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Ceramics Coated Metallic Materials: Methods, Properties and Applications

Dongmian Zang and Xiaowei Xun

Abstract

Surface coating can allow the bulk materials to remain unchanged, while the surface functionality is engineered to afford a more wanted characteristic. Ceramic coatings are considered as ideal coatings on metal which can significantly improve the surface properties of metal materials including anti-fouling, self-cleaning, corrosion resistance, wear resistance, oil/water separation and biocompatibility. Furthermore, various techniques have been utilized to fabricate a range of different ceramic coatings with more desirable properties on metal materials, which make the materials widely used in service environment. This chapter focus will be on the types, fabrication methods, surface properties and applications of ceramics coated metal materials.

Keywords: ceramic coating, metallic materials, surface physicochemistry

1. Introduction

Metallic materials such as Fe, Cu, Ti, Al, Mg and their alloys have excellent mechanical and physical properties showing tremendous application in architecture, marine, aerospace and biomedicine fields, etc. [1–6]. To a certain extents, the surface properties of the metallic materials are playing irreplaceable roles in operating environments. Surface functionalization can improve corrosion resistance, anti-fouling, self-cleaning, wear resistance, oil/water separation and biocompatibility of metallic materials [7–9]. In this context, surface coating is an efficient and resource saving method to realize the surface functionalization of metallic materials. In addition, ceramic coating is environmentally friendly, and has the advantages of low cost, simple preparation, corrosion and wear resistance, thermal stability, and mechanical durability [10]. As such, constructing a ceramic coating on metallic material surface is a rational strategy to realize the surface multi-function [11, 12].

In this chapter, we briefly introduce the types and the properties of ceramic coatings. Then, we summarize the strategies for preparing ceramic coatings on metallic materials and applications of ceramics coated metallic materials.

2. Ceramics coated metallic materials

Ceramics materials can be divided into oxide ceramics and non-oxide ceramics according to their compositions. Many oxide ceramics are metal oxides forming oxide films on their surfaces, which are used as coating materials for the protection

and functional layer of metallic materials (for example, aluminum, stainless steel or titanium alloys). Also, diverse non-oxide ceramic materials are used to functionalize the surfaces of metal materials.

2.1 Ceramic coatings types

Ti and its alloy have excellent corrosion resistant to alkali, chloride and some strong acids because of the compact oxide film (Titania, TiO_2) formed spontaneously on surfaces. Therefore, TiO_2 coating is considered to be an ideal corrosion resistant layer to protect the metal substrate from corrosion. Shen *et al.* fabricated a uniform TiO_2 nanoparticle coating on 316 L stainless steel by using sol-gel technology, the electrochemical results showed that the TiO_2 coating on 316 L stainless steel effectively prevent the substrate from corrosion in chloride containing solution at the room temperature [13]. Furthermore, studies exhibited that the TiO_2 coating with nanostructure had excellent photoactive antibacterial property and hemocompatibility [14, 15].

Alumina (Al_2O_3) exhibits exceptional mechanical property and thermostability possessing a broad range of applications in optics, electronic, and biomedical fields. In addition, the corrosion resistance of Al and its alloys is attributed to inherent Al_2O_3 coating, which can effectively improve the corrosion resistance of metallic substrate. Gao *et al.* prepared the Al_2O_3 ceramic coating on AZ31PH Mg alloy by laser remelting plasma-sprayed coating, it was found that the Al_2O_3 ceramic coating exhibited high hardness as well as wear and corrosion resistance properties [16].

Similarly, silica (SiO_2) is also highly desirable coating materials on metallic materials as wear and corrosion resistant coating. The corrosion-resistant SiO_2 ceramic coating on alloys was prepared by metal organic chemical vapor deposition (MOCVD) [17]. In addition, Sadreddini *et al.* revealed that the corrosion rate and porosity of coating decreased with increasing the quantity of the SiO_2 nanoparticles in the bath [18, 19].

As the most stable oxide of manganese, manganese dioxide (MnO_2) has abundant reserves in the earth, and has the advantages of low cost, environmental friendliness and simple preparation, which is widely used in energy, catalysis and sewage treatment. MnO_2 coating with different crystal structure and surface morphology can be prepared by different methods meeting wanted requirements [20, 21]. Inspired by lotus flower, we used an in situ immersion method to fabricate MnO_2 coating on AZ31B Mg alloy, and post-modification with stearic acid to obtain the superhydrophobic MnO_2 coating. The prepared superhydrophobic Mg alloy surface showed excellent self-cleaning property both in air and under oil (shown in **Figure 1**), as well as mechanical durability and chemical stability [22].

As to non-oxide ceramics, Hydroxyapatite (HA) is the main inorganic component of human and animal bones. It is a kind of bioactive ceramic material, which is widely used in bone tissue engineering. The HA ceramic coating was widely used in surface functionalization of metallic biomaterials. Hiromoto *et al.* prepared the HA coatings on AZ31 magnesium alloy, results showed that the HA coatings can remarkably reduce the Mg ion-release and corrosion current density [23]. In addition, it was reported that HA coating on 316 L stainless steel improved the corrosion behavior and biocompatibility of metallic implant and bone Osseointegration simultaneously [24]. Also, Surmeneva *et al.* prepared the HA coatings with different Ti contents on a Ti-6Al-4 V alloy, which was considered to be a possible candidate for biomedical applications [25].

Additionally, non-oxide ceramics materials such as silicon carbide (SiC), monolithic silicon nitride (Si_3N_4), and aluminum nitride (AlN) exhibit superior high-temperature strength and durability indicating their potential in industrial application [26, 27]. Furthermore, Liu *et al.* used non-oxide ceramics coating (bioactive silica-based glasses) on Ti alloys to promote the formation of HA layers in vivo [28].

Figure 1. Self-cleaning tests on AZ31B Mg alloy. (a, b) time-sequence images showing pristine AZ31B Mg alloy and MnO_2 coated AZ31B Mg alloy surface without self-cleaning properties, time-sequence images showing self-cleaning properties on superhydrophobic surface (c) in air and (d) in oil (isooctane). Scale bar, 1 cm. Reproduced with permission [22]. Copyright 2011, Elsevier.

In this context, oxide ceramic coatings and non-oxide ceramic coatings are playing important roles in the field of surface functionalization of metallic materials.

2.2 Properties of ceramic coating

Different metallic materials, in a sense, have different mechanical properties. Hardness and wear resistance are required to expand application prospect when metallic materials are used for industrial engineering. Numerous studies have shown that rare earth silicate barrier coatings can be potentially used for the application in high temperature aero-engines [29]. Bio-inspired by lotus leaf, Wu *et al.* synthesized the wear-resistant MoS_2 coated BN-TiN composite coating [30]. In addition, Xu *et al.* indicated that electrochemical co-deposition of nano- SiO_2 and nano- CeO_2 particles with Ni-W-P composite coatings on 15[#] steel significantly improved the microhardness and abrasion resistance properties of the substrate [31]. Not only that, nano-structured Ni- Al_2O_3 composite coatings on Al plate exhibited the ultrahigh hardness (657 ± 28 Hv) and wear resistance [32]. Impressively, the $\text{TiO}_2/\text{Al}_2\text{O}_3$ composite coatings were prepared on Ti-6Al-4 V Alloy by micro arc oxidation, and the microhardness up to 11,000 MPa. The wear resistance was increased by 9.5 times than the as-received sample [33].

Metal corrosion is commonly found, hard to prevent, does harm to our environment, and costs several percent of the gross domestic production (GDP) of an

industrialized country. As such, establishing corrosion control systems for metallic materials is very important for the sake of environment and economy harmony. The ceramic coating is widely used to protect metallic materials because of its good corrosion resistance. Like other corrosion-resistant coatings, the ceramic coating provides a barrier on the surface of metallic materials effectively isolating the corrosion solution from the substrate [34]. Moreover, the ceramic coating with micro-nano hierarchical structure can be prepared to obtain a superhydrophobic surface after hydrophobic treatment. In this regard, superhydrophobic ceramic coating has favorable corrosion resistance due to its excellent water-repellent property showing great potential application in corrosion protection of metallic materials [35].

To improve the corrosion resistance of mild steel, Tiwari *et al.* fabricated the conversion coating and sol-gel Al_2O_3 coating on mild steel [36]. The electrochemical results indicated that this coating reduced the corrosion current density of the mild steel by 5 orders of magnitude and increased the corrosion potential up to more than $1.0 V_{\text{SCE}}$. Furthermore, Wang *et al.* used silane coupling agent bonding to the hydrotalcite/hydromagnesite conversion coating on Mg alloy, then the superhydrophobic ceramic coating was obtained, as such, the superhydrophobic ceramic coating had excellent corrosion resistance owing to its anti-water property [37]. In this context, superhydrophobic ceramic coating with hierarchical structure can trapped more air when immersed in the corrosive liquid greatly reducing the corrosive media attacked to the substrate, which provide a new idea for the application of ceramic coating in metallic materials protection.

Owing to their good thermal barrier properties, ceramic coatings are widely used to provide thermal barrier for heat transfer on the surface of metallic material and to improve the thermal stability of the substrate. Ghosh *et al.* evaluated the thermal properties of a thermal barrier coating (TBC) system on nimonic alloy (BaO-MgO-SiO_2 based glass-ceramic bond coating, 8% (mass fraction) yttria stabilized zirconia (8YSZ) top coating), the results showed that thermal barrier ceramic coating has extremely low thermal diffusivity and thermal conductivity than the bare substrate [38].

Ceramic materials can be divided into bioinert materials and bioactive materials according to their biological properties. Bioinert materials do not induce any visible tissue reactions; the majority of ceramics belong to this group. Al_2O_3 and ZrO_2 as bioinert materials have inherently low levels of reactivity, which have great potential for medical application owing to nontoxic, non-allergenic, and non-carcinogenic [39].

Some ceramics regarded as bioactive materials favor organ/tissue repairs and the integration of associated devices, which are essentially used in orthopedics, like favor bone repair and the integration of implants in bone tissues. As the most representative bioactive ceramic material, HA is widely used in bone tissue engineering for it is the main component of bones and teeth of human and animal. To improve the biodegradation performance of AZ91D Mg alloy, Song *et al.* prepared the bioactive HA coating electrodeposited on the Mg alloy, which can obviously reduce the biodegradation rate of AZ91D Mg alloy in stimulated body fluid (SBF) [40]. More importantly, HA-coated implants have been used in clinical research [41].

2.3 Fabrication of ceramic coating on metallic materials

The preparation and application of ceramic coatings have been studied for a long time. In order to adapt to different substrates, various technologies have been developed. These technologies of ceramics coated metallic materials enable to expand the application range in many fields.

Sol-gel method can easily prepare the ceramic coatings on metallic materials. Villatte *et al.* prepared TiO_2 antibacterial coating on fixation pins by using sol-gel

method. This fabrication involved two steps: to create TiO_2 coating via a sol-gel process, and then to anneal at 500°C for 1 h [15]. In order to improve oxidation resistance, Małecka *et al.* used the sol-gel method to obtain a SiO_2 coating on Ti-46Al-7Nb-0.7Cr-0.1Si-0.2Ni alloy [42]. Moreover, sol-gel nanostructured Al_2O_3 coating can be fabricated on mild steel by hydrolysis and polycondensation of aluminum isopropoxide and catalyzed by HNO_3 [36].

Micro-arc oxidation (MAO) has been used as a critical method for many years to prepare much thicker and harder ceramic coatings on metallic materials. Shen *et al.* used the MAO technology to fabricate the $\text{TiO}_2/\text{Al}_2\text{O}_3$ composite coatings on Ti-6Al-4 V alloy in the Na_2SiO_3 -(NaPO_3)₆- NaAlO_2 solution. The growth process revealed that O^{2-} reacted rapidly with Al^{3+} and Ti^{4+} (from substrate) to form the Al_2O_3 and Al_2TiO_5 simultaneously, and then Al_2TiO_5 was immediately decomposed into rutile TiO_2 and $\alpha\text{-Al}_2\text{O}_3$ [33]. In addition, the porous Cu- TiO_2 coatings can be fabricated on titanium through MAO process under the constant current density of 20 A/dm^2 for 5 min, and the high stability TiO_2 coating formed during MAO process improved the corrosion resistance of titanium [43].

Atomic layer deposition (ALD) is a surface modification method through depositing inorganic species on the surface of different substrates, and the materials with arbitrary shape could be modified through vapor phase ALD. After multiple cycles of deposition, a conformal and uniform ceramic coating with good heat resistance and stiffness would be formed [44]. Huang *et al.* deposited the dense TiO_2 thin coatings on Co-Cr alloy with excellent antifungal activity by using ALD process [45]. Impressively, in order to prevent copper from water corrosion, Abdulagatov *et al.* developed an ultrathin barrier film on Cu. In this context, the barrier film was prepared by utilizing Al_2O_3 ALD and then TiO_2 ALD to protect the substrate [46].

Electrochemical method is usually used to fabricate oxide ceramics coated metallic materials. Notably, the electrochemical method is independent on the shape and the size of substrate. As such, Song *et al.* used electrodeposit technology to obtain the HA coatings on AZ91D Mg alloy [40], and Charlot *et al.* employed anodic electrophoretic deposition (EPD) to fabricate the SiO_2 submicron coatings, and found that the thickness of the film was related to the applied electric field [47]. In addition, the anodizing method is another well-established electrochemistry to form the ceramic coatings. Vengatesh *et al.* reported an anodic aluminum oxide surface by using anodizing process to prepare the superhydrophobic Al surface [48]. The prepared aluminum anodizing film not only had strong surface adhesion to the substrate, but also enabled fatty acids graft on the substrate ensuring the stability of superhydrophobic surface.

As a surface-deposited technology, plasma treatment is a simple and effective way to obtain ceramics coated metallic materials showing fine adhesion strength of coating-substrate. To improve corrosion resistance and bioactivity, the HA coating was prepared on AZ91HP Mg alloy by using plasma spraying method [49]. In addition, Sun *et al.* fabricated a TiO_2 coating on titanium substrate by using plasma electrolytic oxidation method in a sodium silicate (Na_2SiO_3) aqueous solution. In this regard, the TiO_2 coating was obtained on the titanium substrate with the best quality of density and adhesion by adjusting the duty ratio, frequency, and positive/negative pulse proportion on the microstructure and phase compositions [50].

Magnetron sputtering is also an efficient method to prepare ceramic coatings on the surface of metallic materials. Krishna *et al.* developed a novel process to improve the tribological and corrosion properties of austenitic stainless steels, a titanium coating deposited onto AISI 316 L stainless steel by magnetron sputtering, and then to partially convert the titanium coatings into titanium oxide by thermal oxidation. The resultant coating showed strong adhesion, good corrosion resistance, together with excellent surface hardness and tribological properties [51].

Solution immersion is a conventional method for fabrication of ceramic coatings on the surface of metallic materials. In this context, it is inexpensive and easy to carry out [52, 53]. In order to obtain a HA coating on Mg and its alloy, Hiromoto *et al.* immersed AZ31 Mg alloy and pure Mg in a 250 mmol/L $C_{10}H_{12}N_2O_8Na_2Ca$ aqueous solution of pH 8.9 [23]. Recently, a superhydrophobic MnO_2 coating was fabricated on AZ31B Mg alloy using two-step in situ immersion method, and post-modification with stearic acid. The superhydrophobic surface showed excellent corrosion resistant and anti-bioadhesion [54].

Laser-cladding is considered to be one of the most effective methods to fabricate a ceramic coating on metallic materials because of the powerful energy of laser to accelerate metal oxidation [55]. Boinovich *et al.* fabricated a superhydrophobic surface on Al alloys by nanosecond laser treatment [56]. After laser etching, a thick oxide film with high roughness was formed after several stages of melting and

Method	Ceramic coating	Substrate	Property	Ref.
Sol-gel	TiO ₂	Stainless steel	Antibacterial and sufficient Mechanical strength	[15]
	SiO ₂	Titanium alloy	Oxidation resistance	[42]
	Al ₂ O ₃	Mild steel	Corrosion resistance	[36]
Micro-arc oxidation	TiO ₂ /Al ₂ O ₃	Ti-6Al-4 V alloy	Wear resistance	[33]
	TiO ₂	Titanium	Corrosion resistance	[43]
Atomic layer deposition	TiO ₂	Co-Cr	Antifungal	[45]
	Al ₂ O ₃ /TiO ₂	Copper	Corrosion resistance	[46]
Electrochemical	HA	Mg alloy	Biodegradation performance	[40]
	SiO ₂	Platinum		[47]
	Al ₂ O ₃	Aluminum	Corrosion resistance	[48]
Plasma treatment	HA	Mg alloy	Corrosion resistance and bioactivity	[49]
	TiO ₂	Titanium	Corrosion resistance	[50]
Magnetron sputtering	HA	Titanium	Corrosion resistance	[25]
	TiO ₂	Stainless steel	Tribological properties and corrosion resistance	[51]
Solution immersion	HA	Mg alloy	Corrosion resistance	[23]
	MnO ₂	Mg alloy	Self-cleaning	[54]
Laser-cladding	Al ₂ O ₃	Aluminum	Corrosion resistance	[56]
	Al ₂ O ₃ /TiB ₂ /TiC	Carbon steel	Microhardness and wear resistance	[57]
Metal organic chemical vapor deposition	SiO ₂	Alloys	/	[17]
Dip-coating	Na ₂ SiO ₃ /Al ₂ O ₃	Stainless steel	High temperature oxidation inhibition and corrosion resistance	[60]

Table 1.
Summary of fabrication methods of ceramic coated metallic materials.

solidifying. Similarly, through laser cladding, Al_2O_3 - TiB_2 - TiC ceramic coatings can be fabricated on carbon steel surface providing high microhardness and good wear resistance due to the results that the cladding thin film was uniformly and densely organized on the substrate [57].

Chemical vapor deposition can produce the ceramic coatings with controlled surface topography. Hofman *et al.* deposited the SiO_2 coatings on alloys by metal organic chemical vapor deposition (MOCVD) in sulphidizing high-temperature environments. The results indicated that the presence of silanol groups in SiO_2 coatings reduced the viscosity of the coating and enhanced the stress relaxation, thereby improving the coating performance [17].

Dip-coating is a time-saving and low-cost method for preparation of ceramic coatings [58, 59]. In 2017, Yu *et al.* produced a chemically robust and corrosion resistant $\text{Na}_2\text{SiO}_3/\text{Al}_2\text{O}_3$ composite coating on the surface of the 304 stainless steel, on which Na_2SiO_3 was incorporated into the nanopore of porous alumina layer by dip-coating heat treatment [60].

The fabrication methods of ceramic coated metallic materials are summarized in Table 1.

3. The applications of ceramics coated metallic materials

Up to now, the ceramics coated metallic materials have great potential in a wide variety of applications due to its unusual properties, such as good mechanical properties, corrosion resistance, thermal stability, and biological properties. It is worth noted that hydrophobic treatment of ceramic coatings on metallic materials ensuring superhydrophobic surfaces with special surface physicochemistry has recently received much attention in many fields.

It is well known that metallic material is irreplaceable in industrial application. The ceramic coatings bestow numerous unusual properties to metallic materials. Early in 1987, Ceramic coating as thermal barrier coating was tested on turbine blades in a research engine. Today, thermal barrier ceramic coatings are used in a low risk location within the turbine section of certain gas turbine engines [11]. In addition, Qin *et al.* reported that multiphase ceramic coatings significantly improved the hardness and wear resistance properties of 5052 Al alloy, which is conducive to industrial application [61]. In 2018, an alumina-titania ceramic coating was fabricated on carbon steel for corrosion protection [62].

Recently, superhydrophobic surface has been extensively developed due to its unique property including corrosion protection, self-cleaning, oil water separation, anti-fouling, anti-icing, and drag reduction [63]. Superhydrophobic ceramic coating was obtained by hydrophobic treatment of ceramic coating with hierarchical rough structure, which greatly expanded the application range of metal materials [64, 65]. In 2020, Emarati *et al.* fabricated a superhydrophobic nano- TiO_2 /TMPSi ceramic composite coating on 316 L steel by using a one-step electrophoretic deposition method, the results indicated that the superhydrophobic ceramic nanocomposite coating had excellent corrosion resistance [66]. Also, the water shear stress and drag can be reduced on superhydrophobic ceramic coated metallic materials surfaces resulting from the air pockets present between the liquid and solid substrate. In this context, the rolling-off droplets can remove contamination particles displaying self-cleaning feature [22]. Furthermore, a superhydrophobic ceramic coating is also reported as an emerging material exhibiting their promising diverse applications for anti-fogging, anti-fouling, and oil water separation [67–69]. **Figure 2** shows the oil/water separation of 1H, 1H, 2H, 2H-perfluorodecyltriethoxysilane-modified CuO-grown copper foam (PCCF).

Figure 2. Separation apparatus with an 18:25 v:v isooctane/water mixture above PCCF. Inset, PCCF was fixed in Cu flange and then sandwiched between two glass tubes (a). Isooctane passed through PCCF whereas water was retained (b). Water is dyed blue. Scale bar, 3 cm. Reproduced with permission [69]. Copyright 2013, Royal Society of Chemistry.

In addition, ceramic coatings have numerous applications in the field of biomedical engineering, mainly because of their biological properties. The bioinert properties of ceramic coatings help them with biocompatibility, and good hardness and wear-resistance properties make them suitable for substitution of hard tissues (bones and teeth). On the contrary, bioactive ceramic coatings such as HA coating have been clinically used onto the metallic implant surfaces combining the mechanical strength of metals and their alloys with the excellent biological properties of ceramics for the enhancement of new bone osteogenesis [70, 71].

Importantly, researching work shows that superhydrophobic surfaces can dramatically reduce the contact between fouling organisms and substrate surfaces

Figure 3. The comparison of properties of unmodified ceramic coating and superhydrophobic ceramic coating on metallic materials.

exhibiting excellent anti-fouling and hemocompatibility properties [72, 73]. Hu *et al.* designed a superhydrophobic SiO₂ biodegradable coating with exceptional anti-bioadhesion through one-step co-electrospraying poly(L-lactide) (PLLA) modified with silica nanoparticles [74]. It was revealed that the superhemophobic TiO₂ surface with a robust Cassie–Baxter state displayed more hemocompatible compared to hemophobic or hemophilic TiO₂ surface [75]. The comparison of properties of unmodified ceramic coating and superhydrophobic ceramic coating on metallic materials is shown in **Figure 3**.

4. Conclusion

In this chapter, we introduce and discuss various techniques utilized to fabricate a range of different ceramic coatings on metal materials with desirable properties such as good mechanical property, corrosion resistance, thermal stability, and biological property. It is not surprising that superhydrophobic ceramic coatings on metallic materials can make the materials be attractive for applications in anti-fouling, self-cleaning, corrosion protection, wear resistance, oil/water separation and biotechnology.

Acknowledgements

This work was supported by the Natural Science Foundation of Jiangxi Province (20192BAB203008).

Conflict of interest

The authors declare no conflict of interest.

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