Enhanced interfacial bonding and superior oxidation resistance of CoCrAlY-TiB$_2$ composite coating fabricated by air plasma spraying

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**Abstract**

In order to enhance oxidation resistance of titanium matrix materials, CoCrAlY-TiB$_2$ coating is introduced by air plasma spray. Tensile test demonstrates that TiB$_2$ addition promoted interfacial bonding strength with a maximum enhancing effect of 22.6%, which alleviated mechanical spallation of the coating and consequently gave rise to the improved physicochemical stability. Cyclic oxidation tests at 700, 800, and 900 °C reveal that weight gain of coated specimens reduced by 66.7%, 73.1%, and 75.2% compared with the TMCs substrate. The significantly enhanced anti-oxidation performance was mostly ascribed to the improved microstructural stability and the formation of dense Al$_2$O$_3$ and Cr$_2$O$_3$ oxides.

1. Introduction

Based on the superior properties, such as high specific strength and stiffness together with outstanding chemical corrosion resistance, titanium matrix composites (TMCs) are considered as promising candidates for structural components in automobile, aviation, and aerospace engineering. However, the discontinuously reinforced titanium matrix composites (DRTMCs) with a homogeneous reinforcer distribution often inevitably suffered from ambient temperature embrittlement challenge, limiting the scope of potential application in multiple fields [1–3]. To combat this problem, it has been documented in literature that the DRTMCs with a special quasi-continuous network architecture fabricated through a cost-effective powder metallurgy (PM) method exhibited appreciable ductility and excellent strength, which overcame the bottleneck problem of DRTMCs, leading to better strength-ductility synergy [2,4,5]. Unfortunately, even though the chemically stable ceramic reinforcements were beneficial for the improvement of oxidation resistance [6], the presence of large volume fraction of titanium matrix still exhibited strong propensity for oxidation especially in the atmosphere environment beyond 550 °C [7,8]. With regard to this, further enhancing the oxidation resistance of network-strengthened TMCs and thereby promoting their service temperature will require the introduction of suitable anti-oxidation coatings.

Coating material systems like aluminide [9], Ti-Al-X (X = Cr, Nb, N) [10], silicide ceramics [11], and MCrAlY (M = Ni, Co, or NiCo) [12–14] were previously reported to possess better oxidation resistance. The most promising candidate amongst them is the MCrAlY alloy showing desirable ductility, high strength, outstanding anti-oxidation performance, and hot corrosion resistance at elevated temperatures [15]. In particular, the slowly formed dense Al$_2$O$_3$ film and the coating microstructures suppressed elemental diffusion, contributing to excellent oxidation resistance [16]. MCrAlY also has capability to produce a continuous and adherent thermally grown oxide (TGO), as well as good cracking/spallation resistance. As a result, this sort of coating system demonstrated the potential to be employed as bond coatings in thermal barrier coating (TBC) application. The commonly used processing methods for MCrAlY coating include: air plasma spray (APS) [12,17,18], vacuum plasma spray (VPS) [19], high velocity oxygen fuel deposition (HVOF) [20], magnetron sputtering [21], electron beam physical vapor deposition [16], and laser deposition [22,23]. Among them, the air plasma spray technique is considered as a suitable method to produce the coatings, because of its appreciable tunability and desirable cost-effectiveness [24]. For instance, Vermaak et al. produced the γ’ strengthened MCrAlY coating by plasma spraying, which presented superior adherence than the NiAl-based coatings [15]. Chen et al. studied the effect of alloying elements (Ta, Mo) on the microstructures and properties of NiCoCrAlY coating by APS technology, revealing that Ta addition improved the oxidation resistance, and Mo addition enhanced the adhesion between coating and substrate [12,17]. Furthermore, it was reported that post treatments could also modify the
MCrAlY coating. For example, Cai et al. found that the high-current pulsed electron beam irradiation refined the grains of as-sprayed CoCrAlY coating, effectively improving the oxidation resistance [25]. Deng et al. reported that the cathode plasma electrolysis treatment also enhanced the anti-oxidation performance of thermal sprayed NiCoCrAlY bond coat [18].

In this work, the anti-oxidation CoCrAlY coating was designed and fabricated on the network structured 3.4 vol.% TiBw/Ti64 composites with the purpose of enhancing the maximum service temperature of TMCs over 800 °C. Our main focus is to examine the coatings' endurance to more aggressive environment. In order to modulate the coating microstructures and the interfacial bonding strength between the coating and substrate, a small number of TiB2 powder was introduced to the CoCrAlY coating system by low-energy ball milling and APS techniques. Additionally, a novel surface roughing method (termed "surface etching pretreatment" in the following) was employed in this study before spraying to improve the bonding strength. Compared with the traditional surface grit blasting process, the surface etching pretreatment is characterized by its low energy consumption, high efficiency and good economic feasibility. Subsequently, the interfacial bonding strength between the coating and substrate has been studied through the uniaxial tensile test, and APS power input is optimized. Furthermore, the cyclic oxidation behavior of CoCrAlY-TiB2 composite coating has been investigated, and the corresponding oxidation mechanisms are further elucidated.

2. Experimental

2.1. Materials and deposition

The substrate material used in this study was as-sintered 3.4 vol.% TiBw/Ti64 composites with a dimension of 10 cm × 10 cm × 2 cm. Commercially available CoCrAlY powders with D50 = 50 μm (Fig. 1(a)) and fine prismatic TiB2 powders (D50 = 3 μm as shown in Fig. 1(b)) were selected as raw materials in this work. The nominal composition of the CoCrAlY powder is Co-24.83-Cr12.74Al-2.68Ta-1.34Si-1.06Y (wt.%). Then the CoCrAlY-1TiB2 (wt.%) composite powders were mixed through ball milling at a speed of 200 rpm for 8 h. From Fig. 1(c), it can be seen that CoCrAlY powder with a diameter between 37–65 μm after ball milling exhibited the similar morphology and size of raw CoCrAlY powder, indicating negligible plastic deformation has taken place. Meanwhile, some tiny particles were adhered to the CoCrAlY powder surface. Table 1 summarizes the chemical analyses of CoCrAlY-TiB2 powder (Fig. 1(c)), revealing that the elements of zones “2, 3” mainly consisted of Ti and B. Therefore, it is realized that fine TiB2 powders were adhered onto the surface of CoCrAlY powder during ball milling. The corresponding schematic of the composite powder is shown in Fig. 1(d). Subsequently, the APS equipment was employed to produce the CoCrAlY coatings with a spray distance of 100 mm under various energy input. Before deposition, the substrate material was preheated by the plasma spraying gun to improve the surface activity and decrease the temperature difference between substrate and the spraying powders.

2.2. Microstructural characterization

The cross section of the coatings was polished by SiC sand paper of grades 120, 400, 800, 1200, 1500# and cleaned by ethanol. Then a Zeiss SUPRA 55 scanning electron microscope (SEM) equipped with energy dispersion X-ray spectroscopy (EDS) system was employed to characterize the morphology, microstructures, and elemental distribution of the as-sprayed coatings before and after cyclic oxidation tests. In addition, a D/Max-2400 X-ray diffractometer (XRD, Cu Kα) was utilized to identify phase constitutions of the coatings before and after the oxidation tests.

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### Table 1

<table>
<thead>
<tr>
<th>Point</th>
<th>Co</th>
<th>Cr</th>
<th>Al</th>
<th>Ta</th>
<th>Y</th>
<th>Ti</th>
<th>B</th>
<th>Si</th>
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<td>1</td>
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<td>0.74</td>
<td>3.44</td>
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<td>–</td>
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<td>6.19</td>
<td>3.60</td>
<td>2.92</td>
<td>–</td>
<td>0.49</td>
<td>27.62</td>
<td>59.17</td>
<td>–</td>
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<tr>
<td>3</td>
<td>0.50</td>
<td>0.36</td>
<td>0.18</td>
<td>–</td>
<td>30.85</td>
<td>68.11</td>
<td>–</td>
<td>–</td>
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<td>4</td>
<td>48.74</td>
<td>23.91</td>
<td>23.63</td>
<td>0.74</td>
<td>0.60</td>
<td>–</td>
<td>–</td>
<td>2.38</td>
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</tbody>
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Fig. 1. SEM micrographs of (a) coarse CoCrAlY powders, (b) fine TiB2 powders, (c) CoCrAlY-TiB2 composite powders, and (d) schematic of the composite powder.
2.3. Bonding strength test

According to the ASTMC633-79 test standard [26], the interfacial bonding strength (namely interfacial bonding strength between coating and substrate, for simplicity, it is described as “bonding strength” in the rest of the text) was analyzed with INSTRON-5569 universal material testing machine at a tensile loading rate of 0.5 mm·min$^{-1}$. Three specimens with each parameter were tested to ensure reproducibility. Fig. 2 illustrates the assembly diagram of the tensile test sample, revealing that the coated cylindrical specimen and a cylindrical TMCs counterpart were glued together by 3M superglue with a strength of 60 MPa, which was sufficient to measure the bonding strength. After tensile test, the samples fractured at the coating/substrate interface. The bonding strength was then evaluated based on these tensile data.

2.4. Cycle-thermal oxidation test

The specimens for high-temperature oxidation experiments were prepared through the following method: two planes of the cubic-shaped TMCs substrate with the dimension of 10 cm × 10 cm were both coated by APS process. Later on, the cyclic oxidation tests were carried out in a muffle furnace at 700 °C, 800 °C and 900 °C with a heating rate of 20 °C·min$^{-1}$ for a total duration of 100 h in air atmosphere respectively. The samples were placed inside alumina crucibles during the test, which were removed from the furnace at a regular interval and air-cooled to room temperature. In this work, the first two cycles were 5 h each, which were followed by the subsequent nine cycles of 10 h each. The weight was monitored using a PTX-FA210 high accuracy electronic balance with a precision of 0.1 mg after each cycle. Meanwhile, the phase constitutions were identified every 20 h. Additionally, the uncoated TMCs substrate was also tested for comparison. Three samples of each cycle were tested, and the average mass gain value is presented in this work.

3. Results and discussion

3.1. Surface pretreatment

It can be seen that TiB whiskers presented a network configuration (Fig. 3(a)) in the substrate material produced by powder metallurgy. The corresponding in situ chemical reaction mechanisms have been demonstrated elsewhere [4]. In order to improve the interfacial bonding strength, the substrate surface roughness was increased through etching pretreatment with a 5HF-15HNO$_3$ (vol.%) aqueous solution. Before spraying, the etched substrates were ultrasonically cleaned in ethanol bath. Fig. 3(b) shows the microstructures of
substrate surface (TiBw/Ti64 composites) after surface etching pre-
treatment with an etching time of 20 s. It was evident that a large
number of TiB whiskers was partially exposed on substrate surface after
the elimination of Ti matrix, of which the average exposed length was
around 2 μm (Fig. 3(b)). Besides, the exposed TiB whiskers exhibited
slant angles on the surface, which was beneficial for pinning the coating
and enhancing the bonding strength.

3.2. Optimization of the power input

The APS power input can directly influence the joining behavior and
thereby properties of the spraying powders [27]. With this regard, the
CoCrAlY and CoCrAlY-TiB2 composite powders were deposited under various
power input to optimize the bonding strength, and the selected
parameters are listed in Table 2. The measured interfacial bonding
strength in Fig. 4 indicates the CoCrAlY-TiB2 coating exhibited lower
bonding strength than the coating without TiB2 addition at 24.75 kW,
which was due to the insufficient energy. Under such condition, the
TiB2 particles could not react with titanium and deteriorated the in-
terfacial bonding strength. Subsequently, the CoCrAlY-TiB2 composite
coating presented comparatively higher bonding strength compared
with that of the CoCrAlY when the energy was higher than 27.50 kW.
During the spraying process with proper power input, the molten
powders collided the substrate surface through a high-velocity inert gas
flow. Moreover, the heated TiB2 also contacted and reacted with Ti64
matrix of the substrate under a certain power input, forming localized
metallurgical cohesion with the substrate. Consequently, the bonding
strength was higher than that of the CoCrAlY coating without TiB2
addition, and the maximum enhancing effect was about 22.6% at
35.75 kW.

Furthermore, Bonding strengths of both types of coatings exhibited
improving trends and peak at 30.25 kW power input (25.13 (5#) and
27.63 (6#) MPa), exceeding which bonding strengths subsequently de-
creased with respect to increasing power input. Fig. 5 shows the in-
terfacial microstructures of the coatings deposited under various power
inputs. The powders of 2# sample were not fully melted and the cor-
responded thickness was inhomogeneous. Solid-state sintering areas
were also frequently formed at the interface during deposition (Fig. 5(a,
b)) due to the insufficient power, which mainly consisted of heavy
elements such as Co and Cr according to the EDS results (Table 3) and
was detrimental to the bonding strength. Besides, Ti and B elements
were also detected in some solid-state sintering areas (area “2”), and
it was deduced as the existence of unmelted TiB2 powders. In addition,
the coating materials were fully melted generating a thickness of
around 45–60 μm as the power input increased to 30.25 kW (Fig. 5(d)).
The coating density was remarkably improved contributing to the
bonding strength. However, the plasma jet under extensive energy
input (35.75 kW) with enhanced flame flow rate interacted with the
adjacent air forming a local vortex, which destroyed the stability of the
plasma jet and sharply reduced the coating thickness to about 23 μm in
Fig. 5(f). Consequently, a plasma power between 27.5–33 kW was op-
timized to improve bonding strength.

According to the XRD patterns presented in Fig. 6, the CoCrAlY-
TiB2 (wt.%) composite coatings were composed of TaC, SiC, Co3Ti,
CrSi2, CrB2, Al-rich β-(Co, Cr)Al and γ-(Co, Cr) solid solution (ss)
phases. With the increase of power input, the intensity of diffrac-
tion peaks (2θ = 43.2°, and 50.5°) was greatly enhanced while the intensity
of peak (2θ = 44.5°) was notably decreased, indicating that the content
of Al-rich β-Al(Co, Cr) and γ-(Co, Cr) solid solution phases changed.
Additionally, the temperature of the melted powders was also increased
with enhanced energy input, which caused a relatively more sufficient
diffusion. Since the coating mainly consisted of solid solution phases,
various temperatures resulted in a small difference on the solid solu-
bility for these phases. Moreover, higher temperature also led to rela-
tively higher residual stress after rapid solidification. As a result, the
XRD peaks also showed a little bit displacement at various power input.
The Co3Ti and CrB2 phases were also gradually formed. Consequently,
the desired phase constituents reported previously [20] could be pre-
bared by the APS technology with appropriate flame temperature and
dwell time.

The detailed microstructures of the as-sprayed CoCrAlY-TiB2 com-
posite coating with the optimized plasma power of 30.25 kW is shown
in Fig. 7. It can be seen that most of the CoCrAlY-TiB2 raw powders
have been melted, and no obvious cracks and other imperfections were
produced except for few tiny pores on the coating surface as a general
characteristic of the APS technique (Fig. 7(a)). In addition, the surface
SEM images were dealt and analyzed by ImageJ software, revealing the
surface porosity of this coating was only 4.67%. Fig. 7(b) shows the
dense microstructures with laminated feature were formed in the
corresponding EDS line profile in Fig. 7(b) reveals that the
dark phase in the laminated microstructure were mainly composed of
Al and O, while the bright phases consisted of Co and Cr elements. In
addition, the chemical composition of different regions marked as “1-6”
in Fig. 7 is also listed in Table 4, confirming that four typical phases
(A12O3, TaC, γ-(Co, Cr)ss and β-Al(Co, Cr)ss, respectively) were formed in
the coating. During APS deposition process, the air can react with the
surface of the melted liquid drop. Among all the elements in the
coating, Al exhibits a strong thermodynamic tendency of oxidation,
leading to the formation of Al2O3 as a dark phase of region “1”
(Fig. 7(b)). While two different solid solution phases were generated at
the inner liquid drop as a result of rapid solidification, the gray phase of

Table 2

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Samples</th>
<th>Energy (kW)</th>
<th>Coatings</th>
<th>Bonding strength (MPa)</th>
</tr>
</thead>
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<tr>
<td>3.4 vol.% TiBw/Ti64 composites</td>
<td>1#</td>
<td>24.75</td>
<td>CoCrAlY</td>
<td>18.76 ± 0.3</td>
</tr>
<tr>
<td></td>
<td>2#</td>
<td>24.75</td>
<td>CoCrAlY-TiB2</td>
<td>16.64 ± 0.5</td>
</tr>
<tr>
<td></td>
<td>3#</td>
<td>27.50</td>
<td>CoCrAlY</td>
<td>22.61 ± 0.5</td>
</tr>
<tr>
<td></td>
<td>4#</td>
<td>27.50</td>
<td>CoCrAlY-TiB2</td>
<td>26.25 ± 0.6</td>
</tr>
<tr>
<td></td>
<td>5#</td>
<td>30.25</td>
<td>CoCrAlY</td>
<td>25.13 ± 0.4</td>
</tr>
<tr>
<td></td>
<td>6#</td>
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<td>CoCrAlY-TiB2</td>
<td>27.63 ± 0.4</td>
</tr>
<tr>
<td></td>
<td>7#</td>
<td>33.00</td>
<td>CoCrAlY</td>
<td>22.52 ± 0.5</td>
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<tr>
<td></td>
<td>8#</td>
<td>33.00</td>
<td>CoCrAlY-TiB2</td>
<td>25.48 ± 0.7</td>
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<tr>
<td></td>
<td>9#</td>
<td>35.75</td>
<td>CoCrAlY</td>
<td>15.63 ± 0.5</td>
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<tr>
<td></td>
<td>10#</td>
<td>35.75</td>
<td>CoCrAlY-TiB2</td>
<td>19.17 ± 0.3</td>
</tr>
</tbody>
</table>

Fig. 4. The interfacial bonding strength of the coated samples under different power input.
region “2” (Fig. 7(c)) was considered as the Al-rich β-Al(Co, Cr)ss, and the bright phase of region “3” (Fig. 7(c)) was summarized as the γ-(Co, Cr)ss. Furthermore, a small quantity of white particles (region “4” and “6”) considered as TaC phase were also generated in the coating, which was beneficial for enhancing the coating strength.

### 3.3. Cyclic oxidation experiment

The cyclic oxidation kinetics of uncoated TiBw/Ti64 substrate and TMCs coated with CoCrAlY-TiB2 composite coating at various temperatures are demonstrated in Fig. 8. The substrate suffered from a rapid oxidation stage at the first 10 h. Then the weight gain value obviously decreased but still followed a linear oxidation law. As a result, the substrate material exhibited an unstable oxidation phenomenon throughout the test, and the mass per unit area after oxidation for 100 h at 700 °C, 800 °C, and 900 °C reached about 10.5 mg·cm$^{-2}$, 14.9 mg·cm$^{-2}$, and 24.5 mg·cm$^{-2}$ (Fig. 8(a–c)). However, the TMCs coated with CoCrAlY-TiB2 experienced a stable oxidation after the initial relatively rapid mass gain stage, following the parabolic rate rule upon the whole procedure. After the cyclic oxidation for 100 h, the corresponding weight gain of the coated specimens was only 2.5 mg·cm$^{-2}$, 4.0 mg·cm$^{-2}$, and 5.4 mg·cm$^{-2}$. Compared with the uncoated substrate, the gained weight was remarkably reduced by 66.7%, 73.1%, and 75.2%.

Moreover, Fig. 8(a1–c1) also show the corresponding first derivative curves of the mass-gain value to quantitatively describe the mass-gain rate over oxidation time. These curves also proved that the TMCs substrate presented higher mass-gain rate compared with the coated specimen. For instance, the initial rate of substrate at 700 °C was about 0.4 mg·cm$^{-2}$ h$^{-1}$ (Fig. 8(a1)), which was two times faster than the coated one (around 0.2 mg·cm$^{-2}$ h$^{-1}$). Subsequently, the mass-gain rate decreased and the substrate exhibited a relatively constant rate of around 0.08 mg·cm$^{-2}$ h$^{-1}$ after 20 h, while the rate of CoCrAlY-TiB2 coated sample was stable and close to only 0.01 mg·cm$^{-2}$ h$^{-1}$. Therefore, the mass-gain rate of the CoCrAlY-TiB2 coated sample was obviously lower than the TiBw/Ti64 substrate, implying the oxidation resistance can be remarkably enhanced by introducing the CoCrAlY-TiB2 coating. In addition, the mass-gain rate of the substrate at high temperatures also experienced a moderate increasing trend after the inflection points “A” (70 h at 800 °C in Fig. 8(b1)) and “B” (60 h at 900 °C in Fig. 8(c1)). When the TMCs substrate was cyclically oxidized at elevated temperature, the oxide scale spalled and detrimentally leading to the exposed fresh surface which was easily oxidized and then caused the inflection points of the mass-gain rate curve. Nevertheless, the rate of the CoCrAlY-TiB2 coated sample exhibited a comparatively stable trend after the initial 20 h. Consequently, the CoCrAlY-TiB2 coating presented stable and excellent anti-oxidation performance contributing to expanding the application fields of TMCs.

Subsequently, the XRD patterns of CoCrAlY-TiB2 composite coating during the cyclic oxidation at different temperatures are shown in Fig. 9. A common phenomenon can be seen is that the change in phase constitution mainly occurred at the first 20 h, and then the transformed phases presented no change during the subsequent test. The main phase constitution change at the initial stage was that the original Al$_6$Cr$_7$Co$_{0.53}$, AlCo, Al$_{60}$Cr$_{20}$, Co$_7$Ti, CrSi$_2$, CrB$_2$ phases were unstable in air atmosphere at elevated temperature, which reacted with oxygen and...
then gradually transformed into Co, Al2O3, Cr2O3. Indicating that Co-CrAlY-TiB2 coating exhibited an enhanced oxidation resistance by forming Al2O3 and Cr2O3 oxides. It is worth noting that the diffraction peak of residual AlCo and Al0.47Co0.53 solid solution phases (2θ = 44.7°) near the metallic Co peak was detected on the oxidized surface at 700 and 800 °C in Fig. 9(a) and (b), but disappeared after oxidizing at 900 °C in Fig. 9(c). In reality, when oxidized at 700 °C, only a portion of Al element transformed into Al2O3, and the rest of Al remained as the original solid solution element state. Therefore, the diffraction peak of residual AlCo or Al0.47Co0.53 was detected in Fig. 9(a) and a certain amount of metallic Co also emerged during this stage. With the increase of oxidation temperature and duration, the quantity of residual AlCo or Al0.47Co0.53 phase on the oxidized surface gradually decreased and the corresponding diffraction peak intensity was reduced in Fig. 9(b) and even disappeared at 900 °C in Fig. 9(c) in association with the increased content of metallic Co. Moreover, there were also some differences in phase constitution change at various temperature. For instance, the diffraction peak of AlCr2O4 phase was observed when testing at 700 and 800 °C, which did not appear at 900 °C. Similarly, the Al0.65Cr0.35Ti0.25 phase could only be detected at 800 °C. The possible reason accounting for this difference might be the instability of the corresponding phases in high-temperature environments.

The surface morphologies of the uncoated TiBw/Ti64 substrate after oxidation for 100 h are shown in Fig. 10. Fig. 10(a) indicates that oxides scales spalled during the test, and the surface morphologies were divided into four regions. Region “A” represented the exposed fresh surface formed when the oxide scale spalled, which presented a slight degree of oxidation. While region “B” revealed the morphology of the thick oxide scale, in which many cracks were initiated and propagated (Fig. 10). Based on the previous works [6,9,28], the oxide scale of TMCs were considered as needle-shaped TiO2 and particle-shaped Al2O3. The thermal expansion coefficient difference between substrate and the oxide scale combined with the cyclic oxidation mode caused a certain thermal stress, which brought about the mechanical spallation [6]. Therefore, the oxide scale lost the protection capability, and the inferior oxidation resistance resulted in the rapid mass-gain rate illustrated in Fig. 8.

As for the coated samples by APS technology, all the oxidized surfaces illustrated in Fig. 11 were free of crack or mechanical spallation. Fig. 11(b) reveals that the oxide formed at 700 °C was fine and the as-sprayed coating microstructures were also observed, indicating a good oxidation resistance at this temperature. Combined with the EDS point analysis in Table 5, the granular Cr2O3 with a diameter of around 1 μm (region “1” in Fig. 11(b)) and fine Al2O3 were generated after oxidizing at 700 °C. Then the corresponding volume and quantity of oxide were enhanced when oxidized at 800 °C. During oxidation process, the stable TaC and SiC ceramic phases remained. While the γ-(Co, Cr)ss and β-Al(Co, Cr)ss reacted with oxygen and transformed into metallic Co, Al2O3, Cr2O3, AlCr2 etc. The oxide dimension was also enlarged over time. As a result, the comparatively continuous and dense Al2O3 and Cr2O3 oxide film formed at 800 °C (Fig. 11(d)) hindered the diffusion of oxygen into the substrate and prevented the substrate from internal oxidation. Moreover, not only the quantity and size, but also the compactness of the oxides formed at 900 °C were further increased as
shown in Fig. 11(e, f). Due to the poor electrical conductivity of Al₂O₃ and Cr₂O₃, some white patterns appeared on the secondary electron image (Fig. 11(e)) referring to the oxide with large scales. In light of Fig. 9, the transformed oxides were relatively stable since the oxide types did not change during oxidation process. Therefore, the uniform and dense oxides without any crack illustrated in Fig. 11(e, f) contributed to the excellent oxidation resistance of CoCrAlY-TiB₂ coating.

Fig. 12 reveals the EDS line profile at interface between the coating and substrate after oxidation for 100 h at 800 °C, indicating that Ti element diffused into the coating zone from the substrate which was beneficial for the interfacial bonding. As a result, the Ti diffusion layer with a thickness of around 5 μm and a closely jointed interface are presented in Fig. 12. Moreover, Co element also diffused into the substrate from the coating with a distance of about 1 μm. As for the O element, the corresponding content was rapidly reduced at the interface. Consequently, the oxygen diffusion behavior was hindered by the CoCrAlY-TiB₂ composite coating during oxidation at high-temperature environment.

3.4. Oxidation mechanisms

In light of the aforementioned experimental results, the poor anti-oxidation performance of the network structured TMCs has been significantly improved by the APS-deposited CoCrAlY-TiB₂ composite coating. In addition, the enhanced bonding strength suppressed the coating from mechanical spallation during oxidation and further improved the physicochemical stability. During the initial oxidation stage, the formation of oxide film led to the relatively rapid oxidation rate. With the extension of oxidation time, the thickness and density of the oxide film gradually increased, resulting in a better oxygen diffusion.
barrier effect. In reality, the oxidation resistance mainly depended on the stress state and properties of the oxide film. Based on the theory of Pilling-Bedworth ratio (PBR) for metals, the volume change due to the oxide formation could be expressed as Eq. (1) [29]:

$$PBR = \frac{V_{\text{ox}}}{V_{\text{m}}} = \frac{M_r \rho_m}{n A_r \rho_{\text{ox}}}$$

(1)

where $M_r$ is the relative molecular weight of the metallic oxide, $A_r$ represents the relative atomic mass of the metal, $n$ is the metal ion valence in the oxide, $\rho_m$ is the density of the metal (kg·m$^{-3}$), $\rho_{\text{ox}}$ represents the density of the oxide (kg·m$^{-3}$). It was previously reported that when PBR > 1, a compressive stress would be developed in the oxide scale, while a tensile stress was generated in the scale with PBR < 1 [29]. As a result, the oxide scale would easily spall under the tensile stress or the excessive compressive stress. While the dense oxide film could be formed under a moderate compressive stress with a PBR value between 1 and 2.5 resulting in an excellent oxidation resistance. In this work, the oxide film was mainly composed of Al$_2$O$_3$ and Cr$_2$O$_3$ with a favorable PBR of 1.28 and 1.99, respectively. Therefore, the coating surface could be covered with a dense oxide scale, contributing to the remarkable oxidation resistance.

Fig. 9. XRD patterns of the CoCrAlY-TiB$_2$ composite coatings during oxidation test at (a) 700 °C, (b) 800 °C and (c) 900 °C.

Fig. 10. Surface morphologies after oxidation test of the uncoated substrate at 800 °C: (a) an overview of the oxidized surface; (b) higher magnification of zone “B” in Fig. 10(a).
The oxidation reaction of alloy could be described as:

\[
M_i + \frac{1}{2}O_2 = M_iO
\]  

(2)

During this reaction, the ions and electrons would diffuse at the metal/oxide interface, and the electrical conductivity of the oxide would affect the diffusion rate. Therefore, the poor conductivity of the dense \(\text{Al}_2\text{O}_3\) (10\(^{-7}\) S cm\(^{-1}\)) and \(\text{Cr}_2\text{O}_3\) (10\(^{-1}\) S cm\(^{-1}\)) scale formed on the CoCrAIY-TiB\(_2\) coating surface reduced the oxidation rate. Moreover, the oxygen partial pressure in the gas atmosphere should also be greater than the pressure required for the metal–metal oxide equilibrium, which is provided by Eq. (3) [30]:

\[
(P_{O_2})^{1/2}_{M_i-M_iO} = \frac{\exp(\Delta G_{M_iO}^0/RT)}{\alpha_{M_i}}
\]  

(3)

Where, \((P_{O_2})_{M_i-M_iO}\) is the oxygen partial pressure of the metal-oxide equilibrium, \(\Delta G_{M_iO}^0\) is the standard Gibbs free energy of \(M_iO\) formation (kJ mol\(^{-1}\)), \(T\) is the absolute temperature, \(\alpha_{M_i}\) is the activity of \(M_i\) in the alloy (mol L\(^{-1}\)). Accordingly, Guo et al. hypothesized oxides of individual metallic element in the alloy were produced at the initial stage due to the sufficient oxygen pressure, while the most thermodynamically stable oxide would eventually cover the alloy surface as a result of selective oxidation [30]. Therefore, the most stable \(\text{Al}_2\text{O}_3\) should be the only oxide. However, \(\text{Cr}_2\text{O}_3\) was also detected in the oxidized CoCrAIY-TiB\(_2\) composite coating, indicating that the oxide formation was controlled by the kinetic factor simultaneously. According to the Wagner’s theory, the minimum quantity of metallic atoms \(N_i\) could be obtained by the followed equation [30]:

\[
N_i = \left(\frac{\pi g N_0 D_0 V_m}{3D_i V_m}\right)^{1/2}
\]  

(4)

Where, \(g\) is a constant, \(N_0D_0\) is the oxygen permeability in the alloy, \(V_m\) is the molar volume of the alloy, \(D_i\) is the diffusion coefficient of \(i\) element, and \(V_m\) is the molar volume of the oxide. Besides, the effective diffusion coefficient \((D_{eff})\) influenced by grain boundary was also decided by Hart as [30]:

\[
D_{eff} = (1 - f)D_b + f D_{gb}
\]  

(5)

Where, \(D_b\) is the bulk diffusion coefficient, \(D_{gb}\) is the diffusion
coefficient along grain boundary, and $f$ is the fraction of the atomic number in the grain boundary. As a result, Guo et al. reported that $D_{\text{eff}}$ increased with the decrease of grain size. In this work, the CoCrAlY coating microstructures could be refined with the addition of 1 wt.% TiB$_2$ particles, which is attributed to two mechanisms based on our most recent report [31]. First, the deposit material experienced a rapid solidification process, during which the TiB$_2$ particles acted as energetically favored heterogeneous nucleation sites, enhancing the nucleation rate and refined the grains. Second, TiB$_2$ addition also enabled a strong pinning effect on the grain boundary (Zener drag), which further hindered the grain growth kinetics. As a result, the microstructures of CoCrAlY-TiB$_2$ was refined compared with the traditional CoCrAlY coating. Therefore, refined microstructures led to an enhanced $D_{\text{eff}}$. Additionally, $N_t$ was then decreased according to Eq. (4). Due to the comparatively low content of Ti (< 1 wt.%), TiO$_2$ could not be generated after oxidation. While the mass fraction of Cr and Al reached 57.36 wt.% and 12.74 wt.% respectively. Therefore, the corresponding oxide scale was finally composed of Cr$_2$O$_3$ and Al$_2$O$_3$ as supported by the XRD patterns in Fig. 9(b).

4. Conclusion

In summary, the CoCrAlY-TiB$_2$ composite coating was synthesized on the TMCs surface by APS technique to enhance the oxidation resistance. The microstructures were characterized and the cyclic oxidation behavior was elucidated in detail. The main findings are listed as follows:

1. The optimized APS power was 30.25 kW, and the corresponding CoCrAlY-1TiB$_2$ (wt.%) coating was composed of TaC, SiC, Co$_3$Ti, CrSi$_2$, CrB$_2$, Al-rich $\beta$-(Co, Cr)Al and $\gamma$-(Co, Cr) solid solution phases;
2. The bonding strength between the coating and substrate experienced an increase first and then decrease trend with the increase of APS power, and maximally reached 27.63 MPa. Besides, the TiB$_2$ addition was beneficial to improving the bonding strength when the power was higher than 27.50 kW, and the maximum enhancement was about 22.6% under 35.75 kW;
3. The anti-oxidation performance was significantly enhanced by introducing CoCrAlY-TiB$_2$ composite coatings. Compared with the uncoated substrate, the weight gain of the coated specimens during cyclic oxidation test reduced by 66.7%, 73.1%, and 75.2% at 700, 800, and 900 °C, respectively. Such enhancement was attributed to the enhanced bonding strength and the formation of uniform and dense Al$_2$O$_3$ and Cr$_2$O$_3$ oxides which hindered internal oxidation.

Data availability

The raw/processed data required to reproduce these findings cannot be shared at this time due to technical or time limitations.

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