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Production of TiB_2 coatings on graphite substrates by electrophoretic deposition in NaF-AlF_3 melt

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Abstract

In this paper a novel method for fabrication of TiB_2 coatings on graphite substrates by electrophoretic deposition of TiB_2 nanoparticles in NaF-AlF_3 melt at 980 °C has been explored. With an applied cell voltage of 1.2 V (i.e. electric field 0.6 V/cm), a flat and dense TiB_2 coating with a thickness of around 50 µm has been prepared. It was found that the surface consisted of TiB_2 flakes with a nanoscale size. In addition, the average value of hardness of the TiB_2 coating was determined as 3585 ± 139 $HV_{0.1}$ (36.6 ± 1.4 GPa) measured by a Vickers micro-hardness tester.

Keywords: *NaF-AlF_3 molten salts, TiB_2 nanoparticles, electrophoretic deposition, TiB_2 coatings*

I. Introduction

Electrophoretic deposition (EPD) was discovered by Ruess in 1808, and it has been studied mostly in aqueous and organic solutions [1] and can be applied for micro/nano fabrication [2–4], self-assembly of nanoparticles [5] and preparation of a wide variety of coatings and films [6–8] for solid oxide fuel cells [9], Li-ion battery electrodes [10] and so on.

Since 2011 molten inorganic salts with a stable suspension of nanoparticles have been investigated as efficient heat transfer and storage materials [11,12] and for catalysis of chemical reactions [13,14]. In 2017, Zhang *et al.* [15] proved the existence of nanoparticles in the form of stable colloids in molten inorganic salts for the first time by means of small angel X-ray scattering and transmission electron microscopy (TEM) characterization. Then a series of studies on the stability of colloidal nanoparticles dispersed in molten inorganic salts have been carried out [16–18]. Motivated by these investigations, our group has found and demonstrated the availability of the EPD of TiB_2 and ZrB_2 nanoparticles in molten salts and thus proposed a new method for preparation of transition metal boride coatings by EPD of the corresponding nanoparticles in molten salts [19]. This approach is advantageous for its simple operation, inexpensive equipment and production of pure product.

It is known that TiB_2 coated graphite materials have significant applications such as wettable cathodes for aluminium electrolysis [20,21] and high-temperature oxidation resistance materials [22]. In this paper the feasibility of preparation of TiB_2 coatings on graphite substrates by EPD of TiB_2 nanoparticles in NaF-AlF_3 melt was investigated.

II. Experimental

2.1. EPD process in NaF-AlF_3 molten salts

The schematic drawing of EPD process used for deposition of TiB_2 nanoparticles suspended in molten NaF-AlF_3 on graphite substrate is demonstrated in Fig. 1. The mixture of NaF and AlF_3 (with molar ratio 61:39) was introduced into a graphite crucible, which was placed in an electric resistance furnace and heated up to a temperature of 980 °C. Actually, the eutectic

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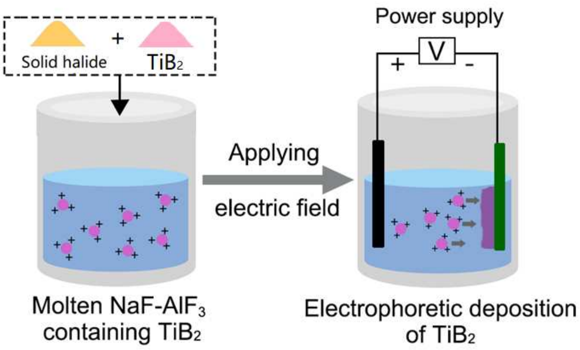

Figure 1. Schematic of EPD of TiB_2 nanoparticles in $NaF-AlF_3$ molten salts

point of $NaF-AlF_3$ (with molar ratio 61:39) is 835 °C, thus 980 °C was selected to obtain a better viscosity of the melt. After the mixed fluorides were melted, the mixture of the $NaF-AlF_3$ and TiB_2 nanoparticles was prepared according to the procedure which could be referred to our previous work [19]. The TiB_2 nanoparticles were added into the molten salts and the concentration was 70 g/l.

Subsequently, a graphite cathode (5 × 1 × 25 mm), with an immersion depth of 10–15 mm, and a graphite anode (⌀6 mm) with an immersion depth of 15–20 mm were placed in the cell, with a distance of 20 mm between them. Pre-electrolysis under 1.5 V cell voltage for 1 h was performed to remove some impurities. EPD was carried out with an applied voltage of 1.2 V (i.e. electric field 0.6 V/cm) for 1 h. A cell voltage less than the theoretical decomposition voltage of the supporting electrolyte ($NaF-AlF_3$) should be selected and there is generally a small amount of dissolved oxygen ions in the fluorides. The theoretical decomposition voltage of Al_2O_3 in this case (using graphite as the anode) is around 1.2 V. So we decided to choose 1.2 V as the cell voltage. A DC power supply (HLR-3660D, Henghui) was employed to regulate the cell voltage. All EPD trials were conducted under an argon atmosphere.

After EPD was finished, the coated cathode was taken out from the cell and immersed in NaCl-KCl molten salts at 710 °C for 5 min to remove the solid fluoride salt remaining on the surface of TiB_2 coating. Then it was soaked in deionized water for 30 min to remove the solid chloride salt residues and in acetone for 5 min to remove the water, followed by drying.

2.2. Characterization

The EPDed TiB_2 coatings were analysed using a scanning electron microscopy (SEM - Regulus 8220, HITACHI) equipped with an energy-dispersive spectroscopy (EDS) detector (ULTIM MAX170, Oxford) and X-ray diffraction (XRD - Smart Lab, Rigaku, voltage: 40 kV, current: 40 mA, scan rate: 10 °/min) with Cu K_α radiation to examine their micromorphology and elements in micro zones and phase composition.

A Vickers micro-hardness tester (MH-5LD, Hengyi) was used to measure the Vickers hardness applying a load of 0.98 N with a dwell time of 15 s. At least six indentation tests on the surface of each TiB_2 coating were carried out.

III. Results and discussion

3.1. Characterization of TiB_2 containing melt

In order to figure out the suspension state of added TiB_2 nanoparticles in $NaF-AlF_3$ melt at 980 °C, the nanoparticles-containing electrolyte was analysed. We sampled the upper part of the molten fluoride suspension with the TiB_2 nanoparticles 5 h after their mixing, cooled it down to room temperature quickly and characterized it by SEM. The typical morphology of the cooled solid salts is shown in Fig. 2a. The elemental EDS mapping analysis (Figs. 2c-f) for Fig. 2a revealed that the main elements were Na, Al and F, corresponding to the composition of the molten $NaF-AlF_3$, while Ti element enriched area was also identified inside the rectangular area in Fig. 2a. This Ti element enriched area was further enlarged (Fig. 2b) confirming the presence of particles (around 50 nm in size), while no nanoparticles were found in the area with the presence of only bulk salts. The existence of the suspended TiB_2 nanoparticles in the cooled solid fluoride salts indicates that TiB_2 nanoparticles could be stable in $NaF-AlF_3$ molten salts for at least 5 h, which ensures the possibility of subsequent EPD of TiB_2 nanoparticles in $NaF-AlF_3$ molten salts. In addition, the enrichment of Ti element in the sampled solid salts may be caused by the segregation of TiB_2 nanoparticles during the cooling process.

3.2. EPD of TiB_2 on graphite substrate in melt

EPD of the TiB_2 nanoparticles on a graphite substrate in the $NaF-AlF_3$ melt at 980 °C was carried out, and the photograph and XRD result of the obtained deposit are shown in Fig. 3. It can be seen that there was an apparent deposited layer on the surface of the graphite cathode. The obvious diffraction peaks of TiB_2 can be observed (Fig. 3b), which indicates that the deposited layer was pure TiB_2.

The surface morphology of the TiB_2 coating was analysed by SEM, as demonstrated in Fig. 4. From Figs. 4a,b, it can be observed that the surface of the TiB_2 coating was relatively flat, which consisted of particles with an average size below 400 nm. The higher magnification of this TiB_2 coating surface, as shown in Fig. 4c, reveals that these hundreds of nanometre scale TiB_2 particles were composed of TiB_2 flakes with an average size less than 100 nm.

The micromorphology of the fractured cross-section of TiB_2 coating is presented in Figs. 4d,e. The surface of the coating was relatively flat and the whole coating was dense and coherent, with a thickness of about 50 μm. Typical EDS analysis result (top-right inset of Fig. 4e) of the cross-section shows that the main components of the coating are Ti and B elements, indicating no inclusion of electrolyte components coming from the molten salts.

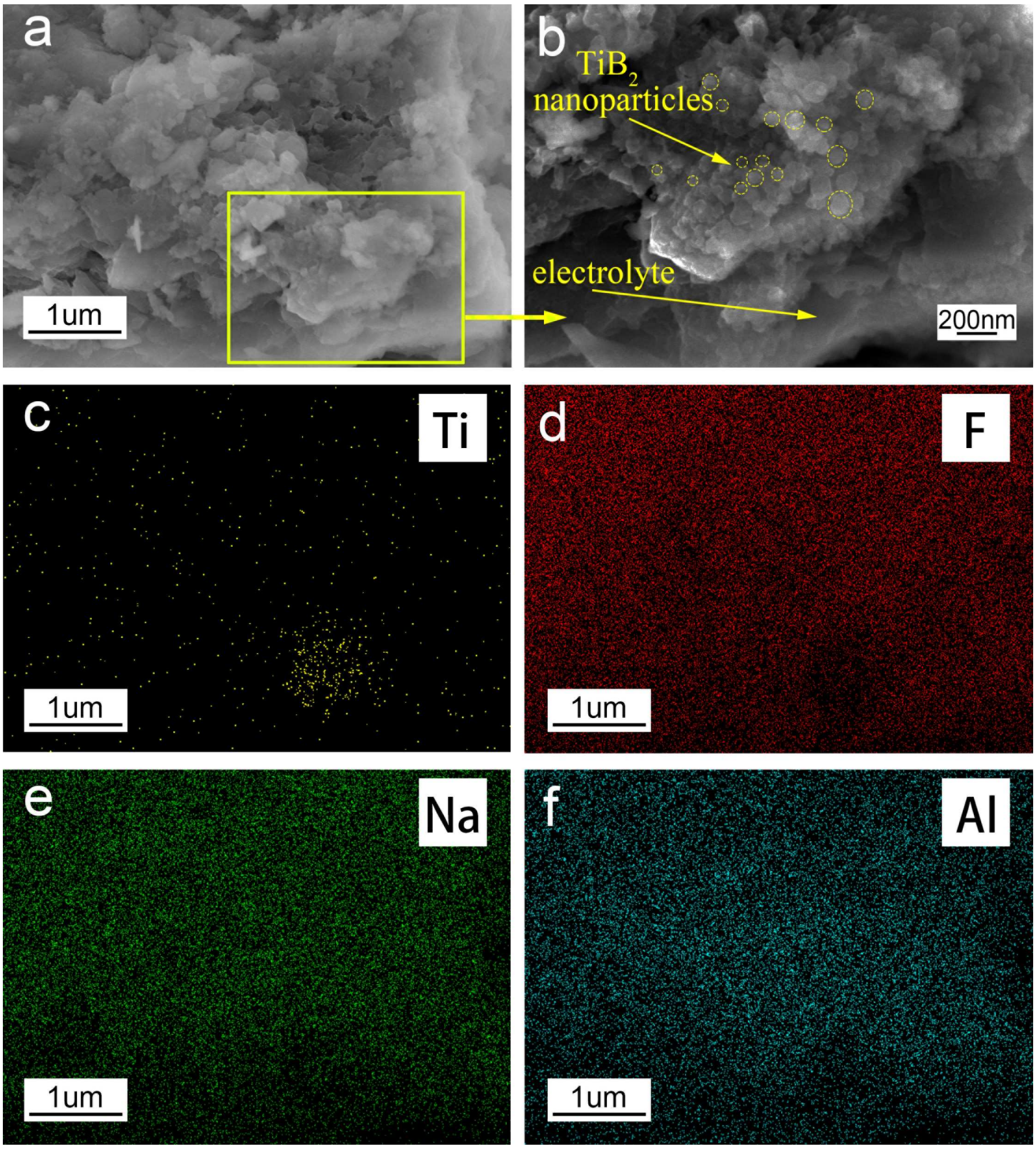

Figure 2. SEM images (a,b) and EDS mapping analysis (corresponding to Fig. 2a) of quenched sample of TiB_2 nanoparticle-containing melt taken from the upper part of molten NaF-AlF_3 system with TiB_2 nanoparticles 5 h after their mixing

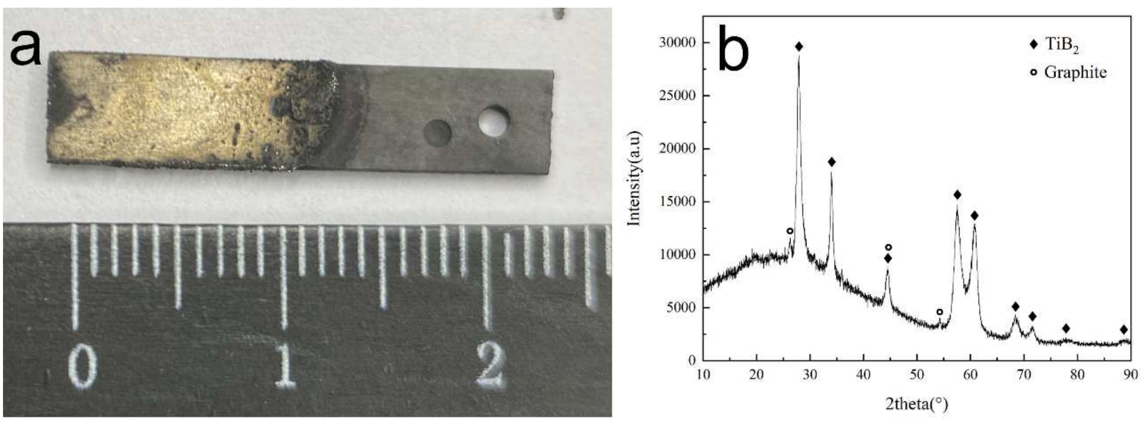

Figure 3. Photograph and XRD result of EPDed TiB_2 coating on a graphite substrate in NaF-AlF_3 melt at 980 °C

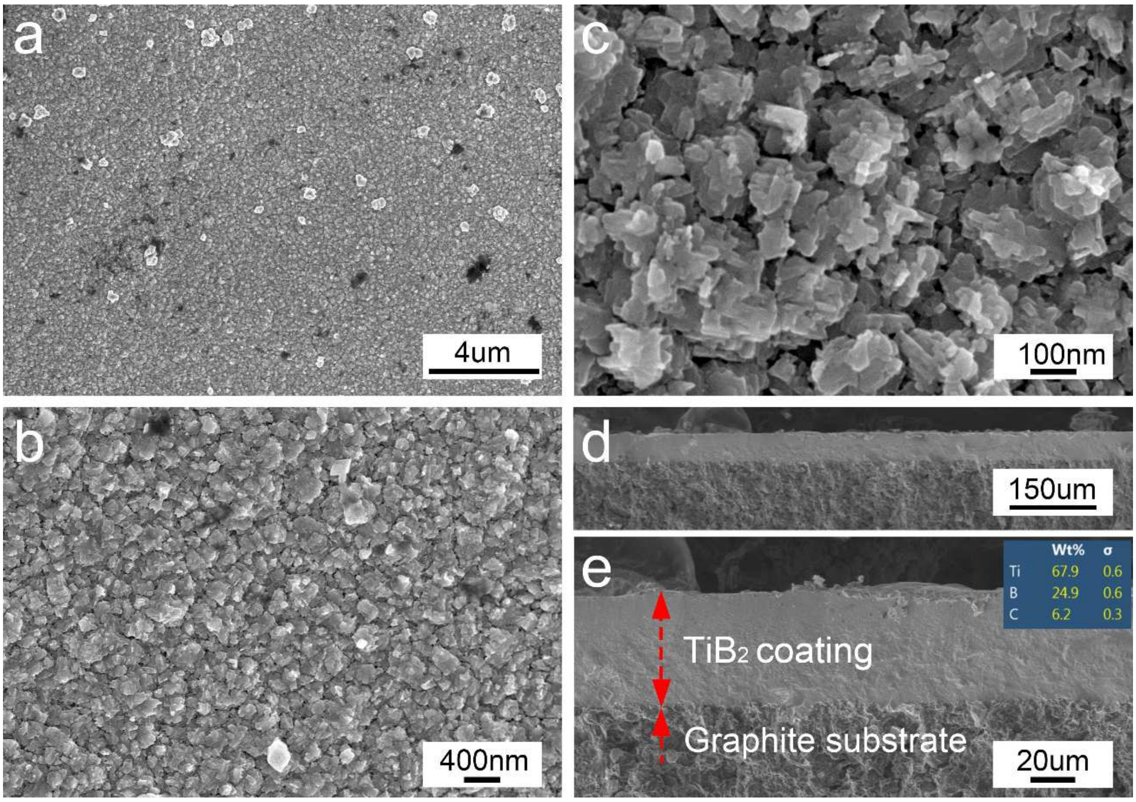

Figure 4. SEM images of the surface (a-c) and fractured cross-section (d,e) of TiB_2 coating prepared by EPD in NaF-AlF_3 melt at 980 °C

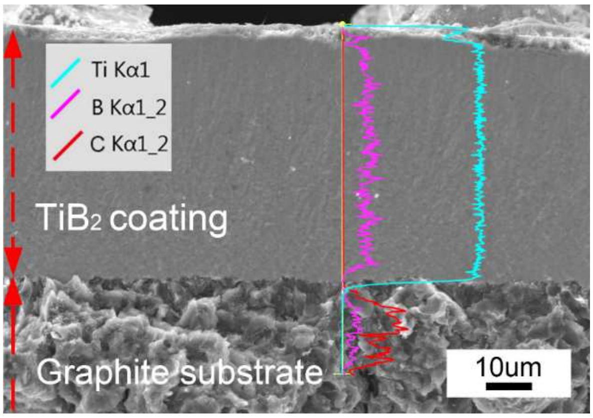

Figure 5. EDS line scan results of the cross-section of TiB_2 coating prepared by EPD in NaF-AlF_3 molten salts at 980 °C

Moreover, EDS line scan of the TiB_2 cross-section was performed with the results shown in Fig. 5. It can be found that there is a tight bond between the TiB_2 coating and the graphite substrate without any inclusion of fluoride electrolyte. According to the line scan results of Ti and B elements, there was no obvious composition transition layer at the interface between the TiB_2 coating and the graphite substrate. In addition, the micro-hardness was tested by a Vickers hardness tester, with the obtained average micro-hardness value of 3585 ± 139 $HV_{0.1}$ (36.6 ± 1.4 GPa), which is higher than the reported values of 25–35 GPa for TiB_2 [22]. This verifies the high density of the TiB_2 coating produced by EPD in NaF-AlF_3 melt.

The above results show that EPD of the TiB_2 nanoparticles in the NaF-AlF_3 molten salts containing TiB_2 nanoparticles was successfully carried out, and dense and flat TiB_2 coatings were obtained on graphite substrates. These initial findings could provide a new approach for manufacturing of TiB_2 coated cathodes for aluminium electrolysis and also fabrication of TiB_2 coated graphite materials for high-temperature oxidation resistance.

Moreover, compared with that in aqueous or organic solutions, EPD in high-temperature molten salts has many advantages. Firstly, the required cell voltages of less than 2 V in high-temperature molten salts are far below the values of 20–300 V generally applied in aqueous or organic solutions [23]. Secondly, EPD in high-temperature molten salts results in a dense and adhesive coating in one step. Contrary to this, in aqueous or organic solutions the resulting deposits with high porosity, low density and poor adhesion generally need further drying and sintering, however, resulting in cracking, which is difficult to be dealt with [23,24]. Therefore, it is our anticipation that the EPD of nanoparticles in molten inorganic salts should become an important method for fabrication of boride coatings and films.

IV. Conclusions

In this paper, an experimental study on the preparation of TiB_2 coatings by EPD on graphite substrates in NaF-AlF_3 molten salts (with molar ratio 61:39) containing TiB_2 nanoparticles at 980 °C, under an applied cell voltage of 1.2 V (i.e. electric field 0.6 V/cm), was carried out, and the following conclusions were obtained:

(1) Analysis of the solid fluoride salts, prepared by sampling the upper part of the NaF-AlF_3 molten salts containing TiB_2 nanoparticles 5 h after their mixing and then cooling it rapidly, shows that there exist TiB_2 nanoparticles with a particle size of about 50 nm in the sampled solid fluoride salts. This indicates that the introduced TiB_2 nanoparticles could probably be stably suspended in the NaF-AlF_3 molten salts for at least 5 h.

(2) A flat and dense TiB_2 coating of about 50 µm thickness has been produced on graphite cathode substrates after EPD in NaF-AlF_3 molten salts containing TiB_2 nanoparticles, and the surface of the TiB_2 coating consists of TiB_2 flakes of less than 100 nm in size. Moreover, the average value of hardness of the TiB_2 coating measured by micro-hardness tests was 3585 ± 139 $HV_{0.1}$ (36.6 ± 1.4 GPa).

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