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Research Progress of Non-oxide and High Entropy Ceramic Coatings

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Abstract
Ceramic coatings play a key role in extending the service life of materials in aerospace and energy fields by protecting materials from high temperature, oxidation, corrosion and thermal stress. Non-oxide and high entropy ceramics are new emerging coating materials which have been researched and developed in recent years. Compared with traditional oxide ceramics, non-oxide ceramics have better high temperature stability, oxidation resistance and erosion resistance. These characteristics make non-oxide ceramics perform well in extreme environments. It is particularly noteworthy that the non-oxide high entropy ceramic is a uniform solid solution composed of at least four or five atoms. Their unique structure and outstanding properties show great potential application in the field of coating. In this paper, the researches about regulating microstructure, preparation technology and properties of nitride and its high entropy system, carbide and its high entropy system and boride and its high entropy system in coating field are summarized, and their future development and prospects are prospected.
Keywords: *Nitride; Carbide; Boride; High entropy ceramic coating*

1 Introduction

Ceramic coatings as the important technology for surface modification and functional enhancement play a significant role in the field of materials science and engineering. Traditional oxide ceramic coatings such as alumina, titania and so on have achieved widespread applications and remarkable achievements in providing surface protection and enhancing performance. However, with the increasing demand for higher performance and the emergence of new challenges, the researches on novel ceramic coatings are still a hot topic in the current coating field. [1-7]

As an emerging research direction, non-oxide ceramic coatings and their high-entropy ceramic coatings have attracted widespread attention. Non-oxide ceramic coatings, including carbides, nitrides, and borides, possess excellent high-temperature stability, mechanical properties, and corrosion resistance, [3-5] making them suitable for applications in various extreme environmental conditions. Additionally, high-entropy ceramic coatings, newly emerging materials, are composed of multiple components and offer more design flexibility and modification capabilities, demonstrating tremendous potential in material surface modification and performance enhancement. [2, 8- 9]

This review aims to discuss the research progress of non-oxide and their high-entropy ceramic coatings, focusing on the preparation, microstructural characteristics, and performance of nitride and their high-entropy ceramic systems, carbide and their high-entropy ceramic systems, as well as boride and their high-entropy ceramic system coatings. Additionally, an outlook on their future development and prospects is proposed.

2 Nitride Coating Systems

2.1 Binary nitride systems

Binary nitrides possess numerous excellent properties, such as high melting points, structural stability, high mechanical hardness, corrosion resistance, wear resistance, and oxidation resistance. These characteristics make them widely used in various fields, [10-14] such as cutting tools and hard coatings. Tielidy et al. [15] deposited titanium nitride on band saw blades using cold plasma technology. Through tribological testing, they found that titanium nitride exhibited low friction coefficients and wear

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values, thereby enhancing the service life of wood cutting tools. Ganeshkumar et al. [16] deposited silicon nitride coatings on SS304 workpieces, and discovered that knives and blades coated with silicon nitride were more wear-resistant and mechanically superior to those without the coating.

Furthermore, specific preparation processes can significantly influence the coating's properties. Takesue et al. [17] prepared coatings with high hardness using the atmosphere-controlled induction heating fine particle projection (AIH-FPP) method, improving the wear resistance of low-alloy steel. Additionally, immersion tests in sodium chloride solutions demonstrated their excellent corrosion resistance.

Moreover, some binary nitrides exhibit excellent biocompatibility, making them suitable for applications in medical implants and other fields. Liao et al. [18] successfully deposited TaN coatings with different nitrogen concentrations on glass slides and medical metal surfaces using magnetron sputtering technology. This coating significantly improved key properties such as adhesion strength, wear resistance, hardness, and biocompatibility. Kim and his team [19] successfully deposited titanium nitride coatings on vascular stents using reactive magnetron sputtering, significantly enhancing their biocompatibility.

Apart from using binary nitrides directly as coating materials, they can also be used to modify other coating materials through doping or addition to enhance their properties, such as improving crack resistance and corrosion resistance. Qian et al. [20] successfully synthesized a novel enamel coating by adjusting the content of silicon nitride. The addition of silicon nitride significantly improved the coating's crack resistance while reducing the overall corrosion rate of the materials.

2.2 Multi-element nitride systems

By adding new elements to binary nitride coatings, it is possible to significantly regulate material properties, including crystal orientation, friction performance, and oxidation resistance. The multi-element nitride ceramics provide broad possibilities and development space for the application of coating technology in areas such as friction pairs and high-temperature environments [21].

Doping new elements into some binary nitrides can alter the crystal orientation of the materials, providing an orientation advantage for the formation of twin crystals and thereby adjusting the mechanical properties of the materials. Yang et al. [22] deposited $TiB_{0.11}N_{1.16}$ coatings on the surface of high-density TBs using direct current magnetron sputtering technology. The doping of boron promoted the orientation transition of the coatings. Compared to the function of TiN as the coating, this approach resulted in higher hardness and toughness.

The doping of some metal elements can change the oxidation resistance of materials. For example, appropriate doping of Al elements can improve the oxidation resistance of materials, making them suitable for applications in metal processing and the aviation industry. Makgae et al. [23] doped Al elements into TiN coatings to prepare $Ti_{1-x}Al_xN$ coatings. When X=0.44, the coverage on the coating was the highest, making the $Ti_{0.56}Al_{0.44}N$ component become the most oxidation-resistant coating. Zhang et al. [24] added Ni to CrN coatings, and the alloying of Ni significantly reduced the surface roughness of the coatings, improved their toughness, and increased the critical fracture stress of CrN coatings. This method reduced the fatigue crack length caused by CrN coating fractures in the substrate, making an important contribution to the widespread application of nitride sand-resistant coatings in the compressor area of aero-engines. Zhang et al. [25] deposited wear-resistant and corrosion-resistant binary TiN and ternary TiZrN coatings using high-power pulsed magnetron sputtering (HiPIMS) technology. It was found that ternary TiZrN exhibited higher surface hardness, elastic modulus and excellent resistance to degradation in acidic solutions.

Moreover, multi-layer coating possesses superior properties compared to single-layer coating. Meanwhile, multi-layer structures have more complex orientations than single-layer structures, and coatings with mixed orientations exhibit better mechanical properties than those with a single orientation. Ma et al. [26] successfully prepared TiZrN coatings on Ti-6Al-4V alloy surfaces using arc plasma deposition technology, demonstrating that coatings with mixed orientations exhibit better strength and toughness than those with a single orientation. Wang et al. [10] prepared a 12 μm Cr/CrN/Cr/CrAlN corrosion-resistant multi-layer coating using arc ion plating. Under high-temperature conditions, the multi-layer coating exhibited superior high-temperature impact resistance and erosion resistance compared to single-layer coatings. At 700℃, the coating remained stable and unchanged, meeting the operating requirements of gas turbine compressor blades. Maksakova et al. [27] deposited multi-layer TiZrN/TiSiN coatings on steel substrates using cathodic arc evaporation. Compared to TiZrN and TiSiN films, the multi-layer films exhibited higher hardness of up to 38.2 ± 1.15 GPa and elastic modulus of up to 430 ± 12.9 GPa, demonstrating higher resistance to plastic deformation. Chemaa et al. [28] performed nitriding treatment on four-layer 304L stainless steel multi-layer coatings deposited using the TWAS process using duplex treatment (PIII+PVD-deposited W-Ti-N coatings). They found that the W-Ti-N coatings exhibited excellent performance in terms of hardness, friction coefficient, and wear rate, indicating the potential for applying this process to austenitic stainless steel.

In summary, in recent years, researches about multi-element nitride coating materials have developed rapidly. By regulating their structure, mechanical properties, corrosion resistance, and other characteristics, new possibilities for enhancing material performance and expanding their applications are provided.

2.3 High-entropy nitride systems

High-entropy ceramics are new multi-component ceramic materials, and their design concept is first derived from high-entropy alloys. The fatigue resistance, corrosion resistance, and mechanical properties can be enhanced through the increase of entropy in high-entropy ceramics. Compared with traditional ceramics, high-entropy ceramics achieve the high-entropy effect by mixing multiple components in equal atomic ratios to form a uniform lattice structure. Among the various high-entropy ceramic coatings, high-entropy nitride coatings exhibit higher hardness, wear resistance, chemical stability, adhesion, excellent thermal conductivity, and multifunctionality. These advantages make high-entropy nitride coatings promising for a wide range of applications in coating technology, providing enhanced and reliable protection and performance enhancement [29-37].

In 2019, Hahn et al. [38] used DC magnetron sputtering to prepare a single-phase (Al,Ta,Ti,V,Zr)N high-entropy nitride coating with nearly equimolar metal components. The coating exhibited a hardness of 30 GPa and a fracture toughness of 2.4 MPa $m^{1/2}$. In 2020, Moskovskikh et al. [39] utilized mechanically activated nanostructured metal precursors to obtain high-entropy nitride phases through exothermic combustion in nitrogen and consolidated them through spark plasma sintering. The high-entropy nitride $(Hf_{0.2}Nb_{0.2}Ta_{0.2}Ti_{0.2}Zr_{0.2})N$ coating had a hardness of up to 33 GPa and a fracture toughness of up to 5.2 MPa $m^{1/2}$, which was suitable for applications in superhard coating fields.

The increasing researches have significant improved the properties of materials through optimized preparation processes. Compared with magnetron sputtering [40-43], MAIP (Magnetron Arc Ion Plating) offers several advantages, including excellent adhesion to the substrate, outstanding diffraction deposition performance, and rapid deposition speed. Xu et al. [44] used a multi-arc ion plating (MAIP) system to deposit a high-entropy ceramic (TiCrZrVAl)N coating on the surface of an alloy. The coating had a maximum hardness of 31.08 ± 1.81 GPa and an elastic modulus of 387.66 ± 12.49 GPa, exhibiting excellent wear resistance with a minimum wear rate of 7.4×10^{-16} m^3 /(N m). The design strategy of high-entropy nitrides provides an optimized solution for nuclear fuel cladding materials. Wang et al. [45] used magnetron sputtering to prepare $TiNbZrTaN/CrFeCoNiN_x$ nitride multilayer films, which exhibited high crystallinity, structural stability, and diffusion resistance under high temperature and irradiation conditions. These findings can be explained by difference in atomic size, Gibbs free energy in mixed systems, and solute-induced chemical inhomogeneity. Moreover, the performance of materials can be improved through the crystal orientation. Lu et al. [46] prepared $(CrAlTiNbV)N_x$ coatings using magnetron sputtering, which was shown in Figure 1(a) and (b). As the substrate bias increased, the coating transformed from a loosely packed columnar crystal structure with a preferred (200) orientation to a dense nanocrystalline structure. In Figure 1(c) and (d), at the substrate biases of -96 V and -126 V, the coating exhibited the lowest average friction coefficient (around 0.06) and wear rate 8.7×10^{-9} mm^3 / (N m).

Recently, machine learning methods have been introduced into the study of high-entropy nitride coatings. Machine learning can be used to predict the properties of high-entropy materials. By collecting and organizing a large amount of experimental data or simulation results from known high-entropy materials, a machine learning model can be constructed. This model can analyze the composition, structural parameters, and correlations of materials, and infer performance characteristics associated with these features, such as the hardness, modulus, and wear resistance of high-entropy nitride coatings. Zhou et al. [47] proposed a data augmentation generative adversarial network (DAGAN)-driven machine learning (ML) design strategy to predict the hardness, modulus, and wear resistance of novel HEN compounds.

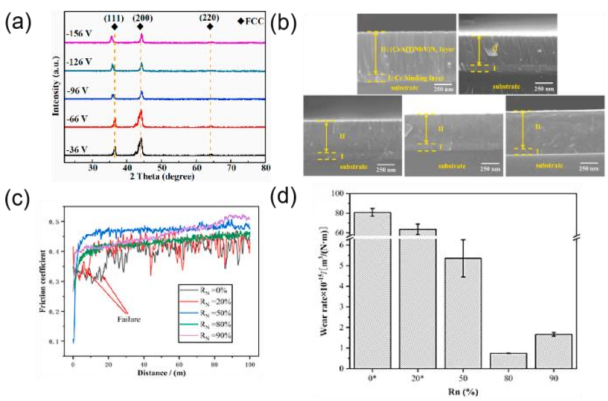

Figure 1 (a) XRD patterns of $(CrAlTiNbV)N_x$ coatings versus substrate bias, (b)SEM cross-section images of $(CrAlTiNbV)N_x$ coatings fabricated at various substrate biases, (c) friction curve of (TiCrZrVAl)N films, (d) wear rate of (TiCrZrVAl)N films [46]

3 Carbide Coating System

3.1 Binary carbide system

Binary carbides possess numerous excellent properties such as wear resistance, high hardness, and corrosion resistance, among which wear resistance stands out as a particularly noteworthy feature. Especially for wear resistance (the abrasion resistance of carbide coatings), binary carbides can be applied in various fields, such as enhancing the service life of cold and hot forging, extrusion, and powder metallurgy molds under abrasive forces.

Micallef et al. [48] employed chemical vapor deposition to deposit tungsten carbide on demanding components. Through corrosion and tribological tests, they discovered that tungsten carbide exhibited a uniform coating structure, which differed from traditional cemented coatings. The low friction coefficient and corrosion rate of tungsten carbide broaden the application prospects. One of the main potential research directions in the future is binder-free tungsten carbide coatings with sub-micron surface smoothness. Zhao et al. [49] thermally pressed niobium with cast iron at high temperatures and used interstitial carburization to precipitate NbC and Nb_2C on the substrate surface, forming a ceramic coating. Observations showed that scratches were not evident on the substrate with the niobium coating. Although the loading of the substrate led to plastic deformation, the coating only peeled off when the surface bearing capacity reached 100 N, indicating strong adhesion between the coating and the substrate (＞ 100 N). Hardness tests revealed a significant improvement in hardness after applying niobium to the substrate. Apart from chemical deposition and surface carburization, Khan et al. [50] employed an in-situ coating method to coat titanium carbide on graphene nanoplates (GNPs). This approach reduced wetting between GNPs and aluminum while enhanced dispersibility. Liu et al. [51] used plasma electrolytic oxidation (PEO) to prepare a titanium carbide coating on aluminum alloy surfaces. TiC particles enhanced the corrosion resistance of PEO coatings of aluminum alloy. Therefore, utilizing PEO technology to coat TiC on aluminum alloy tubing to improve the corrosion resistance of aluminum alloy oil well pipes is both novel and promising.

In addition to using binary carbides directly as coating materials, they can also be doped into other material coating to improve the performance. Chen et al. [52] studied the effects of adding tungsten carbide to graphite coatings on wear resistance and lubrication. They found that when adding 30% tungsten carbide, the graphite coating achieved a good balance in various performance using flame spraying technology.

3.2 Multi-component carbide system

In complex environments with stringent requirements, the performance of materials often needs to be further enhanced based on specific needs and practical situations. The multiple elements in carbide can further improve the properties, enabling their application in various fields such as industry, manufacturing, biology and so on. Therefore, the formation of multi-component carbide coatings on the surface of parts is a practical approach to meet high demands [53]. Li et al. [54] employed the powder immersion reaction method to coat graphite with chromium carbide and niobium carbide. Through studying the microstructure and mechanical properties of the coating, an optimal elemental ratio of 50% chromium carbide and 50% niobium carbide was obtained. The addition of chromium and niobium elements improved the mechanical properties of graphite. Furthermore, within a certain temperature range, the thermal expansion coefficient of the coating is basically consistent with that of the graphite substrate, facilitating good adhesion and preventing peeling.

Some carbides coatings also exhibit the biocompatibility, such as titanium carbide niobium with high corrosion resistance and wear resistance. Pana et al. [55] used cathodic arc evaporation to prepare the coatings for implants on stainless steel substrates. It was found that the titanium carbide niobium coating exhibited the smallest grain size, lowest roughness, low wear rate, highest hardness and adhesion, relatively low porosity, and good corrosion resistance. The niobium-containing titanium carbide coatings as a promising bio-coating has broad application prospects in biological field. Tungsten carbide, a compound with high hardness and thermal conductivity, is widely used as a coating for cutting tools. Based on the high-speed oxygen-fuel spraying process, Govande et al. [56] introduced cobalt into this coating and further conducted low-temperature treatment. The results showed that low-temperature treatment improved the wear resistance of the coating. The densification of the cobalt matrix further enhanced the wear resistance of the coating. Additionally, the coating exhibited better corrosion resistance after low-temperature treatment.

In summary, researches on multi-component carbide coating materials have developed rapidly in recent years. Coating materials with multi-component carbides can enhance their mechanical properties, wear resistance, and corrosion resistance. New exploration of multi-component carbides including component, processing technology, microstructure and properties is still urgent, aiming to further promote the real applications.

3.3 High-entropy carbide systems

High-entropy carbide ceramic coatings possess extremely high hardness, wear resistance, and excellent ablation resistance [34-37, 57]. These characteristics make them applied in aerospace, chemical industries, and other fields [29-30, 32, 58]. Wang et al. [59] prepared (Hf-Ta-Zr-Nb)C high-entropy carbide with excellent mechanical erosion resistance and oxidation-controlled ablation mechanisms at 2100℃ using a plasma flame gun, becoming an ideal candidate for UHTC. Chen et al. [60] prepared porous high-entropy $(Hf_{0.2}Zr_{0.2}Nb_{0.2}Ta_{0.2}Ti_{0.2})C$ ceramics using an in-situ reaction/partial sintering method. Figure 2(a) and (b) showed SEM images of porous $(Zr_{0.2}Hf_{0.2}Ti_{0.2}Nb_{0.2}Ta_{0.2})C$ before and after annealing at

1850℃. The porous structure and grain size of the samples did not change significantly after annealing, and no significant grain growth was observed due to the retarded diffusion effect, indicating good high-temperature stability of the porous high-entropy carbide ceramics. Figure 2(c) shows the XRD patterns of $(Zr_{0.2}Hf_{0.2}Ti_{0.2}Nb_{0.2}Ta_{0.2})C$ sample before and after annealing at 1850℃. The phase composition of the sample still remained to be high-entropy $(Zr_{0.2}Hf_{0.2}Ti_{0.2}Nb_{0.2}Ta_{0.2})C$ phase without phase decomposition or phase transformation, demonstrating excellent phase stability. Figure 2 (d) shows a plot of the linear shrinkage rate (dL/L0) as a function of temperature. It can be seen that no significant size changes during heating, indicating excellent dimensional stability of the porous high-entropy $(Zr_{0.2}Hf_{0.2}Ti_{0.2}Nb_{0.2}Ta_{0.2})C$ ceramics.

High-entropy carbide ceramics exhibit excellent high-temperature radiation resistance and can be used in future advanced nuclear systems. Zhu et al. [61] prepared high-entropy carbide ceramics $(WTiVNbTa)C_5$ using spark plasma sintering, and they were irradiated with 1.0 MeV c-ions at room temperature and 650℃. No amorphization or cavity formation was observed in all samples after irradiation, demonstrating that they had high radiation resistance at high temperatures. Tunes et al. [62] synthesized a novel carbide CrNbTaTiW using magnetron sputtering. The synthesized material with the carbon content of about 50 at.% exhibited the nanocrystalline with single-phase crystal structure. In-situ transmission electron microscopy was used to investigate the irradiation response of the novel high-entropy carbide (HEC) at 573 K, which exhibited better radiation tolerance than high-entropy alloys.

Moreover, the high-entropy carbide ceramic matrix composites prepared through the combination with other materials have excellent performance, realizing the widely applications in new fields. For instance, Zhang et al. [63] employed discharge plasma sintering technology to fabricate $(VNbTaMoW)C_5$-SiC high-entropy ceramics under conditions of 1900℃ and 40 MPa. With the increase in SiC content, the hardness of $(VNbTaMoW)C_5$-SiC multiphase ceramics increased, while the fracture toughness first increased and then decreased. $(VNbTaMoW)C_5$–20 wt.% SiC exhibited the best mechanical properties, with vickers hardness and fracture toughness of 18.2 GPa and 5.7 MPa·m$^{1/2}$, respectively. Cai et al. [64] prepared Cf/$(Ti_{0.2}Zr_{0.2}Hf_{0.2}Nb_{0.2}Ta_{0.2})C$-SiC high-entropy ceramic matrix composites using the precursor infiltration pyrolysis (PIP) method, which exhibited excellent ablation resistance with a linear recession rate of ～2.89 μm/s and a mass recession rate of ～2.60 mg/s. This was primarily attributed to the formation of a dense and stable oxide layer on the surface of the sample. Luo et al. [65] fabricated high-entropy (Ti,Zr,Nb,Ta,Mo)C-Co composites using liquid-phase sintering. When the initial sintering aid was 10 vol% Co, the densification temperature could be reduced to 1350℃ due to liquid-phase sintering. Compared to solid-state sintered (Ti,Zr,Nb,Ta,Mo)C ceramics prepared under conditions of 2000℃ and 35 MPa, the hardness slightly decreased from 25.06±0.32 GPa to 24.11±0.75 GPa, but the toughness increased from 2.25±0.22 MPa·m$^{1/2}$ to 4.07±0.13 MPa·m$^{1/2}$. Significantly reducing the sintering temperature can bring benefits such as energy conservation, improved production efficiency, and reduced material loss. Recently, the combination of simulation calculations and experimental preparation is a commonly used and effective research method for providing a more comprehensive understanding and explanation of material properties, reaction mechanisms, and other related issues. Ye et al. [66] analyzed the formation possibility of novel $(Zr_{0.25}Nb_{0.25}Ti_{0.25}V_{0.25})C$ high-entropy ceramics through first-principles calculations and thermodynamic analysis. They successfully prepared this high-entropy ceramic using hot-pressing sintering, which exhibited high hardness, elastic modulus, and fracture toughness.

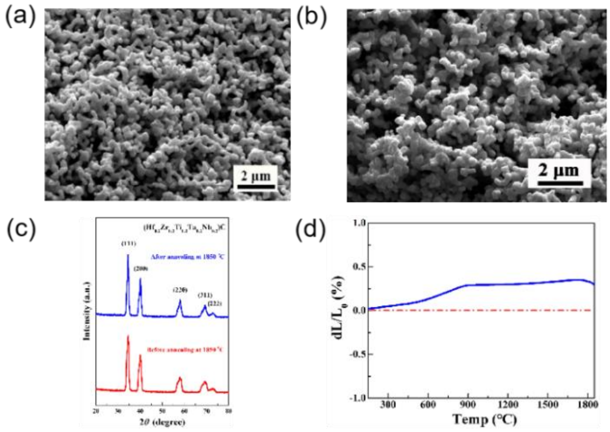

Figure 2 (a-b) SEM micrograph of porous $(Zr_{0.2}Hf_{0.2}Ti_{0.2}Nb_{0.2}Ta_{0.2})C$ sample before and after annealing, (c) XRD patterns of the $(Zr_{0.2}Hf_{0.2}Ti_{0.2}Nb_{0.2}Ta_{0.2})C$ before and after annealing at 1850 ℃, (d)The dL/L0 curve of porous $(Zr_{0.2}Hf_{0.2}Ti_{0.2}Nb_{0.2}Ta_{0.2})C$ [60]

4 Boride Coating Systems

4.1 Binary boride systems

Boride coatings are currently one of the most extensively studied materials in the field of ceramic coatings, including zirconium boride, hafnium boride, and titanium boride. Borides have excellent properties such as corrosion resistance, wear resistance, and excellent oxidation resistance at high temperatures. For instance, boride coatings were coated on surface of metal materials like iron through thermal spraying and infiltration technology, which could significantly improve the tribological properties while enhancing their microhardness. Lindner et al. [67] employed the powder pack infiltration method to harden high-speed oxygen-fuel sprayed Inconel 625 coatings. Further thermochemical treatment was also adopted to intensify the coatings, resulting in a significant increase in microhardness and wear resistance. Khater et al. [57] investigated the mechanical and tribological properties of titanium boride coatings obtained through thermochemical boriding in a salt bath composed of 70% borax and 30% silicon carbide. They found that boriding at 1000 ℃ for 8 hours obtained the highest TiB_2 layer thickness, which reached a value of 50 μm. The formation of the TiB_2 layer increased the surface hardness and elastic modulus of the substrate by 9 times and 2.5 times, respectively, offering a new approach to enhancing the performance of matrix materials or parts. Mirhosseini et al. [68] successfully deposited Al_2O_3-TiB_2 coating on surface of steel substrate using in-situ plasma spraying (IPS). The Al_2O_3-TiB_2 coating exhibited excellent mechanical properties with a hardness of 797.6 HV, a wear track width of 1061.3μm, and a wear rate of 4.2×103 mm^3 /(N ·m).

Additionally, the properties of boride ceramics can be improved by doping other materials. Zeng et al. [69] prepared metal boride MB_x (M = V, Mo, and Fe) and MnO_2 co-doped $NiCr_2O_4$ coatings using atmospheric pressure plasma spraying. These coatings exhibited excellent infrared emissivity within the range of 5 ～ 25 μm and also demonstrated good heat resistance. Salyi et al. [70] employed powder pack infiltration boriding to form boride coatings on steel samples. Both the Fe_2B and FeB phases exhibited excellent corrosion resistance.

4.2 Multi-component boride systems

With the continuous advancement of industrial technology, the demand for high-performance materials is becoming increasingly urgent. Multi-component borides, as a class of promising materials, will play a significant role in various fields. Although the performance of multi-component borides has been significantly improved, the optimization of their preparation processes and further enhancement of their comprehensive properties remains to be issues that need to be addressed in current research to promote their wider application and development.

By reasonably controlling the process parameters, high-quality multi-component boride cladding layers can be obtained, exhibiting excellent adhesion, compactness, and metallurgical bonding. Zhang et al. [71] studied the relationship between the input process parameters (laser power, scanning speed, pre-laid thickness) and the output responses (height, width, dilution rate) of Mo_2FeB_2 coatings through sensitivity analysis. The results showed that laser power had a positive effect on the coating width and dilution rate, while having a negative effect on the coating height. Apart from process regulation, modifying the coating composition can also enhance its performance. Bao et al. [72] prepared the composite coating resistant to high-temperature zinc-aluminum molten liquid corrosion using supersonic flame spraying. Mo-B_4C powders were mixed with WC and Co powders with different proportion to prepare composite powders. An appropriate amount of Mo-B_4C reacted with Co to form ternary borides such as $CoMo_2B_2$ and CoMoB. These ternary borides could formed a perfect and continuous interface, improving the mechanical properties and corrosion resistance of the coating.

4.3 High-entropy boride systems

Currently, researches on high-entropy boride coatings are relatively limited and still in the developing stage. However, due to their outstanding comprehensive properties such as high hardness, high melting point, and excellent corrosion resistance, high-entropy borides are expected to play a significant role in the field of ceramic coatings [73-77]. Mayrhofer et al. [78] prepared ZrB_2, $(Zr,Ti)B_2$, and $(Zr,V,Ti,Ta,Hf)B_2$ coatings using non-reactive magnetron sputtering. Figure 3(a) demonstrated that the prepared boride ceramic coatings exhibit single-phase solid solution. Figure 3(b) showed that the three diboride coatings exhibited very dense morphologies. Compared to ZrB_2 and $(Zr,Ti)B_2$, the $(Zr,Ti,Hf,V,Ta)B_2$ coating exhibited the highest hardness (47.2 ±1.8 GPa). Zhang et al. [79] employed the gas reaction infiltration-assisted slurry spraying (GRSI-SP) method to in situ deposit the high-entropy $(Hf_{0.25}Zr_{0.25}Ti_{0.25}Cr_{0.25})B_2$ ceramic-modified SiC-Si ($HETMB_2$-SiC-Si) coating on the surface of carbon/carbon (C/C) composites to enhance their oxidation resistance at 1973 K. Subsequently, dynamic ablation tests were conducted at ultra-high temperatures (up to 2404 K) using an oxy-acetylene torch (OAT) to investigate the ablation behavior and protective mechanism of the composite coating on C/C composites. Different oxidation deposition were formed under different ablation regions, enhancing high-temperature thermal stability. This study provides the guidance for exploring the heat resistance of high-entropy boride ceramic coatings as high-temperature thermal protection systems under severe conditions. Recently, Guo et al. [80] prepared a multi-component boride $(Hf_{0.5}Zr_{0.5})B_2$-SmB_6-ErB_4-YB_6 (HZRB) coating on the surface of SiC-coated carbon/carbon (C/C) composites using supersonic atmospheric plasma spraying. The excellent ablation resistance was primarily attributed to the formation of a high-density $(Hf_{0.2}Zr_{0.2}Sm_{0.2}Er_{0.2}Y_{0.2})O_{2-\delta}$ high-entropy oxide (HEO) layer during the ablation process.

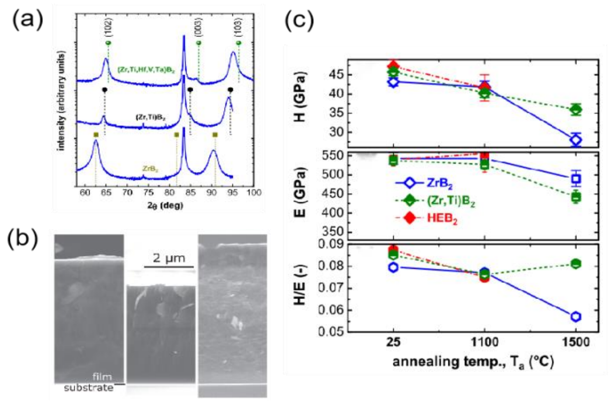

Figure 3 (a) XRD images(b)SEM images; (C)Hardness, indentation modulus and their corresponding ratios of ZrB_2, $Zr_{0.61}Ti_{0.39}B_2$, and $Zr_{0.23}Ti_{0.20}Hf_{0.19}V_{0.14}Ta_{0.24}B_2$ thin films [78]

5 Conclusion and Outlook

Non-oxide ceramics including carbides and their high-entropy ceramics, nitrides and their high-entropy ceramics, as well as borides and their high-entropy ceramics, possessed high hardness, excellent high-temperature resistance, corrosion resistance, and other properties. These characteristics made them application prospects in the field of ceramic coatings. Composition regulation engineering offered significant opportunities to improve the performance of ceramic coatings and promote their applications. The development from binary systems, multi-component coating systems to high-entropy ceramic coating systems had been accompanied by continuous optimization of their properties. In particular, the recently developed high-entropy ceramic coating system had achieved significant innovation in coating materials. High-entropy coatings exhibited advantages such as higher high-temperature stability, corrosion resistance, hardness, and wear resistance, meeting the needs of more application areas and showing broad prospects and tremendous potential. Currently, the regulations of coating composition, coating structure, and internal crystal orientation within the coating are hot research directions, and breakthrough progresses have been achieved. However, the non-oxide ceramic system was still imperfect, especially the researches on high-entropy non-oxide ceramic systems were relatively scarce. The following directions will be developed [79-80].

(1) In the design of non-oxide ceramic coating systems, the introduction of theoretical calculations such as first principles and machine learning can achieve theoretical guidance for experiments, avoiding the need for conducting a large number of experiments. This is conducive to reducing costs and improving research and development efficiency. It also helps to gain a deeper understanding of the properties of high-entropy ceramics. This will provide important guidance for the research and development of non-oxide and their high-entropy ceramic coatings.

(2) The optimization, improvement, and innovation of the preparation processes for non-oxides and their high-entropy ceramic coatings are also critical issues that need to be addressed urgently. Through the optimization and innovation of preparation processes, controllable preparation of high-performance non-oxide coatings can be achieved, enhancing the efficiency of coating preparation and reducing preparation costs.

(3) There exist less researches on the high-temperature mechanical properties, radiation resistance, ablation resistance, and other service properties of non-oxides and their high-entropy ceramic coatings, which need to be further researched to realize their applications.

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