is to investigate the effects of ZrO$_2$ addition on electrical conductivity of nNaF·AlF$_3$−Al$_2$O$_3$ molten salt system, so as to quest for suitable electrolyte composition to produce Al−Zr alloy by molten salt electrolysis technique.

2 Experimental

In this work, sodium fluoride, calcium fluoride, alumina and zirconia were of analytical grade. All reagents were dried at 400 °C for several hours and kept in a dry box before using. Aluminum fluoride was sublimed under low pressure (about 100 Pa) at 1050 °C and kept in a dry box before using. Boron nitride was heat treated as reference [11].

A schematic drawing of the cell is shown in Fig. 1. The cell consisted of a pyrolytic boron nitride tube of 4 mm in inner diameter and 100 mm in length. One electrode consisted of a tungsten rod (1 mm in outer diameter) placed in a fixed position inside the boron nitride (BN) tube, while the graphite crucible served as the other electrode. The crucible containing 10−15 g sample of the salt mixture was placed in a vertical laboratory furnace with argon atmosphere and heated up to the required temperature. The boron nitride tube with the tungsten electrode was immersed in the melt and
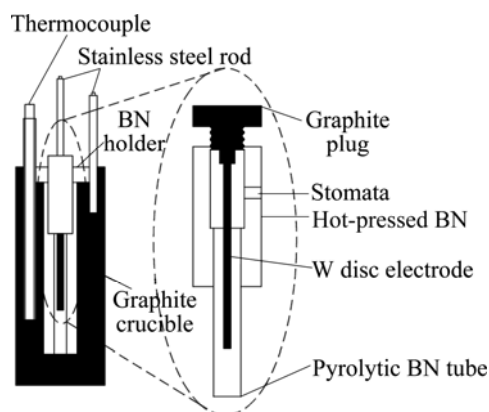
Fig. 1 Sketch of conductivity cell

repositioned several times to make sure that the composition of the electrolyte was homogeneous and any gas bubbles were removed. The temperature was measured with a Pt−Pt 10% Rh thermocouple, and it was stable within 0.5 K. Within a run, the measurements were carried out at different temperatures (typically, at four or five temperatures) for every composition.

Agilent impedance instrument was used to measure the cell impedance, and the electrical conductivity can be calculated by

$$\sigma = G/R \tag{1}$$

where σ is the electrical conductivity; G is the electrical conductivity cell constant; R is the resistance.

3 Results and discussion

3.1 Calibration of electrical conductivity cell

Electrical conductivity cell was firstly used to measure the conductivity of molten KCl and then molten cryolite to determine the cell constant. The data for electrical conductivity of molten KCl were recommended by GRJOTHEIM et al [12]. The experimental results are listed in Table 1.

Table 1 Measurement results of KCl molten salt

$t/°C$	$\sigma/(S·cm^{-1})$ [12]	R/Ω	G/cm^{-1}
814	2.273	17.87	40.62
811	2.266	18.04	40.87
805	2.250	18.20	40.95
800	2.237	18.42	41.20

The cell constant did not vary with the temperature. The average value of electrical conductivity cell constant at different temperatures is 40.91 cm^{-1}.

3.2 Feasibility analysis of method

Table 2 shows the comparison of our measurements with literature values for the electrical conductivity of 2.2NaF$_3$·AlF$_3$−5%CaF$_2$−3%Al$_2$O$_3$ at 959 °C.

Table 2 Relative error of system analysis

No.	$\sigma/(S·cm^{-1})$		Error/%
	This work	Ref. [12]	
1	2.0233	2.0469	1.15
2	2.0384	2.0469	0.42
3	2.0475	2.0469	0.03

The result shows that the error is less than 1.2%, therefore the method is feasible and shows good reproducibility.

3.3 Effect of ZrO$_2$ on electrical conductivity

Figure 2 shows experimenatal data as a function of temperature for different compositions in the system nNaF·AlF$_3$−3%Al$_2$O$_3$−3%CaF$_2$−ZrO$_2$. The results show that the addition of ZrO$_2$ to the melt lowers the conductivity. 1% ZrO$_2$ addition results in a corresponding conductivity decrease of 0.02 S/cm. Some large ion species will generate according to reactions (2) [13] and (3) [14] if ZrO$_2$ is added to the cryolite melt.

$$5AlF_6^{3-} + 2ZrO_2 = 3AlOF_5^{4-} + ZrOF_5^{3-} + ZrF_4 + 2AlF_3 \tag{2}$$

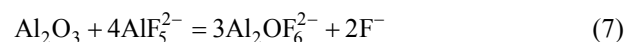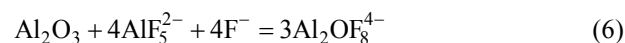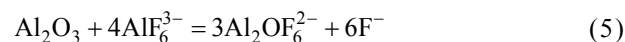$$nZr^{4+} + nxF^- = [ZrF_n^{4-x}]_n \tag{3}$$
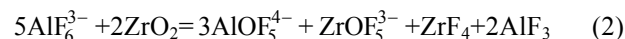
The radiuses (volumes) of these ions are larger than those of AlF$_6^{3-}$ complex [15,16], which already exists in the molten salt system. Correspondingly, it will be more difficult for small ions, such as sodium ion, to move in the melt and then reduces the electrical conductivity of molten electrolyte. Therefore, ZrO$_2$ reduces the electrical conductivity of molten electrolyte.

3.4 Effect of molar ratio of NaF to AlF$_3$ on electrical conductivity

Figure 3 shows the effect of molar ratio of NaF to AlF$_3$ on the electrical conductivity of NaF·AlF$_3$−3%Al$_2$O$_3$−3%CaF$_2$−mZrO$_2$ molten salt system at 985 °C. The results show that the conductivity increases with the increase of molar ratio of NaF to AlF$_3$. When the molar ratio of NaF to AlF$_3$ increases from 2.2 to 2.6, the electrical conductivity increases by 0.189 S/cm.

Ions in Na$_3$AlF$_6$−Al$_2$O$_3$ system include AlF$_6^{3-}$, AlF$_5^{2-}$, AlF$_4^-$, F$^-$ and Al−O−F ion complex [16,17]. The formation of Al−O−F ion complex is shown as follows:

$$2Al^{3+} + 3O^{2-} + 4AlF_6^{3-} = 3Al_2OF_8^{4-} \tag{4}$$

$$Al_2O_3 + 4AlF_6^{3-} = 3Al_2OF_6^{2-} + 6F^- \tag{5}$$

$$Al_2O_3 + 4AlF_5^{2-} + 4F^- = 3Al_2OF_8^{4-} \tag{6}$$

$$Al_2O_3 + 4AlF_5^{2-} = 3Al_2OF_6^{2-} + 2F^- \tag{7}$$

With the increase of molar ratio of NaF to AlF$_3$, the concentration of AlF$_3$ is decreased, and then ion complex
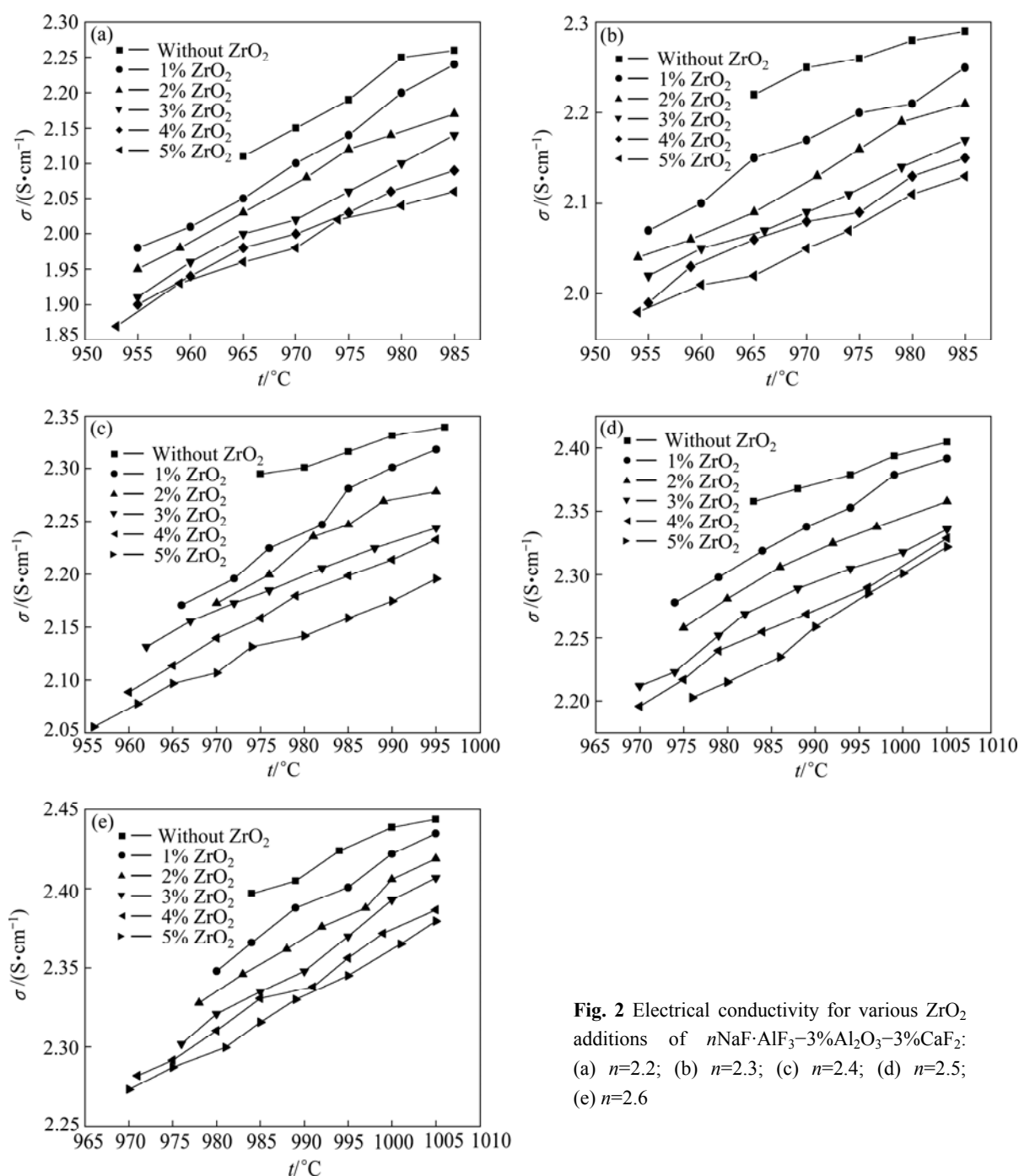
Fig. 2 Electrical conductivity for various ZrO_2 additions of nNaF·AlF$_3$−3%Al$_2$O$_3$−3%CaF$_2$: (a) n=2.2; (b) n=2.3; (c) n=2.4; (d) n=2.5; (e) n=2.6

will decrease according to the reactions. Therefore, the number of mobility ion is increased, which increases the electrical conductivity of molten electrolyte.

3.5 Effect of ZrO_2 on electrical conductivity at different superheats

Figure 4 shows the electrical conductivity of molten salts as a function of ZrO_2 content at superheats of 15, 20 and 25 °C for 2.4NaF·AlF$_3$− 3%Al$_2$O$_3$−3%CaF$_2$−ZrO$_2$ molten salt system. Increasing superheat results in increase of the electrical conductivity. The electrical conductivity increases by about 0.020 S/cm for increase of 5 °C superheat. For 1% ZrO_2, the electrical conductivity increases from 2.215 to 2.271 S/cm when the superheat increases from 15 to 25 °C. For 5% ZrO_2, the electrical conductivity increases from 2.078 to 2.118 S/cm when the superheat increases from 15 to 25 °C.

Because of high price of ZrO_2 and significant effects of superheat on electrolytic conductance, it is reasonable to make the proper concentration of ZrO_2 for industrial practice according to the above study.
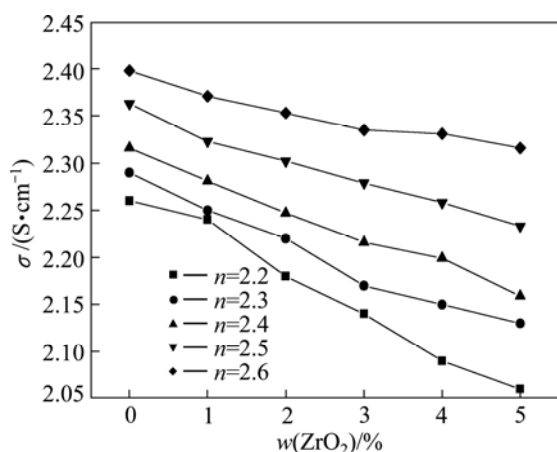
Fig. 3 Electrical conductivity for various molar ratios of NaF to AlF$_3$ at 985 °C
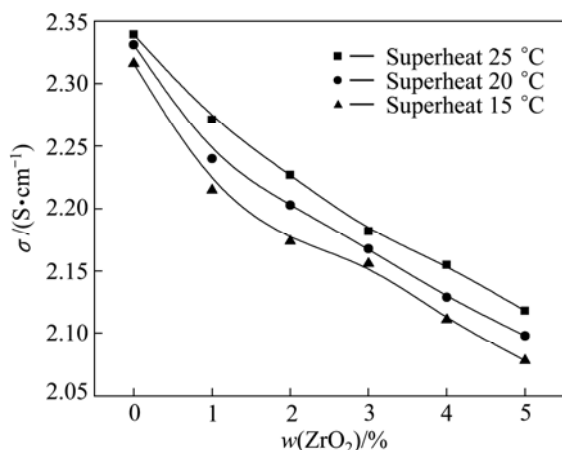

Fig. 4 Electrical conductivity as function of ZrO$_2$ content at different superheats with molar ratio of NaF to AlF$_3$ of 2.4

3.6 Effect of temperature on electrical conductivity

The conductivity of the molten salt is mainly determined by ion movement, and the temperature is one of the most important parameters. Therefore, temperature has a great influence on the electrical conductivity. The temperature dependence of the electrical conductivity of molten salts of predominant ionic characteristic is given in the form of a basic Arrhenius equation:

$$\sigma_s = A\exp(-\frac{E}{RT}) \qquad (8)$$

where σ_s is the specific conductivity; A is the coefficient related to chemical composition of melt; E is the activation energy of conductance; T is the temperature of the melt; R is the gas molar constant.

The A and E are constants, and in the molten salt, the logarithm form of Eq. (8) is

$$\ln\sigma_s = \ln A - \frac{E}{RT} \qquad (9)$$

According to the formula (9), $\ln\sigma_s$ and T^{-1} have a linear relationship. Figure 5 shows the relationship

between $\ln\sigma_s$ and T^{-1} of 2.2NaF·AlF$_3$−3%Al$_2$O$_3$−3%CaF$_2$−ZrO$_2$ molten salt system with different additions of ZrO$_2$. The results show that $\ln\sigma_s$ and T^{-1} have a good linear relationship, and the correlation coefficients are higher than 0.98.
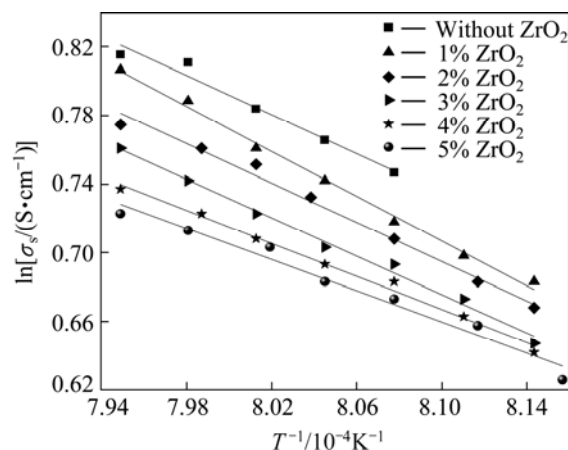

Fig. 5 Relationship between $\ln\sigma_s$ and T^{-1} of molten salts

Figure 5 shows that the electrical conductivity of molten salts increases with increasing temperature. When the temperature increases by 1 °C, the electrical conductivity increases by 0.004 S/cm. The heat movement of particles speeds up when the temperature increases. Bonding energy between ions with contrary charge is weakened because of acceleration of heat movement. Directional movement of ion is easier. The number of free ions increases because of decomposition of more ion complexes with increasing temperature. Decomposition of the ion complexes increases the ion mobility and thereby increases the electrical conductivity.

3.7 Regression equation of electrical conductivity

According to the measured results, the regression equations of electrical conductivity related to temperature and ZrO$_2$ content are obtained by quadratic regression as

For 2.2 NaF/AlF$_3$:
$\sigma=-71.2293+0.1455t+0.448w(ZrO_2)-5\times10^{-4}tw(ZrO_2)-7.2\times10^{-5}t^2+2.2\times10^{-3}w(ZrO_2)^2$ (10)
Scope of application is t=965−985 °C, $w(ZrO_2)$=0−5%.

For 2.3 NaF/AlF$_3$:
$\sigma=-32.1554+0.0662t-0.4223w(ZrO_2)+4\times10^{-4}tw(ZrO_2)-3.18\times10^{-5}t^2+4.8\times10^{-3}w(ZrO_2)^2$ (11)
Scope of application is t=965−985 °C, $w(ZrO_2)$=0−5%.

For 2.4 NaF/AlF$_3$:
$\sigma=2.3516-0.0030t-0.2177w(ZrO_2)+1.92\times10^{-4}tw(ZrO_2)+3\times10^{-6}t^2+2\times10^{-3}w(ZrO_2)^2$ (12)
Scope of application is t=975−995 °C, $w(ZrO_2)$=0−5%.

For 2.5 NaF/AlF$_3$:

$\sigma=-12.455+0.0268t-0.4939w(ZrO_2)+4.8\times10^{-4}tw(ZrO_2)-$
$1.2\times10^{-5}t^2+1.8\times10^{-3}w(ZrO_2)^2$ (13)

Scope of application is $t=985-1005$ °C, $w(ZrO_2)=0-5\%$.

For 2.6 NaF/AlF$_3$:

$\sigma=-12.1895+0.0266t-0.2016w(ZrO_2)+2\times10^{-4}tw(ZrO_2)-$
$1.2\times10^{-5}t^2+1.25\times10^{-3}w(ZrO_2)^2$ (14)

Scope of application is $t=985-1005$ °C, $w(ZrO_2)=0-5\%$.

4 Conclusions

1) Electrical conductivities of (2.2−2.6) NaF·AlF$_3$−3%Al$_2$O$_3$−3%CaF$_2$ molten salt system decrease with increase of ZrO$_2$ content in an interval of 0−5%. 1% ZrO$_2$ results in a corresponding decrease of 0.02 S/cm, and the equivalent conductivity increases with the increase of molar ratio of NaF to AlF$_3$. When the temperature increases by 1 °C, the electrical conductivity increases by 0.004 S/cm.

2) The suitable electrolyte composition for producing Al−Zr alloy by molten salt electrolysis technique is 2.4NaF·AlF$_3$−3%CaF$_2$−3%Al$_2$O$_3$−2%ZrO$_2$ system and the electrolysis temperature is ranging from 970 to 985 °C.

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NaF·AlF$_3$−Al$_2$O$_3$−CaF$_2$−ZrO$_2$ 熔盐体系的电导率

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摘　要：采用改进的固定电导池常数法研究 NaF−AlF$_3$−CaF$_2$−Al$_2$O$_3$−ZrO$_2$ 熔盐体系的电导率。结果表明，NaF−AlF$_3$−3%Al$_2$O$_3$−3%CaF$_2$−ZrO$_2$ 熔盐体系的电导率随着 ZrO$_2$ 含量(0~5%)的增加呈降低趋势。每增加 1%氧化锆，电导率相应地降低约 0.02 S/cm。温度每增加 1 °C 时电导率相应降低约 0.004 S/cm。随着 NaF 与 AlF$_3$ 摩尔比的增加，体系的电导率随之增加。最后采用二次回归正交设计方法，建立分子比相同时电解质的电导率与温度和氧化锆浓度关系的回归方程。

关键词：ZrO$_2$；熔盐电解法；电导率；NaF；AlF$_3$；Al−Zr 合金

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