Article

In Situ Deposition of Amorphous Al₂O₃-GAP Ceramic Coating with Excellent Microstructure Stability and Uniformity via Atmospheric Plasma Spraying

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Abstract: A novel Al₂O₃-GdAlO₃ (GAP) amorphous ceramic coating was in situ prepared via atmospheric plasma spraying (APS). The Al₂O₃/Gd₂O₃ sprayable powders possessed excellent sphericity and fluidity after heat treatment at 1173 K without solid-phase reaction, which indicated that the Al₂O₃-GAP coating deposition process was significantly simplified. The Al₂O₃-GAP amorphous coating showed high glass transition temperature (1155.1 K), initial crystallization temperature (1179.2 K), local activation energy (847.6 kJ/mol) and nucleation resistance (88.3). Compared with almost all amorphous materials, the Al₂O₃-GAP amorphous coating possessed greater crystallization activation energy, which was conducive to its high-temperature microstructure stability. Furthermore, the hardness and elastic modulus of Al₂O₃-GAP coating fluctuated with a tiny range when increasing the nanoindentation depth from 500 nm to 2000 nm, which exhibited excellent uniformity of microstructure and mechanical performance of the coating. Therefore, the results showed that the Al₂O₃-GAP amorphous coating had a better potential for large-scale engineering application under harsh service conditions.

Keywords: plasma spraying; differential scanning calorimetry; mechanical properties; Al₂O₃-GdAlO₃(GAP) coating

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1. Introduction

The friction and wear of materials under high PV (P: contact pressure, V: friction velocity, $PV \geq 15 \text{ MPa} \cdot \text{m} \cdot \text{s}^{-1}$) are often accompanied by high temperature, oxygen enrichment and thermal shock in a wide temperature range [1,2]. Ceramic coatings have to bear large contact pressure, high friction velocity, great friction heat (maximum frictional contact temperature is close to or even exceeds 1000 °C), serious oxidation and strong thermal shock under severe conditions with high PV values [3–5]. Al₂O₃ coatings are considered to be the typical representative of wear-resistant oxide ceramic coatings [6,7]. In the past, investigations on Al₂O₃ coating mainly included optimization of spraying, post-treatment process and variation of coating composition, such as increasing the substrate deposition temperature [8–10], dry-ice blasting [10], laser remelting [11,12], nanostructure [13,14] and adding elemental phases (Al [11], graphene [12], carbon nanotubes [13], etc.) or compounds (ZrO₂ [14], YSZ [15], TiO₂ [16], etc.). Dong S. J. et al. used dry-ice blasting technology to increase the bonding strength of plasma sprayed Al₂O₃ coating by 30% (the value exceeds 60 MPa) and the porosity was reduced from 9.3% to 6.8%. The internal compressive stress of the coating was nearly doubled, which was beneficial to suppress crack propagation and improvement of fracture toughness [10]. Plasma sprayed Al₂O₃ coating surface for laser remelting can increase the content of α -Al₂O₃ phase in the coating and obtain a coating with

fine structure, low porosity and high hardness [11,12]. The nanoscale Al_2O_3 coating with fine-grained strengthening and toughening effect exhibited higher hardness and toughness, better anti-sliding and anti-erosion wear properties [13,14]. However, the common problem is that it is difficult to effectively improve the high-temperature mechanical properties, thermal conduction and wear resistance of the coating simultaneously. Some new methods in our previous work have been applied to solve the above-mentioned problem [17–19]. The “self-healing” and partial coherent interface strengthening and toughening mechanisms of Al_2O_3 coating microcracks filled with in situ generated nanocrystals were discovered and clarified. Moreover, this method for self-toughening Al_2O_3 coatings with in situ regulation of the content of $\alpha\text{-Al}_2\text{O}_3$ nanocrystals via stress-induced phase transformation was put forward [20]. In order to suppress the thermal conductivity of Al_2O_3 coating from showing negative temperature coefficient characteristics and to meet the requirements of more severe wear conditions, the $\text{Al}_2\text{O}_3\text{-Cr}_2\text{O}_3$ composite coatings with positive temperature coefficient characteristics were designed and prepared [18]. Heterogeneous nucleation and partial solid solution strengthened the phase interface, refined the crystalline grains and improved the interlayer bonding of the coating. Meanwhile, it was taken into account thermal conduction, mechanical properties and anti-wear of the coating over the full temperature range [19].

Furthermore, to inhibit the reduction in the coating strengthening effect caused by the long-term high-temperature creep, based on the deep eutectic solidification mechanism, the $\text{Al}_2\text{O}_3\text{-Y}_3\text{Al}_5\text{O}_{12}$ (YAG) amorphous ceramic coating was deposited via plasma spraying with the great under-cooling in our previous investigations [21]. Compared with other thirty kinds of amorphous materials (such as Fe-based alloy, Zr-based alloy, polystyrene and ceramic, etc.), the $\text{Al}_2\text{O}_3\text{-YAG}$ amorphous ceramic coating shows excellent high-temperature microstructure stability [22]. Additionally, the $\text{Al}_2\text{O}_3\text{-YAG}$ coating possesses good plastic toughness, thermal conductivity and crack arrest characteristics, exhibiting superior wear resistance to Al_2O_3 coatings and $\text{Al}_2\text{O}_3\text{-Cr}_2\text{O}_3$ composite coatings under high PV value conditions [23]; however, there still exist some problems in the whole preparation process of $\text{Al}_2\text{O}_3\text{-YAG}$ amorphous coatings:

1. High-temperature calcination for solid-phase reaction (direct heat treatment at 1673–1873 K or step-by-step heating cycle calcination at 1173–1773 K), roughened the surface of the spray powder and resulted in the agglomeration effect of powder, which brought some negative effects on the powder sphericity and fluidity [24]. The step-by-step heating cycle calcination process was very cumbersome, which was difficult to control powder quality and reliability. Moreover, the time and cost were greatly increased;
2. The plasma spheroidization process of the powder needed to be carried out to remove the unfavorable factors caused by high-temperature solid-phase reaction;
3. $\text{Al}_2\text{O}_3/\text{YAG}$ powders obtained by high-temperature solid-phase reaction may lead to gun blockage in the long-term plasma spraying process, which would be adverse to the uniformity of coating preparation.

The fully densified $\text{Al}_2\text{O}_3\text{-GAP}$ ceramics with a eutectic composition prepared by hot-pressing methods described flexural strengths of 556 MPa at room temperature and 515 MPa at 1000 °C [25]. The fracture toughness of the $\text{Al}_2\text{O}_3\text{-GAP}$ bulk eutectic ceramic system ranges from 5 to 6 MPa $\text{m}^{1/2}$ from room temperature to 1600 °C. $\text{Al}_2\text{O}_3\text{-GAP}$ eutectic ceramics have good high-temperature strength and toughness [26,27]. In this current work, a novel $\text{Al}_2\text{O}_3\text{-GdAlO}_3$ (GAP) amorphous ceramic coating was in situ deposited via APS. Being different from the preparation of $\text{Al}_2\text{O}_3\text{-YAG}$ amorphous ceramic coating, no high-temperature solid-phase reaction would occur in the sprayable powders for the deposition of $\text{Al}_2\text{O}_3\text{-GAP}$ coating, and thus the original phases in feedstocks can be retained, namely, $\alpha\text{-Al}_2\text{O}_3$ and $\text{c-Gd}_2\text{O}_3$. The sprayed $\text{Al}_2\text{O}_3/\text{Gd}_2\text{O}_3$ granulated powders had outstanding sphericity and fluidity, which would effectively simplify the whole coating preparation process. Simultaneously, the consistency and reliability of the coating deposition process were greatly improved, which could significantly reduce the time and economic cost of coating deposition. Exceptional mechanical performance, high-temperature microstructure

stability and coating uniformity can be achieved for the as-sprayed Al_2O_3 -GAP coating; therefore, the Al_2O_3 -GAP amorphous ceramic coating had the better potential for large-scale engineering applications under harsh service conditions, such as Turbine pump dynamic seal of a liquid rocket engine, high-speed and over-loading bearing, ultra-high temperature molten salt energy storage system, etc.

2. Experimental Procedure

2.1. Feedstock Preparation and Coating Deposition

Commercially available sub-micro Al_2O_3 and Gd_2O_3 powders (Kouting, China) were used as feedstocks. The median particle size (D_{50}) of Al_2O_3 and Gd_2O_3 powders was $0.486\ \mu\text{m}$ and $0.730\ \mu\text{m}$, respectively. The main phases of the two powders were α - Al_2O_3 and c- Gd_2O_3 , respectively. The homogeneous $\text{Al}_2\text{O}_3/\text{Gd}_2\text{O}_3$ composite powders were prepared by the spray granulation method (PLG-5, China) at the eutectic ratio of $\text{Al}_2\text{O}_3:\text{Gd}_2\text{O}_3 = 77:23$ (mol.%). The Al_2O_3 and Gd_2O_3 powders were put into the ball milling tank, which contained zirconia grinding balls (at the weight ratio of balls: feedstocks: deionized water is equal to 2:1:1). Then the feedstocks were milled with dispersant (Arabic gum, 0.2 wt.%) and binder (polyvinyl alcohol, 0.8 wt.%) for 6 h to obtain a homogeneously mixed suspension. The conventional spray drying process was carried out for the preparation of $\text{Al}_2\text{O}_3/\text{Gd}_2\text{O}_3$ sprayable powders that contain nano/sub-micro scale structures. The main controlled operating parameters included the rotation speed of atomizer (16,800 rpm), the air temperature at the entry ($220\ ^\circ\text{C}$) and the exit ($110\ ^\circ\text{C}$), respectively. The median particle size (D_{50}) of the granulated powder obtained was $15.2\ \mu\text{m}$. The differential scanning calorimetry (DSC) method was used to determine the heat treatment temperature of granulated $\text{Al}_2\text{O}_3/\text{Gd}_2\text{O}_3$ powders and evaluate the thermal stability of as-sprayed Al_2O_3 -GAP coating. The $\text{Al}_2\text{O}_3/\text{Gd}_2\text{O}_3$ granulated powders were sintered at 1173 K for 2 h so as to remove the organic additives and improve the density of granules. The density of sintered $\text{Al}_2\text{O}_3/\text{Gd}_2\text{O}_3$ granulated powders was $0.92\ \text{g}/\text{cm}^3$. The phase composition of the sprayable powder did not change after heat treatment. The heat-treated powders were further sieved to cater to the sprayable demands. The Multicoat APS system equipped with an F4 MB-XL plasma gun (Sulzer Metco AG, Wohlen, Switzerland) was employed to deposit coating. The rectangular stainless steel with the dimension of $30\ \text{mm} \times 15\ \text{mm} \times 1.25\ \text{mm}$ and the round graphite disk with the dimension of $\Phi 30\ \text{mm} \times 3\ \text{mm}$ were used as substrates. Before spraying, the substrates were grit-blasted with 20# white corundum, and then ultrasonically cleaned in alcohol and dried with compressed air. NiCr powder was used to prepare a bondcoat prior to spraying ceramic coating. The density of as-sprayed Al_2O_3 -GAP coating was $2.732\ \text{g}/\text{cm}^3$. The plasma spray parameters of Al_2O_3 -GAP amorphous coatings are listed in Table 1. For performance comparison, Al_2O_3 and Al_2O_3 -YAG coatings were also fabricated according to our previous works [18,24].

Table 1. Plasma spray parameters of Al_2O_3 -GAP coatings.

Parameters	NiCr Bondcoat	Al_2O_3 -GAP Topcoat
Arc current, A	600	650
Primary plasma gas (Ar), slpm	57	49
Secondary plasma gas (H_2), slpm	7.5–8.0	8.5–9.0
Carrier gas (Ar), slpm	3.5	4.0
Powder feed rate, g/min	10	30
Power, kW	40–45	45–50
Stand-off distance, mm	120	110

2.2. Microstructure and Property Characterization

The phase compositions of the as-deposited and annealed Al_2O_3 -GAP coatings were identified by X-ray diffraction (XRD) using a Rigaku D/Max2550 Diffractometer with nickel-filtered $\text{CuK}\alpha$ radiation. The particle size of granulated $\text{Al}_2\text{O}_3/\text{Gd}_2\text{O}_3$ powders was analyzed by a laser particle size instrument (MASTERSIZER-300, UK). Transmission

electron microscopy (TEM) images were taken on JEM 2100F to characterize the microstructures of the coating. Electron backscattered diffraction (EBSD) technology was carried out on Magellan 400 to detect the phase structure of the coating samples and the cross-sectional morphologies of the coating were also characterized by Magellan 400. The crystallization process of the Al_2O_3 -GAP amorphous coating was evaluated by a Netzsh 404C high-temperature DSC tester. The microhardness and elastic modulus of the Al_2O_3 -GAP coating were measured on the cross-section of the coating after being submerged and polished. The measuring instrument was the G-200 nano-indenter produced by Agilent Technologies with Berkovich indenter.

3. Results and Discussion

3.1. Structural Characterization

Figure 1a,b represent the morphology of the original granulated powders and corresponding element distribution, indicating that the powders have good uniformity and dispersibility. A solid-state reaction would occur in granulated powders in the range of 1460~1620 K, as observed in Figure 1c. According to the DSC curve, the sintering temperature of the powder was chosen to be 1173 K, which ensured the improvement effects on density and strength of powders and without solid-state reaction being occurred. The morphology of the heat-treated powders and corresponding element distribution are shown in Figure 1d,e. After heat treatment, powder morphology was not changed, which still possessed good sphericity and fluidity. Figure 1f shows the XRD patterns of the original and heat-treated powders. The phase composition of the heat-treated powder remains unchanged (namely, $\alpha\text{-Al}_2\text{O}_3$ and $\text{c-Gd}_2\text{O}_3$). The angle of repose, Carr index and Hausner ratio of $\text{Al}_2\text{O}_3/\text{YAG}$ and $\text{Al}_2\text{O}_3/\text{Gd}_2\text{O}_3$ sprayable powders are shown in Table 2. The fluidity of the $\text{Al}_2\text{O}_3/\text{Gd}_2\text{O}_3$ powder is obviously better than that of the $\text{Al}_2\text{O}_3/\text{YAG}$ powder in our previous work [28], which is beneficial to the subsequent plasma spraying process.

Figure 1. (a) SEM image of granulated powders (the lower-left corner shows the particle size distribution of granulated powders); (b) the morphology of the single granule and related element distribution; (c) DSC curve of $\text{Al}_2\text{O}_3/\text{Gd}_2\text{O}_3$ granulated powders at the heating rate of 30 K/min; (d) SEM image of granulated powders sintered at 1173 K for 2 h; (e) the morphology of the single granule sintered at 1173 K for 2 h and related element distribution; (f) XRD patterns of $\text{Al}_2\text{O}_3/\text{Gd}_2\text{O}_3$ granulated powder.

Table 2. Angle of repose, Carr index and Hausner ratio of $\text{Al}_2\text{O}_3/\text{YAG}$ and $\text{Al}_2\text{O}_3/\text{Gd}_2\text{O}_3$ sprayable powders.

	Angle of Repose	Carr Index *	Hausner Ratio *
$\text{Al}_2\text{O}_3/\text{YAG}$ powders [24]	46.5°	26%	1.35
$\text{Al}_2\text{O}_3/\text{Gd}_2\text{O}_3$ powders	30.0°	8%	1.09

* When the Carr index is less than 10%, the powder has excellent fluidity; when it is greater than or equal to 38%, the powder fluidity is extremely poor. When the Hausner Ratio is 1.0–1.1, the powder has excellent fluidity; when it is greater than 1.6, the powder fluidity is extremely poor.

There were obvious amorphous scattering peaks in the XRD pattern of the as-sprayed coating, as shown in Figure 2a, indicating that a large amount of amorphous phase was formed in the coating. In addition, few weak diffraction peaks of $\alpha\text{-Al}_2\text{O}_3$ and GAP crystalline phases appeared. According to XRD analysis, the content of the amorphous phase of $\text{Al}_2\text{O}_3\text{-GAP}$ amorphous coating was estimated to be 91.8 wt.%, which means that the as-sprayed coating was mainly composed of the amorphous phase. A small number of $\alpha\text{-Al}_2\text{O}_3$ and GAP crystalline grains was distributed in the amorphous matrix. Figure 2b,c show the cross-sectional morphology of as-sprayed $\text{Al}_2\text{O}_3\text{-GAP}$ amorphous coating deposited on a stainless-steel substrate. Prior to depositing the ceramic topcoat, NiCr bond-coat was prepared. The thickness of NiCr bond-coat and $\text{Al}_2\text{O}_3\text{-GAP}$ topcoat was about 50~60 μm and 250~270 μm , respectively. The results showed that there was no obvious two-phase feature in the SEM morphology of the $\text{Al}_2\text{O}_3\text{-GAP}$ coating, further indicating that the coating matrix mainly consisted of an amorphous phase and the uniformity of coating was good. The black zoom and white zoom were analyzed by EDS in Figure 2c. It presents the enlarged view of the selected area in Figure 2b. The element line scan along the yellow line (marked in Figure 2c as shown in Figure 2d). It can be judged that the black zoom corresponds to the $\alpha\text{-Al}_2\text{O}_3$ phase, and the white zoom corresponds to the GAP phase. On the whole, these phases were well dispersed in the gray amorphous matrix without obvious segregation. The element distribution between the white phase on the left and the black phase on the right was less fluctuating. Consequently, the uniformity of the element distribution in the amorphous matrix demonstrates good consistency of the coating structure. In accordance with the image analysis (IA) method, the porosity of $\text{Al}_2\text{O}_3\text{-GAP}$ coating was $3.71 \pm 0.20\%$. In contrast, the porosity of the plasma-sprayed $\text{Al}_2\text{O}_3\text{-YAG}$ coatings was $8.54 \pm 1.57\%$ in our previous work [21]; therefore, the $\text{Al}_2\text{O}_3\text{-GAP}$ coating had fewer microcracks and higher density than that of the $\text{Al}_2\text{O}_3\text{-YAG}$ coating. The electron backscatter diffractometer (EBSD) and field emission transmission electron microscope (FETEM) were applied to further characterize the coating structure, as shown in Figure 2e,f. The distribution of $\alpha\text{-Al}_2\text{O}_3$ and GAP crystalline grains could be evaluated by EBSD analysis. The content of $\alpha\text{-Al}_2\text{O}_3$ phase marked with yellow was 1.51%. The content of the GAP phase marked with green was 1.73%. Figure 2f shows the TEM image of the as-sprayed $\text{Al}_2\text{O}_3\text{-GAP}$ coating. The coating matrix was chiefly made up of the zone without boundary feature mark with “C”. The corresponding selected area electron diffraction (SAED) pattern (shown in Figure 2f) revealed a diffuse halo, which denoted the obvious amorphous phase feature. There were two kinds of crystalline grains with different morphologies and obvious boundary characteristics in the amorphous matrix, which were labeled with A and B, respectively. The EDS analysis showed that zone A with surface wrinkled and zone B with a darker color were $\alpha\text{-Al}_2\text{O}_3$ and GAP, respectively. A few $\alpha\text{-Al}_2\text{O}_3$ and GAP crystalline grains were distributed in an amorphous phase matrix. Combined with the above-mentioned analysis, the content of the amorphous phase of $\text{Al}_2\text{O}_3\text{-GAP}$ coating was 96.76%, which was consistent with the calculated results from the XRD analysis (as shown in Figure 2a). According to EBSD and TEM analyses, the crystalline size of $\alpha\text{-Al}_2\text{O}_3$ was larger than that of GAP, and the grain number of $\alpha\text{-Al}_2\text{O}_3$ was less than that of GAP. This phenomenon may be ascribed to the fact that one large $\alpha\text{-Al}_2\text{O}_3$ grain is actually originated from many small nuclei; therefore, the difficulty of $\alpha\text{-Al}_2\text{O}_3$ to nucleate is misleading since the larger grain may come from many small nuclei. On the other hand, the small and many grains of GAP may not form larger ones due to the

ineffective Ostwald ripening process [29]. In this case, the diffusivity/mobility of small grains is low, thus preventing the large grain forms.

Figure 2. (a) XRD pattern of as-sprayed Al_2O_3 -GAP coating; (b,c) cross-sectional SEM images of Al_2O_3 -GAP coating; (d) the zoomed morphology image of the Al_2O_3 -GAP coating and line scan from image (c); (e) electron backscattered diffraction (EBSD) images of the Al_2O_3 -GAP amorphous coating; (f) TEM image of as-sprayed Al_2O_3 -GAP coating and selected area electron diffraction (SAED) pattern corresponding to zone C.

3.2. Thermal Stability Analysis

From the DSC curve shown in Figure 3a, the glass transition temperature (T_g), initial crystallization temperature (T_{c1}), supercooled liquid region ($\Delta T = T_{c1} - T_g$), crystallization peak temperature (T_p), local activation energy (E_c) and nucleation resistance (E_g/RT) of Al_2O_3 -GAP amorphous coating can be calculated, as shown in Table 3. In this paper, the glass transformation temperature and initial crystallization temperature of Al_2O_3 -GAP coating were 1155.1 K and 1179.2 K, respectively. The characteristic temperature (T_g and T_c) values of the Al_2O_3 -GAP and the Al_2O_3 -YAG [22] amorphous coatings were very close. E_c can be calculated by the Kissinger equation, which is the most common method to analyze the crystallization behavior [28,29]. The onset activation energy calculated of the Al_2O_3 -GAP amorphous coating was 847.6 kJ/mol, which was greater than that of Al_2O_3 -YAG amorphous coating. Figure 3b compares the initial crystallization activation energy obtained by the Kissinger method for some typical amorphous materials [22,29–48]. Conspicuously, the crystallization activation energy of the Al_2O_3 -GAP amorphous coating reported in this work was higher than that of almost all amorphous materials, which indicated that it was extremely difficult to overcome the energy barrier to precipitate crystalline phase in the Al_2O_3 -GAP amorphous coating. Meanwhile, it can be seen that the initial crystallization temperature of Al_2O_3 -YAG coating is slightly higher than that of Al_2O_3 -GAP coating. This may be due to the fact that the nanocrystals present in the Al_2O_3 -GAP coating can serve as the crystalline core of the amorphous coating during the crystallization process (as shown in Figure 4a,b). Furthermore, the grain size was further analyzed by EBSD technology. Figure 4c,d describe that the GAP grain size range (0.25–0.85 μm) in the as-sprayed Al_2O_3 -GAP coating is indeed smaller than the YAG grain size range (0.25–1.35 μm) in the as-sprayed Al_2O_3 -YAG coating. So, the crystalline phase of the former begins to precipitate at a lower temperature, resulting in a small decrease in the initial crystallization temperature. In addition, E_c/RT_g can also be suggested to evaluate the standard for nucleation resistance of amorphous materials and characterize the degree of difficulty of supercooled liquid crystallization. Greater E_c/RT_g (88.3) of the

Al_2O_3 -GAP amorphous coating indicates higher nucleation resistance, which would show a stronger anti-crystallization tendency and better thermal stability of amorphous materials. In our previous investigations [22], the Al_2O_3 -YAG amorphous coatings possessed greater crystallization kinetic parameters and better high-temperature microstructure stability than thirty kinds of amorphous materials. Particularly, the Al_2O_3 -GAP amorphous coating has greater E_c and E_c/RT than that of the Al_2O_3 -YAG amorphous coating, which indicates the greater efforts needed to overcome the energy barrier during crystallization, directly leading to outstanding microstructure stability of the former.

Figure 3. (a) DSC curve of the Al_2O_3 -GAP amorphous coating at the heating rate of 20 K/min; (b) initial crystallization activation energy $E_c(x)$ obtained by the Kissinger method for some typical amorphous materials reported [22,29–48].

Table 3. A series of evaluation parameters of thermal stability for Al_2O_3 -YAG and Al_2O_3 -GAP amorphous materials.

Amorphous Coatings	T_g (K)	T_{c1} (K)	ΔT (K)	T_{p1} (K)	E_c (kJ/mol)	E_c/RT_g	β (K/min)
Al_2O_3 -YAG [22]	1166.0	1198.4	29.3	1215.5	807.8	83.3	20
Al_2O_3 -GAP	1155.1	1179.2	17.4	1215.0	847.6	88.3	20

3.3. Microstructure and Mechanical Property Uniformity

During coating deposition, some defects such as microcracks, pores and un-melted particles are unavoidable. The presence of these defects degrades material homogeneity and influences corresponding mechanical properties. The nanoindentation tests were carried out to evaluate structure uniformity and mechanical performance of Al_2O_3 , Al_2O_3 -YAG and Al_2O_3 -GAP coatings. To avoid the influence of indentation size effect caused by micro-defects and residual stress on mechanical performance testing, high load conditions should be selected. Ten load-displacement curves were obtained with the nanoindentation process for every kind of coating. It can be seen from the load-displacement curves that the maximum displacement of Al_2O_3 coating was about 1890–4263 nm. However, the maximum displacement of Al_2O_3 -YAG and Al_2O_3 -GAP amorphous coatings were 2034–2393 nm and 2125–2351 nm, respectively, shown in Figure 5a–c. The order of maximum displacement range variation of three kinds of coatings follows the sequence of $\text{Al}_2\text{O}_3 > \text{Al}_2\text{O}_3$ -YAG $>$ Al_2O_3 -GAP.

Figure 4. (a,b) HRTEM images of as-sprayed Al_2O_3 -GAP amorphous coatings after heat treatment at 1173 K and 1223 K for 10 min; (c,d) grain size distribution of different crystalline phases in Al_2O_3 -GAP and Al_2O_3 -YAG amorphous coating.

Meanwhile, the hardness- and modulus-displacement curves are exhibited in Figure 5d–i. The measurement values of the corresponding mechanical property were selected at a depth of 500–2000 nm for statistical analysis. Ten indentation tests were made in each sample and the results were presented in Table 4. The hardness of Al_2O_3 , Al_2O_3 -YAG and Al_2O_3 -GAP coatings were 5.22 ± 1.87 , 9.46 ± 0.63 and 9.25 ± 0.57 GPa, respectively. The corresponding modulus were 158.64 ± 41.89 , 149.71 ± 8.98 and 140.77 ± 7.10 GPa, respectively. It is noteworthy to point out that the hardness of Al_2O_3 coating was significantly smaller than that of Al_2O_3 -YAG and Al_2O_3 -GAP coatings; the corresponding elastic modulus was higher than that of Al_2O_3 -YAG and Al_2O_3 -GAP coatings. With regard to the hardness and elastic modulus of Al_2O_3 -YAG and Al_2O_3 -GAP coatings, the former was slightly higher than the latter. Compared with Al_2O_3 -YAG and Al_2O_3 -GAP coatings, the values of Al_2O_3 coating in the ten nanoindentation tests were quite different. That was ascribed to the cause that Al_2O_3 coating may produce additional defects during non-uniform plastic deformation as the indentation depth increased, namely free volume defects [49]. The existence of these defects greatly reduced the uniformity of the Al_2O_3 coating and affected its micromechanical properties. Relatively speaking, the Al_2O_3 -GAP coating had fewer defects than Al_2O_3 -YAG coating, which was beneficial to its microstructure stability. Furthermore, the ratio of standard deviation to average (denoted as $\Delta\varepsilon$) was used to estimate numerical fluctuation degree. The $\Delta\varepsilon$ of hardness for Al_2O_3 , Al_2O_3 -YAG and Al_2O_3 -GAP coatings were 35.8%, 6.7% and 6.2%, respectively, and that of corresponding modulus values were 26.4%, 6.0% and 5.0%. The $\Delta\varepsilon$ of Al_2O_3 -GAP coating was less than that of Al_2O_3 and Al_2O_3 -YAG coating, indicating that the mechanical performance fluctuation range of Al_2O_3 -GAP coating was the smallest. The load–displacement, hardness–displacement and modulus–displacement

curves of Al_2O_3 -GAP coating basically coincided, indicating that the coating possessed outstanding structural and property uniformity.

Figure 5. The load–displacement (a–c), hardness–displacement (d–f) and modulus–displacement (g–i) curves of the Al_2O_3 , Al_2O_3 -YAG and Al_2O_3 -GAP coatings.

Table 4. The nanoindentation hardness and elastic modulus of several coatings for different nanoindentation depth.

Displacement (nm)	Al_2O_3 Hardness (GPa)	Al_2O_3 Modulus (GPa)	Al_2O_3 -YAG Hardness (GPa)	Al_2O_3 -YAG Modulus (GPa)	Al_2O_3 -GAP Hardness (GPa)	Al_2O_3 -GAP Modulus (GPa)
500–1000	5.16 ± 1.35	157.24 ± 41.90	9.85 ± 0.68	154.78 ± 9.90	9.54 ± 0.68	144.36 ± 6.78
1000–1500	5.22 ± 2.38	157.04 ± 47.02	9.24 ± 0.64	146.66 ± 8.77	9.02 ± 0.69	138.74 ± 8.39
1500–2000	5.61 ± 2.63	161.84 ± 41.30	8.80 ± 0.66	141.29 ± 8.17	8.90 ± 0.70	134.97 ± 8.09
500–2000	5.22 ± 1.87	158.64 ± 41.89	9.46 ± 0.63	149.71 ± 8.98	9.25 ± 0.57	140.77 ± 7.10

4. Conclusions

In summary, this work exhibits the results of an experimental study of the phase structure, microstructure stability and mechanical properties of a novel amorphous Al_2O_3 -GAP ceramic coating produced by APS. Notably, the sprayed powder did not need to undergo high-temperature solid-phase reaction and plasma spheroidization, and then the resulting $\text{Al}_2\text{O}_3/\text{Gd}_2\text{O}_3$ granulated powders possessed excellent sphericity and fluidity. So, the in situ Al_2O_3 -GAP coating deposition process was effectively simplified, which would

be conducive to the consistency and reliability improvement of coating preparation process. The amorphous phase was dominant in as-sprayed Al_2O_3 -GAP coating. The Al_2O_3 -GAP amorphous coating possessed excellent microstructure stability, which was attributed to its greater crystallization activation energy, compared with almost all amorphous materials. Ten nanoindentation experiment results showed that the load, hardness and modulus–displacement curves of Al_2O_3 -GAP coating basically coincided. Moreover, the $\Delta\epsilon$ of hardness and modulus for Al_2O_3 -GAP coating were smaller than Al_2O_3 and Al_2O_3 -YAG coating. In contrast to Al_2O_3 and Al_2O_3 -YAG coatings, Al_2O_3 -GAP coating possessed better microstructure uniformity and performance consistency. The Al_2O_3 -GAP coating retains superior high microstructure stability and structure/performance uniformity, which will provide a fundamental contribution to the engineering applications of the coating under harsh service conditions.

Author Contributions: K.Y. conceived the overall projects; L.Q. designed/performed the experiments, data analysis and wrote the manuscript; X.Z. helped with characterization and discussion; Y.A. helped with the manuscript; Y.Z., J.S. and J.N. deposited the Al_2O_3 -GAP coating. All authors participated in discussions and comments on the paper. All authors have read and agreed to the published version of the manuscript.

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