High speed laser cladded Ti-Cu-NiCoCrAlTaY burn resistant coating and its oxidation behavior

Lou Li-Yan, Zhang Yu, Jia Yun-Jie, Li Yan, Tian Hong-Fang, Cai Yu-Jun, Li Cheng-Xin

1. Introduction

Due to the low density, high specific strength and excellent corrosion resistance, titanium alloy has been widely used in the field of aerospace, such as compressor casing, rotor blade etc. Nevertheless under certain pressure, temperature and flow rate they encounter "spontaneous combustion", commonly known as Titanium Fire, tends to spread very quickly and hence limits the application of titanium alloy in various fields [1]. To inhibit ignition and combustion of titanium alloys, burn resistant titanium alloys including Ti-V-Cr, Ti-Cu-Al and Ti-Nb series have been developed, which can prevent the diffusion of oxygen by forming a dense oxide diffusion barrier layer or avoiding the ignition point of the substrate by rapid distribution of ignition heat [2–3]. Several types of aforementioned burn resistant titanium alloy have been formed for the aviation applications, includes Alloy C (Ti-35V-15Cr) developed by USA [4], BTT-1 (Ti-13Cu-4Al-4Mo-2Zr) and BTT-3 (Ti-18Cu-2Al-2Mo) produced by Russia [4], Ti40 (Ti-25V-15Cr-0.2Si) [5–6], Ti14 (Ti-1Al-13Cu-0.2Si) [2] and WSTi3515S (Ti-35V-15Cr-0.3Si-0.1C) alloy [7–8] designed by China. However, due to the high cost of production and lower strength to weight ratio with the adding of a large amount of heavy alloying elements, the practical systems of burn resistant titanium alloys still need further research.

Since the adding of a protective coating can isolate oxygen, prevent combustion, it becomes an ideal way to solve the problem of “titanium fire" by preparing burn resistant coating on the surface of titanium alloy, along with the cost reduction and retaining high specific strength of titanium alloy. NASA tested 12 kinds of coatings by igniting burn resistant coated titanium alloy to evaluate the flame retardancy and oxidation resistance of the coating [9]. Through grooving and powder pre-implantation, Li et al. [10] fabricated Ti–Cu burn resistant layer on TC4 titanium alloy by friction stir processing technology, revealed the flame retardant mechanism of the coating. Shen et al. [11] prepared Ti–Cr and Ti–Cu coatings on TC4 titanium alloy by surface mechanical alloying and the results of laser spotting test showed an improvement in burn resistance of the substrate for both kinds of coatings. With the diffusion of Cu, Cr, Nb, Mo and other alloying elements on the surface of titanium; Ti–Cu, Ti–Cr, Ti–Nb, Ti–Mo coatings with certain anti-oxidant and flame retardant properties were formed by glow plasma surface alloying technology [12–15].

High Speed Laser Cladding (HSLC) is a novel additive manufacturing technology proposed by Germany in 2017 [16–18]. Under the optimal coupling of laser beam and powder flow by redesigned co-axial powder feeding nozzle, powder particles could be heated to the melting point before guided into the molten pool. Due to limited transmitted laser energy, a micro-molten pool could be formed on the substrate so that the coating with low dilution ratio and metallurgical bonding could
be produced. The deposition speed of HSLC can varies from 25 to 200 m/min [16], overcome the efficiency obstacle of traditional laser cladding technology. HSLC provides a highly efficient and low cost production way for the fabrication of thin coatings on large parts, which can also be applied for the deposition of high quality flame retardant coatings.

MCrAlY (M = Ni, Co or NiCo) coating is an important constituent of thermal barrier coatings (TBCs) due to its good high-temperature oxidation protection and good adhesion to the substrate. And dense α-Al2O3 layer is considered to be the desirable TGO layer due to its low oxidation protection and good adhesion to the substrate. And dense thermal barrier coatings (TBCs) due to its good high-temperature oxidation protection and good adhesion to the substrate.

<table>
<thead>
<tr>
<th>Powder deposited</th>
<th>Laser power (kW)</th>
<th>Working distance (mm)</th>
<th>Carrier/inert gas</th>
<th>Gas flow rate (L/min)</th>
<th>Linear velocity (mm/s)</th>
<th>Overlapping ratio (%)</th>
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<tr>
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<td>Ar</td>
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<td>250</td>
<td>80</td>
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</table>

The operating temperature of the titanium blade of high pressure compressor is up to 600 °C, the burn resistant alloy Ti40 cannot be used above 550 °C [29], and Alloy C is also developed with a maximum operating temperature (non-burning) of 600 °C [30–31]. Simultaneously, literature shows that α trans temperature of TC4 alloy is 880 °C, α completely transforms to β above 1050 °C, if heat treatment process is performed above 1050 °C, the formation of Widmanstatten structure or structure with coarse grain would be promoted [34–35]. Therefore, the oxidation temperature was chosen as 800 °C in this research. High temperature isothermal oxidation tests of Ti-CuNiCoCrAlTaY coating were performed in an atmospheric air furnace. The samples were placed in the furnace and taken out after 5, 15, 25, 35 and 50 h, then cooled to room temperature. The weight change was measured by weighing balance with an electronic sensitivity of 10−5 g and three parallel specimens were measured each time to eliminate measurement error.

Flame-retardant property of TC4 alloy and Ti-Cu-NiCoCrAlTaY coated alloy was evaluated using laser spot melting test. The specimens were irradiated by 500 W laser beam with 2 mm spot diameter and the exposure time of laser was 5 s for each specimen.

Specimens were cut from the as-prepared substrates with coatings using the spark-erosion wire cutting method, then mounted, ground, polished, and etched for the observation of the microstructure. The morphology, microstructure and elemental analysis of as-deposited, oxidized and laser spot melted samples were observed by Hitachi S-3400 Scanning Electron Microscope (SEM) equipped with Energy-Dispersive Spectrometer (EDS). bruker D8 ADVANCE A25 X-ray Diffraction analysis (XRD) was used for phase and crystal structure analysis. The 3D surface morphology of the coating after laser spot melting test was measured by VK9700K color 3D laser microscope. Phantom VEO high-speed camera system was utilized to record the whole laser spot melting process with 4800 fps acquisition frequency.

2. Experimental details

Commercial TC4 (Ti-6Al-4V) titanium alloy rod with a diameter of 28 mm was selected as substrate, cleaned with acetone before the experiment. The Cu (99.9%, < 30 μm) and Amdry 997 NiCoCrAlTaY (Ni-23Co-20Cr-8.5Al-4.0Ta-0.6Y, 35–55 μm) spherical powders were used as raw materials for the deposition of Ti-Cu-NiCoCrAlTaY coating. 2 kW fiber laser machine was used to implement laser cladding with self-designed co-axial powder feeding nozzle. The process parameters are shown in Table 1. In order to deposit a uniform coating with the well combination of Cu and NiCoCrAlTaY, Ti-Cu-NiCoCrAlTaY coating was prepared by depositing NiCoCrAlTaY powder on the surface of Ti–Cu coating rather than directly depositing the powder mixture, considering the obvious differences in melting points and laser absorptivity between Cu and NiCoCrAlTaY. Firstly powder Cu was deposited on TC4 substrate with the optimized process parameters shown in Table 1. Then, clean the Ti–Cu coating with acetone, and readjust the distance between the substrate and the powder feeding head to make sure the working distance was still 15 mm. After that, the powder NiCoCrAlTaY was deposited on the Ti–Cu coating with the process parameter in Table 1 to obtain the composite Ti-Cu-NiCoCrAlTaY coating. In order to prevent oxidation of the coating during fabrication process, the experiment was carried out in a protective gas box with continuously injected argon (99.99%, flow rate 0.5 L/min).

3. As-prepared microstructure and phase analysis of coatings

A dense and homogeneous structure of the Ti-CuNiCoCrAlTaY coating was obtained with a thickness about 170 μm and surface roughness Ra about 12 μm. No visible defects like cracks, pores or bonding errors at the interface were observed on the coating, as shown in Fig. 1.

Due to the formation of the molten pool on the surface of the substrate during the cladding process, interdiffusion of the elements between coating and substrate occurs. The result of EDS analysis is shown in Fig. 2, where Ti element of the TC4 substrate diffused into Ti-CuNiCoCrAlTaY coating and segregated in the transition zone, which proved strong metallurgical bonding between coating and substrate. Fig. 2 shows Ti-Cu-NiCoCrAlTaY coating with relatively uniform distribution of Cr and Ni elements. Cu and NiCoCrAlTaY were homogeneously mixed in the coating.

Fig. 3 presents the elemental distribution of Ti, showing a sudden change at the transition zone caused by the diffusion of element Ti of TC4 into the coating, which also proves strong metallurgical bonding.
between coating and substrate. The dilution ratio was defined as the percentage of the total volume of the surface layer contributed by melting of the substrate, and it could be calculated through the composition of the cladding layer, the formula is as follow [32–33]:

\[
\text{dilution} = \frac{\rho_{\text{powder}} (X_{\text{coating}} - X_{\text{powder}})}{\rho_{\text{substrate}} (X_{\text{substrate}} - X_{\text{coating}}) + \rho_{\text{powder}} (X_{\text{coating}} - X_{\text{powder}})}
\]

where \(\rho\) is the density of the powder or the substrate, and \(X\) is weight percent of element \(X\) in the coating, substrate or powder. Based on the EDS results of element Ti, the dilution ratio was calculated to be lower than 6.8%.

Fig. 4 is showing the XRD patterns of coatings as deposited and after oxidized. It showed Ti-Cu-NiCoCrAlTaY coating was mainly composed of Cu, \(\gamma\)-Ni and Cu3.8Ni. The formation of Cu–Ni solid solution revealed that in-situ reaction occurred during cladding process. While due to the limitation of the XRD effective detection area, phases near the transition zone may not be detected.

The EDS microanalysis (Table 2) revealed Ti-Cu-NiCoCrAlTaY coating was mainly composed of element Cu, Ni, Co and Cr, while the content of Cu was about 40 wt%. As shown in Fig. 5b, the coating was mainly consisted of Cu and Ni (Point 1), which was consistent with XRD results, i.e. Cu, \(\gamma\)-Ni and Cu3.8Ni. And gray spherical structure enriched in Ni, Co, Cr (Point 2) precipitated out from the matrix of the coating. The columnar structure phase formed in the transition zone (Fig. 5c), which was mainly composed of Cu and Ti, as the result of the diffusion of elements the content of Cu and Ti was 50 wt% and 24 wt% (Point 3), respectively.

4. Oxidation behavior of TC4 titanium alloy and Ti-Cu-NiCoCrAlTaY coatings

4.1. Oxidation kinetics curve

The oxidation behaviors of TC4 alloy and Ti-Cu-NiCoCrAlTaY coated alloy were determined after heating at 800 °C for 50 h. The resulting kinetic curves are shown in Fig. 6. An evident weight gain was found in TC4 alloy rather than Ti-Cu-NiCoCrAlTaY coated alloy.

As a grown potential curve versus oxidation time, the kinetic curves exhibited quite frequent weight gain rate of both the coated alloy and the substrate at onset of oxidation, but after 15 h of oxidation, the oxidation kinetic of Ti-Cu-NiCoCrAlTaY coated alloy considerably
decreased, entered to a stable oxidation stage, which indicated a dense and continuous oxide scales were formed on the surface, preventing the diffusion of oxygen and slowing down the oxidation reaction. In this research, the oxidation of Ti-Cu-NiCoCrAlTaY coated alloy and TC4 substrate obeyed Wagner theory \[20,36\], \[\Delta m = k_p t^{n}\], where \(\Delta m\), \(k_p\) and \(t\) are defined as mass gain per unit area/mg·cm\(^{-2}\), oxidation rate constant/mg·cm\(^{-2}\)·h\(^{-1}\), and time of oxidation/h respectively. And \(n\) represents the index of oxidation rate, it should point out that \(n\) is considered as 2 when kinetic model is parabolic. Research have proved that if \(n > 2\), the oxide film formed would be relatively compact and the diffusion coefficient of oxygen could be decreased, while a relatively loose oxide scale would be formed if \(1 < n < 2\) \[37\]. In this research, Ti-Cu-NiCoCrAlTaY coated alloy and TC4 alloy followed the rule \(\Delta m_{2.22} = 0.99 t\) and \(\Delta m_{1.46} = 11.78 t\) respectively, according to the fitting mathematical model. So it can be concluded that a dense and continuous oxide scale would be formed on the surface of Ti-Cu-NiCoCrAlTaY coating during the oxidation process as its index of oxidation rate \(n = 2.22\), while the loose oxide scale formed on TC4 alloy would not help to prevent the penetration of oxygen since its index of oxidation rate lower than 2. Due to the protection of the oxide scale, after 50 h oxidation, the weight gain of the Ti-Cu-NiCoCrAlTaY coated alloy was about 5.93 mg·cm\(^{-2}\), only 0.38 times of the weight gain by TC4 alloy. The decrease in mass gain showed the better oxidation resistance of that the NiCoCrAlTaY coated alloys than the uncoated TC4 substrate.

### 4.2. Oxidized surface analysis

The results of the oxidized surface are summarized in Fig. 7 after 25 h and 50 h exposure at 800 °C. The oxide film of TC4 alloy showed typical lamellar structure and severe spallation occurred after 25 h (Fig. 7a) because of the poor bonding strength between the oxide film and substrate. Due to high solubility of oxygen in titanium and high oxidation rate, the stress of the oxide film cannot be released in time, resulting in a brittle oxide film with high stress and cracks after 50 h oxidation (Fig. 7b). And the oxide scale of TC4 was mainly TiO\(_2\) according to XRD patterns in Fig. 8, which evidently proved the TiO\(_2\) film has no ability to resist high temperature oxidation. XRD pattern of oxidized Ti-Cu-NiCoCrAlTaY coating indicates that the Cu and \(\gamma\)-Ni phases are still the main constituents as in as-prepared coating. The oxide scales were composed Al\(_2\)O\(_3\), CuO, and NiO, CoO, Cr\(_2\)O\(_3\) were also detected along with spinel of (Ni,Co)(Al,Cr)\(_2\)O\(_4\), formed with the combination of NiO, CoO and Cr\(_2\)O\(_3\) \[22,40\]. Although the spinel included mixed oxides, the surface morphology was very different from the typical porous spinel of oxidized MCrAlY coating deposited by thermal spray process such as APS \[21,25,40,38–39\]. The composite oxide scale was relatively dense, no cracks, pores or spallation were observed after oxidation test for 50 h (Fig. 7c, d). The EDS analysis of the oxidized surface shows the content of Al is 11 wt% for 25 h and 17 wt% for 50 h. Both percentages are higher than the as-
deposited coating, means Al diffused outward to the surface of the coating during the oxidation process. Since 5–6 wt% of Al allows the growth of the thermally stable and continuous oxide scale [24,41], dense Al2O3 could be formed for oxidation resistance. It also shows the diffusion of Cr to the surface of the oxidized coating, while no obvious change is observed for Co and Ni in comparison with as-deposited coating. With the outward diffusion of Cr, Co and Ni, white particles were formed on the surface of coating after 25 h oxidation, which proved to be composite oxides mainly consisting Cr2O3 according to EDS analysis (Fig. 7d). As the oxidation proceeded, the composite oxides gradually increased, a relatively continuous oxide film was formed (Fig. 7e). It has been reported that the outward diffusion of Ti could deteriorate the mechanical properties of the substrate [42] and the previous oxidation result of TC4 also indicated TiO2 was non-protective for oxidation resistance. But only about 0.13 wt% Ti was detected in the oxide scale in this research, which means Ti was choked inside the coating, that could be beneficial for the performance of the composite oxide scale.

4.3. Cross section microstructure of oxidized Ti-Cu-NiCoCrAlTaY coating

The Ti-Cu-NiCoCrAlTaY coating was dense, no pores and cracks were found after 50 h oxidation at 800 °C. Al-enriched composite oxide scale was formed on coating surface, commonly known as Thermal Growth Oxides (TGO). TGO prevented the impregnation of oxygen into the coating as shown in the EDS line scans (Fig. 9a). Since the interdiffusion occurred between the coating and substrate driven by the gradient concentration, a zone termed as interdiffusion zone (IDZ) was formed with the thickness of about 20 μm above the transition zone (Fig. 9b). The IDZ’s structure has gray matrix composed mainly of Ti, Ni, Co, Cu and Al (Point 2) with white dotted phase mainly consisted of Cu (Point 1), as observed by EDS analysis in Table 3. And because of the outward diffusion of elemental Ti from TC4 substrate, the content of Ti in the transition zone (Point 3) increased to about 40 wt% from about 24 wt% as-deposited. Pores appeared at the interface between the IDZ and the substrate due to the mismatch of thermal expansion coefficient. Wang and others had revealed that the IDZ could become the weakest
area in the coating and severe interdiffusion can promote the exfoliation of oxide scale and weaken the adhesion strength of the coating [43–44].

The magnified image of the TGO, that is the composite oxide formed on NiCoCrAlTaY coating, is shown in Fig. 9c and d, representing a double-layered structure. The top layer of composite oxides mainly composed of Cr2O3 (Point 5) and a layer with high proportion of Al2O3 distributed beneath it (Point 4), in accordance with the elemental distribution result in Fig. 10 along the linear scanning direction in Fig. 9d. The double-layered oxide scale acted as a barrier to prevent the penetration of oxygen into the coating.

4.4. Microstructural evolution and oxidation mechanism of Ti-Cu-NiCoCrAlTaY coating

TGO formed on the coating surface during thermal exposure in air played a decisive role in the thermal cyclic failure of the coating when acting as a thermal barrier. It can be seen that the Ti-Cu-NiCoCrAlTaY coating formed bi-layered TGO, an inner continuous layer consisting mainly of aluminium oxide and an outer layer of mixed oxides. The same morphology is obtained in the TGO of MCrAlY coating prepared via APS, HVOF and other thermal spray (TS) techniques [24,39,19–21]. But the Ti-Cu-NiCoCrAlTaY coating deposited by HSLC had a relatively compact TGO layer after thermal exposure which was quite different from the porous spinel TGO of APS coating, although the XRD pattern indicated the presence of spinel based mixed oxides. There is a difference in the mechanism of TGO formation between HSLC and APS coating.

At the initial stage of oxidation process, oxygen reacted with the alloying elements on the coating surface and oxide scales are formed. The interfacial reaction rate between oxygen and alloying elements is the controlling factor for the growth of oxidation scale. Walker [45] proposed that the electronegativity of element affected the formation of oxides, the greater the electronegativity, the more difficult to form oxide scales. The electronegativity of main elements, i.e. Ni, Cr, Al, Co, Ti and Cu in the Ti-Cu-NiCoCrAlTaY coating was 1.91, 1.66, 1.61, 1.88, 1.54 and 1.90, respectively, according to the Pauling electronegativity of elements, which meant Al, Ti and Cr were more likely to be oxidize with relatively lower electronegativity, while Cu and Ni were relatively difficult to form oxides. Meanwhile, the O affinity and the oxide stability could be reflected through standard Gibbs free energy [37]. According to Ellingham diagram [20,37,46], oxide stability would be increased in the order of CuO, NiO, CoO, Cr2O3, TiO2 and Al2O3. So that,
Al₂O₃ with the negative standard Gibbs free energy (ΔG₀ = RT lnP₀₂) i.e. lowest characteristic equilibrium oxygen pressure, would be formed firstly at the oxygen/coating interface, while CuO was the most unstable oxides in contrast, which was difficult to form. Therefore, even though the content of Cu in Ti-Cu-NiCoCrAlTaY coating was about 40 wt%, porous CuO was not the main part of the oxide scales after thermal exposure. Although oxide nuclei of NiO, Cr₂O₃, CoO, CuO, TiO₂ and Al₂O₃ was expected to form rapidly on the coating surface at onset of oxidation, after a closed oxide layer was developed, it was likely that the oxygen partial pressure at the reaction interface decreased, only Al₂O₃ could grow at the oxide/coating interface owing to its lowest standard Gibbs free energy. Thus, with the increasing of oxidation time, the TGO formed on Ti-Cu-NiCoCrAlTaY coating deposited by HSLC became continuous and stable owing to Al₂O₃ as the primary component. And many researchers also noted the initial stage of the oxidation of MCrAlY coating prepared by APS (19,27,38) generally proceed by the simultaneous formation of dense alumina layer and non-protective oxides such as NiO, CoO, (Ni,Co)Cr₂O₄ and (Ni,Co)Al₂O₄.

As the oxidation proceeds, the elemental diffusion rate and phase formation for the coating obtained by different spray method differed. Coatings deposited by APS technique usually have similar typical lamellar structure with inter-splat pores, micro-cracks and oxide stringers, since the coating is generally attained through the stacking of spray particles in a completely or partially melted state [47-48]. The presence of porosity, inter-splat gaps and cracks in APS coating resulting from splashing could provide gas access channels, which permit the penetration of oxygen to the coating, lead to the internal oxidation and decrease the high temperature oxidation resistance [48]. In contrast, HSLC coating could generate dense coating with almost zero porosity content, and no cracks, bonding errors, preventing the inward diffusion of oxygen. The HSLC coatings was obtained through non-equilibrium solidification reaction, under severely high cooling speed, have smaller grain sizes than the coatings deposited by traditional laser cladding technology [49]. The fine grained coating are more desirable for the TGO formation, since the refinement microstructure could enhance short-path diffusion of the elements for forming oxide scale and increase the diffusion rate of element to the surface [19,40]. So the Ti-Cu-NiCoCrAlTaY coating deposited by HSLC could have a higher nucleation rate of alumina [21] due to the smaller grain size, the diffusion rate of Al element could also get increased, which accelerates the selective oxidation of Al and promotes the formation of dense alumina scale of HSLC coating.

Once the alumina enriched oxide scale formed, it serves as a diffusion barrier to retard further oxidation of the coating [48]. It has been proved that TGO should be continuous, dense and slow grown in order to enhance the life expectancy during thermal exposure in air. And dense Al₂O₃ layer is the most desirable oxide scale due to its low oxygen diffusivity, superior adherence and lower growth rate. The model of D. Renusch [50] indicated that the coatings with larger Al content have longer service life. Since internal oxidation is common in TS coatings particular APS coating, owing to the high temperature environment and oxidizing atmosphere, an oxide film would be formed on the particle surface, then splattered onto the substrate during the spraying operation [51]. While under the protection of inert atmosphere, no obvious internal oxidation is observed in the HSLC process. Due to the significant particle oxidation during the APS process, numerous oxide stringers mainly composed of Al₂O₃ is formed. Aluminium in such oxidation regions is isolated form the remaining coating, which restrained the diffusion of Al to the surface [25,47], and lead to localized Al depletion. During high temperature exposure, the internal oxides continuously grow within the coating, accelerating the Al depletion [48]. Weng et al. [49] observed the formation of inner β-depleted zone (IBDZ) caused by the inward diffusion of Al to the substrate which also accelerated the consumption of Al. While for HSLC coating, without oxide stringers generated by internal oxidation, elemental Al in the coating can diffuse outwards into the TGO freely. The composition of the coating as-deposited was changed with the diffusion of elements. And Al-enriched irregular sphere gray structure (Fig. 9c, Point 7) was formed with Al content increased from about 6% (Fig. 5b, Point 2) to about 13%. Since this Al-enriched irregular sphere gray structure was distributed uniformly near the surface of the coating, it could act as the Al reservoirs and ensure that the enough Al content to form Al₂O₃. And the element distribution maps (Fig. 11) describes the Al segregation on the coating surface contributed to the formation of Al₂O₃. After 50 h oxidation, no Al depletion was observed, proved that the Al reservoirs was sufficient for consumption during oxidation. Thus, both the activity and the content of Al available for the formation of Al₂O₃ were optimized in the coating deposited by HSLC.

Since the growth rate of Al₂O₃ was much lower than Ni, Co, Cr oxides, an outer oxidation layer of mixed oxides would be formed attributed to the outward diffusion of Ni, Co, Cr and Ta through the Al₂O₃ scale. Therefore, a duplex TGO having inner layer of mainly Al₂O₃ and outer layer of the mixed oxides of Ni, Cr, Co and spinels could be formed for HSLC coating, which was also be observed in APS coating [25,51]. In HSLC coating, CuO also existed in the outer oxidation layer because of its higher content in as-deposited coating. Due to the lower standard Gibbs free energy of element Cr, the oxides of Ni and Co could be deoxidized by Cr₂O₃, and a large amount of Cr₂O₃ would be formed [40], resulting the higher content of Cr on the coating surface than other elements, proved by EDS analysis in Fig. 11 and element distribution on the surface of coating after 25 h and 50 h thermal exposure shown in Table 3. Cr₂O₃ could decrease the diffusion rate of oxygen and reduce the activity of oxygen between oxide film and coating interface [21]. Consequently, an oxide scale composed of two layers was formed and randomly distributed over the surface of Ti-Cu-NiCoCrAlTaY coating deposited by HSLC, the outer of mixed oxides with Cr₂O₃ as the major component and the inner oxide layer mainly consisted of Al₂O₃.

Previous studies had demonstrated the durability of MCrAlY coatings in thermal exposure mainly relied on the microstructure, morphology and growth rate of TGO [21,25,51]. The failure of the coatings

<table>
<thead>
<tr>
<th>Point</th>
<th>O</th>
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<th>Ti</th>
<th>V</th>
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Table 3 EDS results of oxidized Ti-Cu-NiCoCrAlTaY coating at different position.
mainly resulted from the excessive growth of non-protective oxides, such as spinel, NiO, and CoO. Due to the dense, continuous and refined microstructure of as-deposited coating and slowly grown TGO, HSLC coatings exhibit great oxidation resistance and durability in thermal exposure.

5. Burn resistance behavior of TC4 titanium alloy and Ti-Cu-NiCoCrAlTaY coated alloy

5.1. Surface morphology after laser melting test

Laser spot melting test was carried out with the irradiation of 500 W laser for 5 s on TC4 titanium alloy and Ti-Cu-NiCoCrAlTaY coated TC4 alloy. After laser spot melting, the surfaces of the samples were all severely oxidized and burnt. Some part of the melted alloy was evaporated or spattered and a hole was left on the laser-melt surface.

For TC4 titanium alloy, the diameter of the laser-melt area was about 3200 μm, including surrounding burning products and a central round-like blind hole with a diameter of about 2000 μm and depth of about 1400 μm (Fig. 12a, b).

Laser-melt area of Ti-Cu-NiCoCrAlTaY coated alloy (Fig. 12c, d) was relatively flat, exhibited chrysanthemum-like appearance and the central blind hole was basically disappeared. Under the same laser beam and heat input, the diameter of the laser-melt area was about 3200 μm, same as TC4, while the depth of the hole was only about 500 μm. The surrounding burning products also decreased significantly. The results illustrated with the protection of the Ti-Cu-NiCoCrAlTaY coating, the appearance of the blind hole on the burning area of TC4 alloy was avoided and the ablation decreased obviously.

The cross-sectional image of TC4 alloy’s burning area is shown in Fig. 13a–c. The morphology of the burning area at the top and bottom of the blind hole was quite different. Burnt products gathered at the top of the blind hole, showing loose structure with pores and cracks (Fig. 13a), which can act as the diffusion channel of oxygen. And a cracked titanium oxide scale existed on the surface of the burning products, as seen in Fig. 13b. The burnt products mainly consist of high valence oxides of titanium with a small amount of Al oxides (Points 1 and 2), showed by EDS analysis in Table 4. Only titanium oxide appeared on the surface of TC4 alloy at the bottom of the blind hole, as shown in Fig. 13c.

For Ti-Cu-NiCoCrAlTaY coated alloy, the morphology of the burning area at different positions was almost the same. Titanium oxides segregated on the edge of the burning area, that is the combustion front, and the atomic percentage of O to Ti was 1.65:1, between 1:1 (TiO) and 2:1 (TiO₂), which meant the principal phase compositions were TiO and TiO₂, shown in Fig. 13d. In the other burning areas, titanium oxide (Point 3) distributed on the matrix which was mainly composed of Ti and Cu (Point 4), as observed by EDS analysis in Table 4. The morphology of titanium oxide was changed from cellular structure to dendritic crystals under different cooling rates, and the grain size became smaller from the surface to the deep burning area, as shown in Fig. 13e, which meant the diffusion of oxygen was prevented and the precipitation of titanium oxide was restrained. There was a transition zone between the substrate and the burning area which was mainly consisted of Ti and Cu, as shown in Fig. 13f. The EDS analysis results shows that Cu was 26 wt% in region 5 and 45 wt% in region 6.

High-speed camera images acquired during the laser spot melting process under 500 W continuous laser on TC4 titanium alloy are shown in Fig. 14. The surface of TC4 alloy was fused to form the molten pool at 25 ms (Fig. 14a). Since the heat source of the laser beam was Gaussian distributed heat resource, the beam density reached the peak value in the center of the molten pool where the keyhole began to appear at 30 ms (Fig. 14b). It indicated that the oxide scale generated on the surface of the burnt TC4 alloy cannot prevent the expansion of thermal effect, the combustion heat penetrated to TC4 titanium alloy immediately after ignition. The depth of keyhole increased gradually and the range of the molten pool expanded steadily between 100 and 300 ms (Fig. 14c–d). Melt and oxidized products accumulated at the edge of molten pool at 500 ms (Fig. 14e).

With the keyhole acted as oxygen and heat transfer channel, the ablation of TC4 alloy proceeded, the vaporization of the molten pool occurred, and the surface of molten pool became depressed at 1500 ms.
As burning proceeded, the diameter of the keyhole increased and the surface of the molten pool collapsed deeper. More burnt products accumulated at the edge of the molten pool between 2000 and 3000 ms, shown in Fig. 14(i–j). At 4000 ms almost all the molten pool collapsed, the keyhole still exited. At 5000 ms the molten pool collapsed completely and the blind hole appeared instead of a keyhole. Since the blind hole was developed from the molten pool, the diameter of the blind hole was almost the same as the laser spot (2 mm) and the burnt products distributed around the blind hole under the action of heat flow.

High-speed camera images for Ti-Cu-Ni-CoCrAlTaY coated titanium alloy are shown in Fig. 15. The surface of Ti-Cu-NiCoCrAlTaY coating was fused and the molten pooling was formed at 500 ms (Fig. 15b), that is 20 times of TC4 alloy. Subsequently, the molten pool expanded continuously between 800 and 3000 ms (Fig. 15c–f). The oxidized and melted coating effectively prevented the penetrating of the laser power to the base metal. At 3500 ms (Fig. 15g), a small hole began to appear in the center of the molten pool which meant the heat began to spread to the base metal. But the coating still exhibited the function as the thermal barrier. The surface of the molten pool only collapsed slightly.
creased gradually. The oxide produced a series of oxides from low to high valence, the density decreased and a molten pool was formed. For TC4 alloy, titanium both TC4 alloy and Ti-Cu-NiCoCrAlTaY coated alloy were melted immediately. NiCoCrAlTaY coating is depicted in Fig. 16. At onset of the ignition, the combustion process was delayed. With the elimination of the keyhole, only a small hole was left instead of the blind hole, proved the ablation was decreased. Thus, the burning damages into the TC4 substrate were not formed, with a small hole appeared instead.

The combustion process and burn resistant mechanism of Ti-Cu-NiCoCrAlTaY coating is only 0.38 times of TC4 alloy, so that the diffusion ratio of oxygen is prevented gradually. Table 4 shows that the oxygen mainly existed in the form of titanium oxide and the grain size become smaller from the surface to the deep burning area, that is, the oxygen mainly existed in the form of titanium oxide and the grain size become smaller from the surface to the deep burning area, showing that the oxygen mainly existed in the form of titanium oxide and the grain size become smaller from the surface to the deep burning area.

5.2. Mechanism of flame-retardant functions of TC4 and Ti-Cu-NiCoCrAlTaY coating

The combustion process is a rapid and intense oxidation reaction which including oxidation at high temperature, ignition and continuous combustion. The oxygen, heat and fuel are necessary factors for the combustion process was delayed. With the elimination of the keyhole, only a small hole was left instead of the blind hole, proved the ablation was decreased. Thus, the burning damages into the TC4 substrate were retarded, Ti-Cu-NiCoCrAlTaY coating exerted the functional effects of flame-retardant property.

The combustion process and burn resistant mechanism of Ti-Cu-NiCoCrAlTaY coating is depicted in Fig. 16. At onset of the ignition, both TC4 alloy and Ti-Cu-NiCoCrAlTaY coated alloy were melted immediately and a molten pool was formed. For TC4 alloy, titanium produced a series of oxides from low to high valence, the density decreased gradually. The oxide film on the surface had a certain resistance to the interdiffusion of oxygen. However, it had been proved that with the increase of temperature, the solubility of oxygen in titanium increased which resulted in anoxic environment in oxide, and the oxidation reaction would turn into reduction reaction. With the decrease in the density of oxide film, the oxide film cracked and even fell off during the unbalanced process. As a result, the interdiffusion speed of oxygen increased sharply, and the heat generation rate exceeded the heat loss rate, with the rapid increase of the temperature, the oxidation reaction developed into combustion quickly [53]. Previous studies [54] had demonstrated that the oxidation reaction of titanium was quite intense in the combustion process, as the combustion temperature exceeded the boiling points, Ti and TiO2 evaporated and spattering occurred during the laser spot melting test.

While for Ti-Cu-NiCoCrAlTaY coated alloy, with the protection of the coating, the combustion process was delayed and the ablation was less. The reason was that, firstly, the high thermal conductivity of Cu. According to the calculation results based on JMatPro, the thermal conductivity of Cu, Ti and Ni is 462, 21, 74 W/M·K at 800 °C, and 464, 22, 76 W/M·K at 900 °C, respectively, which indicated that the thermal conductivity of Cu is much higher than that of other elements, even 20 times higher than that of titanium. Since the content of Cu in Ti-Cu-NiCoCrAlTaY coating was about 40 wt%, enough Cu can increase the heat dissipation rate, reduce the accumulation of heat and make the heat distribution more uniformly, resulting in the reduction of the ignition probability. At the same time, the heat release from the oxidation reaction of Cu is much lower than that of Ti, which can decrease the combustion heat. Since the melting point of CuO and Cu2O was 1050 °C and 1235 °C [55], lower than other oxide, CuO and Cu2O would evaporate before other oxides melted. Because the evaporation of CuO and Cu2O is endothermic reaction, part of the combustion heat can be taken away to reduce the temperature of the coating system.

Then, the burning product is formed through the outward diffusion of alloy elements and inward diffusion of oxygen. Although the burning product for both TC4 and Ti-Cu-NiCoCrAlTaY coated alloy was mainly titanium oxide, the diffusion ratio of oxygen was different for them. According to Fick's first law, the diffusion ratio is proportional to the oxidation rate [56], it can be seen the oxidation mass gain ratio of Ti-Cu-NiCoCrAlTaY coating is only 0.38 times of TC4 alloy, so that the diffusion ratio of oxygen was lower in Ti-Cu-NiCoCrAlTaY coated alloy. And the formation of Al2O3, Cr2O3, CuO, Cu2O and spinels in the coating could consume oxygen, the diffusion rate and transmission capacity of oxygen could be diminished. Burning area shown in Fig. 13 shows that the oxygen mainly existed in the form of titanium oxide and the grain size become smaller from the surface to the deep burning area, means the diffusion of oxygen is prevented gradually.

Thirdly, with the penetration of the laser energy, the substrate connected to the coating is melted, and Ti of TC4 will diffuse to the molten pool. So that low melting eutectic could be formed, with the
reaction of Ti and Cu, whose eutectic temperature is 925–990 °C, and the transition zone is formed in Fig. 13f. The ignition temperature of titanium in air was about 1600 °C, higher than the melting point of Ti–Cu eutectic. The intermetallic compounds will melt and precipitate liquid phases before ignited [57], and part of the combustion heat can be absorbed as the liquid precipitation was endothermic process. Meanwhile, the diffusion of Ti to the molten pool was prevented. Besides, the generated liquid phase can act as lubricant during dramatic impact or high speed friction situation to avoid rigid friction and if the titanium fire occurred, the spread of the titanium fire would be restrained then.

The laser heat source creates local overheating in the center of the molten pool. The molten pool would flow under Marangoni phenomenon induced by surface tension gradients [58], which is caused by temperature gradients, so that Ti flows in the molten pool under the convection of the fused liquid. Since TiO2 has lower Gibbs free energy, titanium is readily oxidized as compared to other oxides, titanium oxide was formed and segregated in the combustion front as shown in Fig. 13d. With the oxidation of titanium, the combustion was inevitable, the same as TC4 alloy.

Both TC4 and Ti-Cu-NiCoCrAlTaY coated alloy could be ignited if the heating time is enough. For Ti-Cu-NiCoCrAlTaY coated alloy, under the great heat dissipation rate, lower diffusion ratio of oxygen, and the existence of Ti–Cu eutectic transition zone, the combustion process is delayed. Meanwhile, due to the formation of transition zone, less titanium diffused and oxidized in the combustion front, and the ablation can be decreased. So Ti-Cu-NiCoCrAlTaY coating showed good flame-retardant property on TC4 substrate.

6. Conclusion

(1) Novel high speed laser cladding technology is used to successfully develop a pores and cracks free Ti-Cu-NiCoCrAlTaY coating over TC4 alloy, having compact microstructure with suitable thickness and surface roughness.

(2) Compared to TC4 alloy, Ti-Cu-NiCoCrAlTaY coated alloy follows the rule $\Delta m^{2.22} = 0.99t$ with the index of oxidation rate of 2.22, and exhibits good oxidation performance at 800 °C with double layered oxide scales. The outer layer consists of mixed oxides where Cr2O3 is the major component and the inner oxide layer mainly composed of Al2O3.

(3) Under the great heat dissipation rate, lower diffusion ratio of oxygen, and the existence of Ti–Cu eutectic transition zone, the combustion process is delayed, and the ablation is decreased, Ti-Cu-NiCoCrAlTaY coating exerts functional effects of flame-retardant property on TC4 substrate.

CRediT authorship contribution statement

Lou Li-Yan: Data curation, Writing - review & editing,
Methodology. **Zhang Yu:** Investigation. **Jia Yun-Jie:** Visualization. **Li Yan:** Investigation. **Tian Hong-Fang:** Validation. **Cai Yu-Jun:** Supervision. **Li Cheng-Xin:** Resources, Conceptualization.

**Declaration of competing interest**

We declare that we have no financial and personal relationships with other people or organizations that can inappropriately influence our work. There is no professional or other personal interest of any nature or kind in any product, service or company that could be construed as influencing the position presented in, or the review of, the manuscript entitled “High Speed Laser Cladded Ti-Cu-NiCoCrAlTaY Burn Resistant Coating and its Oxidation Behavior”.

**Fig. 15.** High-speed camera images of Ti-Cu-NiCoCrAlTaY coated titanium alloy during laser spot melting process.

**Fig. 16.** Schematic illustration of flame-retardant mechanism of Ti-Cu-NiCoCrAlTaY coated alloy.


