



# Production of $\text{TiB}_2$ coatings on graphite substrates by electrophoretic deposition in $\text{NaF-AlF}_3$ melt

Jun Zhang<sup>1,2</sup>, Jie Pang<sup>1</sup>, Weiliang Jin<sup>1</sup>, Shaojun Chu<sup>2</sup>, Geir Martin Haarberg<sup>3</sup>, Saijun Xiao<sup>1,\*</sup>

<sup>1</sup>School of Metallurgy Engineering, Anhui University of Technology, Ma Xiang Road, Yushan District, Maanshan 243032, China

<sup>2</sup>School of Metallurgical and Ecological Engineering, University of Science and Technology Beijing, Xueyuan Road, Haidian District, Beijing 100083, China

<sup>3</sup>Department of Materials Science and Engineering, Norwegian University of Science and Technology, Trondheim 7491, Norway

Received 22 May 2022; Received in revised form 14 August 2022; Accepted 20 November 2022

## Abstract

In this paper a novel method for fabrication of  $\text{TiB}_2$  coatings on graphite substrates by electrophoretic deposition of  $\text{TiB}_2$  nanoparticles in  $\text{NaF-AlF}_3$  melt at  $980^\circ\text{C}$  has been explored. With an applied cell voltage of 1.2 V (i.e. electric field 0.6 V/cm), a flat and dense  $\text{TiB}_2$  coating with a thickness of around  $50\ \mu\text{m}$  has been prepared. It was found that the surface consisted of  $\text{TiB}_2$  flakes with a nanoscale size. In addition, the average value of hardness of the  $\text{TiB}_2$  coating was determined as  $3585 \pm 139\ \text{HV}_{0.1}$  ( $36.6 \pm 1.4\ \text{GPa}$ ) measured by a Vickers micro-hardness tester.

**Keywords:**  $\text{NaF-AlF}_3$  molten salts,  $\text{TiB}_2$  nanoparticles, electrophoretic deposition,  $\text{TiB}_2$  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 angle 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 avail-

ability of the EPD of  $\text{TiB}_2$  and  $\text{ZrB}_2$  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.

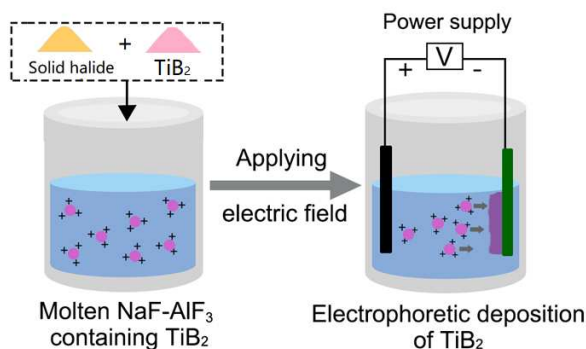
It is known that  $\text{TiB}_2$  coated graphite materials have significant applications such as wettable cathodes for aluminium electrolysis [20,21] and high-temperature oxidation resistance materials [22]. In this paper the feasibility of preparation of  $\text{TiB}_2$  coatings on graphite substrates by EPD of  $\text{TiB}_2$  nanoparticles in  $\text{NaF-AlF}_3$  melt was investigated.

## II. Experimental

### 2.1. EPD process in $\text{NaF-AlF}_3$ molten salts

The schematic drawing of EPD process used for deposition of  $\text{TiB}_2$  nanoparticles suspended in molten  $\text{NaF-AlF}_3$  on graphite substrate is demonstrated in Fig. 1. The mixture of  $\text{NaF}$  and  $\text{AlF}_3$  (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  $980^\circ\text{C}$ . Actually, the eutectic

\*Corresponding author: tel: +86 18255576998  
e-mail: [xiaosaijunzj@yahoo.com](mailto:xiaosaijunzj@yahoo.com)



**Figure 1. Schematic of EPD of  $\text{TiB}_2$  nanoparticles in  $\text{NaF-AlF}_3$  molten salts**

point of  $\text{NaF-AlF}_3$  (with molar ratio 61:39) is  $835^\circ\text{C}$ , thus  $980^\circ\text{C}$  was selected to obtain a better viscosity of the melt. After the mixed fluorides were melted, the mixture of the  $\text{NaF-AlF}_3$  and  $\text{TiB}_2$  nanoparticles was prepared according to the procedure which could be referred to our previous work [19]. The  $\text{TiB}_2$  nanoparticles were added into the molten salts and the concentration was 70 g/l.

Subsequently, a graphite cathode ( $5 \times 1 \times 25$  mm), with an immersion depth of 10–15 mm, and a graphite anode ( $\varnothing 6$  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 ( $\text{NaF-AlF}_3$ ) should be selected and there is generally a small amount of dissolved oxygen ions in the fluorides. The theoretical decomposition voltage of  $\text{Al}_2\text{O}_3$  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  $\text{NaCl-KCl}$  molten salts at  $710^\circ\text{C}$  for 5 min to remove the solid fluoride salt remaining on the surface of  $\text{TiB}_2$  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  $\text{TiB}_2$  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:  $10^\circ/\text{min}$ ) with  $\text{Cu K}_\alpha$  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  $\text{TiB}_2$  coating were carried out.

## III. Results and discussion

### 3.1. Characterization of $\text{TiB}_2$ containing melt

In order to figure out the suspension state of added  $\text{TiB}_2$  nanoparticles in  $\text{NaF-AlF}_3$  melt at  $980^\circ\text{C}$ , the nanoparticles-containing electrolyte was analysed. We sampled the upper part of the molten fluoride suspension with the  $\text{TiB}_2$  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  $\text{NaF-AlF}_3$ , 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  $\text{TiB}_2$  nanoparticles in the cooled solid fluoride salts indicates that  $\text{TiB}_2$  nanoparticles could be stable in  $\text{NaF-AlF}_3$  molten salts for at least 5 h, which ensures the possibility of subsequent EPD of  $\text{TiB}_2$  nanoparticles in  $\text{NaF-AlF}_3$  molten salts. In addition, the enrichment of Ti element in the sampled solid salts may be caused by the segregation of  $\text{TiB}_2$  nanoparticles during the cooling process.

### 3.2. EPD of $\text{TiB}_2$ on graphite substrate in melt

EPD of the  $\text{TiB}_2$  nanoparticles on a graphite substrate in the  $\text{NaF-AlF}_3$  melt at  $980^\circ\text{C}$  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  $\text{TiB}_2$  can be observed (Fig. 3b), which indicates that the deposited layer was pure  $\text{TiB}_2$ .

The surface morphology of the  $\text{TiB}_2$  coating was analysed by SEM, as demonstrated in Fig. 4. From Figs. 4a,b, it can be observed that the surface of the  $\text{TiB}_2$  coating was relatively flat, which consisted of particles with an average size below 400 nm. The higher magnification of this  $\text{TiB}_2$  coating surface, as shown in Fig. 4c, reveals that these hundreds of nanometre scale  $\text{TiB}_2$  particles were composed of  $\text{TiB}_2$  flakes with an average size less than 100 nm.

The micromorphology of the fractured cross-section of  $\text{TiB}_2$  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  $\mu\text{m}$ . 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.



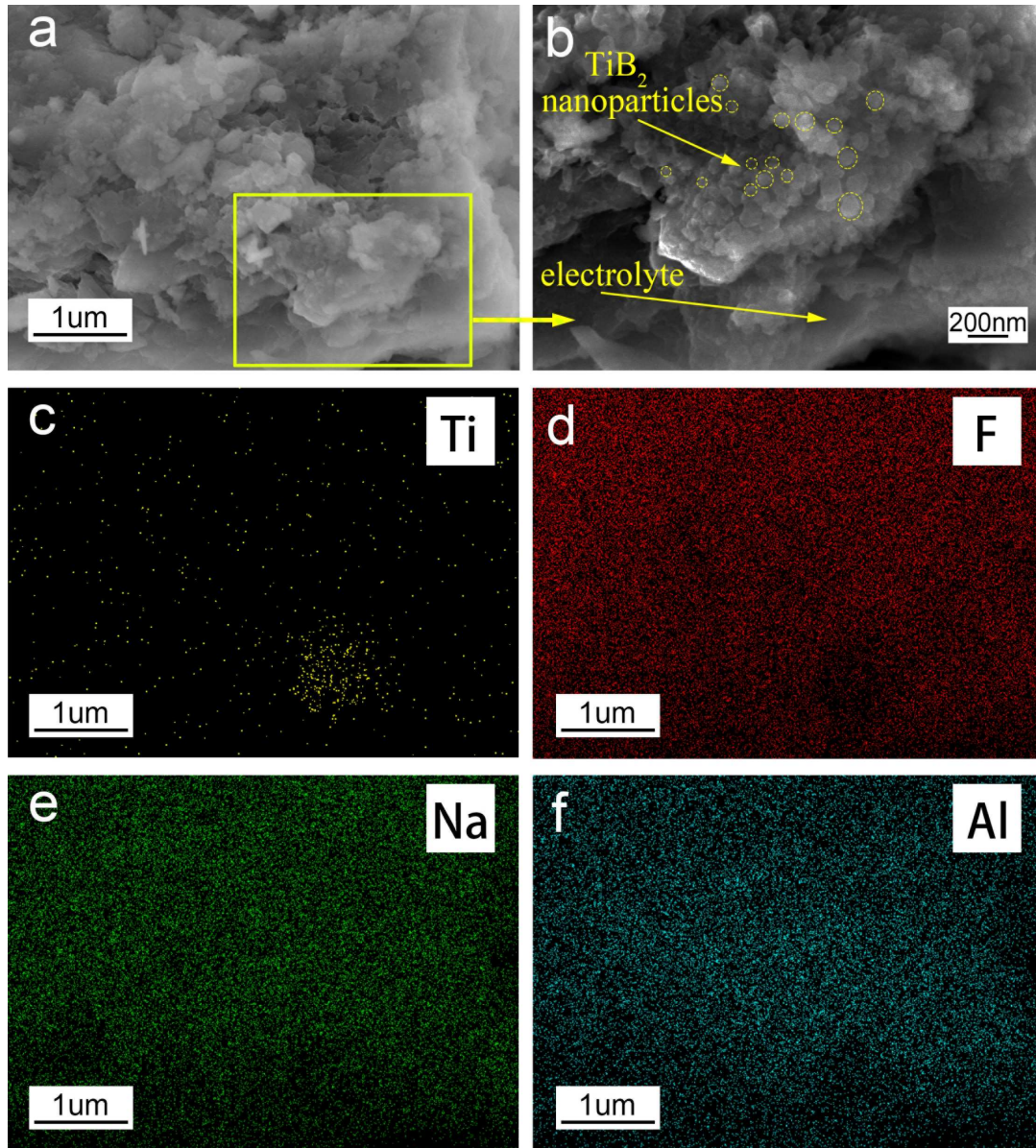


Figure 2. SEM images (a,b) and EDS mapping analysis (corresponding to Fig. 2a) of quenched sample of  $\text{TiB}_2$  nanoparticle-containing melt taken from the upper part of molten  $\text{NaF-AlF}_3$  system with  $\text{TiB}_2$  nanoparticles 5 h after their mixing

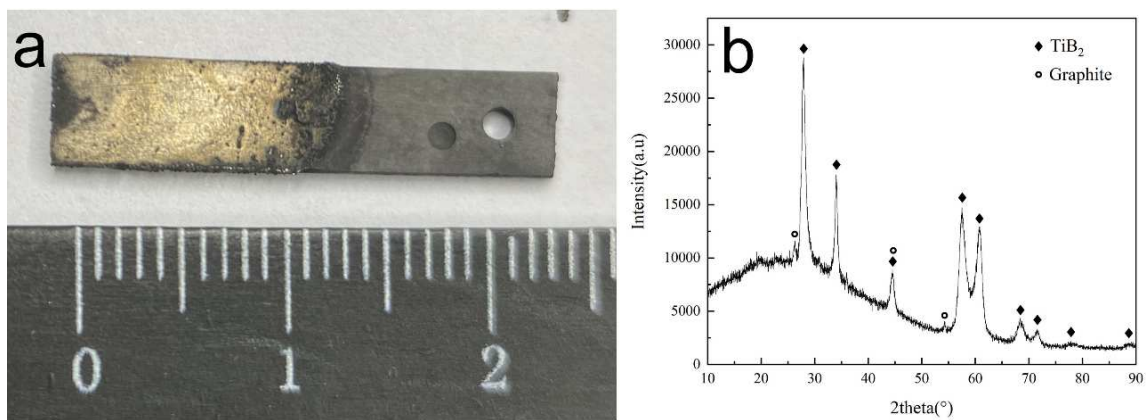


Figure 3. Photograph and XRD result of EPDed  $\text{TiB}_2$  coating on a graphite substrate in  $\text{NaF-AlF}_3$  melt at  $980^\circ\text{C}$



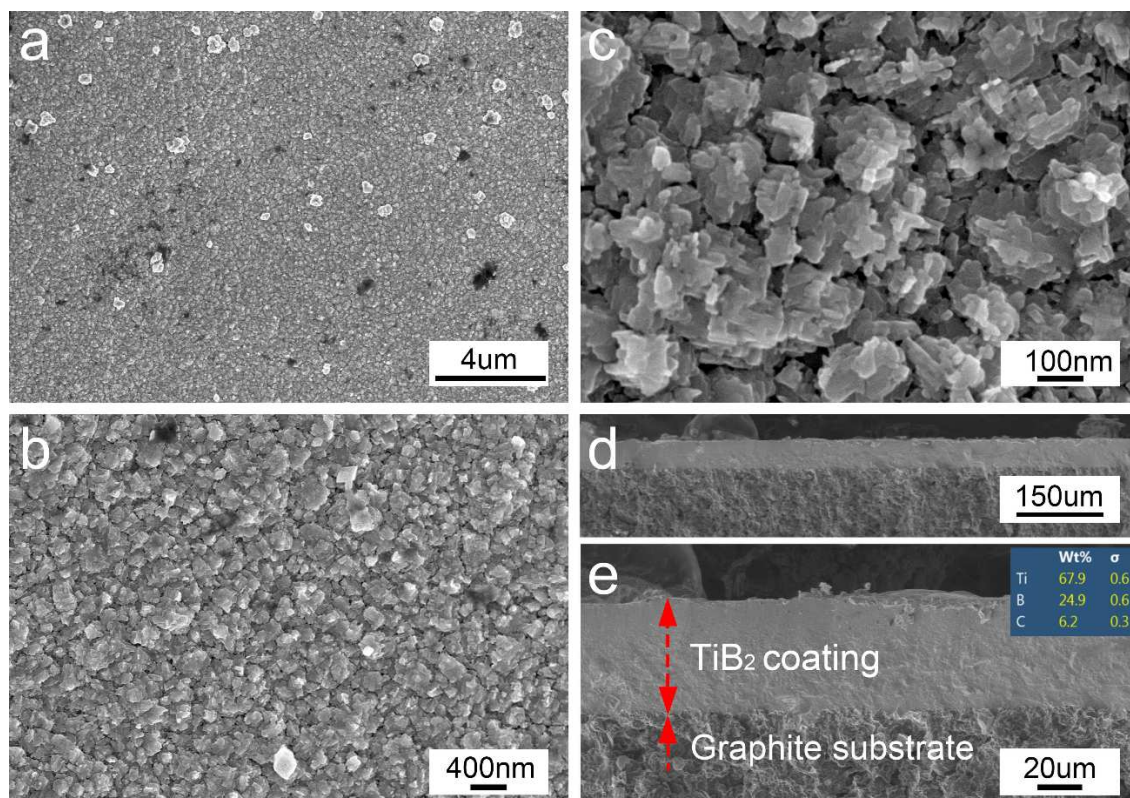


Figure 4. SEM images of the surface (a-c) and fractured cross-section (d,e) of  $\text{TiB}_2$  coating prepared by EPD in  $\text{NaF-AlF}_3$  melt at  $980^\circ\text{C}$

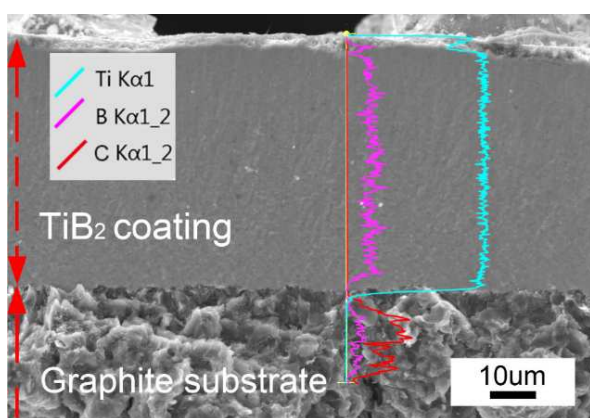


Figure 5. EDS line scan results of the cross-section of  $\text{TiB}_2$  coating prepared by EPD in  $\text{NaF-AlF}_3$  molten salts at  $980^\circ\text{C}$

Moreover, EDS line scan of the  $\text{TiB}_2$  cross-section was performed with the results shown in Fig. 5. It can be found that there is a tight bond between the  $\text{TiB}_2$  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  $\text{TiB}_2$  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  $3585 \pm 139 \text{HV}_{0.1}$  ( $36.6 \pm 1.4 \text{GPa}$ ), which is higher than the reported values of 25–35 GPa for  $\text{TiB}_2$  [22]. This verifies the high density of the  $\text{TiB}_2$  coating produced by EPD in  $\text{NaF-AlF}_3$  melt.

The above results show that EPD of the  $\text{TiB}_2$  nanoparticles in the  $\text{NaF-AlF}_3$  molten salts containing  $\text{TiB}_2$  nanoparticles was successfully carried out, and dense and flat  $\text{TiB}_2$  coatings were obtained on graphite substrates. These initial findings could provide a new approach for manufacturing of  $\text{TiB}_2$  coated cathodes for aluminium electrolysis and also fabrication of  $\text{TiB}_2$  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  $\text{TiB}_2$  coatings by EPD on graphite substrates in  $\text{NaF-AlF}_3$  molten salts (with molar ratio 61:39) containing  $\text{TiB}_2$  nanoparticles at  $980^\circ\text{C}$ , 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<sub>3</sub> molten salts containing TiB<sub>2</sub> nanoparticles 5 h after their mixing and then cooling it rapidly, shows that there exist TiB<sub>2</sub> nanoparticles with a particle size of about 50 nm in the sampled solid fluoride salts. This indicates that the introduced TiB<sub>2</sub> nanoparticles could probably be stably suspended in the NaF-AlF<sub>3</sub> molten salts for at least 5 h.

(2) A flat and dense TiB<sub>2</sub> coating of about 50 μm thickness has been produced on graphite cathode substrates after EPD in NaF-AlF<sub>3</sub> molten salts containing TiB<sub>2</sub> nanoparticles, and the surface of the TiB<sub>2</sub> coating consists of TiB<sub>2</sub> flakes of less than 100 nm in size. Moreover, the average value of hardness of the TiB<sub>2</sub> coating measured by micro-hardness tests was 3585 ± 139 HV<sub>0.1</sub> (36.6 ± 1.4 GPa).

## References

- I. Corni, M.P. Ryan, A.R. Boccaccini, "Electrophoretic deposition: From traditional ceramics to nanotechnology", *J. Eur. Ceram. Soc.*, **28** [7] (2008) 1353–1367.
- L. Besra, M. Liu, "A review on fundamentals and applications of electrophoretic deposition (EPD)", *Prog. Mater. Sci.*, **52** [1] (2007) 1–61.
- S. Bonnas, H.J. Ritzhaupt-Kleissl, J. Haußelt, "Electrophoretic deposition for fabrication of ceramic microparts", *J. Eur. Ceram. Soc.*, **30** [5] (2010) 1159–1162.
- M. Aliofkhaezrai, A. Makhlof, *Handbook of Nanoelectrochemistry*, Springer, Berlin, Germany, 2016.
- B. Vigneashwari, S. Satyanarayana, "Self-assembly of CdSe nanorod arrays by electrophoretic deposition of CdSe nanoparticles", *Int. J. Nanosci.*, **10** [6] (2011) 1215–1223.
- L. Mostafapour, S. Baghshahi, M. Rajabi, S. Mahdi Siahpoosh, F. Esfehiani, "Kinetic evaluation of YSZ/Al<sub>2</sub>O<sub>3</sub> nanocomposite coatings fabricated by electrophoretic deposition on a nickel-based superalloy", *Process. Appl. Ceram.*, **15** [1] (2021) 1–10.
- N. Ramezannejad, H. Farnoush, "Effect of graphene oxide on micro-tribological and electrochemical properties of electrophoretically deposited HA-TiO<sub>2</sub>-GO composite coatings", *Process. Appl. Ceram.*, **16** [1] (2022) 30–41.
- Y. Liu, Y. Zu, H. Tian, J. Dai, J. Sha, "Microstructure and mechanical properties of continuous carbon fiber reinforced ZrB<sub>2</sub> based composites via combined electrophoretic deposition and sintering", *J. Eur. Ceram. Soc.*, **41** [3] (2021) 1779–1787.
- E.Y. Pikalova, E. Kalinina, "Electrophoretic deposition in the solid oxide fuel cell technology: fundamentals and recent advances", *Renew. Sust. Energ. Rev.*, **116** (2009) 109440.
- N.P. Benekohal, M.J. Sussman, H.C. Chiu, M. Uceda, R. Gauvin, G.P. Demopoulos, "Enabling green fabrication of Li-ion battery electrodes by electrophoretic deposition: Growth of thick binder free mesoporous TiO<sub>2</sub> carbon anode films", *J. Electrochem. Soc.*, **162** [11] (2015) 3013–3018.
- Z. Tong, L. Li, Y. Li, Q. Wang, X. Cheng, "The effect of in situ synthesis of MgO nanoparticles on the thermal properties of ternary nitrate", *Materials*, **14** [19] (2021) 5737.
- Z. Li, B. Li, X. Du, H. Wu, "Experimental investigation on stability of thermal performances of solar salt based nanocomposite", *Renew. Energ.*, **146** (2020) 816–827.
- S. Licht, B. Cui, B. Wang, F.-F. Li, J. Lau, S. Liu, "Ammonia synthesis by N<sub>2</sub> and steam electrolysis in molten hydroxide suspensions of nanoscale Fe<sub>2</sub>O<sub>3</sub>", *Science*, **345** [6197] (2014) 637–640.
- T. Harada, P. Brown, T.A. Hatton, "Nonvolatile colloidal dispersion of MgO nanoparticles in molten salts for continuous CO<sub>2</sub> capture at intermediate temperatures", *ACS Sustain. Chem. Eng.*, **7** [8] (2019) 7979–7986.
- H. Zhang, K. Dasbiswas, B. Ludwig, G. Han, B. Lee, S. Vaikuntanathan, D.V. Talapin, "Stable colloids in molten inorganic salts", *Nature*, **542** (2017) 328–331.
- V. Srivastava, V. Kamysbayev, L. Hong, E. Dunietz, R.F. Klie, D.V. Talapin, "Colloidal chemistry in molten salts: synthesis of luminescent In<sub>(1-x)</sub>Ga<sub>x</sub>P and In<sub>(1-x)</sub>Ga<sub>x</sub>As quantum dots", *J. Am. Chem. Soc.*, **140** [38] (2019) 12144–12151.
- N. Navarrete, A. Gimeno-Furió, J. Forner-Escrig, J.E. Juliá, R. Mondragón, "Colloidal stability of molten salt-based nanofluids: Dynamic light scattering tests at high temperature conditions", *Powder Technol.*, **352** (2019) 1–10.
- V. Kamysbayev, V. Srivastava, N. Ludwig, O.J. Borkiewicz, H. Zhang, J. Ilavsky, B. Lee, K.W. Chapman, S. Vaikuntanathan, D.V. Talapin, "Nanocrystals in molten salts and ionic liquids: experimental observation of ionic correlations extending beyond the Debye length", *ACS Nano*, **13** [5] (2019) 5760–5770.
- W. Jin, S. Xiao, Q. Kou, D. Ding, J. Zhang, X. Fang, C. Ge, C. Zhong, H. Zhu, G.M. Haarberg, "Preparation of diboride coatings by electrophoretic deposition in nanoparticle containing molten inorganic salts", *Mater. Lett.*, **306** (2022) 130908.
- E. Yvenou, B. Davis, D. Guay, L. Rou, "Electrodeposited TiB<sub>2</sub> on graphite as wettable cathode for Al production", *J. Am. Ceram. Soc.*, **104** [3] (2021) 1247–1254.
- Y. Étienne, B. Alexandre, B.E. Fadhel, D. Ali, D. Boyd, G. Daniel, M. Christian, R. Lionel, "TiB<sub>2</sub> deposited on graphite by suspension plasma spray as Al wettable cathode", *J. Therm. Spray Technol.*, **30** [6] (2021) 1535–1543.
- B.R. Golla, A. Mukhopadhyay, B. Basu, S.K. Thimmappa, "Review on ultra high temperature boride ceramics", *Prog. Mater. Sci.*, **111** (2020) 100651.
- J.H. Dickerson, A.R. Boccaccini, *Electrophoretic Deposition of Nanomaterials*, Springer, Berlin, Germany, 2011.
- E. Teimouri, E. Darabi, M. Hantehzadeh, A. Khajehzad, "The electrophoretic deposition of TiB<sub>2</sub> nanoparticles produced by pulsed laser ablation: Case study on microstructural features and micromorphology properties", *Microsc. Res. Techniq.*, **85** (2022) 2140–2151.