



Coating titanium on carbon steel by in-situ electrochemical reduction of solid TiO₂ layer

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Abstract: Ti coating on A3 steel was successfully prepared by direct electrochemical reduction of high-velocity oxy-fuel (HVOF) thermally sprayed and room-temperature dip-coating titanium dioxide coating on A3 steel in molten CaCl₂ at 850 °C. The interfacial microstructure and mutual diffusion between coating and steel substrate were investigated using scanning electron microscopy (SEM) and energy dispersive X-ray (EDX) spectroscopy. The results show that the precursory TiO₂ coating prepared by HVOF has closer contact and better adhesion with the A3 steel substrate. After electrolysis, all of the electro-generated Ti coatings show intact contact with the substrates, regardless of the original contact situation between TiO₂ layer and the steel substrate in the precursors. The inter-diffusion between the iron substrate and the reduced titanium takes place at the interface. The results demonstrate the possibility of the surface electrochemical metallurgy (SECM) is a promising surface engineering and additive manufacturing method. **Key words:** Ti coating; molten salt; surface metallurgy; electrochemical reduction; additive manufacturing

1 Introduction

Titanium and titanium alloys have many desirable properties such as light mass, high strength, biocompatibility, good conductivity and corrosion resistance. They are attractive materials in various fields such as metallurgy, navigation, aerospace, chemical industries and biomedicine. However, their widespread application has been retarded due to the costly and environmentally unfriendly production and processing [1]. Currently, Ti metal is normally extracted through the KROLL process [2]. Briefly, TiO₂ reacts with Cl₂ to generate TiCl₄ at first, and then TiCl₄ is reduced by liquid Mg to sponge Ti. And the resulting by-product, viz. MgCl₂ is separated from titanium by vacuum distillation and can be electrochemically recovered to metallic Mg and chlorine. Although enormous efforts have been devoted to improving the KROLL process over the past years [3–5], the cost of titanium and titanium alloy is still high because of the multistep process of titanium sponge production and the complicated procedure of titanium processing. Therefore, cost-affordable fabrication of Ti-based materials and components has drawn worldwide interests in recent decades. An

alternative way might be manufacturing composite materials with a titanium thin layer in which only a small quantity of Ti-based materials is needed. It was reported that a thin Ti coating on substrates (e.g., steels) can enhance the corrosion resistance against salt water, hardness and biocompatibility of the resulting composites, with the steel substrate maintaining high strength [6]. However, due to its high melting point and negative deposition potential, titanium coating can be prepared neither by hot-dipping nor by electroplating in aqueous solution. Alternatively, preparation of titanium oxide coating is much easier and commercially available via physical methods [7–9]. An idea of transforming an oxide layer into metal layer might lead to an alternative way for the preparation of the refractory and corrosion-resistant metallic coating.

In 2000, CHEN et al [10] reported a promising route for the electrochemical reduction of solid titania to titanium metal in high temperature molten chloride salts. The process has been applied to the preparation of refractory metals [11–14], ceramics [15,16], semi-metals [17,18] and alloys [19,20] from their oxides/compounds. Afterwards, SCHWANDT and FRAY [21] first reported an approach to prepare titanium coating on steel through electro-reduction of titania layer. The process involves

two key steps, namely coating the steel substrate with TiO_2 and then electro-conversion of the titania layer into titanium in molten CaCl_2 . The cost-affordable and abundant titania in solid state is used as the precursor and metallic coating is directly from the oxide ore by electrochemical method. This process can be named as surface electrochemical metallurgy (SECM), which represents a simple and cost-effective route to clad refractory metals on common metallic materials by direct electro-reduction of the corresponding metal oxide layers. The schematic diagram of SECM is shown in Fig. 1.

Although the first proof of concept of the process has been demonstrated by SCHWANDT and FRAY [21], it is far from being optimized either on the preparation of the pre-films of metal-oxides or the understanding of the inter-diffusion of the metals at the interface between the substrate and the reduced coating metals. In this work, the formation of titanium film on A3 steel substrate was studied by the direct electrochemical reduction of TiO_2 coating prepared by high velocity oxy-fuel (HVOF) spraying at high temperature and slurry-dipping at room temperature, with the focus on optimizing of the coating preparation and investigating the inter-diffusion behavior at the interface.

2 Experimental

2.1 Preparation of TiO_2 coating on A3 steel substrate through HVOF spraying technique

In the HVOF route, A3 steel cylinders ($d=2$ cm and $h=2$ cm) were used as the substrate, which were previously cleaned and grit-blasted with corundum. TiO_2 powders with particle sizes ranging from 45 to 90 μm were thermally sprayed via the high velocity oxy-fuel (HVOF) spraying technique (about 3100 $^\circ\text{C}$) using FS-4 multifunctional powder spray gun (plum-like nozzle, Germany). Ethyne was used as the fuel gas and the powder carrier gas was compressed air. The pressure of ethyne, oxygen, and compressed air was controlled at 0.1, 0.5 and 0.4 MPa, respectively. The spray distance was fixed at 120 mm.

2.2 Preparation of TiO_2 coating on A3 steel through dip-coating method

A3 steel sheets (1.0 cm \times 3.5 cm \times 0.3 cm) were used as the substrates. The surface of the substrate was

mechanically ground with 800-grit silicon carbide sand paper previously and degreased in 5% NaOH solution at 50 $^\circ\text{C}$, and then etched in 3% HCl solution for 5 min. After that, the matrixes were rinsed with distilled water and dried in vacuum oven before dipping into the titania ink. The ink was made from ball-milling of TiO_2 and some additives. TiO_2 powder (10 g), isopropanol (20 mL) and stearic acid (0.24 g) were mixed by ball milling for 10 h with a rotation speed of 250 r/min, and then, poly(vinyl butyral-co-vinyl alcohol-co-vinyl acetate) (1.0 g) and poly(ethylene glycol) (0.8 g) were added into the slurry and ball-milled for another 10 h. The resulting slurries were placed into fume cupboard at room temperature and viscous slurries were obtained by slow evaporation of isopropanol for several hours. The pre-cleaned substrates were dipped into the ink and suspended vertically in it for about 30 s, and then the sheets were pulled out slowly and dried in air. In the typical process, the above dip-coating procedure was repeated several times to ensure the formation of a thick coating. After drying at room temperature, a uniform TiO_2 film with a thickness of about 150 μm was formed on the substrate. It was shown in our preliminary experiments that the TiO_2 coating peeled off from the substrate upon annealing in air at 400 $^\circ\text{C}$. Therefore, no further annealing was employed in the present work, with the residual organic compounds being in-situ burned out in the following molten-salt electrolysis.

2.3 Electro-reduction of titania coating on A3 steel substrate

The titania coated steel substrate was wrapped with foamed Ni and used as cathode. Constant cell voltage electrolysis was performed at 850 $^\circ\text{C}$ under a cell voltage of 3.1 V between the cathode and the graphite anode, controlled and recorded by a DC power system (Shenzhen Neware Electronic Ltd., China). All experiments were performed under Ar atmosphere, and the outlet gas was absorbed by NaOH aqueous solution. After electrolysis, the cathode was pulled out from the molten salt and cooled in the upper part of the reactor before being taken out of the reactor. After each experiment, the residual solid salt on the coating was washed by de-ionized water, and then, the cathode products were dried in vacuum oven at 60 $^\circ\text{C}$ before further analysis.

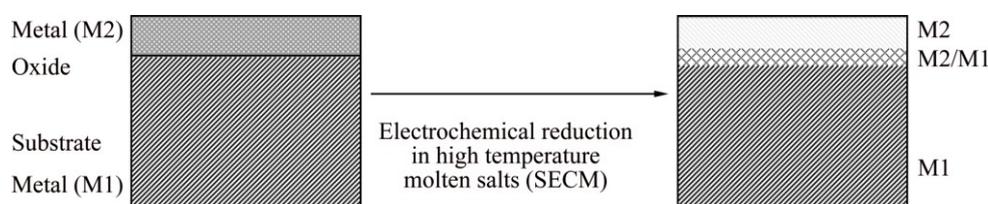


Fig. 1 Schematic diagram of surface electrochemical metallurgy (SECM) method

2.4 Materials characterization

For the analysis of the cross section of the samples, the precursors and the electrolysis products were mounted into resin and then cut and polished carefully. The surface and interface of samples were characterized by scanning electron microscopy (SEM, FEI Quanta 450 FEG) and energy-dispersive X-ray spectroscopy (EDX, EDAX GENESIS 7000).

3 Results and discussion

3.1 TiO₂-coatings on A3 steel by HVOF spraying and dip-coating

Figure 2(a) shows the interface cross-section of TiO₂-coated steel obtained by HVOF spraying. The thickness of the TiO₂ layer is about 300 μm. And the TiO₂ coating is quite uniform with some small pores, which is a typical phenomenon for thermal spraying coating. The pores are formed due to the high particle velocity and gas entrapment during the rapid solidification process and the volume variation during cooling process. As shown in the inset of Fig. 2(a), a typical layered structure of thermal-spray coating is observed [22]. Such architecture is built up by well-melted titania particles, indicating a rather dense ceramic

TiO₂ coating. Usually, a high temperature driven process, like thermal spray, tends to facilitate a good adhesion between the coating and substrate due to the melting/near melting of the coating material during deposition process that solidifies during cooling of the substrate [23]. The high kinetic energy and heat enthalpy of sprayed particles can produce sufficient deformation when the particles impact the substrate, which is beneficial to the combination of particle and substrate. Figure 2(b) shows the microstructure and EDX analysis result in the interface region of the sample. An intimate contact and interlock between sprayed TiO₂ coating and the substrate can clearly be observed, implying a good adhesion between TiO₂ coating and the steel substrate. As can be seen from the EDX line-scanning analysis (inset of Fig. 2(b)), mutual diffusion occurs at the interface, with Fe species from the A3 steel diffusing towards TiO₂ coating and Ti species from the sprayed coating transferring towards the substrate. This is because the substrate was impacted by the high-speed, hot, melted TiO₂ particles when TiO₂ coating was formed through HVOF spraying, which lead to iron and titania dissolving and diffusing mutually in the localized melt zone. As a result, the good adhesion between the coating and the substrate was generated. The interface morphology of

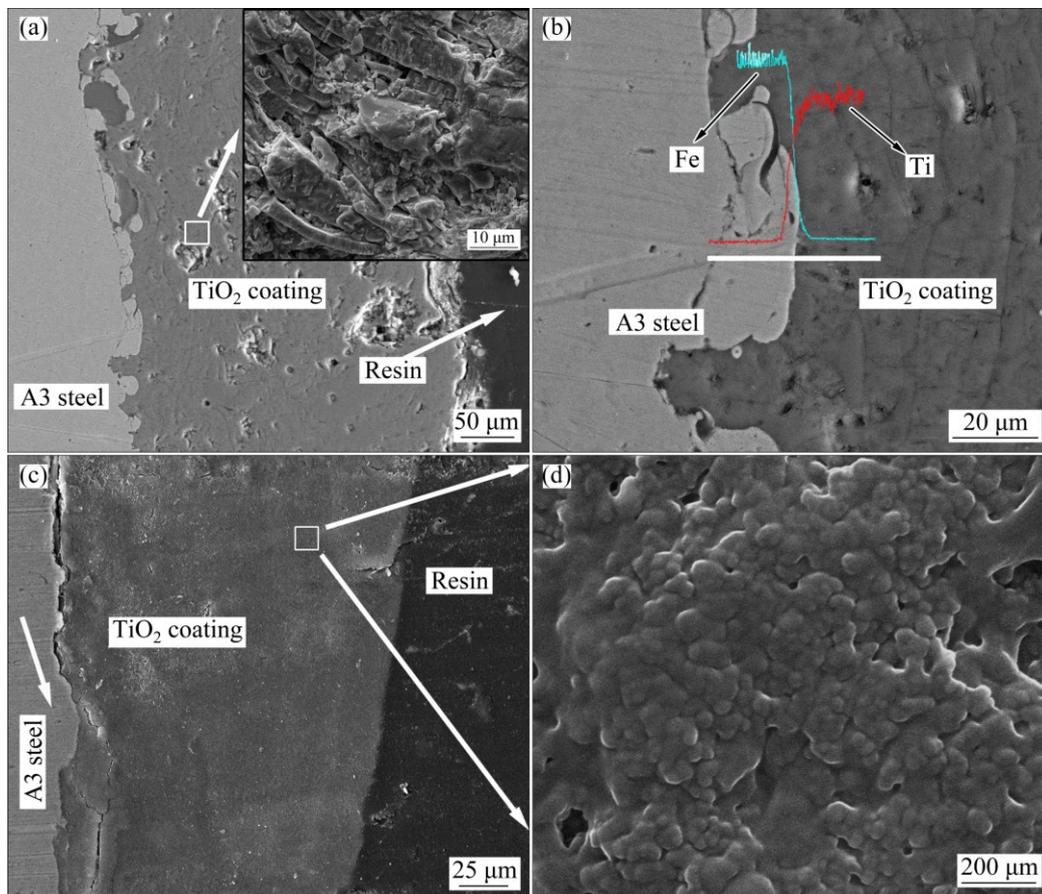


Fig. 2 SEM images of polished cross-sections of HVOF TiO₂ (a, b) and dip-coating sample (c, d) (inset of (b) exhibits elemental analysis along line near interface of titanium coating/steel sample (HVOF))

the dip-coating $\text{TiO}_2/\text{steel}$ composite is shown in Fig. 2(c). It can be seen that the thickness of the coating is about 150 μm . The coating is uniform in general, although some small crevices clearly occur between the substrate and the coating. Figure 2(d) shows the magnified SEM image of dip-coated TiO_2 (the marked area in Fig. 2(c)). It can be found that the coating consists of nano-size TiO_2 particles and some polymer binders.

Different from the HVOF coating, the dip-coating is looser and more porous and the particle size of TiO_2 is several orders smaller than that of the HVOF coating. Both of the porosity of TiO_2 pellet and the particle size of TiO_2 will greatly affect the electro-reduction kinetics of TiO_2 [24–26]. It is therefore very interesting to know whether these differences will significantly affect the formation of the titanium coating.

3.2 Molten salt electro-metallization of TiO_2 coating

The $\text{TiO}_2/\text{A3}$ steel composite cathode was electrolyzed under constant cell voltage of 3.1 V in molten CaCl_2 at 850 °C. Typical current–time curves recorded during the electrolysis are presented in Fig. 3. The $I-t$ curves of both coating cathode exhibit very similar features with an initial increasing and then decreasing profile, which can be explained based on the three-phase-interline (3PI) model [27]. Since most of metal oxides are poor electronic conductors, the electro-reduction of solid oxides takes place initiatively at the current collector/solid oxide/electrolyte (molten salt) three-phase interlines. The 3PIs expand with the generation of fresh metals by the reduction of oxides, which leads to the increase of the electrolysis current at the initial stage. Generally, the expanding speed of 3PIs in the depth direction is much slower than that in the surface direction due to the diffusion barrier. Along with the consuming of oxides and slowing-down of the 3PIs expanding rate in the depth direction, the electrolysis current decreases and gradually reaches the background value after the complete metallization of the oxides. The process can be schematically shown in Fig. 4. Reduction of TiO_2 first occurs at the site of the conductor/ $\text{TiO}_2/$

CaCl_2 3PIs at the initial stage and quickly expands along the initial oxide/ CaCl_2 interface (Stage I in Fig. 4). Afterward, the current decreases monotonically to a background current, representing the consuming of TiO_2 and the penetration electro-reduction in the depth direction (Stage II). The reaction rate is controlled mainly by diffusion of oxygen ions in the coating. It is acknowledged that the dense TiO_2 coating tends to retard the diffusion of oxygen ions and reduction kinetics therefore increases the energy consumption of the process. Generally, it takes 10–20 h to reduce a TiO_2 pellet with a thickness of about 2 mm. In this work, due to the fact that the thickness of the TiO_2 coating is less than 300 μm , the reduction kinetics is much faster and the energy consumption becomes less concerned. According to Fig. 3, the current decreased to the background value within 180 min for the sprayed-coated electrode and 100 min for the dip-coated electrode, respectively. The less reaction time for the dip-coated electrode is due to the less thickness and more porous features. After reaching the background current, the electrolysis was maintained for another 1–2 h in order to trigger potential solid diffusion between electro-generated Ti and steel substrate [28]. Such a process (Stage III) is believed essential to generate good contact between Ti coating and steel substrate, especially for

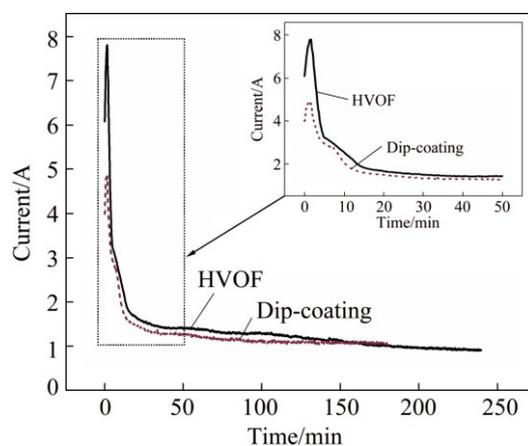


Fig. 3 Current–time curves of electro-reduction of TiO_2 -coated substrates in 850 °C molten CaCl_2 at cell voltage of 3.1 V

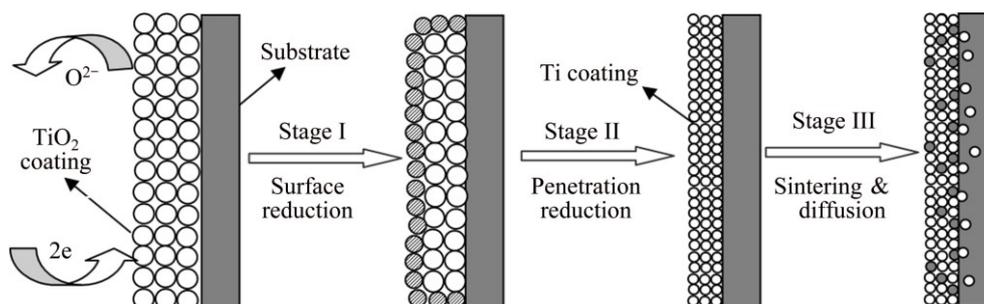


Fig. 4 Electrochemical reduction process of TiO_2 coating on steel substrate

the dip-coated TiO_2 sample which initially shows much looser contact with the substrate. As the electro-reduction of TiO_2 , the generated fresh titanium atom tends to sinter to each other to form a titanium sponge through surface diffusion and/or bulk diffusion. It is expected that the inter-diffusion of Ti and Fe will take place at the Ti/A3 steel interface so that a firm joint between two metals can form.

3.3 Characterization of electrolytic Ti/A3 composite

The typical photos of the cross section of the samples with HVOF spraying coating and dip-coating after electrolysis are shown in Figs. 5(a) and (b). The morphology and composition of the reduced coatings were characterized and analyzed by SEM and EDX, respectively, which are presented in Figs. 5(c) and (d). After electrolysis, the TiO_2 was converted into Ti in both coatings. As can be seen from the SEM images, interconnected particles were formed after electrolysis, with significant increase in the porosity of the coating. The porous structure of the coating after electrolysis is ascribed to the decrease in molar volume from TiO_2 ($20.8 \text{ cm}^3/\text{mol}$) to Ti ($10.7 \text{ cm}^3/\text{mol}$). Such morphology is in line with that of the Ti sponge prepared from molten-salt electrolysis of solid TiO_2 [21]. To increase its

density and anti-corrosion property, post-treatment such as cold rolling might be needed. On the other hand, the micro/nano porous structure is beneficial to its application as medicine implant materials [29].

Furthermore, it can be found from the SEM images that both of the electro-generated Ti coatings have good contact with the A3 substrates. Although there were some cracks between the TiO_2 layer and the substrate in the precursor of the dip-coating (Fig. 2(c)), the cracks did not appear between the electrolytic Ti coating and substrate any more. The good connection between the Ti coating and the A3 substrate should be due to the inter-diffusion of Fe and the fresh-reduced Ti atom at the interface. Therefore, EDX line analysis was conducted along the cross-section of the interface. The obtained results are also presented in Figs. 5(a) and (b). It was indicated that mutual diffusion behavior did happen between titanium and the steel substrate. The distribution curve of titanium and iron concentration across the interface in both cases clearly shows that the penetration distance of iron on the Ti side is larger than that of Ti on A3 steel side. These results agree well with the earlier report [30]. The freshly reduced titanium atoms tend to sinter together through surface diffusion and lead to a lot of vacancies in the coating matrix, which may promote

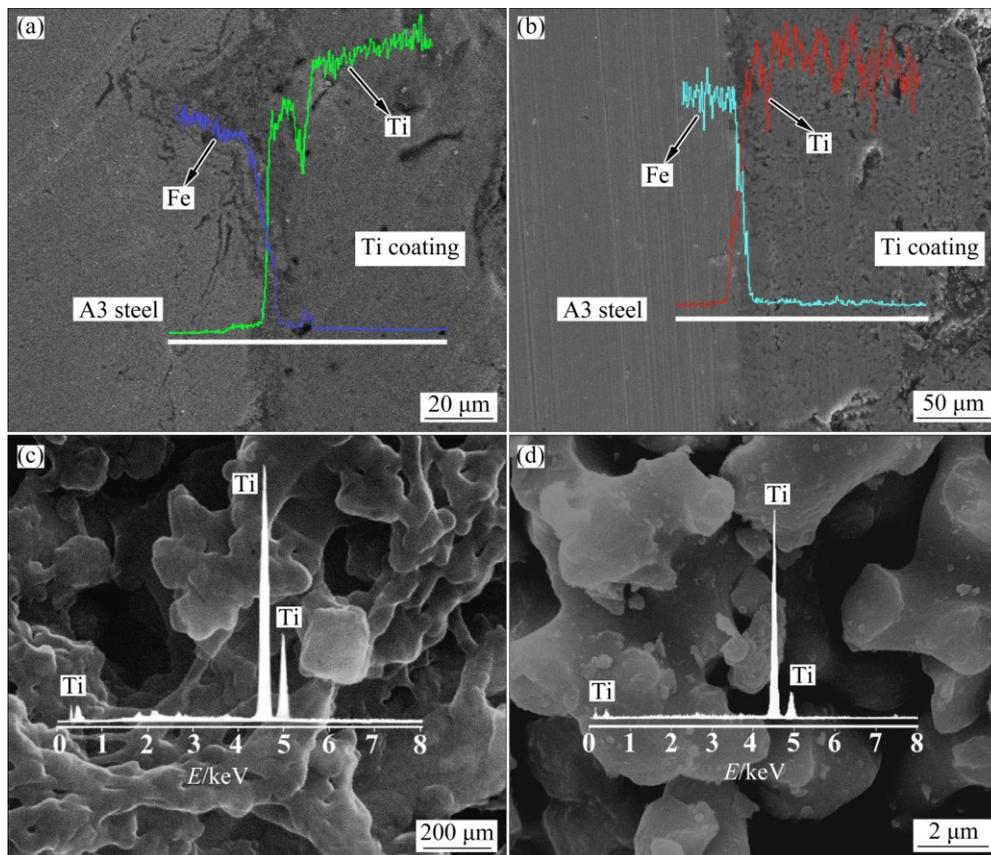


Fig. 5 SEM images of polished cross-section of titanium/steel sample with HVOF route (a) and dip-coating route (b) and line scanning analysis near interface of samples gained by electro-reduction of titania/steel; microstructures and EDX results of titanium coating obtained through electro-reduction of titania/steel samples with HVOF route (c) and dip-coating route (d)

the diffusion of iron in the titanium coating, leading to a larger diffusion distance of Fe on the Ti side. On the other hand, steel has a close packed face centered cubic structure, and it is not beneficial to atom diffusion of titanium. The atomic radius of iron (0.127 nm) is smaller than that of titanium (0.147 nm). Consequently, larger titanium atoms are more difficult to diffuse into steel. Nevertheless, the Fe and Ti atoms have intimated molecular level intermix at the interface, which is also beneficial to the adhesion strength of the coating and the matrix.

4 Conclusions

1) TiO₂ coating on A3 steel substrate, prepared either through high velocity oxy-fuel (HVOF) spraying or dip-coating was successfully converted into titanium coating on the steel by electro-reduction in molten CaCl₂. The precursory TiO₂ coating prepared by HVOF-derived method has closer contact and better adhesion with the A3 steel substrate and has a larger particle size than that prepared by dip-coating. However, two kinds of TiO₂ can be transformed into uniform Ti coating on the substrates under the selected electrolysis condition in molten CaCl₂.

2) The obtained Ti coatings show a good connection with the steel substrate due to the sintering of the reduced Ti atoms and mutual diffusion between the titanium and the substrate at the high temperature, which eliminates the initial difference between the HVOF coating and the dipping coating. However, compared with the HVOF spraying route, dip-coating method has merits on low temperature, facile operation and low cost.

3) The present work confirmed surface electrochemical metallurgy (SECM) a potential simple surface engineering method for preparing refractory material coating or for additive manufacturing.

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在碳钢上直接电还原固态二氧化钛制备金属钛涂层

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摘要: 采用超音速火焰喷涂(HVOF)技术和室温提拉法在碳钢上制备致密和多孔两种 TiO_2 涂层, 然后在 CaCl_2 熔盐中直接电化学还原 TiO_2 得到金属钛涂层, 利用 SEM、EDX 等技术对涂层与基体界面的显微组织和金属互扩散行为进行研究。结果表明, 与提拉法相比, 虽然超音速火焰喷涂(HVOF)法制备的 TiO_2 涂层与碳钢基体有更强的附着力和更致密的结构, 但二者熔盐电解还原后所得钛涂层与碳钢基体都有较好的结合, 在界面处发生了铁、钛互扩散, 表明表面电化学冶金(SECM)可能是一种颇具发展潜力的表面工程/增材制造方法。

关键词: Ti 涂层; 熔盐; 表面冶金; 电化学还原; 增材制造

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