

## Effect of borate coating on corrosion resistance of pure nickel in molten $\text{LiCl-Li}_2\text{O}$ <sup>①</sup>

LIU Rui-yan(刘瑞岩), WANG Xu(王旭), ZHANG Jun-shan(张俊善),  
WANG Xiu-min(王秀敏), ZHU Mei-Li(祝美丽)

(Department of Materials Engineering, Dalian University of Technology, Dalian 116024, China)

**Abstract:** The pack boriding process was used to treat pure nickel at a boriding temperature of 950 °C for a boriding time of 5 h. A dense and continuous borided layer with 40 μm thickness was obtained on pure nickel. Corrosion behavior of the borided layer was investigated in molten  $\text{LiCl-10% Li}_2\text{O}$  (mass fraction) at 750 °C in air. The mass loss of the boriding coating was  $8.4 \text{ mg} \cdot \text{cm}^{-2}$  after being corroded for 50 h in the melt, which is about three times lower than that of unborided pure nickel. The preferential corrosion of B in borided layer effectively prevents the corrosion of nickel, which improves the corrosion resistance of pure nickel in molten  $\text{LiCl-Li}_2\text{O}$ .

**Key words:** pure nickel; borided nickel; molten  $\text{LiCl-Li}_2\text{O}$ ; corrosion

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### 1 INTRODUCTION

At the end of the twentieth century, a lithium reduction technique was developed to dispose of nuclear fuel ( $\text{UO}_2$ ) used<sup>[1]</sup>. In this process, the oxide ( $\text{UO}_2$ ) is reduced to the metallic form (U) by reaction with lithium dissolved in molten  $\text{LiCl}$  at 750 °C. The technique can effectively reduce the volume and radiation of spent nuclear fuel, which is convenient to store and manage. Unfortunately, the containment materials used in the technique undertake severe corrosion owing to the strong basic oxide  $\text{Li}_2\text{O}$  formed and dissolved in molten  $\text{LiCl}$ . Several reports have been published on the metals in molten  $\text{LiCl-Li}_2\text{O}$ <sup>[1-4]</sup>. Their attentions focused on the selection of the ferrous and nickel-based high-temperature alloys in molten  $\text{LiCl-Li}_2\text{O}$  mixture, such as 304, 316SS, heat resistant cast steel Morel and super 22H, Ni-base superalloys Inconel600, Inconel601 and Hastenloy C-276, but it was observed all these alloys undertaken serious corrosion being accompanied with duplex oxide  $\text{LiCrO}_2$  and/or  $\text{LiFeO}_2$  formed. Ni exhibited more stability than Cr and/or Fe in molten  $\text{LiCl-Li}_2\text{O}$  because no corrosion products of Ni were observed in the above-mentioned reports. Search for suitable coating materials in molten carbonate full cell environment mainly induced by the  $\text{Li}_2\text{O}$  suggests that B is one of suitable non-metallics elements<sup>[5]</sup>. Accordingly, this work was conducted to study the effect of boriding on corrosion resistance of pure Ni and the possibility of protective Ni-B compound coat-

ing in molten  $\text{LiCl-Li}_2\text{O}$ .

In this article, the pack boriding process, a conventional thermochemical diffusion proceeding, was used to treat pure Ni in order to explore the possibility of improving its corrosion resistance in molten  $\text{LiCl-Li}_2\text{O}$ . The effect of boriding on the corrosion resistance of pure Ni was investigated through immersion experiments in molten  $\text{LiCl-10% Li}_2\text{O}$  performed at 750 °C in air.

### 2 EXPERIMENTAL

#### 2.1 Specimen preparation

Pure nickel (99.9%) sheet was used for the metallic specimens. Specimens of rectangular, size of 12 mm × 10 mm × 5 mm, were cut from the sheet. The specimens were finely ground through 220, 400, and 800 grit silicon carbide paper and ultrasonically cleaned in acetone followed by air drying.

#### 2.2 Boriding

The pack boriding process was performed in boriding powers, consisting of 60% FeB, 1.5%  $\text{B}_4\text{C}$  (as boron donor), a mixture of 5%  $\text{KBF}_4$ , 1%  $\text{NH}_4\text{Cl}$  (as activator), and balance absorbent carbon (as filler). The pure nickel specimens were packed into a stainless-steel crucible of 60 mm in diameter and 200 mm in length. Filled with a sufficient amount of boriding powers, the crucible was heated at  $950 \pm 5$  °C in a muffle furnace for 5 h. During boriding, the pressure of reactive atmosphere caused

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**Correspondence:** LIU Rui-yan, PhD; Tel: + 86-411-4708469; E-mail: jszhang@dlut.edu.cn

by the decomposition and relative reaction of the boriding powers in the furnace was controlled at about  $(3-5) \times 10^5$  Pa for enhancing the absorption rate of boron. When the boriding process finished, the crucible was removed from the furnace and cooled in air. The borided specimens were cleaned in water for the metallographic examination and corrosion tests.

The borided surface of pure nickel specimens was examined by scanning electron microscopy (SEM) coupled with energy dispersive X-ray microanalysis (EDX). The structure of borided layers was identified with X-ray diffraction (XRD).

### 2.3 Corrosion tests

Immersion experiments were carried out at 750 °C in a LiCl-10% Li<sub>2</sub>O melt in air. For every group of experiments, the 22 g salt contained in an alumina crucible of 25 mL was used. After a selected period of time, the specimens were taken out of the melt, rinsed with distilled water, dipped in a 10% HNO<sub>3</sub> solution to strip corrosion products, dried, and weighed by microbalance. To evaluate the effect of the salt on the corrosion of the materials, the oxidation of these materials without the salt under air at 750 °C was also conducted by their discontinuous mass change.

The corrosion products were also identified XRD. The morphology and distribution of elements of corrosion scales on the surface of the specimens were investigated by SEM/EDX and electron probe microscope analysis (EPMA), respectively.

## 3 RESULTS AND DISCUSSION

### 3.1 Metallography and structure of borate coating

Fig. 1 shows the cross-sectional SEM photograph of the borided layer of pure nickel. It is clearly seen that the borided layer is a dense and continuous layer with 40 μm in thickness and few voids were observed in the borided layer. At the interface of matrix/coating, the borided layer shows lingulate. The borided surface was smooth and argent in color. The EDX analysis indicates that the composition of the borided layer is composed of Ni and B element. The XRD pattern of the borided surface as shown in Fig. 2 indicates that the borided layer is composed of Ni<sub>2</sub>B and Ni<sub>3</sub>B.

### 3.2 Corrosion test of pure nickel and borided layers

The mass change curves for the corrosion of unborided pure nickel and borided nickel are shown in Fig. 3. The mass change curves of both unborided pure nickel and borided nickel without melt show parabolic, and no visible distinction in the corrosion speed between them is seen. The presence of the molten LiCl-Li<sub>2</sub>O significantly accelerates the corrosion

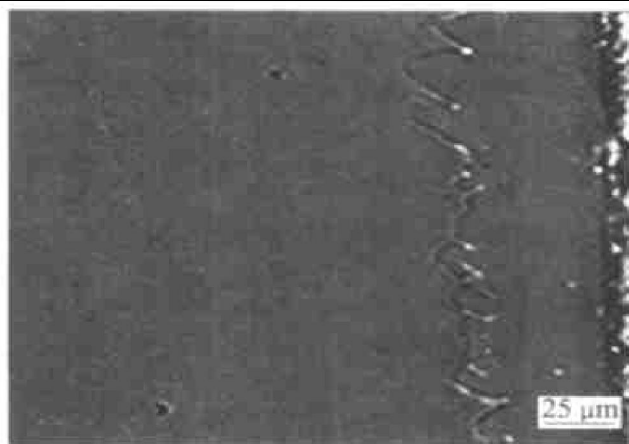


Fig. 1 Microstructure in borided layer of pure nickel

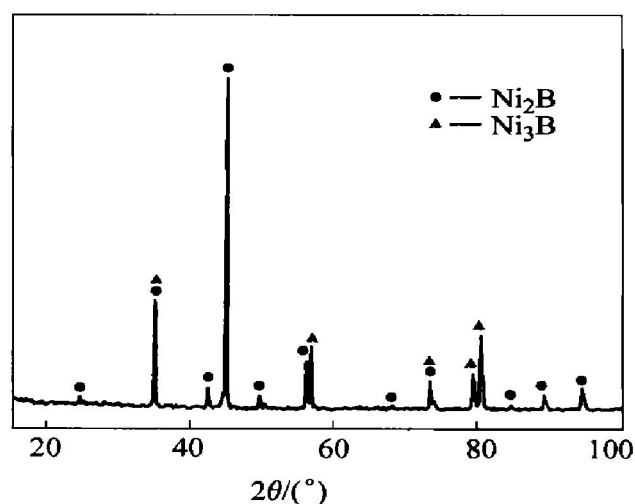


Fig. 2 X-ray diffraction pattern of borided pure nickel

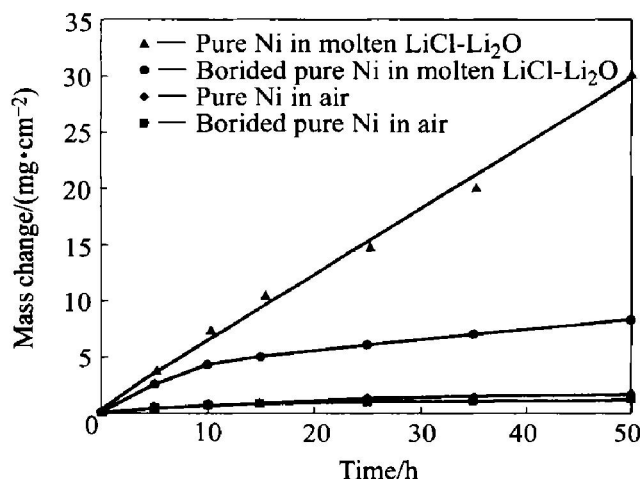


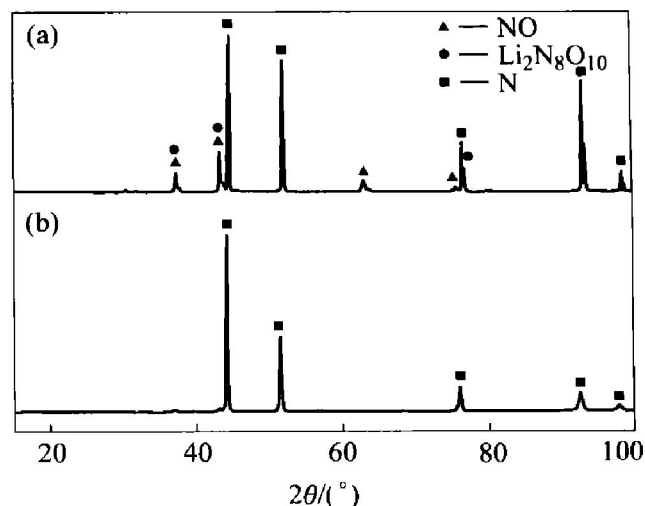
Fig. 3 Corrosion kinetic curves for pure nickel with and without melt at 750 °C in air

sion of the materials. In molten LiCl-Li<sub>2</sub>O, the mass change of unborided pure nickel increases linearly and the mass change of borided nickel increases parabolically. The corrosion of the borided nickel is slower than that of unborided pure nickel in molten salt. The

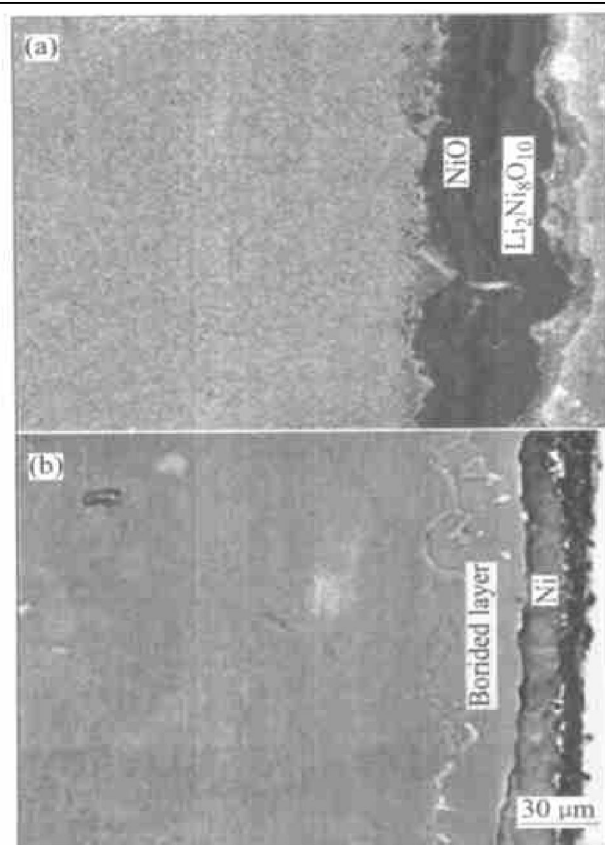
maximum value of borided nickel mass change in the melt is  $8.34 \text{ mg} \cdot \text{cm}^{-2}$ , which is about 3 times lower than that of unborided pure nickel. Thus it can be deduced that the borided coating obviously improves the corrosion resistance of pure nickel in molten LiCl-Li<sub>2</sub>O during the experimental period.

### 3.3 Corrosion products

In Fig. 4, XRD pattern of the corrosion products that are formed on unborided pure nickel and borided nickel in molten LiCl-Li<sub>2</sub>O is shown. The scale growing on the pure nickel consists of NiO and duplex oxides Li<sub>2</sub>Ni<sub>8</sub>O<sub>10</sub>. Only the peaks of nickel are identified on the surface of borided nickel corroded in the melt. Figs. 5(a) and (b) give the cross-sectional SEM photographs of the unborided nickel and borided nickel specimens corroded in the melt at 750 °C for 35 h. The corrosion scale formed on the surface of pure nickel has two layers, and an obvious vertical crack is observed at the interface of layers. The EDX analysis shows that the atomic percentage of oxygen in outer layer is 56.46 and that in inner layer is 48.37 (lithium cannot be detected by EDX). Based on the analysis of EDX and XRD, the outer-layer oxide on pure nickel is rich in Li<sub>2</sub>Ni<sub>8</sub>O<sub>10</sub> and the inner-layer is rich in NiO. The formation of the vertical crack may be attributed to the thermal stress induced by different cubic expansion coefficients of NiO and Li<sub>2</sub>Ni<sub>8</sub>O<sub>10</sub> during the cooling process<sup>[6]</sup>. Fig. 5(b) shows clearly that the borided layer also has two layers after corroded in the melt. Both B element and Ni element were detected in the inner-layer by EDX, but only Ni element was detected in the outer-layer. According to the analysis of EDX and XRD, the inner ligulate layer is uncorroded borided layer and the outer-layer is nearly composed of Ni. It is an interesting phenomenon that no oxide is detected on the surface of the borided nickel after corroded in molten LiCl-Li<sub>2</sub>O. A further investigation on the corroded borided nickel specimen by EPMA was carried out aiming at exploring the phenomenon more detailedly. The examination of EPMA of the corrosion layer of the borided nickel after immersion for 35 h is shown in Fig. 6. The analysis of line profile (Fig. 6(a)) shows clearly that the gradation changes of Ni appear at both the interfaces of matrix/inner-layer and inner-layer/out-layer, which indicates that the content of Ni in outer-layer is nearly the same as that in matrix and higher than that in inner-layer. Moreover, the visible peaks of B can only be seen in the inner-scale and no visible peaks of O can be seen in Fig. 6(a). The element (Ni, B and O) distribution is shown in Figs. 6(b), (c) and (d). The outer-layer is rich in Ni and seriously poor in O and B, the inner-layer is rich in Ni and B and poor in O. In combination with the analysis of EDAX and XRD, it is reasonable to



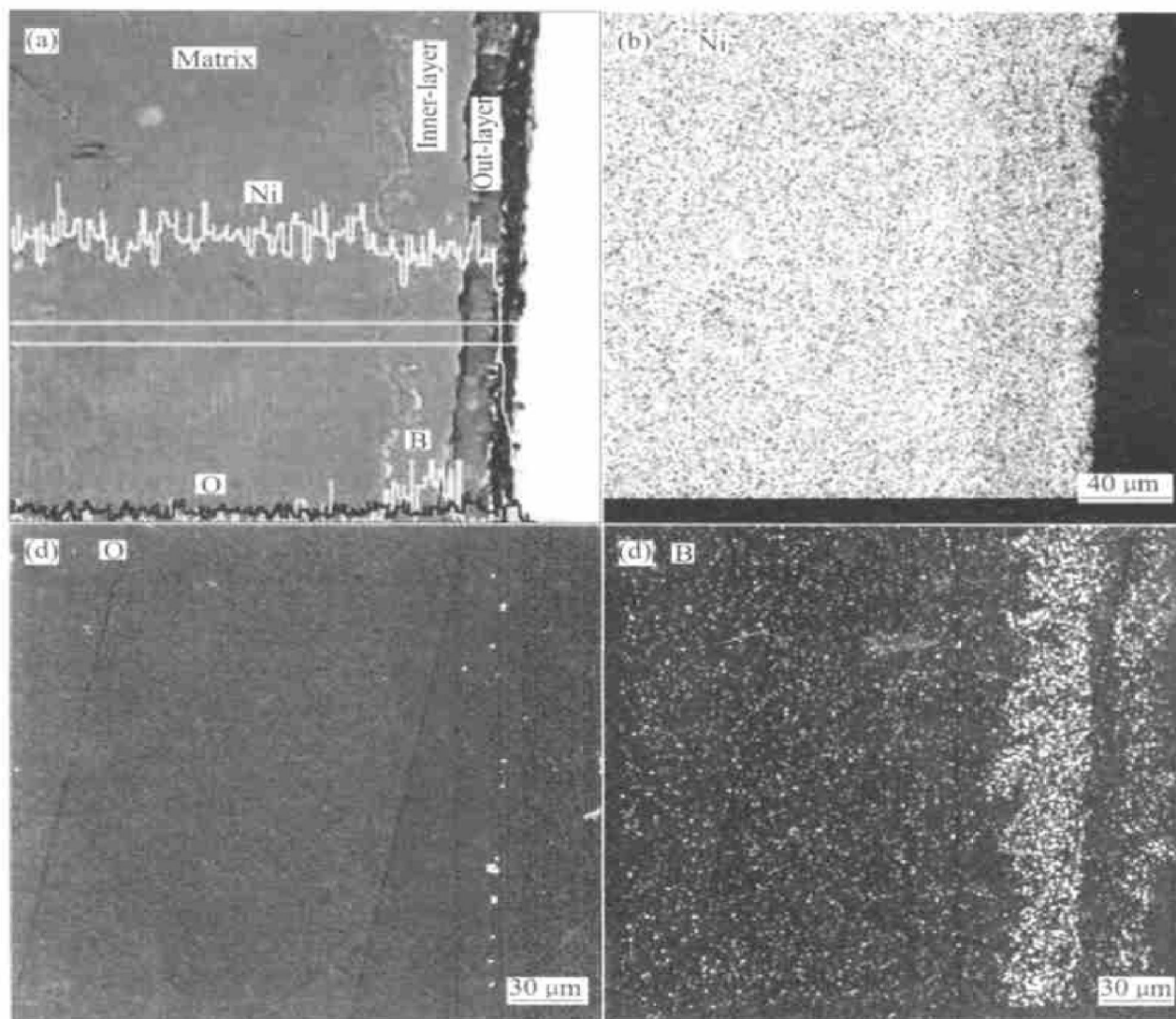
**Fig. 4** X-ray diffraction pattern of pure nickel and borided nickel corroded in molten LiCl-Li<sub>2</sub>O at 750 °C for 35 h  
(a) —Pure nickel; (b) —Borided nickel



**Fig. 5** Corrosion in molten LiCl-Li<sub>2</sub>O at 750 °C for 35 h  
(a) —Pure nickel; (b) —Borided nickel

believe that the inner-layer is uncorroded borided layer and the out-layer is composed of nickel. Thus it can be deduced that only B in the borided layer is corroded in molten LiCl-Li<sub>2</sub>O.

Corrosion in molten salts is characterized as two steps<sup>[7,8]</sup>. The first is oxidation of the metal, and the second is basic or acidic dissolution of oxide scale. For oxidation, oxygen has to diffuse through the melt to



**Fig. 6** Cross-section EPMA analysis of borided pure nickel in  $\text{LiCl-Li}_2\text{O}$  at  $750\text{ }^\circ\text{C}$  for 35 h  
(a) —Ni, B, O; (b) —Ni; (c) —O; (d) —B

metal surface. It may also be provided by dissolution from the gas phase in the molten salts. In this work, the concentration of basic  $\text{Li}_2\text{O}$  in the melt is 10%, so basic dissolution should take place in the corrosion process. During immersion in molten  $\text{LiCl-Li}_2\text{O}$ , initially,  $\text{NiO}$  was formed by reaction with oxygen dissolved from the air in the melt. With the development of corrosion, the basic dissolution of  $\text{NiO}$  happened through the lithiation process. The lithiation reactions of  $\text{NiO}$  with Li and O took place at interface of the corrosion-layer/melt ( $2\text{Li}_2\text{O} + 4\text{NiO} + \text{O}_2 = 4\text{LiNiO}_2$ )<sup>[8]</sup>. Due to less oxygen in melts under air atmosphere, the incomplete lithiation process of  $\text{NiO}$  led to products of  $\text{Li}_2\text{Ni}_8\text{O}_{10}$  ( $\text{Li}_2\text{Ni}_8\text{O}_{10}$  can be regarded as  $2\text{LiNiO}_2 + 6\text{NiO}$ )<sup>[9]</sup>. Based on the theory of Wagner<sup>[6,10]</sup>, when the corrosion curve follows linear law, the corrosion process is controlled by the reaction at the interface and the corrosion speed is independent of the thickness of the corrosion layer. The corrosion curve of pure nickel in molten  $\text{LiCl-Li}_2\text{O}$  is linear (Fig. 3), so the corrosion of pure nickel is controlled by the lithiation reaction at the interface of

corrosion-layer/melt.  $\text{Li}_2\text{Ni}_8\text{O}_{10}$  was firstly developed by the reaction of  $\text{NiO}$  with the  $\text{Li}_2\text{O}$  component and oxygen dissolved in the melt at the interface of  $\text{NiO}/\text{melt}$ . The growth of  $\text{Li}_2\text{Ni}_8\text{O}_{10}$  must take into account of the outward diffusion of nickel through the whole layer<sup>[9]</sup>. In the growth process of  $\text{Li}_2\text{Ni}_8\text{O}_{10}$ , nickel diffused through the corrosion layer and reacted with oxygen and Li at the interface of  $\text{Li}_2\text{Ni}_8\text{O}_{10}/\text{melt}$  (The reactions can be regarded as:  $\text{O}_2 + 4\text{Ni}^{2+} + 2\text{Li}_2\text{O} + 4\text{O}^{2-} = 4\text{LiNiO}_2$  and  $6\text{Ni}^{2+} + 2\text{LiNiO}_2 + 6\text{O}^{2-} = \text{Li}_2\text{Ni}_8\text{O}_{10}$ ). Because the corrosion layer was not protective and could not form a barrier for the outward diffusion of nickel, the corrosion continued with a fixed speed in the melt.

Although no protective oxide layer is detected on the surface of borided nickel, Fig. 3 indicates that the boriding treatment obviously improves the corrosion resistance of pure nickel in the molten  $\text{LiCl-Li}_2\text{O}$ . The analysis of SEM and EPMA shows that the matrix is not corroded in the melt, which indicates that the borided layer provides an effective barrier to prevent the outward diffusion of Ni in the matrix. The



analysis of EPMA shows that the outer-layer is rich in Ni and poor in B and O. Thus it can be deduced that only B in the borided layer participates in the corrosion through outward diffusion. The preferential corrosion of B may be due to the following matters. Firstly, the borided layer consists of Ni<sub>3</sub>B compound, and the complicated structure of the compound greatly decreases the speed of outward diffusion of Ni in both the matrix and the borided layer<sup>[11]</sup>. Secondly, B in the borided layer has higher activity for oxidation than Ni in the borided<sup>[6]</sup>. Additionally, the low oxygen in the melt may be a reason for the preferential corrosion of B. Only the more active B in the borided layer is corroded because the oxygen is in short supply in the melt. At the initial stage of corrosion, B in the borided layer is corroded and formed B<sub>2</sub>O<sub>3</sub> at the interface of borided layer/melt. B<sub>2</sub>O<sub>3</sub> with a low melting point (460 °C) can completely dissolve with the basic oxide at high temperature (> 600 °C)<sup>[12]</sup>. In this experiment, B<sub>2</sub>O<sub>3</sub> may completely dissolve with Li<sub>2</sub>O in the melt. This may be regarded as the basic dissolution of B<sub>2</sub>O<sub>3</sub>. Moreover, the molten B<sub>2</sub>O<sub>3</sub> may directly dissolve in the melt. Based on the theory of Wagner<sup>[6, 10]</sup>, when the corrosion curve follows parabolic law, the corrosion process is controlled by the diffusion of metallic (or oxide) ion. The corrosion curve of borided nickel in the melt shows parabolic which indicates that the corrosion process is controlled by the outward diffusion of B. With the development of the corrosion, B should diffuse from the borided layer to the interface of borided layer/melt for making up its consumption at here. During the experimental time, the oxidation and basic dissolution (or dissolution) dominate the total corrosion process and the corrosion products dissolve in the melt, which induces that no oxide is detected in the results of EDX, XRD and EPMA. It is difficult to clarify the detailed corrosion mechanism in molten LiCl-Li<sub>2</sub>O because no concrete corrosion products are detected. However it can be deduced that the preferential corrosion of B in borided layer effectively prevents the formation of oxide of nickel, which results in the improvement on the resistance of nickel in molten LiCl-Li<sub>2</sub>O.

#### 4 CONCLUSIONS

The pack boriding process of pure nickel at 950 °C for 5 h produces a dense and continuous borided layer with 40 μm in thickness which is composed of Ni<sub>3</sub>B compound (Ni<sub>2</sub>B and Ni<sub>3</sub>B). The effect of borided coating on the corrosion resistance of pure nickel in molten LiCl-10% Li<sub>2</sub>O at 750 °C under air

was studied. The experimental results indicate that the borided coating can greatly improve the corrosion resistance of pure nickel in molten LiCl-Li<sub>2</sub>O, which is ascribed to the preferential corrosion of B in the borided layer that prevents the severe corrosion of nickel.

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