Novel High-Temperature-Resistant Phosphates: Thermal Ablation Behavior of La–Al System Phosphates at 2000 °C

Shuai Shuai Zhang, Wei Sun,* Zi Zhang Zhan, Hong Bo Zhang, and Xiang Xiong

ABSTRACT: The saturation-free and directionless cross-linking and interpenetration processes between La\(^{3+}\) and [(H\(_2\)PO\(_4\))\(_2\)Al(HPO\(_4\))] \(-\)plasma in La–Al phosphate by mixing Al(OH)\(_3\), CrO\(_3\), and H\(_2\)O\(_2\) dissolved in H\(_3\)PO\(_4\) and La\(_2\)O\(_3\) as a curing accelerator, as well as the thermal stability of the La–Al phosphate bulk materials and the evolutions of the phase composition and morphology at different temperatures were studied using thermogravimetric/differential scanning calorimetry under different temperatures in a muffle furnace. The La–Al phosphates showed good thermal stability, and the thermal weight loss rate of the materials decreased from 18% before heat treatment to ~2% after heat treatment. In addition, the La–Al phosphates showed excellent resistance to ablation when subjected to ablation by an oxyacetylene flame at 2000 °C for 30 s. It evolved into a dense LaPO\(_4\) and AlPO\(_4\) high-temperature phase layer on the sample surface, which prevented further ablation damage to the sample and significantly improved the temperature resistance of the La–Al phosphate bulk material.

1. INTRODUCTION

With the rapid development of science and technology, a large number of new energy technologies have been studied and applied. The devices used in many fields, such as aerospace and nuclear engineering, are subjected to extreme high-temperature, high-pressure, and high-speed environments. Therefore, it is necessary to develop high-temperature engineering materials. In the research of high-temperature-resistant materials, phosphate materials have shown excellent temperature resistance and phosphate has excellent oxidation resistance, integrated molding, and doping properties, providing good application prospects.

Current research on phosphate matrix materials has mainly focused on aluminum phosphate, chromium phosphate, and aluminum chromium phosphates. Aluminum phosphate, chromium phosphate, and phosphophosphate bulk materials cured at a temperature range of 150–200 °C exhibit good temperature resistance at 1500 °C. Although the above-mentioned cured phosphate materials have good temperature resistance, they require a high curing temperature (150–200 °C) without the addition of a curing agent. To address the problem of phosphate curing, metal oxides are typically introduced as curing agents into the phosphate matrix, and the activity of metal oxide cations is utilized to cross-link the polycondensation and exothermic reactions with phosphate and thereby to reduce the curing temperature of phosphate. For example, Wang used aluminum dihydrogen phosphate as the main component and ZnO and MgO as curing agents to prepare a type of high-temperature-resistant phosphate block material that could be cured at 120 °C. Xu used the nanoparticle surface coating technology to employ synthesized MgO–SiO\(_2\) as a curing agent to reduce the curing temperature to 80 °C. Zhan added CuO and Al(OH)\(_3\) in proportion to a phosphoric acid solution, stirred at room temperature, and solidified, significantly reducing the curing temperature; however, the low Cu–O bond energy led to poor temperature resistance. Although the above-mentioned reduction in curing temperature can be achieved, the temperature resistance below 1500 °C limits the further development and application of phosphate materials.

To improve the temperature resistance of phosphate, metal oxides and other curing agents are typically used to react with phosphate to generate high-temperature products or a high Me–O bond energy to improve the temperature resistance of phosphate. For example, Khlystov introduced salts containing Al and Fe into phosphoric acid to form an iron–aluminum phosphate, which can be used at 1400 °C for a long duration. Liu used a composite material obtained by sintering a mixture of Al\(_2\)O\(_3\), Cr\(_2\)O\(_3\), Fe\(_2\)O\(_3\), and MnO\(_2\) at 1050 and 1250 °C as the curing agent based on aluminum chromium oxides and other curing agents, as well as the thermal stability of the La–Al phosphate bulk materials and the evolutions of the phase composition and morphology at different temperatures were studied using thermogravimetric/differential scanning calorimetry under different temperatures in a muffle furnace. The La–Al phosphates showed excellent resistance to ablation when subjected to ablation by an oxyacetylene flame at 2000 °C for 30 s. It evolved into a dense LaPO\(_4\) and AlPO\(_4\) high-temperature phase layer on the sample surface, which prevented further ablation damage to the sample and significantly improved the temperature resistance of the La–Al phosphate bulk material.

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phosphate, and the temperature resistance of which could be significantly reduced. Wang\textsuperscript{3} used CuO, Si, and B\textsubscript{4}C to cure aluminum phosphate and improved the temperature resistance of phosphate to more than 1600 °C. Gladkikh\textsuperscript{18} proposed a new type of phosphate material with good temperature resistance under an inert environment of 1800 °C by curing with ZrO\textsubscript{2} and high-melting-point carbides. Ma\textsuperscript{12} adopted modified nanoCuO, nanoTiO\textsubscript{2}, and nanoAlN nanoparticles as curing agents, which could maintain good phosphate integrity at 1700 °C and significantly improve the temperature resistance of phosphate materials.

In summary, phosphate has drawbacks such as high curing temperature and low temperature resistance. Therefore, first, in this study, the curing and temperature resistance of phosphate are improved, then the characteristics of aluminum chromium phosphate and metal oxide as curing agents are combined, and the metal oxide La\textsubscript{2}O\textsubscript{3} with a high melting point is introduced into the aluminum chromium phosphate. The low-temperature self-curing mechanism of the La−Al phosphate block material was analyzed. Finally, the temperature resistance of the La−Al phosphate block material was tested in a muffle furnace at different temperatures and under a 2000 °C oxyacetylene flame.

2. EXPERIMENTS

2.1. Preparation of Aluminum Chromium Phosphate (ACP). First, we diluted 0.9 mol of H\textsubscript{3}PO\textsubscript{4} (analytically pure) with 60−80 mL of distilled water, and diluted phosphoric acid was placed in a water bath maintained at 80−85 °C for preheating and stirring. Subsequently, 0.3 mol of Al (OH)\textsubscript{3} was added to the preheated dilute phosphoric acid and stirred for ~30 min until the solution reached a certain transparent state.
At this time, 0.1 mol of \( \text{CrO}_3 \) and \( \text{H}_2\text{O}_2 \) were added to the transparent solution. Finally, the mixed solution was stirred for 20–30 min to prepare an aluminum chromium phosphate adhesive solution (Figure 1).

### 2.2. Preparation of the La–Al-Based Phosphate Block

In this study, \( \text{La}_2\text{O}_3 \) was used as the curing agent, and mass fractions of 10, 20, 30, and 40 parts of \( \text{La}_2\text{O}_3 \) were mixed into the prepared aluminum chromium phosphate solution and then constantly stirred in a water bath at 80–85 °C until the appropriate viscosity was reached. \( \text{La}_2\text{O}_3 \) was poured into a special mold, placed in an oven at 50 °C for curing, and then released. A self-curing La–Al phosphate block material was obtained. Finally, the temperature resistance and phase morphology of the self-curing La–Al phosphate block materials were tested in a muffle furnace at temperatures of 300, 500, 700, 1000, 1500, and 1700 °C and the material was also subjected to an oxyacetylene flame ablation at 2000 °C.

### 2.3. Characterization Methods

A Rigaku D/Max (2550) automatic (18 kW) rotating target X-ray diffractometer (XRD) was used to analyze the phases on the surface of the La–Al phosphate bulk material. A Quanta FEG 250 field emission scanning electron microscope (SEM) and Czech Nova NanoSEM scanning electron microscope were employed to observe the surface microstructure and phase distribution of the material. A model SDT650 synchronous thermal analyzer (TA Instruments) was used to perform the thermogravimetry-differential thermal scanning calorimetry (TG-DSC) analysis under air atmosphere conditions by heating the specimen to a specific experimental temperature at a heating rate of 10 °C/min. The temperature resistance of the sample was tested by ablation under an oxyacetylene flame at 2000 °C for 30 s.

### 3. RESULTS AND DISCUSSION

#### 3.1. Analysis of the Evolution of the Physical Phase.

To study the effects of different material ratios and treatment temperatures on the phase, \( \text{La}_2\text{O}_3 \) phosphate with addition amounts of 30 and 40% (wt %) was subjected to the corresponding heat treatment. The heat-treated samples were sintered at a given temperature for 2 h. Finally, the heat-treated samples were analyzed via XRD.

The diffraction peaks of the self-curing La–Al phosphate block materials in Figure 2a,b show that the diffraction peaks of raw materials, such as \( \text{La}_2\text{O}_3 \) and \( \text{Al(OH)}_3 \), remain undetected, indicating that the reaction between raw materials is sufficient. From the XRD spectra, the phases of the self-cured samples were mainly composed of \( \text{La(OH)}_3 \), \( \text{Al(PO}_4)_3 \cdot 3\text{H}_2\text{O} \), \( \text{CrPO}_4 \), and \( \text{LaPO}_4 \), and the spectra show wide diffraction peaks, indicating that the macromolecular polyphosphate forms an amorphous network, which is the main reason for the self-curing of phosphate at room temperature. The self-curing nature of La–Al phosphate bulk materials mainly comes from the formation of the macromolecular network in phosphate and the volatilization of water. Although the addition amounts of \( \text{La}_2\text{O}_3 \) are different, both can form a macromolecular network structure and solidify, but their reaction rates are different. As listed in Table 1, with the increase in the addition of \( \text{La}_2\text{O}_3 \), the phosphate solidification is faster, which shows that \( \text{La}_2\text{O}_3 \) promotes the formation of network macromolecules. Conversely, an increase in \( \text{La}_2\text{O}_3 \) content not only improves the macroscopic adhesive property of phosphate but also promotes the evaporation of water, thus shortening the curing time.

With the increase in the treatment temperature, after 300 °C, the 30% \( \text{La}_2\text{O}_3 \) phosphate appears as an AlPO4 phase because in the process of heat treatment, \( \text{Al(PO}_4)_3 \cdot 3\text{H}_2\text{O} \) dehydration and other reactions generate AlPO4, among which the \( \text{La(OH)}_3 \) phase decomposes and disappears at 300 °C and participates in the transformation into LaPO4 phase. With an increase in the processing temperature, the phases of 30% La-containing phosphates tend to be the same after 300 °C, forming AlPO4 and LaPO4; however, the AlPO4 phase with strong diffraction peaks is not formed until the temperature exceeds 1000 °C. The spectrum shows that the diffraction peak of AlPO4 is higher and narrower, indicating that more AlPO4 phases are generated. A possible reason is that the amount of added \( \text{La}_2\text{O}_3 \) is less than that of \( \text{Al(PO}_4)_3 \), and the raw material provides more Al, making PO4+ more combined with Al3+ and then generating more AlPO4 substances.

The analysis of the XRD pattern data of the 40% La-containing phosphate shows that there are low-temperature phases of \( \text{Cr(OH)}_3 \) and \( \text{CrO}_2 \) below 700 °C. A comparative analysis showed that in the 40% La-containing phosphate at 300 and 500 °C, \( \text{La(OH)}_3 \) did not participate in the formation of LaPO4. This is sufficient to show that the phase-transition temperature increases with increasing La. With an increase in the treatment temperature, the graph shows a large number of LaPO4 phases at 1000 °C and no \( \text{La(OH)}_3 \) phase can be detected, indicating that \( \text{La(OH)}_3 \) was involved in the formation of LaPO4 at 1000 °C. When the heat treatment temperature exceeds 1500 °C, AlPO4 with good crystallinity can be detected; unlike phosphate containing 30% La, the diffraction peak of AlPO4 is stronger than that of AlPO4. The reason may be that with the increase in \( \text{La}_2\text{O}_3 \) addition, more \( \text{La}_3^+ \) is provided for the generation of LaPO4.

#### 3.2. Microscopic Morphology Analysis

The self-curing of phosphate is realized through the intermolecular polymerization reaction, and the added \( \text{La}_2\text{O}_3 \) reacts with phosphate molecules to promote intermolecular cross-linking and condensation, thus reducing the curing temperature of phosphate and shortening the curing time. As shown in Figure 3a, the self-curing La–Al phosphate at room temperature is relatively dense, and there are no cracks or pores on the surface.

However, as shown in Figure 3a–c, the compactness of the sample decreases with an increase in the temperature, which may be due to two reasons. First, the low-temperature curing temperature of the sample is far lower than the evaporation temperature of water, resulting in free water and bound water to seal inside and on the sample surface. When the sample is heat-treated, the free water and bound water absorb heat and volatilize, leaving behind “pores.” Second, in combination with the XRD analysis, \( \text{La(OH)}_3 \) and \( \text{Al(PO}_4)_3 \cdot 3\text{H}_2\text{O} \) were decomposed during the heating process from room temperature to 300 °C, and the water molecules generated by the

### Table 1. Molar Ratio of La–Al-Based Phosphate Reactants and Their Corresponding Curing Time

| sample no. | \( \text{H}_3\text{PO}_4 \) | \( \text{Al(OH)}_3 \) | \( \text{CrO}_3 \) | \( \text{H}_2\text{O}_2 \) | \( \text{La}_2\text{O}_3 \) (wt %) | curing time (h) |
|-----------|----------------|----------------|----------------|----------------|----------------|------------------|
| a         | 1.8            | 0.6            | 0.2            | 0.2            | 10             | >2               |
| b         | 1.8            | 0.6            | 0.2            | 0.2            | 20             | 1.5–2 (bubbling) |
| c         | 1.8            | 0.6            | 0.2            | 0.2            | 30             | 0.5–1            |
| d         | 1.8            | 0.6            | 0.2            | 0.2            | 40             | <0.5             |

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decomposition are endothermic in nature and evaporate, leaving behind "pores," thus reducing the compactness of the La–Al phosphates. With an increase in the treatment temperature, the micromorphologies of Figure 3d–g show that the sample surface has a densification trend. This is because the sample begins to undergo a large degree of phase transformation at 1000 °C, and the phase change volume gradually fills in the pores left by the low-temperature-treated free water, bound water, and volatile substances, thus causing the sample to exhibit a densification trend. As shown in Figure 3e, the 30% La-containing phosphate appears to be of two phase above 1000 °C.

However, combined with the XRD analysis, the sample formed a relatively uniform phase composition after 300 °C, while the crystallinity of the AlPO₄ phase below 1000 °C is poor; therefore, no evident two phase is captured by the SEM below 1000 °C. The XRD data showed that the La–Al series phosphates formed AlPO₄ phases with better crystallinity at 1000 °C, and the same SEM image of the sample treated at the same temperature could capture this phase. As the temperature continued to rise, the La–Al phosphates gradually formed more uniform LaPO₄ and AlPO₄ phase compositions.

Figure 4 shows the micromorphology of the La–Al phosphates with 40% La content; a comparative analysis showed that the density of 30% LaAl decreased from room temperature to 500 °C, while 40% LaAl showed a densification trend. The reason may be that with the increase in La³⁺, the cross-linking polycondensation reaction between La³⁺ and AlCr phosphate becomes more intense and sufficient, releasing more heat and taking away more free water. Furthermore, in the heating process, more heat is used to remove phase transition and CrPO₄ decomposition reaction, and the volume of the phase transition is used to supplement the pores, making the sample show a certain densification trend. As shown in Figure 4F, with increasing temperature, the La–Al phosphates form 40% La content form two distinct phases at 1500 °C. From the XRD data, we find that the La–Al phosphates form LaPO₄ and AlPO₄ with good crystallinity at 1500 °C. As shown in Figure 4G, there are many fine particles on the sample surface. From the EDS results, the particles are mainly from the growth and transformation of Al-containing substances on the La substances. Similarly, combined with the XRD data and point-sweep data, the phase composition of the samples heat-treated at 1500 and 1700 °C is mainly composed of gray-white LaPO₄ phase and black AlPO₄ phase.

We compared and analyzed the microtopography with La contents of 30 and 40%. As shown in Figure 3a–c, the density of the self-curing 30% La-containing phosphates decreases during the temperature treatment. However, the 40% La-containing phosphate showed a densification tendency at the corresponding treatment temperature, and it was verified that 30% of the low-temperature curing materials containing LaAl phosphate mainly had contained bound water that was not volatilized in time, while 40% of the low-temperature curing materials containing La–Al phosphate had most of their moisture removed due to the continuous exothermic reaction. Therefore, the density of the materials did not decrease due to defects, such as pores, after subsequent heat treatments at 300 and 500 °C. By comparing (b), (c), (d), (e), (B), (C), (D), and (E) with the XRD data, it can also be seen that the decomposition and phase-transition temperatures of CrPO₄, Cr(OH)₃, and La(OH)₃ increased with increasing La content.

Figure 3. Micromorphology of the 30% La–Al phosphate treated at different temperatures: (a) RT, (b) 300 °C, (c) 500 °C, (d) 700 °C, (e) 1000 °C, (f) 1500 °C, and (g) 1700 °C.
After the heat treatment, the crystal growth and grain boundary between the grains were evident in the sample containing 30% La phosphate, and the phase distribution of LaPO₄ and AlPO₄ was more uniform. However, at 1700 °C, the 40% phosphate-containing La formed finer LaPO₄ particles with a small amount of AlPO₄ mixed in.

In summary, during the heat treatment, the sample microstructure maintained a flat and compact structure, and the phase transition was relatively stable. The LaPO₄ and AlPO₄ ceramic phases with good high-temperature resistance and crystallinity were formed at 1000 and 1500 °C, respectively.

### 3.3. Thermal Properties

#### 3.3.1. TGA–DSC Analysis

The La–Al-based phosphate polymer is used as a composite material, and its composition change during the high-temperature treatment directly affects the performance of the composite material. To study the thermal properties of the La–Al-based phosphate matrix, the La–Al-based phosphate was analyzed via TG-DSC from room temperature to 1000 °C. Figure 4 shows the analysis results, which shows the TG-DSC curves of the La–Al phosphates containing 30 and 40% La.
heated to 1000 °C at a heating rate of 10 °C/min in an air environment. The total weight loss rate of the samples (a) and (e) is ∼18% from room temperature to 1000 °C, in which the fastest weight loss occurs before 400 °C, the weight loss is relatively gentle between 400 and 800 °C, and the weight loss remains unchanged after 800 °C. Three distinct endothermic peaks appeared in samples (a) and (e) before 300 °C, and their temperatures were ~60, 145, and 233 °C. Among them, the endothermic peak at 60 °C might indicate that the sample at room temperature cures fast, resulting in incomplete basic reaction, leading to further heating or free water evaporation. The heat absorption peak at 145 °C may be attributed to inorganic phosphate radical polymerization cross-linking curing; in addition, the volatilization of bound water and the small endothermic peak around 233 °C may be the reason for the polymerization combined water loss. The samples (b), (c), (d), (f), (g), and (h) were subjected to high-temperature thermal testing and exhibited no evident endothermic peak, and the weight loss rate of the samples was within 2%. The weight loss rate of the samples could be significantly improved after heat treatment (Figure 5).

3.3.2. Ablation Performance. In this study, the La–Al phosphates still had a good morphology after being tested in a 1700 °C muffle furnace for 2 h. Therefore, a 2000 °C oxygen-acetylene flame was used to test its heat resistance at a higher temperature. Many defects (such as bound water) were detected in the self-curing La–Al phosphate at room temperature, which can cause serious damage to the sample when directly used in a high-temperature environment. To avoid such damage as much as possible, it is necessary to heat treat the La–Al phosphates at a certain temperature. According to Kingery,19,20 the self-cured phosphate can be directly used in a high-temperature thermal environment only after heat treatment at ∼427 °C, and, combined with thermogravimetric analysis, indicates that volatile substances such as free water were largely removed below 427 °C. Therefore, in this study, the La–Al phosphate block material was heat-treated at 427 °C, and the treated samples were directly used for the oxygen-acetylene ablation test at 2000 °C.

Figure 6 shows the micromorphology of the 30% La–Al phosphates after being treated at 427 °C and then by oxygen-acetylene flame ablation at 2000 °C for 30 s. Figure 6a–c shows the microscopic morphologies of the central, transition, and edge regions of the ablated sample, respectively. From the microscopic morphology after ablation of the sample surface, several irregular edge areas of round bars are formed, and there are large holes; the possible reason is that the edge zone temperature rise rate is lower, making the surface sintering growth slower, prompting abnormal grains to increase, and, in turn, generating a large number of round bars. However, the stresses generated by the ablative impact in the central area are transferred to the edge area, resulting in a large number of large-sized holes in the edge area. The surface of the ablation transition zone shows a densification trend compared with the ablation edge zone, but there are still a large number of

Figure 6. Micromorphology of 30% La–Al phosphate after heat treatment at 427 °C by oxyacetylene flame ablation at 2000 °C (a, a1) ablation central area, (b, b1) ablation transition area, and (c, c1) ablation edge area.

Figure 7. XRD after ablation of La–Al phosphates.
micron-sized pores on the surface, and there are more shallow pits and small cracks. The probable reason is that the heat makes the transition zone combine with water volatilization and leave pores, coupled with the ablation transition zone getting closer to the ablation center, allowing more heat through the air “heat wave” to the surrounding transmission, resulting in the formation of the transition zone “side down” characteristics. The same ablation center stress transmission occurs, resulting in the transition zone micro-cracking, the transition zone surface heat, and uneven stress. This affects the growth rate of the grains and makes more shallow pits to form in the transition zone. Through a comparative analysis, it is found that the central ablation zone has a denser micro-structure than the edge and transition zones. As shown in Figure 6a, there are two evident phases in the central ablation zone, forming microscopic morphological features of irregular light gray sheets growing on the dark gray matrix. Combined with the XRD and EDS data analyses, light gray LaPO₄ and dark gray AlPO₄ high-temperature-resistant phases were generated in the central region. Evidently, cracks also appeared in the ablation center, and the main reasons for the cracks may be the volatilization of the phase with a low melting point under high-temperature ablation and the uneven growth and

Figure 8. Micromorphology of 40% La–Al phosphate after heat treatment at 427 °C via oxyacetylene flame ablation at 2000 °C (a, a1) ablation central area, (b, b1) ablation transition area, and (c, c1) ablation edge area.

Figure 9. Mechanism of the La–Al system phosphate ablation process.

Figure 10. Spatial structure of the aluminum phosphate polymer.

Figure 11. Cross-linking reaction between aluminum chromium phosphate and La₂O₃.
stress accumulation in the phase transition area under the action of heat and impact force (Figure 7).

Similarly, the La–Al phosphate block material with a 40% La content after 427 °C treatment was subjected to an oxygen acetylene ablation test at 2000 °C, and the phosphate block sample showed excellent heat resistance after 30 s of oxygen acetylene flame ablation at 2000 °C. Figure 8a–c, respectively, represents the ablation center, ablation transition, and ablation edge. As shown in the SEM images, the entire surface of the ablation samples shows a smooth, dense microstructure, and there are microcracks in the ablation transition and ablation edge area, which may be due to the high flame impact force in the ablation center, resulting in the stress accumulation and stress “transfer,” as well as the volatilization of volatile substances, which generate microcracks and other defects in the uneven heating zone of the sample. From Figure 8c, we find that in the ablation fringe area, there are many “flat bubble” shapes in the phase structure, and there is a small number of microcracks, and the reason for this may be the slow heating rate of the edge zone leading to abnormal grain growth, coupled with the transition zone not being flatter so that the “heat wave” generated by the ablation center can better reach the edge zone and the abnormal growth of grain “up and down” grain growth is affected to a certain extent. There are many “fish scale” morphological characteristics in the ablation transition zone. The reason may be that the heat of the ablation center and the force generated by the flame converge into the heat wave to sinter the surface of the transition zone and then form the special morphology of “fish scales.” Based on the data analysis shown in Figure 8a and EDS, a large number of LaPO4 particles were formed in the ablation center area, with a relatively uniform particle size, mixed with a slightly dark gray AlPO4 phase and distributed evenly on the sample surface.

Figure 9 shows a schematic of the La–Al system phosphate ablation process. From the above analysis, it is clear that the ablation process of this type of phosphate is dominated by two types of reactions, namely, physical and chemical reactions. The physical reaction mainly includes the melting and sublimation of phosphate materials under the high temperature and high pressure of oxyacetylene ablation, while the chemical reaction mainly refers to the decomposition of phosphate materials at high temperatures, grain sintering, and growth, among other processes.

\[
\text{CrO}_2 \rightarrow \text{Cr}_2\text{O}_3 + \text{O}_2 \dagger \\
\text{Cr(OH)}_3 \rightarrow \text{Cr}_2\text{O}_3 + \text{H}_2\text{O} \dagger 
\]

La–Al-based phosphates undergo a series of reactions under the ablation of an oxyacetylene flame. At the beginning of the ablation reaction, La–Al phosphates undergo decomposition and volatilization of low melting point substances. For example, the decomposition equations of reactions 1 and 2 produce H2O and O2 gases. The gases escape and leave micro-pits on the surface. These micro-pits increase the contact area between the sample and the flame, and the unstable La–Al(PO4) turns into stable LaPO4 and AlPO4 phases in the middle stage of ablation. Then, the AlPO4 phase melts and has a high viscosity at a high temperature, which fills the above-mentioned micro-pores; lays flat on the surface, stabilizing the LaPO4 particles well, and effectively reduces mechanical peeling. The LaPO4 particles sinter and grow up in the later stage of ablation and form a dense La–Al phosphate-resistant layer with AlPO4, as shown in Figure 9, which in turn further reduces the further ablation damage of the phosphate to a certain extent.

3.4. Self-Curing Mechanism. The low-temperature self-curing phenomenon of phosphate is due to the cross-linking and polycondensation of aluminum chromium phosphate and metal cations into macromolecules and the accompanying exothermic reaction. A large amount of heat is released in the process of cross-linking dehydration of phosphate, and free water volatilizes rapidly with the help of heat, thereby increasing the viscosity of the solution, because of which the self-curing phenomenon of phosphate can occur without the application of high temperature or heat treatment. At the beginning of the reaction, a large number of trivalent [PO4]3− ions can be found in the phosphate solution. After the reaction with aluminum hydroxide, [PO4]3+ polymerization occurs to generate [HPO4]2− ions, which become the “endpoints” of chain-like polymerization. Such two “endpoints” can be combined to form tetravalent phosphate. As the reaction continues, the [HPO4]2− ion transforms into the intermediate state of \((H_2PO_4)2Al(HPO_4)\)−, which is cross-linked into a 3D network, showing a certain macroscopic adhesive effect, as shown in Figure 10.

As the reaction continued, the stability of the phosphate solution could be improved by the introduction of Cr3+. Because Cr2O3 is insoluble in water, Cr2O3 is reduced to Cr3+ by hydrogen peroxide. Because the outer electron orbital of Cr3+ is d5sp2 hybridization, it is a central ion complex with the ligand H2O molecule, forming an inner-orbital-type complex \([\text{Cr}(\text{H}_2\text{O})_6]^{3+}\). The structure of the electron layer of the central ion changes, but there are no or a few unpaired electrons, and the orbital energy is low; therefore, the inner orbital-type complex ion is highly stable. This complex may form complex salts with phosphate ions and hydrogen phosphate ions. At the same time as the formation of this complex, the energy of the crystal water in the phosphate decreases, and the phosphate dehydrates faster with an increase in temperature. The aluminum chromium phosphate reaction process can be described by the following equations:

\[
\text{Al(OH)}_3 + 3\text{H}_2\text{PO}_4 \rightarrow \text{Al(H}_2\text{PO}_4)_3 + 6\text{H}_2\text{O} \\
\text{Al(H}_2\text{PO}_4)_3 \rightarrow [(\text{H}_2\text{PO}_4)_2\text{Al(HPO}_4)\]^{-} + \text{H}^+ \\
4\text{Cr}_3\text{O}_3 + 6\text{H}_2\text{O}_2 + 12\text{H}^+ \rightarrow 4\text{Cr}^{3+} + 6\text{O}_2 \uparrow + 12\text{H}_2\text{O} \\
4\text{Cr}^{3+} + 12[(\text{H}_2\text{PO}_4)_2\text{Al(HPO}_4)\]^{-} \rightarrow 12[(\text{H}_2\text{PO}_4)_2\text{Al(HPO}_4)\]^{2-}
\]

Finally, to improve the temperature resistance of the phosphate and reduce the curing temperature of the phosphate, La2O3 was used as the curing agent to undergo a cross-linking reaction with the aluminum chromium phosphate solution. As an alkaline oxide, La2O3 has strong activity and a relatively high melting point of 2300 °C. As a curing agent, La3+ reacts with \((\text{H}_2\text{PO}_4)_2\text{Al(HPO}_4)\]− to cross-link and polymerize to form a macromolecular structure. La3+ partially replaces the positions of Cr3+ and Al3+ and releases a large amount of heat. As the reaction continues, the macromolecules develop rapidly and continuously expand into space, gradually forming a 3D network. The solution gradually exhibits macroscopic viscosity.
until the sample is completely solidified. Figure 11 illustrates this process.

4. CONCLUSIONS
An appropriate amount of metal oxide $La_2O_3$ as a curing agent can make aluminum chromium phosphate fully cure and form within 1 h in an oven at an atmospheric pressure of 50 °C. This significantly reduces the curing temperature of phosphate, and a $La-Al$ phosphate block material can be prepared.

The $La-Al$ phosphates exhibited good thermal stability. During the heat treatment at different temperatures ranging from 300 to 1700 °C in a muffle furnace, the samples showed excellent temperature resistance. The entire sample was relatively complete, and the surface gradually transformed into dense high-temperature-resistant phases of $LaPO_4$ and $AlPO_4$.

The $La-Al$ phosphates showed excellent temperature and oxidation resistances. In terms of the La content, the $La-Al$ phosphate containing 40% La showed better temperature resistance and oxidation resistance under the 2000 °C oxyacetylene flame. After ablation, the surface was more compact and flatter. The ablation center formed a granular layer with $LaPO_4$ as the main phase and mixed with a small amount of the $AlPO_4$ phase. This provided a solid “backing” to resist ablation at 2000 °C.

The $La-Al$ phosphate block material has relatively high-temperature resistance in domestic and international phosphate research worldwide (see Table 2 for a summary of such research). $La-Al$ phosphates can directly undergo ablation damage within 2000 °C after heat treatment at ~427 °C in the later stage; therefore, the material does not need to undergo other complex processes such as high-temperature sintering.

### Table 2. Domestic and Foreign Phosphate Research on Temperature Resistance

| system | temperature (°C) | source | remarks |
|--------|------------------|--------|---------|
| $AlPO_4:\text{Si}_2\text{C}-\text{AlIF}_3$ | 1300 | an engineering ceramic-used high-temperature-resistant inorganic phosphate-based adhesive self-reinforced by in situ growth of mullite whisker | air |
| $AlPO_4:\text{SiO}_2$ | 1300 | effect of $Al/P$ ratio on the bonding performance of high-temperature-resistant aluminum phosphate adhesive | air |
| $AlPO_4:\text{SiO}_2-B_4\text{C}$ | 1500 | a new practical inorganic phosphate adhesive applied under both air and argon atmospheres | air, argon gas |
| $AlPO_4$ | 1500 | preparation and characterization of high-temperature-resistant and high-strength alcohol-soluble phosphate/phenol-formaldehyde hybrid adhesives | air |
| $AlPO_4-CuO-Si_2\text{C}-\text{Si-Al-Rglass}$ | 1600 | multiple high-temperature-resistant phases modified phosphate-based adhesive for engineering ceramic connection in extreme environments | air |
| $AlPO_4$ | 1700 | effects of nano-aluminum nitride on the performance of an ultrahigh-temperature inorganic phosphate adhesive cured at room temperature | air |
| $AlPO_4$ | 1800 | heat- and high-temperature-resistant adhesives for joining carbon and ceramic materials | nitrogen |

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