

Electrochemical behaviors of Mg^{2+} and B^{3+} deposition in fluoride molten salts

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Abstract: By using cyclic and linear sweep voltammetry, the electrochemical deposition behaviors of Mg^{2+} and B^{3+} in fluorides molten salts of $KF-MgF_2$ and $KF-KBF_4$ at 880 °C were investigated, respectively. The results show that the electrochemical reduction of Mg^{2+} is a one-step reaction as $Mg^{2+}+2e^{-}\rightarrow Mg$ in $KF-1\%MgF_2$ molten salt, and the electrochemical reduction of B^{3+} is also a one-step reaction as $B^{3+}+3e^{-}\rightarrow B$ in $KF-KBF_4$ (1%, 2% KBF_4) molten salts. Both the cathodic reduction reactions of Mg^{2+} and B^{3+} are controlled by diffusion process. The diffusion coefficients of Mg^{2+} in $KF-MgF_2$ molten salts and B^{3+} in $KF-KBF_4$ molten salts are $6.8\times 10^{-7} cm^2/s$ and $7.85\times 10^{-7} cm^2/s$, respectively. Moreover, the electrochemical synthesis of MgB_2 by co-deposition of Mg and B was carried out in the $KF-MgF_2-KBF_4$ (molar ratio of 6:1:2) molten salt at 750 °C. The X-ray diffraction analysis indicates that MgB_2 can be deposited on graphite cathode in the $KF-MgF_2-KBF_4$ molten salt at 750 °C.

Key words: magnesium diboride; electro-deposition; fluoride molten salts; diffusion coefficient

1 Introduction

MgB_2 , which is a kind of superconductive material with simple structure [1], has attracted much attention in the fundamental physics and engineering application. There are many methods such as pulse laser deposition, chemical vapor deposition (CVD), DC magnetron sputtering, to prepare high quality alkali metal boride [2] and alkaline-earth metal boride [3]. By electro-deposition, magnesium and boron will co-deposit on the cathode, and then react spontaneously with each other by the reaction:



Recently, YANG et al [4], HIROSHI et al [5] and KENJI and HIDEKI [6] successfully fabricated MgB_2 by electro-deposition in chloride-based molten salts. However, the evolving of Cl_2 from anode will reduce the concentration of chlorine ion in the electrolyte which consists of B_2O_3 or MgB_2O_4 as solute, and make the MgB_2 not uniform and costly. If using the fluoride electrolyte with B_2O_3 , MgB_2O_4 or MgO as solute for MgB_2 electrochemical deposition, the anode product is O_2 (with inert anode) or CO_2 (with carbon anode). Thus

the concentration of fluorine ion will keep stable during electro-deposition, which will make the electro-deposition process more easily be controlled.

Although several articles have reported the electrochemical behavior of Mg^{2+} in ionic liquid [7] and B^{3+} in the fluoride molten salts [8–9], the electrochemical behaviors of MgB_2 in $KF-MgF_2-KBF_4$ molten salt systems are not involved. Therefore, the aim of this study is to investigate the reduction mechanism of Mg^{2+} and B^{3+} in $KF-MgF_2$ and $KF-KBF_4$ molten salts.

2 Experimental

Electrochemical research was conducted in a three-electrode system with tungsten wire ($d0.48 mm$, $\geq 99.95\%$) as work electrode, platinum wire ($d2.4 mm$, 99.99%) as reference electrode and graphite rod as counter electrode. A high pure graphite crucible with holding capacity of 70 g electrolyte, which has a specification of 45mm in diameter and 80 mm in depth with a sidewall thinness of 5 mm, was used. The whole apparatus was protected in argon gas. The used chemicals of KF , MgF_2 and KBF_4 are anhydrous and analytically pure reagents, respectively. Cyclic voltammetry and linear sweep voltammograms were

performed with an AUTO Lab 30 potentiostat instrument.

3 Results and discussion

3.1 Electrochemical behavior of Mg^{2+} in $KF-MgF_2$

Cyclic voltammograms were carried out on a tungsten wire working electrode in a $KF-1\%MgF_2$ molten salt system at $880\text{ }^\circ\text{C}$. The cyclic voltammograms under different scanning rates of 0.4, 0.6 and 0.8 V/s are shown in Fig. 1. It is clear that magnesium deposition occurs from -1.7 V (Point A) to -1.9 V (Point B), while potassium deposition occurs from -2.0 V (vs Pt, Point C) to -2.5 V (Point D) versus the quasi-reference electrode. During the reverse sweep, the oxidation peaks of magnesium and potassium run at -2.15 V (Point E) and -1.6 V (Point F), respectively.

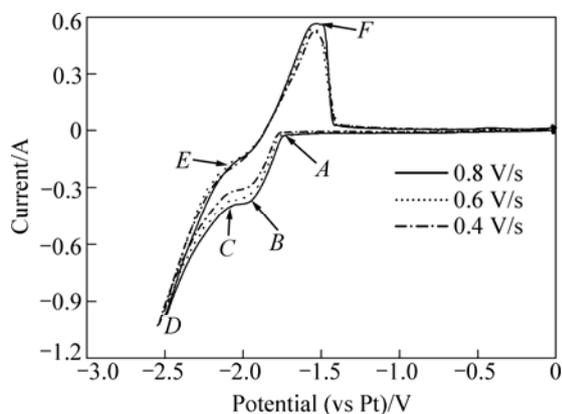


Fig. 1 Cyclic voltammograms in $KF-1\%MgF_2$ molten salt system at $880\text{ }^\circ\text{C}$

It is confirmed that the reduction peak at Point B (-1.9 V , vs Pt) is associated with the electrochemical reduction of Mg^{2+} . As seen in Fig. 1, the change in the scanning rate range of $0.4-0.8\text{ V/s}$ does not make the reduction potential shift in the voltammograms. According to Refs. [10–11], the number of exchanged electrons can be deduced from the cyclic voltammograms. For the magnesium reduction peak, the plot of potential φ vs $\ln[I/(I_{PC}-I)]$ (I_{PC} is the reduction peak current, and I is the current) is linear, as seen in Fig. 2. From the slope (RT/nF) of linear equation in Fig. 2, the exchanged electron number of Mg^{2+} reduction is approximately equal to 2 ($n \approx 2$). So, it can be concluded that two electrons are exchanged in this reduction. That is to say, the electrochemical reduction of Mg^{2+} proceeds as follows: $Mg^{2+}+2e^- \rightarrow Mg$. It is a single step for the reaction of Mg^{2+} reduction.

Furthermore, the relationship between the reduction peak current (I_{PC}) and the square root of the scanning rate ($v^{1/2}$) is plotted in Fig. 3. From Fig. 3, it is concluded that the reduction peak current (I_{PC}) is linearly related with

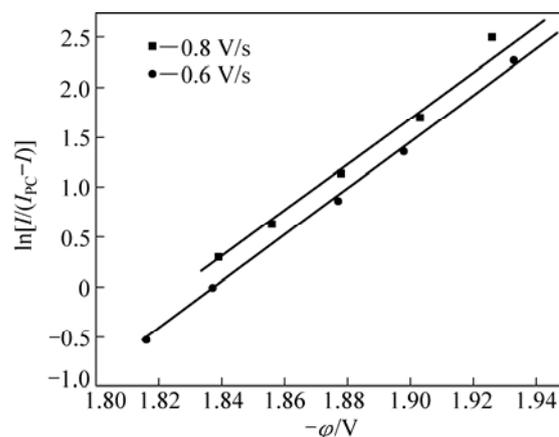


Fig. 2 $\ln[I/(I_{PC}-I)]$ as function of potential (φ) in $KF-1\%MgF_2$ system

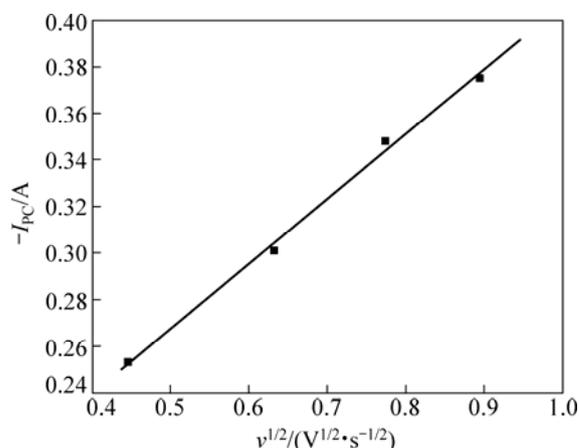


Fig. 3 Plot of peak current (I_{PC}) vs square root of scanning rate ($v^{1/2}$) in $KF-1\%MgF_2$ system at $880\text{ }^\circ\text{C}$

the square root of the scanning rate ($v^{1/2}$). It satisfies the Randles-Sevcik equation completely, which indicates that magnesium electrochemical reduction is a diffusion control process [11]. The diffusion coefficient D can be deduced by the Randles-Sevcik equation as follows [10]:

$$I_{PC} = -0.4463nFSc(nFD/RT)^{1/2}v^{1/2} \quad (2)$$

where S is the electrode area; c is the solute concentration; D is the diffusion coefficient; F is the Farady constant; n is the number of exchanged electrons; v is the scanning rate; T is the thermodynamic temperature.

From Fig. 3, we can get the value of slope, which is equal to the value of $I_{PC}/v^{1/2}$:

$$I_{PC}/v^{1/2} = -31\text{ mA}\cdot\text{s}^{1/2}/\text{V}^{1/2} \quad (3)$$

Taking all parameters ($n=2$, $S=0.226\text{ cm}^2$, $c=4.29 \times 10^{-4}\text{ mol/cm}^3$, $F=96\,487\text{ C/mol}$, $R=8.314\text{ J/(K}\cdot\text{mol)}$, $T=1\,153\text{ K}$) into Eq. (2), and combining Eqs. (2) and (3), we can obtain the diffusion coefficient of magnesium cation $D(Mg^{2+})$ under the experiments

condition. The calculated $D(\text{Mg}^{2+})$ is $6.8 \times 10^{-7} \text{ cm}^2/\text{s}$. This value is less than $(7.2\text{--}9.9) \times 10^{-6} \text{ cm}^2/\text{s}$ in $\text{MgCl}_2\text{--CaCl}_2\text{--NaCl}$ chloride system [12] and $5.3 \times 10^{-6} \text{ cm}^2/\text{s}$ in chloride-fluoride $\text{MgCl}_2\text{--MgF}_2$ system [13]. This difference is caused by the different operating temperatures and different molten salt systems.

3.2 Electrode behavior of B^{3+} in KF-KBF_4 molten salts

Figure 4 shows the linear sweep voltammograms of B^{3+} on tungsten electrode in KF-1\%KBF_4 and KF-2\%KBF_4 molten salts at 880°C . Only one reduction peak (Point B) in the voltammograms is found, which indicates that the reduction of B^{3+} occurs in a one-step reaction. It is clear that boron deposition occurs from near -0.8 V (vs Pt, Point A) to -1.25 V (vs Pt, Point B). The reduction peak of boron in the cathode is at -1.25 V (vs Pt, Point B).

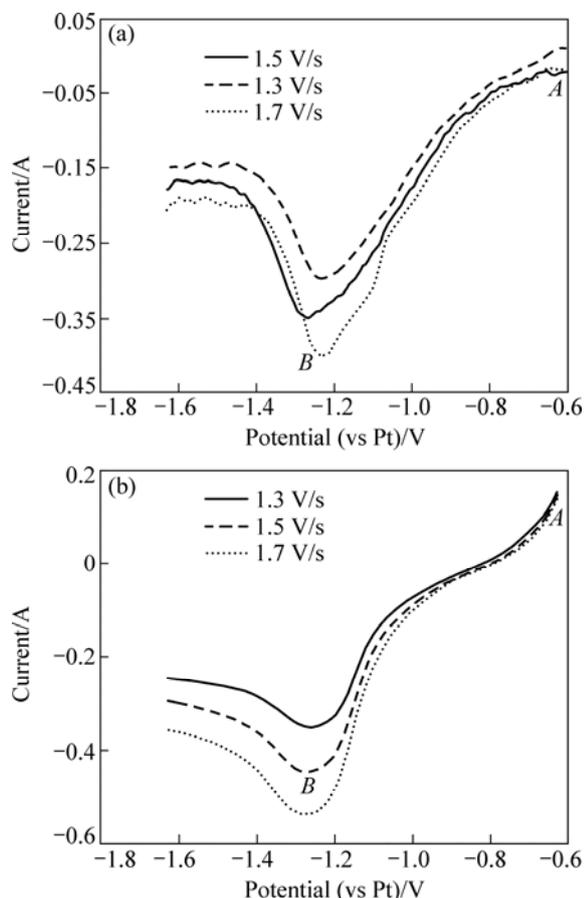


Fig. 4 Linear sweep voltammograms at 880°C with different scanning rates: (a) KF-1\%KBF_4 ; (b) KF-2\%KBF_4

From Fig. 4, it is observed that the change in the scanning rate does not make the reduction potential shift in the voltammograms. The number of exchanged electrons of boron reduction can be deduced with the same method of Mg^{2+} . The relationship between the potential (ϕ) and $\ln[I/(I_{\text{PC}}-I)]$ are plotted in Fig. 5. By

calculating the slope (RT/nF) of these linear equations, the average number of exchanged electrons for B^{3+} reduction reaction (existing as BF_4^- complex anion actually [14]) is approximately equal to 3. Therefore, it can be concluded that three electrons are exchanged in this reduction. That is to say, the electrochemical reduction of B^{3+} proceeds as follows: $\text{B}^{3+} + 3\text{e}^- \rightarrow \text{B}$.

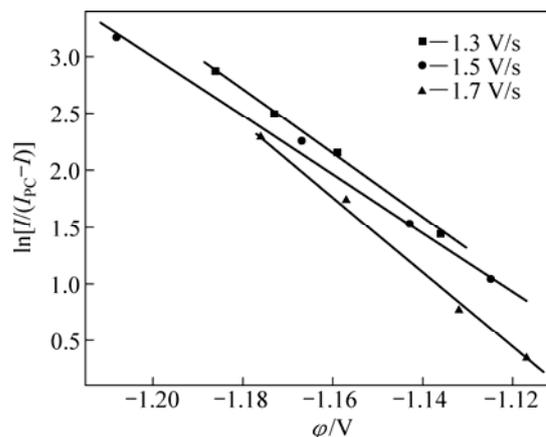


Fig. 5 $\ln[I/(I_{\text{PC}}-I)]$ as function of potential (ϕ) in KF-KBF_4 system

Moreover, the relationship between the reduction peak current (I_{PC}) and the square root of the scanning rate ($v^{1/2}$) is also plotted, as shown in Fig. 6.

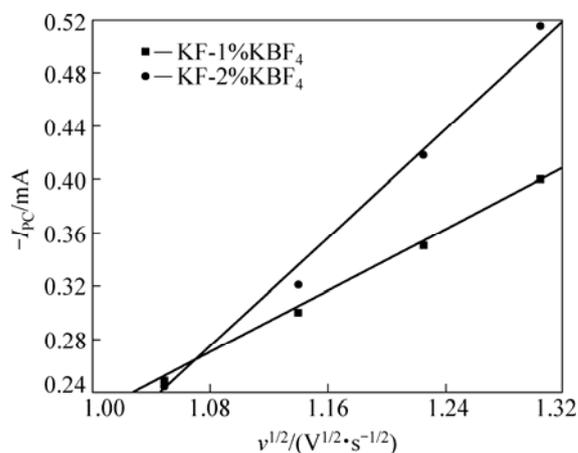


Fig. 6 Plot of peak current (I_{PC}) vs square root of scanning rate ($v^{1/2}$) in KF-KBF_4 system at 880°C

From Fig. 6, we can conclude that the B^{3+} reduction peak current (I_{PC}) is also linearly related with the square root of scanning rate ($v^{1/2}$) like Mg^{2+} . So, the electrochemical reduction process is also controlled by the diffusion of boron cation in the solution. The value of $I_{\text{PC}}/v^{1/2}$ is as follows.

1) In KF-1\%KBF_4 molten salt,

$$I_{\text{PC}}/v^{1/2} = -61.03 \text{ mA}\cdot\text{s}^{1/2}/\text{V}^{1/2} \quad (4)$$

2) In KF-2%KBF₄ molten salt,

$$I_{PC}/V^{1/2} = -118.40 \text{ mA}\cdot\text{s}^{1/2}/V^{1/2} \quad (5)$$

Taking all the parameters into Eq. (2), the diffusion coefficient of boron cation at 880 °C can be calculated as follows:

1) In KF-1%KBF₄ molten salt, $D(B^{3+}) = 7.9 \times 10^{-7} \text{ cm}^2/\text{s}$;

2) In KF-2%KBF₄ molten salt: $D(B^{3+}) = 7.8 \times 10^{-7} \text{ cm}^2/\text{s}$.

These diffusion coefficient values are more than $4.5 \times 10^{-10} \text{ cm}^2/\text{s}$ on steel cathode at 800 °C and $1.13 \times 10^{-10} \text{ cm}^2/\text{s}$ on molybdenum cathode at 830 °C in KF-LiF-KBF₄ molten fluorides [15–16]. The difference is caused by the different substrates, temperatures and molten salt systems.

The concentration of B³⁺ does not much affect the diffusion coefficient of B³⁺. Therefore, the corresponding diffusion coefficient of B³⁺ can be treated using an average value as $7.85 \times 10^{-7} \text{ cm}^2/\text{s}$.

3.3 Electro-deposition of MgB₂ in KF-MgF₂-KBF₄ system

In the above experiments, the operating temperatures were 880 °C in both KF-1%MgF₂ and KF-1%KBF₄ molten salts system. However, in an eutectic MgF₂-KF-KBF₄ system, the electro-deposition could be carried out near 750 °C, which is lower than the melting point of MgB₂ (800 °C). According to the Gibbs free energy of Eq. (1), the value of $\Delta G_{1023K}^{\ominus}$ is significantly negative, so MgB₂ coating could be deposited at a suitable deposition potential.

An electro-deposition of MgB₂ experiment was conducted in a close system of argon environment at 750 °C. The electrolyte consisted of MgF₂, KF and KBF₄ with a molar ratio of 1:6:2. The graphite crucible ($d75 \text{ mm} \times 80 \text{ mm}$, sidewall thickness of 7.5 mm) acted as an anode, and the cathode was high cylinder pure graphite ($d10 \text{ mm} \times 50 \text{ mm}$). The current density was $0.35 \text{ A}/\text{cm}^2$. At the beginning of the electro-deposition process, pre-electrolysis was performed for 10 min.

During the course of electro-deposition, the cell voltage fluctuated in a range of 3.6–3.9 V, as seen in Fig. 7. After experiment, the cathode surface was analyzed with XRD, and MgB₂ was found, as seen in Fig. 8.

According to the ionic structure of KF-MgF₂-KBF₄ molten salt, the electrode reactions are given as follows:

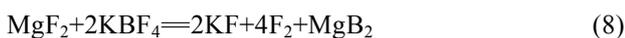
Anodic reaction,



Cathodic reaction,



The overall reaction is



Using graphitic anode, the anodic gas of fluorine will react with carbon at 750 °C:

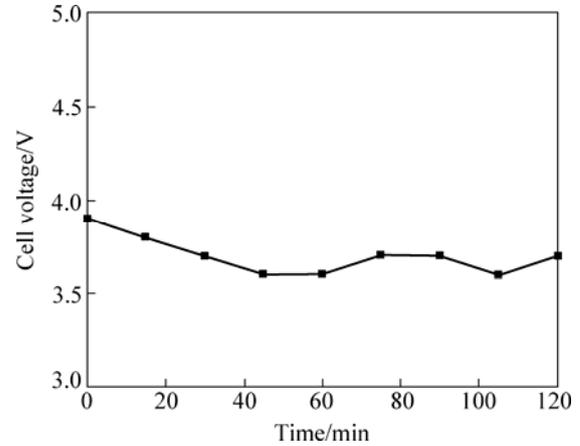


Fig. 7 Relationship between cell voltage and time during MgB₂ electrochemical deposition

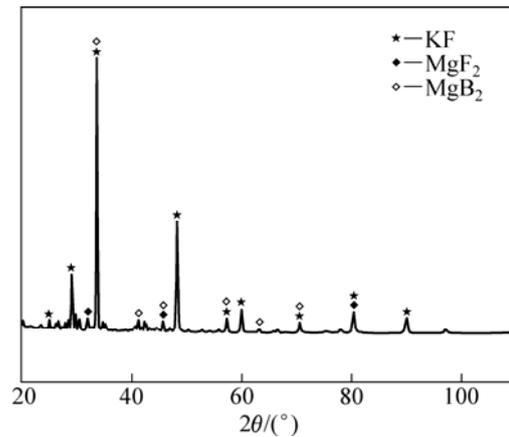
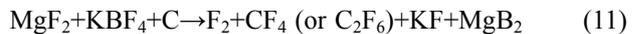


Fig. 8 XRD pattern of electro deposited product from KF-MgF₂-KBF₄ system

Therefore, the following expression could describe this process:



When using oxides MgO and B₂O₃, CO₂ (with carbon anode) or oxygen (with inert anode) could be evolved, which is similar to the Hall-Heroult aluminium reduction process [15]. This will provide an environmental friendly, low cost and high efficiency process for MgB₂ synthesis.

4 Conclusions

1) Both electrochemical reduction processes of Mg²⁺ in the KF-MgF₂ and B³⁺ in the KF-KBF₄ molten salts are governed by the diffusion process. The diffusion coefficient of Mg²⁺ in KF-1%MgF₂ is $6.8 \times 10^{-7} \text{ cm}^2/\text{s}$,

while the diffusion coefficient of B^{3+} in $KF-KBF_4$ is $7.85 \times 10^{-7} \text{ cm}^2/\text{s}$ at $880 \text{ }^\circ\text{C}$.

2) The deposition processes of Mg^{2+} in the $KF-MgF_2$ molten salt and B^{3+} in the $KF-KBF_4$ molten salt are one-step reaction process at $880 \text{ }^\circ\text{C}$.

3) MgB_2 could be fabricated by electro-deposition on graphite electrode in the $KF-MgF_2-KBF_4$ molten salt at $750 \text{ }^\circ\text{C}$. The overall reaction may be: $MgF_2+KBF_4+C \rightarrow F_2+CF_4(\text{or } C_2F_6)+KF+MgB_2$.

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氟化物熔盐体系中 Mg^{2+} 和 B^{3+} 的电化学沉积行为

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摘要: 采用循环伏安和线性扫描伏安技术, 研究在 $880 \text{ }^\circ\text{C}$ 下 Mg^{2+} 和 B^{3+} 分别在 $KF-MgF_2$ 和 $KF-KBF_4$ 氟化物熔盐体系中的电化学沉积行为。结果表明: Mg^{2+} 在 $KF-1\%MgF_2$ 熔盐体系中的还原是一步两电子反应, $Mg^{2+}+2e^- \rightarrow Mg$; B^{3+} 在 $KF-KBF_4$ 熔盐体系中的还原是一步三电子反应, $B^{3+}+3e^- \rightarrow B$ 。 Mg^{2+} 和 B^{3+} 的还原过程受扩散控制, Mg^{2+} 在 $KF-MgF_2$ 体系中的扩散系数为 $6.8 \times 10^{-7} \text{ cm}^2/\text{s}$, B^{3+} 在 $KF-KBF_4$ 熔盐体系中的扩散系数为 $7.85 \times 10^{-7} \text{ cm}^2/\text{s}$ 。在温度为 $750 \text{ }^\circ\text{C}$ 、摩尔比为 6:1:2 的 $KF-MgF_2-KBF_4$ 熔盐体系中进行电沉积制备 MgB_2 。X 射线衍射分析结果表明, 在石墨阴极的表面得到了 MgB_2 。

关键词: 二硼化镁; 电沉积; 氟化物熔盐; 扩散系数

(Edited by YANG Hua)