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Degradation of TiB_2/TiC Composites in Liquid Nd and Molten $\text{NdF}_3\text{--LiF--Nd}_2\text{O}_3$ System

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Abstract: The degradation of titanium diboride (TiB_2)/titanium carbide (TiC) composites in the liquid Nd and molten $\text{NdF}_3\text{--Nd}_2\text{O}_3\text{--LiF}$ salts is investigated at 1,060 °C, respectively. The penetration of TiB_2/TiC composites by liquid Nd mainly depended on the grain boundaries and residual pores, even if the coherent interface is formed between TiB_2 and TiC . The oxidation of TiB_2 led to further interfacial chemistry reactions, which speeded up the degradation of TiB_2/TiC composites at the initial stage in $\text{NdF}_3\text{--LiF--Nd}_2\text{O}_3$ system. After that, the degradation was slowed because of the formation of diffusion boundary layer, and then chemical penetration was replaced gradually by the physical penetration. The dissolved Ti in liquid Nd and $\text{NdF}_3\text{--LiF--Nd}_2\text{O}_3$ melts are used to evaluate the corrosion rate of TiB_2/TiC composites, and the calculated values were about 0.56 and 7.8 mm/year, respectively. After the penetration by liquid Nd and $\text{NdF}_3\text{--LiF--Nd}_2\text{O}_3$ melts, the bending strengths of TiB_2/TiC composites decreased and the fracture mode changed from transgranular to intergranular due to the decreased grain boundary force.

Keywords: TiB_2/TiC composites, grain boundary, penetration, fracture mode, corrosion rate

Introduction

Titanium diboride (TiB_2) demonstrates wide application advantages as drained and inert cathode materials in aluminum and neodymium electrolysis cells [1–4]. Despite the desirable potential of TiB_2 materials, inert cathodes based on TiB_2 materials have not yet been

applied in industrial cells. The main challenge lies in the sintering difficulty of monolithic TiB_2 to full density without microcracking due to its high melting point, low diffusion coefficient and anisotropic structure [5–7]. The resistance toward infiltration of liquid metals along grain boundaries is most likely dependent on the microstructure of the materials, such as the grain boundaries, the grain size and finally the porosity and the degree of microcracking. Titanium carbide (TiC) is a desirable choice for avoiding some of these problems, because it has five independent slip systems and good thermodynamic compatibility with TiB_2 [5, 8, 9]. Therefore, TiB_2/TiC composites could exhibit higher densities compared to that of monolithic TiB_2 , which could lead to the improved corrosion resistance of TiB_2/TiC cathodes in aluminum and neodymium electrolysis cells. At present, most studies mainly focus on the preparation and mechanical properties of TiB_2/TiC composites [10–14]. The application in the high-temperature electrolytic systems, especially for the degradation of TiB_2/TiC composites in neodymium electrolysis cells, is rarely reported.

In this work, the degradation of TiB_2/TiC composites in liquid Nd and molten $\text{NdF}_3\text{--LiF--Nd}_2\text{O}_3$ salts was investigated, involving the penetration mechanisms, the decreased mechanical properties and corrosion rates calculated according to the dissolved Ti in the melts. The results obtained here are highly significant for guiding the application of TiB_2/TiC inert cathodes in neodymium electrolysis fields, especially for the submerged neodymium reduction cells.

Experiments

Materials

The metal neodymium (Nd, purity > 99%) from the supplier (Baotou Lanthanide New Material Technology Co. LTD, Baotou, China) and the chemical agents (NdF_3 , LiF and Nd_2O_3) from the supplier (Second Chemical Agent Co. LTD, Suzhou, China) are used as raw materials. In order to obtain finer grains and higher densities, TiB_2/TiC composites were prepared by mechanical alloying (48 h)

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followed by pressureless sintering technique. The details, involving phase evolution, preparation process and mechanical properties of the TiB₂/TiC composites, have been reported in our previous studies [15, 16].

Exposure to the liquid neodymium and molten NdF₃–LiF–Nd₂O₃ salts

By electrical discharge machining, the TiB₂/TiC plates for tests were cut off from the bulk into pieces with dimensions of 25 × 5 × 5 mm³. The sample surface was ground by the SiC abrasive and then polished with 5 and 1 μm diamond paste. To exclude the effect of impurities, ultrasonic cleaning in ethanol was performed prior to further testing. Due to the density difference between the TiB₂/TiC composites and liquid Nd, special molybdenum crucible was used to carry out the hot corrosion experiments. The schematic diagram is shown in Figure 1, where the test bars were immersed in the bottom liquid Nd and the upper molten NdF₃–LiF–Nd₂O₃ salts (NdF₃:LiF = 7.5:1, Nd₂O₃ accounted for 3% of the total mass), respectively. The test bars were held at 1,060 °C for determined intervals along with the flowing argon. After the exposure, the residual Nd on the surface of TiB₂/TiC bars was removed first by etching in 0.5 mol L⁻¹ HCl followed by cleaning with deionized water several times. The residual salts on the surface of TiB₂/TiC bars were removed by scraper blade followed by polishing with SiC abrasive paper. The corrosion rates of TiB₂/TiC degraded in liquid Nd and NdF₃–LiF–Nd₂O₃ melt were estimated according to

the dissolved Ti in the melts. To exclude the effect of Ti concentration gradients in the melts, samples were collected from top, middle and bottom portions and then mixing for inductively coupled plasma (ICP) characterization. The average corrosion rate was calculated according to the following formula:

$$V = \frac{\Delta w}{s \times t} \quad (1)$$

where V is the corrosion rate (g/h/cm²), Δw is the changing weight of TiB₂/TiC composites (g), s is the superficial area (cm²) and t is the exposure time (h).

Characterization

Three-point bending bars (25 × 5 × 5 mm³) were prepared according to the CTM9100 test standard. After testing, the bars were cut using an automatic cut-off machine employing a diamond blade to obtain cross sections of specimens. The cross sections were ground and polished to mirrors for further characterization. The microstructures of TiB₂/TiC composites, polished cross sections and fracture surfaces of the tested bars were investigated using a Hitachi-S-4800N scanning electron microscope (SEM) attached with an energy-dispersive spectrometer (EDS). The phase component of the TiB₂/TiC composites was characterized using X-ray diffraction (XRD) (PW3040/60) with Cu-Kα radiation by comparing the peak positions and the intensities with those from the JCPDS databases.

Figure 1: Schematic diagram for infiltration of melts.

Results and discussion

Micrographs of pristine TiB₂/TiC composites

The microstructures and phase component of the TiB₂/TiC composites have been shown in Figure 2. As shown in Figure 2, the mechanical alloyed powders mainly consisted of 30–50 nm TiB₂ and TiC particles (Figure 2(a)), corresponding to the broad XRD peaks shown in Figure 2 (b). Because of the role of mechanical alloying, high activity and metastable particles were obtained, which were benefited for the subsequent sintering process. The dark elongated grains are TiB₂, and the irregular but more equiaxed grains are TiC (Figure 2(c)), in agreement with the results of XRD analysis (Figure 2(d)). Sorrell et al. [17] used lattice parameter values and estimated the lattice mismatch between TiB₂ and TiC to be only about 1.6%.

Figure 2: Images and XRD analysis of TiB_2/TiC materials. (a, b) Micrographs and XRD of mechanical alloyed powders; (c, d) SEM and XRD analysis of TiB_2/TiC composites; (e, f) TEM and HRTEM images between TiB_2 and TiC (selected areas in the areas marked by red dash square).

Due to the good lattice match between TiB_2 and TiC , the coherent interface could be observed in dense TiB_2/TiC composites (Figure 2(e) and (f)), which led to the improved corrosion resistance properties of TiB_2/TiC composites, especially for the penetration along the grain boundaries.

Infiltration of liquid Nd and molten $\text{NdF}_3\text{--LiF--Nd}_2\text{O}_3$ salts in TiB_2/TiC composites

Comparing the exposed and pristine TiB_2/TiC materials, the samples exposed to the liquid Nd showed mechanically soften and became more pronounced during the

subsequent polishing. The samples exposed to the $\text{NdF}_3\text{--LiF--Nd}_2\text{O}_3$ melt exhibited the structure soften and lots of pores at the surface of the TiB_2/TiC materials. Figure 3 shows the morphologies and elemental distributions of polished cross sections close to the penetration front exposed in liquid Nd and molten $\text{NdF}_3\text{--LiF--Nd}_2\text{O}_3$, respectively. As shown in Figure 3(a), a thick gradient layer (about $50\text{ }\mu\text{m}$) is formed after 48 h of static corrosion in the $\text{NdF}_3\text{--Nd}_2\text{O}_3\text{--LiF}$ system, and a small amount of melt is allowed to infiltrate slowly into the interior through the gradient layer. The interfaces were sparse and discrete compared with those in the interior of materials, suggesting the degradation of the TiB_2/TiC composites during the corrosion process. A completely different phenomenon is observed when

the TiB₂/TiC composites were exposed to the liquid Nd. The gradient layer is hardly detected around the cross section (Figure 3(b)). The element traces of Nd and Ti along the cross sections could be also observed from the EDS analysis (Figure 3(a₁), (a₂), (b₁) and (b₂)), indicating the penetration sites of the melts in TiB₂/TiC materials. The elemental distributions along the cross section

suggested that residual pores were the main sites for the penetration of TiB₂/TiC composites by liquid Nd, because of the Nd energy peaks detected at the supposed locations of missing Ti energy peaks (compare Figure 3(b₁) and (b₂)). Comparing the energy peaks of Nd obtained in molten NdF₃–LiF–Nd₂O₃ melts and that in liquid Nd (Figure 3(a₂) and (b₂)), more Nd traces were

Figure 3: Micrographs and EDS analysis of the cross sections close to the penetration front of the TiB₂/TiC composites exposed to (a) molten NdF₃–Nd₂O₃–LiF salts and (b) liquid Nd; as well as the element distributions (a₁, a₂) corresponding to molten NdF₃–Nd₂O₃–LiF salts and (b₁, b₂) corresponding to liquid Nd (a₃, b₃) showing the XRD results of the corresponding cross sections after penetration.

detected in molten NdF₃-LiF-Nd₂O₃ melts, indicating that the penetration mechanism of TiB₂/TiC composites by molten NdF₃-LiF-Nd₂O₃ melts was different from that by liquid Nd. The penetration can cause a weakening of the grain boundary cohesion and possibly cracking, and then pull out of grains and failure of TiB₂/TiC composites as cathodes during neodymium electrolysis. There are several possible mechanisms for explaining the infiltration of Nd or molten NdF₃-LiF-Nd₂O₃ melts along the grain boundaries or residual pores in polycrystalline ceramic materials. First, the resistance toward the infiltration of melts along the grain boundaries and residual pores most likely depend on the microstructure of the materials, especially the second-phase composition at the grain boundaries and final porosity. Although the observed grain boundaries between TiB₂ and TiC are free of pores (Figure 2(c)), the residual pores and grain boundaries are inevitable because of the discrepant thermal expansion coefficient of TiB₂ hexagonal structure and the lattice plane orientation between TiB₂ and TiC. Second, infiltration of the grain boundaries will result in the increase of internal stresses due to the anisotropic thermal expansion after infiltration. Lastly, penetration due to the direct or indirect reactions is also possible. If the reaction forms new phases with increased molar volume, internal stress will build up and possibly induce microcracking formation and by this way increase the corrosion rate. As shown in Figure 3(b₃), no reaction between Nd and TiB₂/TiC composite is observed according to the results of XRD analysis. However, some new phases, such as TiO₂, Nd₂Ti₄O₁₁ and Nd(BO₂)₃, are detected from the cross sections of exposed samples in the molten NdF₃-LiF-Nd₂O₃ melts, indicating the direct or indirect reactions occurring between the TiB₂/TiC composites and the melts (Figure 3(a₃)). Due to slight oxygen mixed in the flowing argon, TiB₂ is more vulnerable to be oxidized than that of TiC at high temperature according to the reported literature [18], which leads to further reactions between the oxidized productions, such as TiO₂, and molten NdF₃-LiF-Nd₂O₃. The possible reaction mechanisms could be deduced in the following:

Due to the penetration of liquid Nd and molten NdF₃-LiF-Nd₂O₃, the degradation of TiB₂/TiC composites is inevitable. The changes between corrosion rate and exposure time profile, corresponding to the materials

exposed to the liquid Nd and molten NdF₃-LiF-Nd₂O₃, are shown in Figure 4. It should be noticed that the conversion between Ti content detected by ICP and TiB₂/TiC composites is based on the target composition of 2TiB₂/TiC, and then the corrosion rate is calculated according to formula (1). The data used for calculating the corrosion rate are listed in Table 1. A steep linear increase (to about 0.00041 g/cm²/h) is observed and deems to be related to the rapidly dissolved TiB₂/TiC composites in molten NdF₃-LiF-Nd₂O₃ salts when the exposure time is only up to 12 h. Afterward, the increase becomes less significant and even descends sharply between 24 and 48 h, confirming that the chemical penetration is replaced gradually by the physical penetration when the diffusion gradient layer is formed after some time. Similar results are also observed for the infiltration of liquid Nd.

Figure 4: Relation between corrosion rate and exposure time for TiB₂/TiC composites.

Table 1: Data used for calculating the corrosion rate.

Corrosion media	Melt weight/g	Corrosion area/cm ²	Corrosion time/h	Ti content/wt %	Weight of 2TiB ₂ /TiC/g
Nd	100	5.5	12	0.0017	0.0024
			24	0.0033	0.0048
			36	0.0038	0.0051
			48	0.0041	0.0055
NdF ₃ -Nd ₂ O ₃ -LiF	100	5.5	12	0.02	0.028
			24	0.041	0.055
			36	0.044	0.061
			48	0.048	0.065

Notably, due to the oxidation reactions of TiB₂/TiC composites and further reactions between the melts and intermediates, the corrosion rate of TiB₂/TiC composites in NdF₃-LiF-Nd₂O₃ melts is higher than that in liquid Nd, which is less than 0.00003 g/cm²/h. It is also of great importance to understand that the corrosion rate obtained in the present investigation fluctuates with prolonged exposure time. With prolonged time, the diffusion boundary layer becomes increasingly thicker, which can impede or delay the further infiltration of melts along the grain boundaries and open porosities in TiB₂/TiC composites. Therefore, the corrosion rate obtained in this study is higher than that produced in actual industrial production, indicating the promising applications of TiB₂/TiC composites in submerged neodymium reduction cells.

Influence of the infiltration on the mechanical properties

As shown in Figure 5, the test bars show the gradually decreased bending strengths with prolonged exposure time. Comparing the bending strengths of test bars penetrated by liquid Nd and those penetrated by NdF₃-Nd₂O₃-LiF melts, the descended range detected in liquid Nd are, however, not so pronounced probably due to a crack-bridging effect of the ductile Nd located at the grain boundaries and open porosities. Figure 6 shows the fracture morphologies of the pristine materials and those of

Figure 5: Bending strength as a function of exposure time for TiB₂/TiC composites.

penetrated materials. The grain boundary cohesion is weakened because of the infiltration of melts, which resulted in a change of fracture mode. As shown in Figure 6, the fracture mode changes from mainly intra-granular to intergranular due to the soften grain boundaries and induced microcracking (compare Figure 6(a), (b) and (c)). Similar results have also been reported in the literature [19, 20].

Potential for inert cathodes based on TiB₂/TiC composites

According to the dissolved Ti in liquid Nd and molten NdF₃-Nd₂O₃-LiF melts, the estimated corrosion rates are about 0.56 and 7.8 mm/year, respectively. The values obtained here is a little higher than that reported by Thonstad, who estimated a wear rate of ~0.2 mm/year for a commercial Al electrolysis cell [21]. However, the results obtained here are more instructional for developing the submerged neodymium electrolysis cell equipped with the TiB₂/TiC cathodes, where the TiB₂/TiC cathodes are mainly corroded by the liquid Nd. Furthermore, in order to improve the corrosion resistance of TiB₂/TiC composites, dense microstructures and strengthened grain boundaries between TiB₂ and TiC are pursued in future.

Conclusions

The degradation of TiB₂/TiC composites in liquid Nd and molten NdF₃-Nd₂O₃-LiF salts has been investigated. Although the observed grain boundaries between TiB₂ and TiC are free of pores, the penetration of liquid Nd and NdF₃-Nd₂O₃-LiF along the grain boundaries and residual pores is evitable. Interfacial chemistry reactions occurring in NdF₃-Nd₂O₃-LiF system led to the fast penetration by melts and high corrosion rates of TiB₂/TiC composites. However, the penetration is slowed because of the formation of diffusion boundary layer with prolonged exposure time, and then the chemical penetration is replaced gradually by the physical penetration. The dissolved Ti in liquid Nd and NdF₃-Nd₂O₃-LiF are used to estimate the corrosion rates of TiB₂/TiC composites, and the calculated values were about 0.56 and 7.8 mm/year, respectively. After the penetration of liquid Nd and NdF₃-Nd₂O₃-LiF, the bending strengths of TiB₂/TiC composites decreased with prolonged exposure time and the fracture mode changed from transgranular to intergranular.

Figure 6: SEM micrographs of fracture surface for (a) pristine TiB_2/TiC composites, TiB_2/TiC exposed in (b) Nd and (c) molten $\text{NdF}_3\text{--LiF--Nd}_2\text{O}_3$ salts.

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