**In-situ synthesis, microstructure, and properties of NbB$_2$–NbC–Al$_2$O$_3$ composite coatings by plasma spraying**

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**Abstract:** The high melting point and strong chemical bonding of NbB$_2$ pose a great challenge to the preparation of high-density nanostructured NbB$_2$ composite coating. Herein, we report a novel, simple, and efficient method to fabricate *in-situ* NbB$_2$–NbC–Al$_2$O$_3$ composite coating by plasma spraying Nb$_2$O$_5$–B$_4$C–Al composite powder, aiming at realizing the higher densification and ultra-fine microstructure of NbB$_2$ composite coating. The microstructure and properties of *in-situ* NbB$_2$–NbC–Al$_2$O$_3$ composite coating were studied comparatively with *ex-situ* NbB$_2$–NbC–Al$_2$O$_3$ composite coating (plasma spraying NbB$_2$–NbC–Al$_2$O$_3$ composite powder). The reaction mechanism of Nb$_2$O$_5$–B$_4$C–Al composite powder in plasma jet was analyzed in detail. The results showed that the *in-situ* nanostructured NbB$_2$–NbC–Al$_2$O$_3$ composite coating presented a lower porosity and superior performance including higher microhardness, toughness and wear resistance compared to the plasma sprayed *ex-situ* NbB$_2$–NbC–Al$_2$O$_3$ coating and other boride composite coatings. Densification of the *in-situ* NbB$_2$–NbC–Al$_2$O$_3$ coating was attributed to the low melting point of Nb$_2$O$_5$–B$_4$C–Al composite powder and the exothermic effect of *in-situ* reaction. The superior performance was ascribed to the density improvement and the strengthening and toughening effect of the nanosized phases. The *in-situ* reaction path could be expressed as: Nb$_2$O$_5$ + Al → Nb + Al$_2$O$_3$, and Nb + B$_4$C → NbB$_2$ + NbC.

**Keywords:** NbB$_2$–NbC–Al$_2$O$_3$ composite coating; plasma spray; *in-situ* synthesis; Nb$_2$O$_5$–B$_4$C–Al system

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1 Introduction

NbB₂, one of the transition metal diborides, is widely applicable to many fields such as aerospace, military, and metallurgy due to its high hardness, high chemical stability, high thermal and excellent wear resistance [1–4]. Moreover, it is also regarded as a promisingly protective coating material for the nose cones of hypersonic vehicles and components in abrasive conditions [5]. Currently, NbB₂ composite coatings have been fabricated and studied by various technologies, such as the chemical vapor deposition (CVD) [6], boronizing [7,8], pack cementation method [9–11], magnetron sputtering [12–15], laser cladding [16], and plasma spraying [17]. Among them, the plasma spraying has unique advantages for manufacturing a refractory ceramic coating due to the high jet temperature, high production efficiency, and convenient operation. Up to now, some scholars have successfully prepared TiB₂ and ZrB₂ composite coatings by plasma spraying [18,19]. Nevertheless, the high melting point and strong chemical bonding of borides lead to a poor sinterability [1], which finally results in the high porosity of the as-sprayed coating. For example, Han et al. [20] and Zou et al. [21] fabricated TiB₂–TiC composite coatings with porosity as high as 20% and 12.7% by plasma spraying, respectively. High porosity will inevitably weaken the mechanical properties of the composite coating. To realize the densification of the boride composite coating by plasma spraying, some scholars have proposed many solutions: (i) Doping modification by the introduction of metals with a low melting point, but the hardness and wear resistance of the coating by this approach were reduced [22]. (ii) Eutectic composition, namely the melting point of the composite powder was reduced by forming a eutectic phase to increase the coating compactness [23,24]; however, this process is complicated and requires preprocessing the induction plasma spheroidization (IPS) on the composite powder, which increases the cost. (iii) Reactive plasma spraying (RPS). RPS combines the advantages of the atmospheric plasma spraying (APS) with in-situ reaction, and submicron-sized or nano-sized grains can be formed in the coating prepared by RPS, which can dramatically improve the mechanical properties of the ceramic coatings. Meanwhile, the exothermic reactions as a second heat source can further promote the melting of the powder and improve the compactness of coating [25,26]. In recent years, numerous scholars have prepared TiB₂–TiC [19,27] and ZrB₂–ZrC [28] coatings by different reaction systems. Therefore, RPS is a potential method for preparing NbB₂ composite coating.

In our previous work [17], NbB₂–NbC composite coating was successfully synthesized by the in-situ reaction of Nb–B₄C system, and the density of the coating was improved compared with ex-situ NbB₂–NbC composite coating. To further reduce the porosity of NbB₂–NbC composite coating, the doping modification by the introduction of Al₂O₃ was carried out in this study. Meanwhile, a ternary reactive system (Nb₂O₅–B₄C–Al) was designed to prepare the compact NbB₂–NbC–Al₂O₃ composite coating. In this system, Nb₂O₅ was used as a niobium source, and the high exothermic effect of thermite reaction between Nb₂O₅ and Al could further reduce the porosity of the NbB₂ composite coating. The microstructure and properties of these two NbB₂–NbC–Al₂O₃ composite coatings were investigated comparatively, and the formation mechanism of these two coatings and reaction mechanism of Nb₂O₅–B₄C–Al system were revealed. This study provides a novel idea for the densification of other boride ceramic coatings.

2 Materials and experimental procedure

2.1 Experimental materials and coating process

Commercial pure Nb₂O₅ powder (99.9%, ~1 μm, Qinhuangdao Taijihan Nano Products Co., Ltd., China), B₄C powder (99.9%, ~1.5 μm, Mudanjiang Boron Carbide Factory, China), and Al powder (99.8%, 6–9 μm, Ansteel Industrial Micro Aluminum Powder Co., Ltd., China) were used as raw materials of Nb₂O₅–B₄C–Al system, and the molar ratio of theoretical composition was Nb₂O₅ : B₄C : Al = 3 : 2 : 10. NbB₂ powder (99.5%, 5–10 μm, Shanghai Xianxin New Material Technology Co., Ltd., China), NbC powder (99.9%, 1–3 μm, Shanghai Xianxin New Material Technology Co., Ltd., China), and Al₂O₃ powder (99%, ~40 nm, Shanghai Pantian Nano Powder Co., Ltd., China) were used as raw materials of NbB₂–NbC–Al₂O₃ system, and the molar ratio of theoretical composition was NbB₂ : NbC : Al₂O₃ = 4 : 2 : 5. Figure 1 is the XRD patterns of the raw powder. In Fig. 1, Nb₂O₅, B₄C, Al, and NbC powder existed as a stable α-phase and NbB₂ powder existed as a single phase without impurity, Al₂O₃ powder existed as a stable α-phase and NbB₂ powder contained little Nb₂B₃ and Nb₅B₆.

The dispersant (sodium polyphosphate), binder (CMC
solution), and deionized water were added into these two kinds of feedstocks. After ultrasonic vibration for 30 min and centrifugal stirring for 1.5 h, the slurry with homogeneous mixture and good fluidity was obtained. Then two obtained mixed slurries were spray-dried to prepare spherical agglomerate powder. The specific experimental parameters of the spray drying process were as follows: (i) the inlet temperature was 230 °C; (ii) the outlet temperature was 120 °C; (iii) the feed pump rate was 35 r/min; and (iv) the rotation speed of the atomization disc was 3000 r/min. Finally, two kinds of composite powder were dried at 150 °C and sieved through the sieve of 200–300 mesh.

TC4 titanium alloy (Al 5.5–6.5 wt%, V 3.5–4.5 wt%, Fe, Si, C, and O slight, Ti balance, Beijing Qianshuo Nonferrous Metal Products Co., Ltd., China) with the dimension of 10 mm × 10 mm × 10 mm was used as a substrate material, and its surface was grit blasted to obtain a rough surface. Before spraying, in order to improve the bonding strength between the coating and substrate, a NiAl bonding layer (Ni 80 wt%, Al 20 wt%, Hangtian Zhenbang Co., Ltd., China) with a thickness of 50–100 μm was sprayed on the surface of the substrate. Two feedstocks were deposited onto the substrate by using a GP-80 type plasma spraying system (Jiu Jiang Spraying Device Co., Ltd., China). The specific experimental parameters of the plasma spraying were as follows: (i) the voltage and current were 70 V and 500 A, respectively; (ii) the primary gas (Ar) and secondary gas (H2) flow rate were 1.33 and 0.33 L/s, respectively; (iii) the spray distance was ~100 mm; and (iv) the carrier gas flow rate was 6.67 × 10⁻³ L/s and the powder feed rate was 0.15 g/s.

2.2 Characterization

The phase compositions of powder and as-sprayed NbB₂–NbC–Al₂O₃ coatings were identified by the X-ray diffraction (XRD, Rigaku Smartlab 2500/PC, Cu Kα radiation, step size of 0.02°), and the spectra were collected in the 2θ range of 20°–80°. The microstructure of the coatings and powder were characterized by the scanning electron microscope (SEM, HITACHI S-4800) equipped with the energy dispersive spectroscopy (EDS). Furthermore, the microstructure and crystallographic features of Nb₂O₅–B₄C–Al coating were determined by the transmission electron microscopy (TEM, Philips Tecnai F20). The porosity measurement of the coatings with cross-section was performed on ten SEM images per coating, each recorded at a magnification of 500×.

The thermodynamic calculation was carried out for exploring the reaction mechanism of Nb₂O₅–B₄C–Al system. To explain the specific reaction process, differential thermal analysis and heat treatment were performed. Differential thermal analysis (DTA)/thermogravimetric analysis (TG) of Nb₂O₅–B₄C–Al composite powder was carried out under the protection of Ar gas, the heating rate was 10 °C/min, and the temperature was up to 1250 °C. Heat treatment for composite powder was performed at 900, 1000, 1100, and 1200 °C, and the holding time was 1 h.

2.3 Property characterization

The microhardness of as-sprayed NbB₂–NbC–Al₂O₃ coatings was measured by a Vickers indenter (SHIMADZU HMV-2) at a load of 0.98 N with a dwell time of 15 s (twenty indentations for each sample). The indentation morphology test was performed with a load of 4.9 N for 15 s, and the toughness of the coatings was characterized by observing the indentation morphology and fracture morphology of the coatings under a scanning electron microscope. The fracture samples without substrates
were stripped off by a procedure utilizing mismatch in the thermal expansion coefficients. These coatings were deposited onto an unheated and polished 45 steel substrate. Then, the as-prepared samples were immediately placed in water (25 °C), and the coatings peeled off. The setup of the wear test was ball-on-disc (SFT-2M tribometer), the counter body material of ball was Si3N4 with a diameter of 4 mm, and the parameters were set as follows: the normal load on each disc 30 N, the rotation speed 6.67 r/s, the wear time 10 min and the measurement method cyclic friction. Wear rate and wear scar profile were used to evaluate the wear resistance. Wear rate was calculated according to Eq. (1):

$$W = \frac{V}{2\pi nrtF}$$

where $W$ is the wear rate (mm$^3$/N·m), $V$, $t$, and $F$ are the worn volume (mm$^3$), the wear time (s), and the load (N), respectively, $r$ is the center distance (m), and $n$ is the rotation speed (r/s).

3 Results and discussion

3.1 Microstructure of two composite powder and coatings

Figures 2(a) and 2(b) show the morphology of two composite powder after spray drying. The composite powder with smooth surfaces were spherical or ellipsoidal in a diameter range of 20–70 μm. The fluidity of spherical powder was superior to other shapes of powder, which was conducive to stable and uniform powder feeding, thus improving the deposition efficiency of powder [29]. It is worth noting that Nb$_2$O$_5$–B$_4$C–Al powder exhibited a smaller and more uniform size than NbB$_2$–

![Fig. 2](image-url)  
**Fig. 2** SEM micrographs of composite powder: (a) NbB$_2$–NbC–Al$_2$O$_3$, and (b) Nb$_2$O$_5$–B$_4$C–Al.

...was beneficial to the full melting of the powder. According to the XRD patterns (Fig. 3), NbB$_2$–NbC–Al$_2$O$_3$ composite powder were composed of NbB$_2$, NbC, α-Al$_2$O$_3$, and a small amount of NbB and Nb$_5$B$_6$ (from raw powder). Nb$_2$O$_5$–B$_4$C–Al composite powder comprised Nb$_2$O$_5$, B$_4$C, and Al, without other impurity phases. In summary, the raw powder with high sphericity were prepared via spray drying, which could ensure the uniform heating of composite powder.

The XRD patterns of as-sprayed NbB$_2$–NbC–Al$_2$O$_3$ composite coatings by the ex-situ and in-situ methods are shown in Fig. 4. NbB$_2$–NbC–Al$_2$O$_3$ coating was mainly comprised of NbB$_2$, NbC, α-Al$_2$O$_3$, and γ-Al$_2$O$_3$, and small amounts of NbB and Nb$_5$B$_6$ were also presented in the coating. The phase transition (from stable α-Al$_2$O$_3$ to metastable γ-Al$_2$O$_3$) occurred in a part of Al$_2$O$_3$ relative to NbB$_2$–NbC–Al$_2$O$_3$ composite powder during the plasma spray. There were two reasons for the formation of metastable phase γ-Al$_2$O$_3$ [30]: (i) γ-Al$_2$O$_3$ possessed lower nucleation energy compared with α-Al$_2$O$_3$, so γ-Al$_2$O$_3$ was formed firstly as the molten droplet cooling; and (ii) the formation of γ-Al$_2$O$_3$ was also attributed to the rapid cooling (10$^6$ K/s) of molten Al$_2$O$_3$. It is noteworthy that α-Al$_2$O$_3$ phase still was contained in the coating, which might be ascribed to the following two reasons: (i) the existence...
of α-phase was inherited from the partially melted or unmelted α-Al2O3 phase primary particles of the feedstocks [31,32]; and (ii) during the cooling process of the deposited coating, the phase transformation from γ-Al2O3 to α-Al2O3 was caused by the reheating of plasma jet [33]. For Nb2O5–B4C–Al coating (Fig. 4(b)), which was composed of NbB2, NbC, α-Al2O3, γ-Al2O3, Nb2O5, NbO2, and Nb2C, new phases NbB2, NbC, α-Al2O3, NbO2, and γ-Al2O3 appeared in the coating relative to composite powder, demonstrating that new phases were formed as a result of the reaction between Nb2O5, B4C, and Al. Moreover, the diffraction peaks of Nb2O5–B4C–Al coatings were wider than its composite powder, which meant that finer grains were formed during the RPS. An obvious phenomenon is that the peak intensity of NbC was low. The decrease of NbC diffraction peak intensity was mainly caused by the following two aspects: (i) a part of the product NbC decarbonize to form Nb2C at a high temperature, which could be confirmed by XRD (Fig. 4(b)); and (ii) according to Bao et al.’s study [34], serious decarbonization will occur when B4C participates in SHS reaction at a high temperature. Therefore, speculating that the carbon loss was caused by the decarbonization of B4C in plasma spraying, which could lead to the decrease of the diffraction peak intensity of NbC. It should be noted that obvious broad peaks (30° < 2θ < 45°) were observed in the XRD spectra of Nb2O5–B4C–Al coating, which meant that amorphous existed in this composite coating.

Figure 5 shows the cross-sectional structure of two composite coatings. Lamellar structure in NbB2–NbC–Al2O3 coating was not obvious, and the coating had some obvious pores. In contrast, Nb2O5–B4C–Al coating possessed the typical lamellar structure of thermal spraying coatings. Furthermore, nanoscale particles could be observed in Nb2O5–B4C–Al coating, and they might be NbB2 and NbC obtained by the in-situ reaction. The porosities of NbB2–NbC–Al2O3 and Nb2O5–B4C–Al coatings was 7.9% and 6.2%, respectively, and Nb2O5–B4C–Al coating showed better compactness. In the preparation of NbB2–NbC–Al2O3 coating process, although the pores could be filled by Al2O3 with a low melting point, the NbB2 (3050 °C) and NbC (3610 °C) could not be fully melted in plasma jet due to their inherent high melting point. The unmelted ceramic particles did not merge with each other during the deposition of the coating and cooling induced shrinkage, and they became detached from each other, thus causing
porosity. In the preparation of Nb₂O₅–B₄C–Al coating process, the composite powder had a well-melted state in plasma jet because of the low melting point of Nb₂O₅, B₄C, and Al. Moreover, in addition to the heat provided by the plasma jet, another source of heat that originated from the *in-situ* reaction promoted the further melting of the feedstocks [35]. Hence, the porosity of Nb₂O₅–B₄C–Al coating was lower than that of NbB₂–NbC–Al₂O₃ coating. Compared with the NbB₂–NbC composite coating (9.6%) prepared by plasma spraying Nb–B₄C composite powder in the previous study [17], the porosity was reduced by 35.4% (*in-situ* approach) and 21.5% (*ex-situ* approach). The porosity results show that the doping modification by introducing Al₂O₃ with a low melting point and the design of ternary reactive system (Nb₂O₅–B₄C–Al) can obviously improve the density of NbB₂ composite coating, and the latter shows better densification.

The EDS results of the cross-sectional macrostructure of the composite coatings are listed in Table 1. Combining with the XRD results, it can be inferred that the white irregular area (region A) in NbB₂–NbC–Al₂O₃ coating was rich in NbB₂ and NbC phases, and the dark gray structure in the region B was rich in Al₂O₃. In Nb₂O₅–B₄C–Al coating, all the regions contained five elements, indicating that a well-mixed melt was formed during plasma spraying. White structure (region C) was mainly composed of NbB₂ and NbC, light gray (region D) mainly contained NbB₂, NbC, and Nb₂O₅, and dark gray (region E) might consist of NbB₂, NbC, Al₂O₃, and Nb₂O₅. The black structure (region F) mainly consisted of Al₂O₃, and it might contain B₄C.

By combining EDS and the cross-sectional structure of NbB₂–NbC–Al₂O₃ coating, nano-particles are observed. To further characterize the phase composition of the coating, the TEM images of the coating are shown in Fig. 6. NbB₂–NbC–Al₂O₃ coating comprised many nanograins with sizes ranging from tens to hundreds of nanometers. In Fig. 6(a), the whole area was composed of a large number of equiaxed grains with good uniformity, and they were identified as NbB₂. There were many spherical nanoparticles uniformly distributed in Fig. 6(b), and they were identified by selected area electron diffraction (SAED) analysis as NbC. Spherical grains with a size range of 10–50 nm was observed in Fig. 6(c), the ultrafine-sized grains were uniformly distributed, and they were identified as γ-Al₂O₃. In addition, there were two irregular regions A and B in Fig. 6(d), and they were identified as amorphous based on their SAED. The EDS results (Figs. 6(e) and 6(f)) indicate that the region A was consisted of Al, Nb, and O, while the region B was composed of Al and O. The presence of amorphous diffraction spots was also consistent with the broad peaks in the XRD (Fig. 4(b)). The formation of amorphous phase structure in the coating was mainly attributed to the rapid cooling and solidification of the droplet during plasma spraying. According to McDonald et al.’s report [36], the cooling rate of droplet could reach up to 10⁷ K/s in plasma spraying.

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**Table 1 coatings**

| EDS results of two NbB₂–NbC–Al₂O₃ composite (Unit: wt%) |
|---|---|---|---|---|
| Element | B | C | O | Al | Nb |
| A | 49.15 | 8.07 | 1.66 | 0.81 | 40.31 |
| B | — | — | 37.87 | 62.13 | — |
| C | 40.48 | 16.41 | 3.39 | 1.14 | 38.58 |
| D | 28.41 | 15.55 | 16.33 | 0.64 | 39.07 |
| E | 25.52 | 7.05 | 23.30 | 21.37 | 22.85 |
| F | 16.92 | 7.33 | 32.85 | 40.86 | 2.040 |
| G | 50.29 | 9.29 | 3.16 | 3.17 | 34.09 |

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Fig. 6  TEM and EDS images of Nb_2O_5–B_4C–Al coating: (a) the microstructure of NbB_2 area, (b) the microstructure of NbC area, (c) the microstructure of γ-Al_2O_3 area, (d) the microstructure of amorphous area, and (e, f) EDS of regions A and B, respectively.

At such high cooling rate, the possibility of nucleation and crystal growth into crystals for the melt during solidification was greatly reduced. TEM results show that a large number of equiaxed nano-sized NbB_2 grains as well as spherical NbC and Al_2O_3 grains appeared in Nb_2O_5–B_4C–Al coating, and it is of great significance for improving the hardness, toughness, and other mechanical properties of the composite coating. Moreover, the existence of in-situ reaction was further confirmed.

3.2  Reaction mechanism of Nb_2O_5–B_4C–Al system

3.2.1  Thermodynamic calculation of Nb_2O_5–B_4C–Al system

NbB_2–NbC–Al_2O_3 composite coating was prepared by the in-situ approach in Nb_2O_5–B_4C–Al system, which not only had the physical change of traditional plasma spraying such as flight, impact, deformation, and solidification, but also had the corresponding chemical reactions and the release of considerable amounts of heat [37,38]. Through the analysis of reaction thermodynamics, the direction and degree of the reaction can be understood, and it is of great significance for the subsequent exploration of the reaction mechanism in Nb_2O_5–B_4C–Al system.

The reaction process of Nb_2O_5–B_4C–Al system was complex, and the possible reaction products included NbB_2, NbC, Al_2O_3, and NbO_2. Because plasma spraying was carried out in the atmosphere, O_2 should also be taken into account. The following reactions were likely to happen during the plasma spraying of Nb_2O_5–B_4C–Al composite powder.

\[
\begin{align*}
6\text{Al} + 3\text{Nb}_2\text{O}_5 & = 6\text{NbO}_2 + 3\text{Al}_2\text{O}_3 \\
4\text{Al} + 3\text{NbO}_2 & = 3\text{Nb} + 2\text{Al}_2\text{O}_3 \\
10\text{Al} + 3\text{Nb}_2\text{O}_5 & = 6\text{Nb} + 5\text{Al}_2\text{O}_3 \\
3\text{Nb} + \text{B}_4\text{C} & = 2\text{NbB}_2 + \text{NbC} \\
\text{B}_4\text{C} + 4\text{O}_2 & = 2\text{B}_2\text{O}_3 + \text{CO}_2 \\
4\text{Al} + 3\text{O}_2 & = 2\text{Al}_2\text{O}_3
\end{align*}
\]

According to thermodynamic data in the reference [39], the Gibbs free energy of the reactions was calculated. The Gibbs free energy of Eqs. (1)–(6) was negative from 298 to 3000 K in Fig. 7, indicating that all the reactions may occur. Equation (6) had the lowest Gibbs free energy, followed by Eqs. (5) and (3). It can be inferred that in the equilibrium reaction condition, the oxidation of raw powder (especially Al) in Nb_2O_5–B_4C–Al system was most likely to occur and form Al_2O_3 and B_2O_3. B_2O_3 would evaporate above 1200 °C, so the coating may not contain B_2O_3 phase [40]. It is noteworthy that there was only a small amount of oxidation of Al and B_4C due to the protection of Ar gas. The reaction between Al and Nb_2O_5 had relatively low Gibbs free energy, and liquid aluminum has good wettability, so the reaction would proceed faster once the temperature of the reaction reached critical temperature. Nb with significant activity was replaced by the reaction between Al and Nb_2O_5, and considerable amount of heat was generated to promote the reaction of Nb and B_4C. In addition, Nb_2O_5 would be surplus because of the loss of B_4C and Al, and NbO_2 might play the role of intermediate phase. Hence, the NbB_2, NbC, Al_2O_3, NbO_2, and NbO_2 might be the possible phases in view of the thermodynamic calculation, which was basically consistent with the actual XRD results (Fig. 4(b)).

Based on Merzhanov et al.’s empirical criterion [41],
the adiabatic temperature $T_{ad} \geq 1800 \, ^\circ C$ was required for the self-propagating reaction of the system to be self-sustaining. The reaction equation of $\text{Nb}_2\text{O}_5$–$\text{B}_4\text{C}$–$\text{Al}$ powder could be written as

$$3\text{Nb}_2\text{O}_5 + 2\text{B}_4\text{C} + 10\text{Al} \rightarrow 4\text{NbB}_2 + 2\text{NbC} + 5\text{Al}_2\text{O}_3 \quad (7)$$

$T_{ad}$ of Eq. (7) could be calculated by using Eq. (8):

$$\Delta H^\theta_{298} + \int_{298}^{T_{ad}} \sum n_i c_p (P_i) dT + \sum n_i L (P_i) = 0 \quad (8)$$

where $\Delta H^\theta_{298}$ is the reaction enthalpy at 298 K, $n_i$ and $c_p$ are the mole of each product and the molar heat capacity, respectively, and $L$ is the latent heat. The calculation result shows that the $T_{ad}$ of $\text{Nb}_2\text{O}_5$–$\text{B}_4\text{C}$–$\text{Al}$ system was 3734.1 K. Whereupon the self-propagating reaction of $\text{Nb}_2\text{O}_5$–$\text{B}_4\text{C}$–$\text{Al}$ system could be self-sustained from the perspective of adiabatic temperature. Also, $T_{ad}$ exceeded the melting point of $\text{NbB}_2$ (3300 K) and $\text{Al}_2\text{O}_3$ (2352 K), and just slightly below $\text{NbC}$ (3798 K) when the initial temperature was 298 K. In fact, the temperature of plasma jet was considerably higher than 298 K. Therefore, the reactants and products of $\text{Nb}_2\text{O}_5$–$\text{B}_4\text{C}$–$\text{Al}$ system could be fully melted in plasma spraying and this would help explain subsequent the formation of $\text{B}$–$\text{C}$–$\text{O}$–$\text{Al}$–$\text{Nb}$ liquid melt.

To quantitatively analyze whether the heat released from the reaction of $\text{Nb}_2\text{O}_5$–$\text{B}_4\text{C}$–$\text{Al}$ system promotes the melting of composite powder, the total energy needed to melt the stoichiometric ratio of the raw powder ($Q$) and the absolute value of the change in enthalpy ($|\Delta H|$) of Eq. (7) were calculated and compared. The total energy needed to melt the stoichiometric ratio of the raw powder could be expressed as

$$Q = \sum n_i \bar{c}_p (T_{melt} - T_0) + H \quad (9)$$

where $n_i$ is the stoichiometry at each of the reactants in Eq. (9), $\bar{c}_p$ is the average molar heat capacity of each reactant from $T_{melt}$ to $T_0$, $T_{melt}$ is the melting temperature of each reactant, $T_0$ is the room temperature, and $H$ is the change in enthalpy during a phase change. The result indicates that the $Q$ (2122.69 kJ) was less than the $|\Delta H|$ (3826.59 kJ), which indicated that the exothermic reaction of $\text{Nb}_2\text{O}_5$–$\text{B}_4\text{C}$–$\text{Al}$ system greatly promoted the melting of the raw powder to achieve the purpose of coating densification.

3.2.2 Reaction mechanism of $\text{Nb}_2\text{O}_5$–$\text{B}_4\text{C}$–$\text{Al}$ system during plasma spraying

To explain the microstructure evolution and reveal the specific reaction process of $\text{Nb}_2\text{O}_5$–$\text{B}_4\text{C}$–$\text{Al}$ system, the differential thermal analysis and heat treatment were performed.

The DTA/TG curve of $\text{Nb}_2\text{O}_5$–$\text{B}_4\text{C}$–$\text{Al}$ composite powder is illustrated in Fig. 8. As shown in the DTA curve, the endothermic peak at 649–670 $^\circ C$ and the exothermic peaks at 951–980 $^\circ C$ and 1018–1110 $^\circ C$ could be observed. The melting point of $\text{Al}$ was 660 $^\circ C$ and accompanied by thermal absorption; hence, the
endothermic peak at 649–670 °C corresponded to the melting of Al. As demonstrated by Mostaan et al. [42], the exothermic peak at 951–980 °C was attributed to the occurrence of Eq. (1). The exothermic peak at 1018–1110 °C was wide, the broadening of the exothermic peak indicated that multiple reactions may be involved [43], and the possible reactions included Eqs. (2)–(4). The exothermic peak at this stage was relatively high, which was beneficial to the full melting of raw powder. As shown in the TG curve, Nb2O5–B4C–Al composite powder experienced two stages, namely the weight gained stage and weight loss stage, during heating. The oxidation of Al resulted in the mass increase before 600 °C. The mass reduction in the range of 600–1200 °C might be caused by the oxidation of B4C into CO2. However, the weight change was negligible on the subsequent reactions.

The XRD patterns of Nb2O5–B4C–Al composite powder after heat treatment at 900, 1000, 1100, and 1200 °C are shown in Fig. 9. At 900 °C, several new phases such as NbO2 and α-Al2O3 appeared compared with Nb2O5–B4C–Al composite powder, and Al has melted at this moment. It could be inferred that the melting of Al took place preferentially, and then Nb2O5 reacted with molten Al in Eq. (1) to form NbO2 and α-Al2O3, which corresponded to the exothermic peak of 915–980 °C in the DTA curve. As compared to 900 °C, the diffraction peak of Al and Nb2O5 disappeared at 1000 and 1100 °C, which indicated that the thermite reaction (Eqs. (1) and (3)) has completed. New phases of NbB2, NbC, Nb, and NbB were presented, and B4C phase also existed, indicating that Eq. (4) was in progress, and NbB might exist as an intermediate phase. The phase composition at 1000 °C was basically the same as that at 1100 °C, which showed that Eq. (4) was also in progress. At 1200 °C, the diffraction peak intensity of NbB decreased and the diffraction intensity of NbB2 increased in contrast to 1100 °C, which may be caused by the reaction between NbB and B4C. Heat treatment at 1000–1200 °C corresponded to exothermic peaks of 1018–1110 °C in the DTA curve. The phase composition obtained by heat treatment was basically consistent with plasma spraying, but there was no γ-Al2O3, wherein the principal reason is that the heat treatment was a stable process, and the degree of supercooling and cooling rates was not as large as that in plasma spraying, so the α-Al2O3 had sufficient time to nucleate and grow. According to the results of DTA/TG and heat treatment, the liquid–solid reaction of the composite powder took place preferentially, namely Al melted and enveloped Nb2O5 and B4C powder, meanwhile triggering the self-propagating reaction. Then according to the above-inferred result of composite powder formed melt during the process of plasma spraying, suggesting the liquid–liquid reaction also existed. Therefore, the reaction mechanism of Nb2O5–B4C–Al system could be described as a liquid–solid-reaction–liquid–liquid-reaction. Firstly, Al melted and effectively filled the gap between Nb2O5 and B4C powder, and accelerated their melting, meanwhile triggering the self-propagating reaction to promote the formation of B–C–O–Al–Nb liquid melt. The orders of the whole process were Eqs. (1), (2), (3), and then (4).

3.3 Formation mechanism of two NbB2–NbC–Al2O3 composite coatings

The formation mechanism of NbB2–NbC–Al2O3 composite coating can be revealed by means of the phase analysis and microstructural analysis (the SEM micrographs of the cross-section). In the process of plasma spraying, only a part of Al2O3 phase transition (α→γ) occurred in NbB2–NbC–Al2O3 composite powder, and there was no chemical reaction between other feedstock particles, wherein the composite powder underwent melting and deposition. When the composite powder approached the plasma jet, the low-melting Al2O3 was preferentially melted and infiltrated into the gaps between NbB2 and NbC particles and enveloped them to promote their melting. Then most of NbB2 and NbC began to melt under the plasma jet and molten Al2O3, and the melted
droplets were formed. Finally, the Al$_2$O$_3$-based melt contained melted NbB$_2$/NbC deposited on the substrate. Significantly, Al$_2$O$_3$ melt and NbB$_2$/NbC melt did not mix well, and they tended to keep segregated, which was resulted from the different density and chemical bond between them. Schematic graphs of NbB$_2$–NbC–Al$_2$O$_3$ coating formation process are shown in Fig. 10(a).

The formation mechanism of Nb$_2$O$_5$–B$_4$C–Al coating can be described as the melting–reaction–deposition–precipitation, which can be schematically illustrated in Fig. 10(b). The melting of Al preferentially occurred, and the molten Al infiltrated into the B$_4$C and Nb$_2$O$_5$ particles, filled the gaps between B$_4$C and Nb$_2$O$_5$ powder, and increased the contact area and surface atom activity of reactants. Then, the self-propagating reaction was triggered by the molten Al, and it was accompanied by the release of a large amount of heat. The release of heat from the plasma jet and in-situ reaction promoted the formation of the B–C–O–Al–Nb liquid melt. Subsequently, the liquid melt was deposited on the substrate of sprayed NiAl. Then finely particles NbC and NbB$_2$ precipitated from the melt successively, and Al$_2$O$_3$ melt was pushed to the edge and solidified, eventually NbB$_2$–NbC–Al$_2$O$_3$ composite coating being synthesized.

3.4 Properties of as-sprayed NbB$_2$–NbC–Al$_2$O$_3$ composite coatings

3.4.1 Microhardness of NbB$_2$–NbC–Al$_2$O$_3$ coatings

The microhardness values of two composite coatings were 937.4 HV$_{0.1}$ (ex-situ) and 1188.7 HV$_{0.1}$ (in-situ). Obviously, the hardness of NbB$_2$–NbC–Al$_2$O$_3$ coating prepared by the in-situ approach was higher than that prepared by the ex-situ approach. The microhardness of the coating is closely linked to the microstructure and phase composition [44]. The denser the microstructure, the higher content of hard phase, and the higher microhardness of the coating. The hard phases of NbB$_2$ and NbC were the main source of the high microhardness of NbB$_2$–NbC–Al$_2$O$_3$ coating. Compared with ex-situ NbB$_2$–NbC–Al$_2$O$_3$ coating, the higher microhardness of in-situ NbB$_2$–NbC–Al$_2$O$_3$ coating was attributed to the compact microstructure, the low porosity, and the fine grain strengthening of NbB$_2$ and NbC.

3.4.2 Toughness of NbB$_2$–NbC–Al$_2$O$_3$ composite coatings

The indentation morphology of two composite coatings is illustrated in Fig. 11. The indentation edge of NbB$_2$–NbC–Al$_2$O$_3$ composite coating had obvious cracks (Fig. 11(a)) but no spalling. Crack propagation paths were intragranular and intergranular modes as shown in the local enlarged image (Fig. 11(b)). Crack branching and deflection could be observed, which demonstrates that the phase boundary toughening existed in this coating. In contrast to NbB$_2$–NbC–Al$_2$O$_3$ coating, the porosity of Nb$_2$O$_5$–B$_4$C–Al coating was lower, and cracks in the
indentation edge were not obvious (Fig. 11(c)). According to the partial enlarged image (Fig. 11(d)), the crack size was small, the crack propagation path was zigzag and was mainly intergranular modes, the phenomenon of crack branching and deflection also existed, and the toughening mechanism was chiefly a grain boundary toughening. Moreover, some cracks stopped propagating when they reached the fine grain zone (white dotted box zones), indicating that the fine grain by the in-situ reaction can effectively blunt the crack and prevent their propagation.

Figure 12 is the fracture morphology of two NbB$_2$–NbC–Al$_2$O$_3$ composite coatings. The fracture of as-sprayed NbB$_2$–NbC–Al$_2$O$_3$ coating by the ex-situ approach was flat. The existing morphology of NbB$_2$ and NbC in coating were blocky and there are some fine particles which could be seen in the region A. It is speculated that the fine particles (region A) were mixtures of NbB$_2$ and NbC, because their morphologies are similar to the NbB$_2$–NbC phase in Fig. 5(b). In addition, the formation of fine particles could be attributed to crystallization of the melt. Also, this coating had many pores, the size and shape of pores are different and irregular, and the stress concentration may occur. In Nb$_2$O$_5$–B$_4$C–Al coating, the fracture surface of sags and crests could be observed, and the crack propagation paths were zigzag, suggesting that more energy was consumed during fracture process. Furthermore, there were also some pores existed in this coating, and most of them were spherical. In contrast to the non-spherical pores, the spherical pores can significantly weaken the stress intensity factor of the crack tip, leading to blunting of crack tip to improve the toughness of the composite coating [45]. Therefore, it is fortunate that they existed as spheres although pores are inevitable.

In light of the indention and fracture morphology, the toughness of NbB$_2$–NbC–Al$_2$O$_3$ coating through the in-situ reaction was better than that through the ex-situ approach, which could be attributed to the following three reasons: (i) refinement strengthening of NbB$_2$, NbC, and Al$_2$O$_3$ by the in-situ reaction. The refinement of grains could increase the number of crystal boundaries and make the crack propagation path more zigzag (Fig. 11(d)) when crack extension occurred, so the toughening effect was achieved. Also, the smaller grain size, the smaller initial crack size, and correspondingly the higher fracture strength of the coating since the cracks were usually initiated at grain boundaries. (ii) The high fracture strength of Nb$_2$O$_5$–B$_4$C–Al coating was resulted from low porosity. Generally, the fracture strength of ceramic coating decreases with the increase of porosity. In the stress concentration zone, pores were prone to produce cracks and induce cracking under the load. Thus, the coating with lower porosity prepared by the in-situ approach had higher fracture strength [46]. Also, the existence of spherical pores in this coating could refrain the deterioration of toughness to a certain extent. And (iii) partially unmelted NbB$_2$ and NbC particles (due to their high melting point) located in NbB$_2$–NbC–Al$_2$O$_3$ coating would generate significant residual stress and might induce microcracks. In contrast, Nb$_2$O$_5$–B$_4$C–Al composite powder melted fully under the heating of plasma jet and exothermic heat from the reaction, so Nb$_2$O$_5$–B$_4$C–Al coating showed higher toughness than NbB$_2$–NbC–Al$_2$O$_3$ coating.

### 3.4.3 Tribological performance of two NbB$_2$–NbC–Al$_2$O$_3$ composite coatings

The coefficient of friction of two NbB$_2$–NbC–Al$_2$O$_3$ composite coatings is shown in Fig. 13(a). The wear process of two composite coatings was composed of the run-in stage and the stable wear stage. For NbB$_2$–NbC–Al$_2$O$_3$ coating, the run-in stage was approximately

![Fig. 12 Fracture morphology of two composite coatings: (a) NbB$_2$–NbC–Al$_2$O$_3$, and (b) Nb$_2$O$_5$–B$_4$C–Al.](www.springer.com/journal/40145)
180 s, and the coefficient of friction was increased with the increase of wear time. At this stage, the contact surface between Si$_3$N$_4$ ball and coating expanded from a point to an arc. The increase of the friction coefficient was the result of the increase of the contact area. Then it tended to decrease when it reached the maximum value, which was caused by the uneven microstructure of the coating. After 180 s, the wear process entered a stable stage with a certain fluctuation. The average friction coefficient of the whole stage was 0.63. As-sprayed coating by the in-situ approach presented a great difference compared with the coating by the ex-situ approach. The coefficient of friction increased to a stable value after about 20 s in the run–in stage, and the short run-in stage demonstrates that the coating quickly reached the stable stage due to its high microhardness [41]. The average friction coefficient of Nb$_2$O$_5$–B$_4$C–Al coating was 0.58, lower than that of NbB$_2$–NbC–Al$_2$O$_3$ coating, and the fluctuation range was small. Figure 13(b) shows a worn surface profile of two composite coatings. The depths of wear scar of two composite coatings were 119.6 and 89.1 μm. Also, the wear rates were $0.69 \times 10^{-3}$ and $0.53 \times 10^{-3}$ mm$^3$/N·m by Eq. (1). All the above discussions demonstrate that NbB$_2$–NbC–Al$_2$O$_3$ composite coating prepared by the in-situ approach exhibited better wear resistance than that prepared by the ex-situ approach, which attributed to the compact and refined microstructure as well as high microhardness. From Nb$_2$O$_5$–B$_4$C–Al coating, a uniform distribution of the microstructure ensured the uniformity of hardness, so the fluctuation of the coefficient of friction was low. The coating with high microhardness could effectively resist the abrasion of Si$_3$N$_4$ ball. From NbB$_2$–NbC–Al$_2$O$_3$ coating, the inhomogeneous microstructure led to much fluctuation of friction coefficient; particularly, the existed unmelted particles in the coating could also cause the decrease of compactness.

To explain the wear mechanism of two composite coatings, the morphology of the worn surfaces is observed. Figure 14 presents the morphology of the worn surfaces consisted of smooth and rough areas. The smooth area was the deformation layer formed by friction between Si$_3$N$_4$ ball and the dense microstructure in the coating, while the rough area was the chipping pit formed by the pores in the coating or the abrasion of the coating [47]. In NbB$_2$–NbC–Al$_2$O$_3$ coating, the smooth area was small, and there was a lot of lamellar spalling on the worn surface, which was a typical feature of adhesive wear, as shown in Fig. 14(a). Based on Fig. 14(b), a lot of debris was attached to the smooth area of worn surface, and furrows appeared along the direction of sliding friction, indicating that the abrasive wear had also occurred. The abrasive wear mainly ascribes to two aspects; (i) the unmelted NbB$_2$ and NbC particles were prone to peel off due to the weak bonding force between them and the coating, and the peeled particles would participate in the wear of the friction pairs, leading to abrasive wear during the wear process; and (ii) the lamellar spalling would participate in the friction wear of the friction pairs after peeling off. Blocky spalling could be seen in Fig. 14(b), which was a transitional form of lamellar spalling and would eventually ground into fine abrasive particles to cause abrasive wear. Compared with NbB$_2$–NbC–Al$_2$O$_3$ coating, Nb$_2$O$_5$–B$_4$C–Al coating had a distinct difference in which the proportion of smooth area increased (Fig. 14(c)), and there was no peeling phenomenon. The furrows could be also observed along the direction of sliding friction, which explains that the wear mechanism was mainly abrasive wear. By magnifying the smooth area (Figs. 14(e) and 14(f)), this area was composed of many...
Fig. 14 Wear morphology of two NbB$_2$–NbC–Al$_2$O$_3$ composite coatings: (a) NbB$_2$–NbC–Al$_2$O$_3$; (c) Nb$_2$O$_5$–B$_4$C–Al; (b, d) enlarged views of (a) and (c), respectively; (e) the orange dotted box zones in (c); (f) magnification of the yellow dotted box zones in (e), and EDS mapping.

Nanoscale particles with uniform size and dispersion distribution. By comparing the element distribution in Fig. 14(f), it can be inferred that the fine grains were mainly NbB$_2$ formed via the *in-situ* reaction. The size of NbC particles was small based on Fig. 6(b), while the distribution of C element was uniform. Thereby it can be inferred that NbC was uniformly dispersed in the coating. The synthesized NbB$_2$ and NbC by the *in-situ* approach played the role of fine grain strengthening, and they were regarded as a fixed barrier of pinning reinforcement and could effectively resist the cutting of the friction pairs during wear process [21]. Also, according to the solidification theory of melt [48], the degree of refinement of solidification structure was significantly related to the solidification speed and the degree of melt melting. In the process of plasma spraying Nb$_2$O$_5$–B$_4$C–Al composite powder, a large amount of heat was released by the *in-situ* reaction, which promoted the composite powder to be melted fully and was beneficial to the grain refinement of ceramic layer. Therefore, NbB$_2$–NbC–Al$_2$O$_3$ composite coating prepared by the *in-situ* approach had an excellent tribological performance.

At present, the literature on NbB$_2$–NbC–Al$_2$O$_3$ composite coating has not been reported, but there are numerous pieces of literatures about other boride composite coatings by APS, as shown in Table 2. NbB$_2$–NbC–Al$_2$O$_3$ composite coating by the *in-situ* approach exhibits an excellent comprehensive performance, i.e., the lowest porosity, the higher microhardness, and lower coefficient of friction, than other boride composite coatings. It is worth mentioning that its wear rate is higher than that of other boride composite coatings, which is resulted from the difference in the friction pair,

| Coating composition | Porosity (%) | Hardness (HV) | Model and counterpart | Wear condition | Coefficient of friction | Wear rate | Ref. |
|---------------------|--------------|---------------|----------------------|----------------|------------------------|-----------|------|
| TiB$_2$–TiC         | 12.7         | 1031 HV$_{0.1}$ | Pin-on-disc, 600# SiC abrasive paper | 10 N           | > 0.5 × 10$^{-10}$ m$^3$/m | [27]      |
| ZrB$_2$–ZrC         | > 9.6        | 500.6 HV$_{0.1}$ | Pin-on-disc, 600# SiC abrasive paper | 20 N, 7.854 m  | > 6 × 10$^{-10}$ m$^3$/m | [28]      |
| TiB$_2$–TiC–Al$_2$O$_3$–Al | 439.9 HV$_{0.1}$ |                | Pin-on-disc, 600# SiC abrasive paper | 60 r/min, 7.854 m | −5 × 10$^{-10}$ m$^3$/m | [21]      |
| TiB$_2$–40Ni        | 11.7         | 1200 HV$_{0.2}$ | Linear reciprocating tribo-tester, GCr15 (hardness, 61–65 HRC) | 150 N, 1 m/s | 0.71 | 6.41 mm$^3$ | [49]      |
| Al$_2$O$_3$–30 wt% B$_4$C | 18.5       | 925 HV$_{0.1}$ | Ball-on-disk, Si$_3$N$_4$ (06 mm, hardness 16 GPa) | 9.8 N, 0.188 m/s, 30 min | 0.75–0.8 | (3.5–4) × 10$^{-4}$ mm$^3$/N·m | [51]      |
| TiB$_2$–TiC–30 wt% Co | 1196 HV$_{0.1}$ |                | Pin-on-disc, 600# SiC abrasive paper | 20 N           | 4.6–10 m$^3$/m | [52]      |
| NiCoCrAlY/TiB$_2$–B$_4$C | 7            | −1000 HV$_{0.2}$ | Ball-on-disk, Ni$_3$Al (06 mm, hardness 16 GPa) | 9.8 N, 0.188 m/s, 1200 s | 0.47 | −1.3 mm$^3$ | [53]      |
| Nb–B$_4$C           | 9.6          | 1062 HV$_{0.1}$ | Ball-on-disk, Si$_3$N$_4$ (04 mm, hardness 16 GPa) | 30 N, 0.13 m/s, 600 s | 0.67 | 1.04 × 10$^{-7}$ mm$^3$/N·m | [17]      |
| NbB$_2$–NbC–Al$_2$O$_3$ | 7.9          | 937.4 HV$_{0.1}$ | Ball-on-disk, Ni$_3$Al (06 mm, hardness 16 GPa) | 30 N, 0.13 m/s, 600 s | 0.63 | 0.69 × 10$^{-7}$ mm$^3$/N·m | [17]      |
| Nb$_2$O$_5$–B$_4$C–Al | 6.2          | 1188.7 HV$_{0.1}$ | Ball-on-disk, Ni$_3$Al (04 mm, hardness 16 GPa) | 30 N, 0.13 m/s, 600 s | 0.58 | 0.53 × 10$^{-7}$ mm$^3$/N·m | Present work |
applied load, ball diameter, stress, and sliding speed. Actually, NbB2–NbC–Al2O3 composite coating by plasma spraying Nb2O3–B4C–Al composite powder possesses good wear resistance. In contrast to NbB2–

Applied load, ball diameter, stress, and sliding speed. Actually, NbB2–NbC–Al2O3 composite coating by plasma spraying Nb2O3–B4C–Al composite powder possesses good wear resistance. In contrast to NbB2–

4 Conclusions

A novel in-situ reaction system, Nb2O3–B4C–Al, was used to fabricate NbB2–NbC–Al2O3 composite coating by plasma spraying for obtaining the high-density NbB2 composite coating. The microstructure, properties, and formation mechanism of the composite coatings obtained by plasma spraying NbB2–NbC–Al2O3 composite powder (ex-situ approach) and Nb2O3–B4C–Al composite powder (in-situ approach) were comparatively studied.

(1) NbB2–NbC–Al2O3 composite coating prepared by the in-situ approach presented a dense microstructure compared with the as-sprayed coating by the ex-situ approach, and a great deal of NbB2 and NbC nanoparticles were uniformly distributed in the in-situ NbB2–NbC–Al2O3 coating. Densification of the coating and the formation of ultrafine microstructure could be attributed to the low melting point and the in-situ reaction of Nb2O3–B4C–Al composite powder.

(2) The reaction path of Nb2O3–B4C–Al composite powder during plasma spraying was proposed as follows: Nb2O3 + Al → Nb + Al2O3, and Nb + B4C → NbB2 + NbC. The formation mechanisms of NbB2–NbC–Al2O3 coatings by the ex-situ and in-situ approaches were described as the melting–deposition and melting–reaction–deposition–precipitation.

(3) NbB2–NbC–Al2O3 composite coating prepared by the in-situ approach exhibited higher microhardness and fracture toughness, as well as excellent tribological performance compared with that prepared by the ex-situ approach. It was ascribed to a dense microstructure and strengthening and toughening effect of the nanoscale phases formed by the in-situ reaction.

(4) The density and properties of NbB2–NbC–Al2O3 composite coating obtained by the in-situ approach are obviously improved compared with other boride composite coatings. Therefore, plasma spraying combined with the in-situ reaction (Nb2O3–Al–B4C) is a prospective way to prepare the nanostructured boride composite coatings with high density and excellent performance.

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Declaration of competing interest

The authors have no competing interests to declare that are relevant to the content of this article.

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