

Review

The Oxidation Process and Methods for Improving Reactivity of Al

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Abstract: Aluminum (Al) has been widely used in micro-electromechanical systems (MEMS), polymer bonded explosives (PBXs) and solid propellants. Its typical core-shell structure (the inside active Al core and the external alumina (Al_2O_3) shell) determines its oxidation process, which is mainly influenced by oxidant diffusion, Al_2O_3 crystal transformation and melt-dispersion of the inside active Al. Consequently, the properties of Al can be controlled by changing these factors. Metastable intermixed composites (MICs), flake Al and nano Al can improve the properties of Al by increasing the diffusion efficiency of the oxidant. Fluorine, Titanium carbide (TiC), and alloy can crack the Al_2O_3 shell to improve the properties of Al. Furthermore, those materials with good thermal conductivity can increase the heat transferred to the internal active Al, which can also improve the reactivity of Al. Now, the integration of different modification methods is employed to further improve the properties of Al. With the ever-increasing demands on the performance of MEMS, PBXs and solid propellants, Al-based composite materials with high stability during storage and transportation, and high reactivity for usage will become a new research focus in the future.

Keywords: aluminum; oxidation process; reaction mechanism; modification method; development trend



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1. Introduction

Aluminum (Al) is an important solid metal fuel, which has been widely used in connection between crystalline silicon [1], micro-electromechanical systems (MEMS) [2–5], polymer bonded explosives (PBXs) [6–12], and solid propellants [13–18] to provide energy. As a combustion agent, Al displays obvious advantages, such as low oxidant consumption, high combustion calorific value (31,070 J/g), and high measured specific impulse [19–21]. The dense and high melting point (about 2000 °C) alumina (Al_2O_3) shell will be formed when Al is exposed to air, which can improve the safety of aluminum powder in the process of production, storage, transportation and usage [22–24]. However, the oxidation process of Al is also closely related to the Al_2O_3 shell, which causes the inside active Al to become hindered (it cannot come into contact with oxidation components) [25–28]. As a result, the ignition and combustion reaction activity of Al is limited by the Al_2O_3 shell [21,29–31]. In addition, the combustion product Al_2O_3 will wrap onto the surface of the active Al again, which further hinders the combustion chemical reaction, resulting in an incomplete combustion of Al, and reduced energy release efficiency [29].

To solve the problem of the Al_2O_3 shell limiting oxidation activity and combustion efficiency, the oxidation process of Al has been studied extensively. To describe the ignition and combustion process of Al, some mechanisms, such as the oxidant diffusion mechanism [32–34], the Al_2O_3 crystal transformation mechanism [35–41], and the melt-dispersion mechanism [42–46], have been proposed. Meanwhile, to improve the activity of Al, some new composite materials, such as Al-based metastable intermixed composites (MICs), flake Al-based composite materials, alloying and so on, have been found and used gradually [12,47–57].

A large number of reviews on Al have been published. Xiang Zhou [58] summarized the synthesis, ignition and combustion modeling, and applications of Al-based nanocomposites. Wei He [59] introduced the preparation and characterization of Al-based MICs. In addition, Xiaoxia Ma [60] focused on the preparation and fundamental properties of the Al-based core-shell structured nanoenergetic. However, they discussed the preparation and characterization methods, and hardly any reviews systematically summarized the relationship between the modification method and the different ignition mechanism of Al during the past decades. This review examines systematically the key influencing factors and the mechanisms during the Al oxidation process, and classified modification methods by the influencing factors of its transformation. Furthermore, it provides ideas for selecting modification methods of Al under different application conditions. What is more, the new trend of Al-based composite materials has been indicated.

2. The Key Influencing Factors and the Reaction Mechanism during the Al Oxidation Process

The Al particle is a typical core-shell structure with active Al wrapped in dense Al_2O_3 . Therefore, the oxidation process of the Al particle is the evolution process of the oxidant, the alumina shell, and the inside active Al. Furthermore, the diffusion of the oxidant, the growth and rupture of the Al_2O_3 shell, and the melting and gasification of the inside active Al are the key influencing factors of the Al oxidation process.

2.1. Effect of Diffusion of the Oxidant on the Al Oxidation Process

The diffusion of the oxidant is a necessary process for Al oxidation. Zachariah [32–34] proposed a three-step oxidation process of Al (oxidant diffusion mechanism) on the basis of a well-known idealized “shrinking core” mechanism for spherical particles, which involves a reaction front moving radially inward separating an unreacted core with a completely reacted ash outer layer. As shown in Figure 1, the diffusion of the oxidant is influenced by three factors: the Al_2O_3 shell (generated on the surface in air), the Al_2O_3 ash (the product of oxidation reaction) and the chemical reaction of the oxidant with the inside active Al.

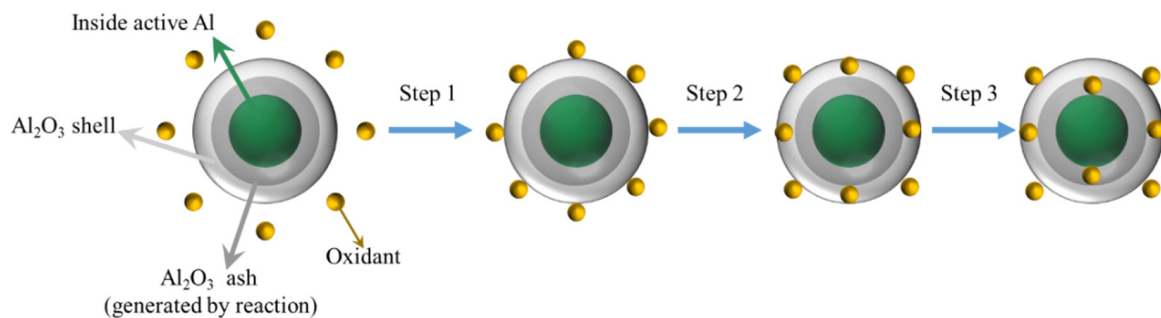


Figure 1. The three-step oxidation process of Al proposed by Zachariah.

Step 1: Diffusion of the oxidant through the Al_2O_3 shell to ash (Al_2O_3 generated by reaction, Al_2O_3 shell resistance).

Step 2: Diffusion of the oxidant through the ash (Al_2O_3 generated by reaction) to the surface of the inside active Al (ash resistance).

Step 3: Chemical reaction of the oxidant with the inside active Al at the unreacted core surface (chemical reaction resistance).

Since ash (Al_2O_3 generated by reaction) forms very rapidly, step 1 (Al_2O_3 shell resistance) can be ignored. This still leaves steps 2 and 3 from which to deduce the rate-limiting step. Then it is proved by experiments that the reaction of Al is controlled by diffusion. Therefore, the diffusion of the oxidant through the Al_2O_3 ash to the inside active Al is the rate-limiting step.

2.2. Effect of the Al_2O_3 Shell on the Al Oxidation Process

The Al_2O_3 shell on the surface of Al has a crucial effect on the oxidation process of Al. Trunov [35] analyzed the processes of simultaneous growth and phase transformations of Al_2O_3 during oxidation of the Al particle (Al_2O_3 crystal transformation mechanism). The process of Al oxidation can be divided into four stages, which can be seen in Figure 2. Firstly, amorphous Al_2O_3 on the Al surface gradually grows thicker and the reaction rate is controlled by the outward diffusion of Al cations [36]. Secondly, amorphous Al_2O_3 on the Al surface transforms to γ - Al_2O_3 when the critical thickness is approached, or when the temperature becomes sufficiently high [37–40]. Since the density of γ - Al_2O_3 exceeds that of the amorphous Al_2O_3 , the Al_2O_3 shell on the Al surface ruptures. In addition, the inside active Al can come into contact with oxide, which greatly increases the reaction rate. With the growth and healing of the γ - Al_2O_3 shell, the reaction rate decreases significantly. Eventually, a regular polycrystalline layer of γ - Al_2O_3 forms by the end of the second stage. In stage three, the growth of γ - Al_2O_3 continues. In the meantime, γ - Al_2O_3 transforms the crystal phase to δ - Al_2O_3 or θ - Al_2O_3 . Due to the density of δ - Al_2O_3 , and θ - Al_2O_3 is similar to that of γ - Al_2O_3 , the shell of Al_2O_3 will not rupture and the reaction will not change significantly. Additionally, the reaction rate is limited by the inward grain boundary diffusion of oxidant anions in stage three [36,41]. When the stable and denser α - Al_2O_3 forms by increased temperature, stage three ends. Stage four starts when Al_2O_3 is completely transformed to α - Al_2O_3 . In stage three, the thickness of the γ - Al_2O_3 layer decreases, and the oxidation rate increases momentarily. Once most of the oxide layer is transformed to coarse and dense α - Al_2O_3 , the contact between the internal active aluminum and the oxidized components is completely blocked, and the reaction rate decreases rapidly.

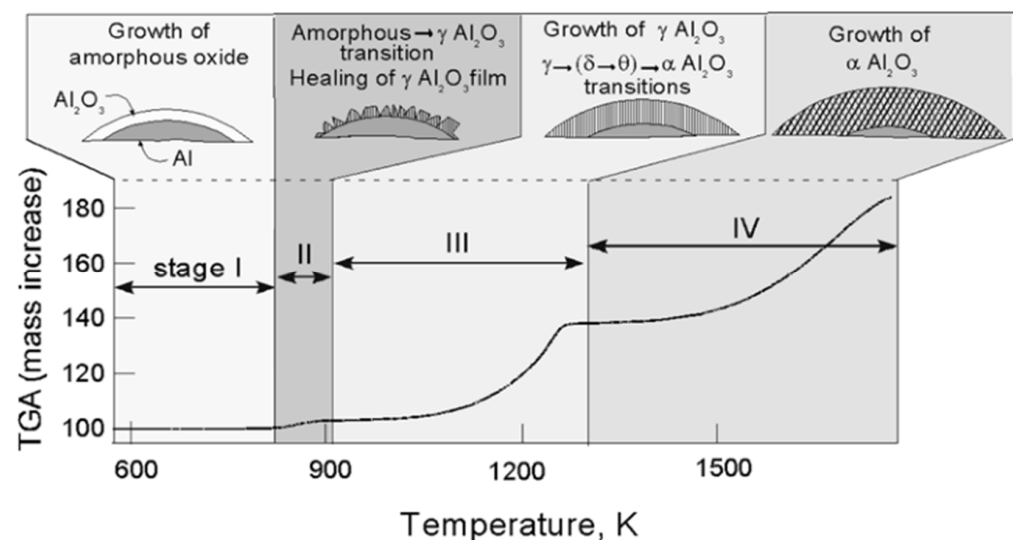


Figure 2. The change of the Al_2O_3 shell during the oxidation process of the Al particle, reprinted/adapted with permission from Ref. [35]. 2006, Dreizin, E. L.

2.3. Effect of the Inside Active Al on the Al Oxidation Process

Levitas [42–46] proposed a melt-dispersion mechanism when Al is heated rapidly. As shown in Figure 3, the volume change (6% volume expansion) due to the melting of the inside active Al can make the pressure of the Al_2O_3 shell reach about 11 GPa. That can cause spallation of the Al_2O_3 shell and the inside active Al can come into contact with the oxidant. Furthermore, the pressure inside the molten active Al will disperse the active Al into small droplets. Then the oxidation process of the active Al would occur rapidly.

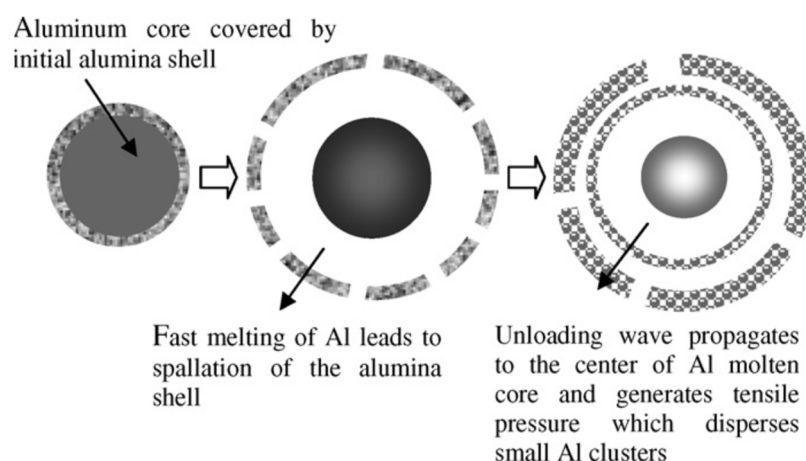


Figure 3. The process of melt and dispersion of the active Al during the oxidation process of the Al particle, reprinted/adapted with permission from Ref. [46]. 2008, Levitas Valery I.

From the above discussion, it can be seen that the diffusion of the oxidant, the crystallization and the growth of the Al_2O_3 shell, and the melting and dispersion of the internal active Al, all have a crucial impact on the oxidation process of Al. The leading factors will change with the particle size and the heating rate of Al. Therefore, the oxidation process of Al under different conditions is not the same. At a slow heating rate, the diffusion of the oxidant plays a leading role, and the oxidation process of nano Al, which has a large specific surface area, conforms to the three-step oxidation process (proposed by Zachariah [32,33]). At the slow heating rate, the transformation and growth of the Al_2O_3 shell have the greatest influence on the oxidation process of micron Al, so the oxidation process of micron Al conforms to the Al_2O_3 shell transformation and growth mechanism (proposed by Trunov [35]). At a fast heating rate, the melting and dispersion of the internal active Al have the greatest influence on the oxidation process of nano Al, so the oxidation process of nano Al conforms to the melting diffusion mechanism (proposed by Levitas [42–46]).

The three crucial factors that determine the oxidation process of Al are: the diffusion of the oxidant, the transformation and growth of the Al_2O_3 shell, and the melting and dispersion of the internal active Al. As the key factors affecting the oxidation process of Al have been investigated, the oxidation process of Al under different conditions can be accurately described. Then the method of changing the Al oxidation process can be found, and the properties of Al can be improved.

2.4. Effect of the Gas Phase Reaction on the Al Oxidation Process

The gasification temperature of the internal active Al is lower than that of the Al_2O_3 shell, which leads to the gas phase reaction involving gas phase Al during Al oxidation [61]. As the models of the combustion process of micron Al, which were introduced both by Law [62] and Glassman [61], and later expanded upon by Brooks and Beckstead [63], the gas phase flame can drive the surface reactions of the Al particle. However, it is difficult to accurately characterize the process and products of gas phase reactions. Lynch [64,65] found that volatile suboxides existed during Al combustion, and Tappan [66] found the reaction between the gas phase Al and the Al_2O_3 shell. Although the gas phase reaction has been found, the reaction process under the different reaction conditions has not been accurately confirmed, and its effect on the oxidation of Al continues to be studied.

3. Methods for Improving Al Properties

To improve the properties of Al, the following methods have been investigated: metastable intermixed composites (MICs, reducing the diffusion of the oxidant), nano Al and flake Al (increasing the specific surface area of Al) for improving diffusion efficiency, fluorine modification [67], Titanium carbide (TiC) modification and alloying for cracking

the Al_2O_3 shell and the modification of good thermal conductivity materials (Ag, graphene) for improving heat transfer efficiency.

3.1. Improving Diffusion Efficiency

3.1.1. MICs

Metastable intermixed composites (MICs) are usually composed of a metal fuel and an oxidizer. The Los Alamos National Laboratory in the US was the first to study the combustion performance of MICs. Aumann [68] prepared the Al/MoO₃ nano Al, which bulk energy density can reach 16 kJ/cm³, and the combustion rate is more than 1000 times that of the traditional thermit. The oxidizer of the Al-based MICs is usually metal oxide (bismuth oxide (Bi₂O₃), copper oxide (CuO), cuprous oxide (Cu₂O), molybdenum oxide (MoO₃), ferric oxide (Fe₂O₃), nickel oxide (NiO), tungsten trioxide (WO₃)), halate (potassium perchlorate (KClO₄), potassium periodate (KIO₄), iron iodate (Fe(IO₃)₃), copper iodate (Cu(IO₃)₂), bismuth iodate (Bi(IO₃)₃)), and persulfide (potassium persulfate (K₂S₂O₈)) etc. Al-based MICs effectively reduce the diffusion distance of oxidation, which has significant advantages in volume energy density, ignition, and burning rate [59]. Although, MICs have not been able to achieve efficient, safe and low cost batch preparation, and the reaction process of MICs is difficult to accurately control. Therefore, MICs are difficult to apply in solid propellants and PBXs these days [69].

Ludovic Glavier [70] prepared Al-based MICs by Al, Bi₂O₃, CuO and MoO₃. Among them, as shown in Table 1, Al/Bi₂O₃ have the shorter the ignition delay time (5 μ s), the highest burning rate (420 m/s), and the fastest pressurization rate (5762 kPa/ μ s). Egor A. Lebedev [71] prepared the MICs layer composed of Al, CuO and Cu₂O by electrophoretic deposition, and the maximum heat release of MICs layer is 1954 J/g. Aifeng Jiang [72] prepared Fe₂O₃/nano Al by ball milling. The initial combustion temperature of Fe₂O₃/nano is about 600 °C. Ning Wang [73] prepared a Al@NiO core-shell structure composite micro-unit; the ignition temperature can be advanced to 531.5 °C, the heat release is 1410.2 J/g. Chunpei Yu [74] prepared 3D ordered macroporous Al/NiO MICs. Its heat releases up to 2462.27 J/g. Wei He [75] prepared Al/Energetic metal organic frameworks (EMOF) MICs, which can activate Al by eliminating Al₂O₃ shell and produce metal oxide by decomposing of EMOF. The heat release of Al/EMOF is 3464 J/g; the burning rate is 2.8 m/s.

Table 1. The thermal and combustion properties of Al-based MICs, reprinted/adapted with permission from Ref. [70]. 2015, Rossi Carole.

Sample	Heat Release J/g	Delay Time μ s	Burning Rate m/s	Pressurization Rate kPa/ μ s
Al/Bi ₂ O ₃	1541	5	420	5762
Al/CuO	1057	15	340	172
Al/MoO ₃	1883	110	100	35

W. Lee Perry [76] prepared WO₃·H₂O/Al MICs, which had an energy release of approximately 1.8 MJ/kg at a rate of approximately 215 GW/m². They found that the enhanced behavior of the hydrated MICs formulation resulted from the reaction of Al with the interstitially bound H₂O, which had additional energy release and generated hydrogen gas.

Ahmed Fahd [77] compared and analyzed the thermal behavior of different nanothermite tertiary compositions based on nano Al, graphene oxide (GO), various salt and metallic oxidizers (as shown in Figure 4). The addition of GO enhances the reactivity of nanothermites with both salt and metallic oxidizers by reducing the reaction onset temperature, activation energy and increasing the heat release. For nanothermites with oxidizing salts, the heterogeneous solid–gas reaction mechanism plays a more important role than the condensed phase reactions. In general, nanothermites based on oxidizing salts are more reactive than those with metallic ones, as indicated in both theoretical and experimental data. Among them, the GO/Al/KClO₄ nanothermite exhibits the highest

heat release (9614 J/g), while the GO/Al/K₂S₂O₈ nanothermite shows the lowest onset temperature and activation energy (380 °C and 105 kJ/mol^{−1}).

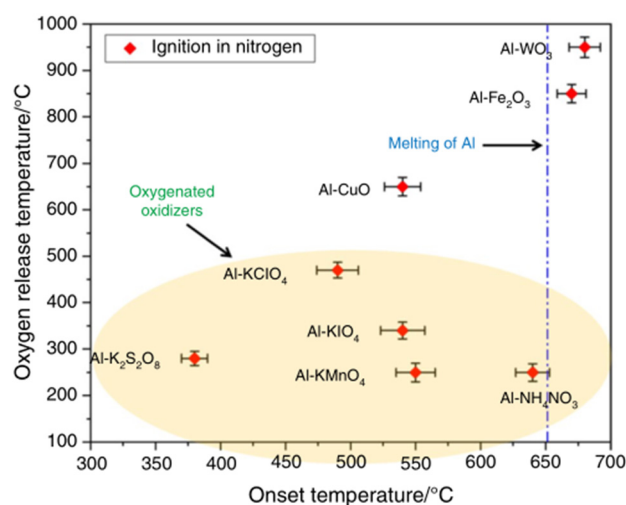


Figure 4. Relation between the oxidant release temperature of different oxidizers and the onset temperature of their nanothermites, reprinted/adapted with permission from Ref. [77]. 2022, Dubois, Charles.

3.1.2. Flake Al and Nano Al

Flake Al and nano Al have larger specific surface areas than that of sphere Al, which can improve the diffusion efficiency of oxidation [12,49–51,78–82]. However, the large-scale preparation process of nano Al and the effective Al content are still the key problems restricting its application.

Al has good ductility when it is subjected to external force, which would deform firstly. So flake Al is usually prepared by ball milling. As shown in Figure 5, in the process of ball milling, the sphere Al is extruded and sheared by ball milling beads. Under the action of force, sphere Al is changed to cake-like, firstly. In the second stage, the caked Al continues to be subjected to force and becomes flake Al; in the third stage, the flake Al would be broken and becomes smaller flake Al. So different thicknesses of flake Al can be prepared by controlling the parameters of ball milling.

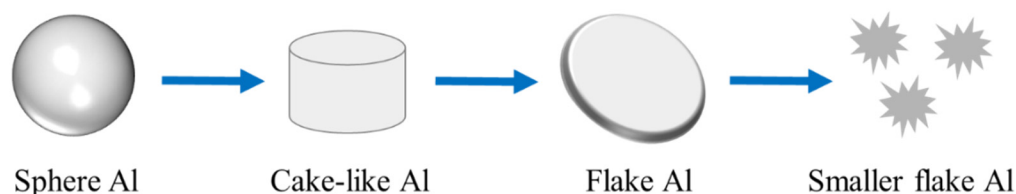


Figure 5. The deformation process of Al during ball milling.

Lei Xiao [51] prepared flake Al powder by ball milling, which could increase the detonation heat of Al-containing explosives by 6.48%. William Wilson [49] found that the flake Al became small particles more easily by shock waves during combustion. Qingming Liu [78] found that the flake Al dust–air mixture could be ignited, and self-sustained detonation by an electric spark of 40 J. DeQi Wang [81] applied the flake Al powder to a solid propellant, which increased the burning rate of the propellant by 5.5%. A.L. Kuhl [50,82] found the flake-Al could increase the impulse of the TNT composite charges by the fast combustion of the flake-Al.

The main methods of preparing nano Al include the electric explosion of wires method [83] and the plasma-arc recondensation [84]. In order to protect the nano Al from oxidation during storage, it is usually necessary to form a coating film on the surface of the nano Al. Deluca L T [21,85] prepared a nano-coated Al with stearic acid (L-ALEX), palmitic acid (P-ALEX), and trihydroperfluoro-undecyl alcohol (F-ALEX), et al. (as shown in Figure 6).

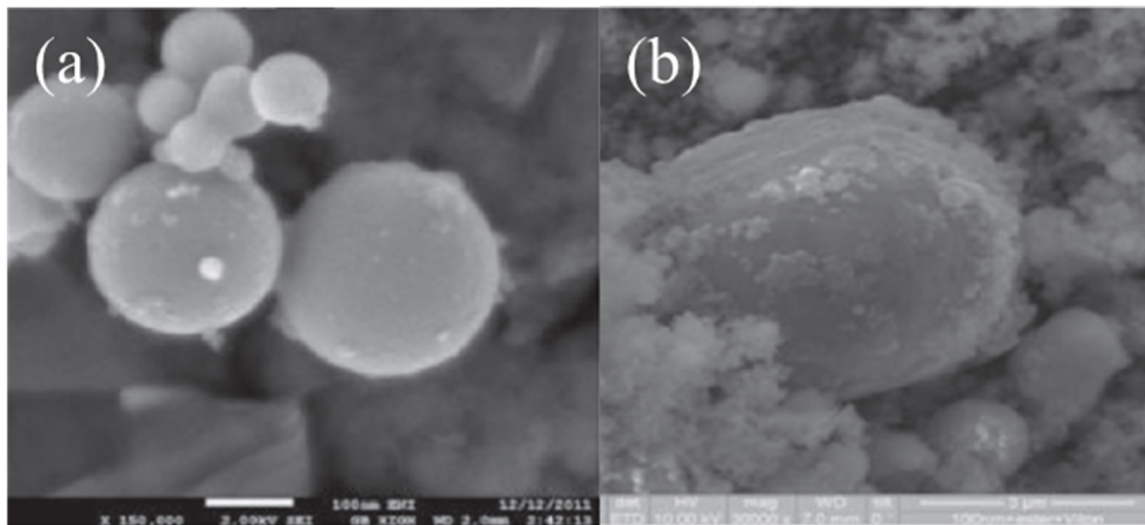


Figure 6. The SEM image of P-ALEX (a) and F-ALEX (b), reprinted/adapted with permission from Ref. [21]. 2017, Deluca, L.T.

Nano Al is widely used in MICs and solid propellants, etc [86]. Deyun Tang [87] used tannic acid (TA) to coat on nano Al as an interfacial layer to bind with $(\text{Fe}(\text{IO}_3)_3)$, copper iodate ($\text{Cu}(\text{IO}_3)_2$), bismuth iodate ($\text{Bi}(\text{IO}_3)_3$), respectively. For the energy release, $\text{Fe}(\text{IO}_3)_3$ -based MICs can be increased to 24.1 kJ/cm^3 (14.5% higher), whereas the $\text{Cu}(\text{IO}_3)_2$ -based MICs to 22.8 kJ/cm^3 (19.4%), and $\text{Bi}(\text{IO}_3)_3$ -based MICs to 20.2 kJ/cm^3 (3.1%). Deluca L [85] found that 100–200 nm Al can clearly increase the burning rate of the propellant.

Nano Al has high reactivity, which also produces some problems such as a high safety risk, a low content of active aluminum and sintering during combustion. Uncoated nano Al is classified by the International Air Transport Association as a highly flammable solid [88]. Weismiller [52] researched the effect of the particle size of Al and the oxidant on the properties of Al/CuO and Al/MoO₃. As shown in Table 2, the properties of Al/CuO and Al/MoO₃ are greatly improved due to the rapid decomposition of nano oxidants. However, due to the high Al₂O₃ content of nano Al, the nano Al does not show theoretical property advantages.

Table 2. Properties for Al/CuO and Al/MoO₃, reprinted/adapted with permission from Ref. [52]. 2011, Weismiller, M. R.

Sample	Linear Burning Rate m/s	Mass Burning Rate kg/s	Pressurization Rate MPa/ μs
Nano Al/nano CuO	980	3.8	0.67
Micron Al/nano CuO	660	4.8	1.82
Nano Al/micron CuO	200	1.3	0.28
Micron Al/micron CuO	180	2.0	0.11
Nano Al/nano MoO ₃	680	2.0	0.68
Micron Al/nano MoO ₃	360	1.5	0.44
Nano Al/micron MoO ₃	150	0.45	0.20
Micron Al/micron MoO ₃	47	0.52	0.17

Zachariah [89] found that the combustion product of nanothermites has two distinct populations of particles, as shown in Figure 7. The large particles include aluminum, oxidant, and reduced metal while the nano-sized particle is composed of reduced metal/metal oxide. As such large particles cannot be formed from the vapor phase condensation during the available transit time to the substrate, they must be formed in the condensed state as molten material.

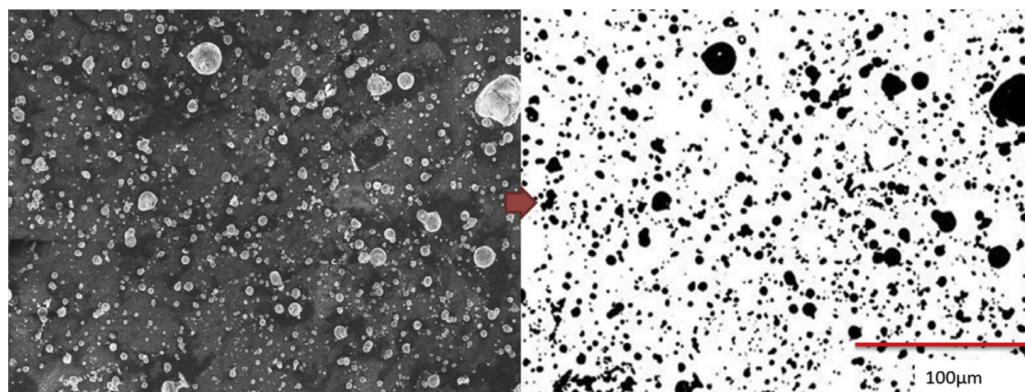


Figure 7. The combustion product of nanothermites, reprinted/adapted with permission from Ref. [89]. 2015, Zachariah, Michael R.

3.2. Cracking the Al_2O_3 Shell

3.2.1. Fluorine Modification

Fluoropolymers and fluorides can crack the Al_2O_3 shell of Al by the reaction between fluorine and Al_2O_3 shell. The curve of DSC will appear as a small exothermic peak before the main exothermic peak, caused by oxidation of Al. This phenomenon is known as preignition reaction (PIR), which is found by Osborne [90], and is verified by Zachariah by a quadrupole mass spectrometer and TG-DSC-MS coupling techniques [91]. The properties of the fluorine-modified Al are greatly improved due to the crack of the Al_2O_3 shell by PIR. Fluorine-modified Al can be used in MEMS and PBXs, but compatibility of fluoride with a propellant system is a key problem to realize its application in the propellant system.

Siva K. Valluri [92] prepared composite micro-units containing Al and NiF_2 by reaction inhibition ball milling, which shortened the ignition delay time and improved the combustion efficiency of Al powder. Sergey Matveev [48] prepared Al/ BiF_3 , which could produce 3200 K temperatures. Aifeng Jiang [72] prepared $\text{FeF}_3/\text{Al@vinyltrimethoxysilane}$ by ball milling, which had a large specific surface area ($26.33 \text{ m}^2/\text{g}$) and could be well-preserved from the air atmosphere and water. Additionally, the maximum heat release of $\text{FeF}_3/\text{nano Al@vinyltrimethoxysilane}$ can go up to $12,852 \text{ J/g}$.

Jena McCollum [93] composited Al with perfluoropolyethylene to advance the ignition temperature of Al to about 330°C . Dong Won Kim [94] coated polyvinylidene fluoride (PVDF) onto the surface of Al (Al@PVDF), and the heat release of Al@PVDF at 900°C was $11,040 \text{ J/g}$. Jun Wang from the Institute of Chemical Materials [95] prepared Carbon nanotubes/polytetrafluoroethylene (PTFE)/Al nanocomposites, which had a lower initial reaction temperature (reduced by 80°C) and a shorter ignition delay time (reduced by 0.21 ms). Xiang Ke [96] coated PVDF onto the surface of Al to prepare reactive film materials, which appear PIR at 430°C .

3.2.2. TiC Modification

The reaction (as shown in Equation (1)) of Al_2O_3 and Titanium carbide (TiC) has been found during the preparation process of ceramics, which also can generate gas [97–99]. If this reaction can take place before the oxidation reaction of Al, the Al_2O_3 shell can be removed effectively, and the generated gas can also break the Al into small particles under high pressure. DeQi Wang [56] prepared the thick flake Al/TiC, which can crack the Al_2O_3 shell in-situ before 633°C . As shown in Figure 8, the reaction of TiC with the Al_2O_3 shell on the Al surface to produce gas has been experimentally confirmed. The heat release of it can reach $21,419 \text{ J/g}$, and this powdered material has good application prospects in solid propellants and polymer bonded explosives (PBXs). This provides a new research idea

for solving the limitation of the Al_2O_3 shell on the Al oxidation process. However, the application of it in PBXs and the propellant system needs further exploration.

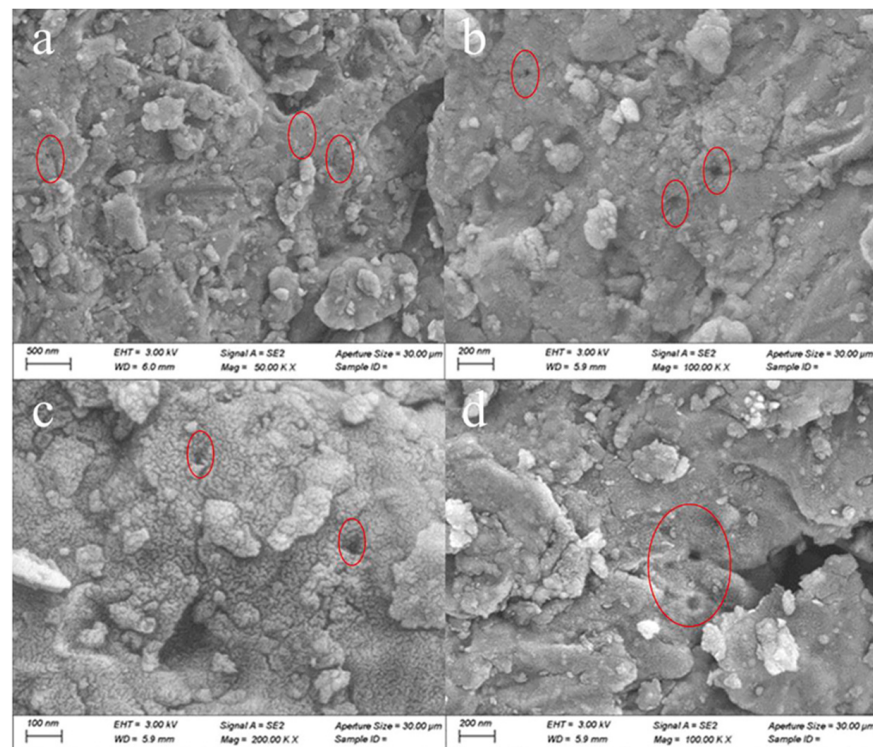
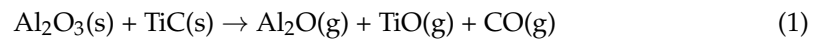


Figure 8. The pores morphology of TF-Al/5%TiC surface at different temperature: 633 °C (a), 650 °C (b), 670 °C (c) and 690 °C (d), reprinted/adapted with permission from Ref. [56]. 2021, Jie Liu.

3.2.3. Alloying

The oxide film on the surface of the Al-alloy particle may not be pure Al_2O_3 shell, which may have higher transmittance to oxidation. Therefore, the Al-alloy can be oxidized at lower temperatures. The oxidation product is not a dense structure like the Al_2O_3 shell. Accordingly, alloying is one of the effective ways to destroy the structure of the Al_2O_3 shell. Some metals (such as Li, Mg and Zr et al.) can be oxidized at a lower temperature than Al and can provide activation energy for the oxidation of Al, so that oxidation activity of Al-alloy is higher [53–55]. The preparation method of the high-density alloy is the key factor restricting the application of this modification method.

Hao Fu [55] prepared the Al-europium (Eu) alloy, which could be oxidized at 1065 °C and the heat release of the Al-Eu alloy is almost 5 times that of pure Al. Aobo Hu [53,54] prepared the Al-Zr alloy and the Al-W alloy. New alloy phases, ZrAl_3 , formed in the Al-Zr alloy, which changed the oxidation process (as shown in Figure 9a). Therefore, the Al-Zr alloy can complete combustion under high pressure. Furthermore, the Al-W alloy is almost completely oxidized in air at 1500 °C. In addition, as shown in Figure 9b,c, the gas product, WO_3 , increases the contact area between the active Al and the oxidant. As a result, the properties of the Al-W alloy have been improved greatly. Fahad Noor [100] prepared the Al-Cu alloy, which had the lower ignition temperature (565 °C).

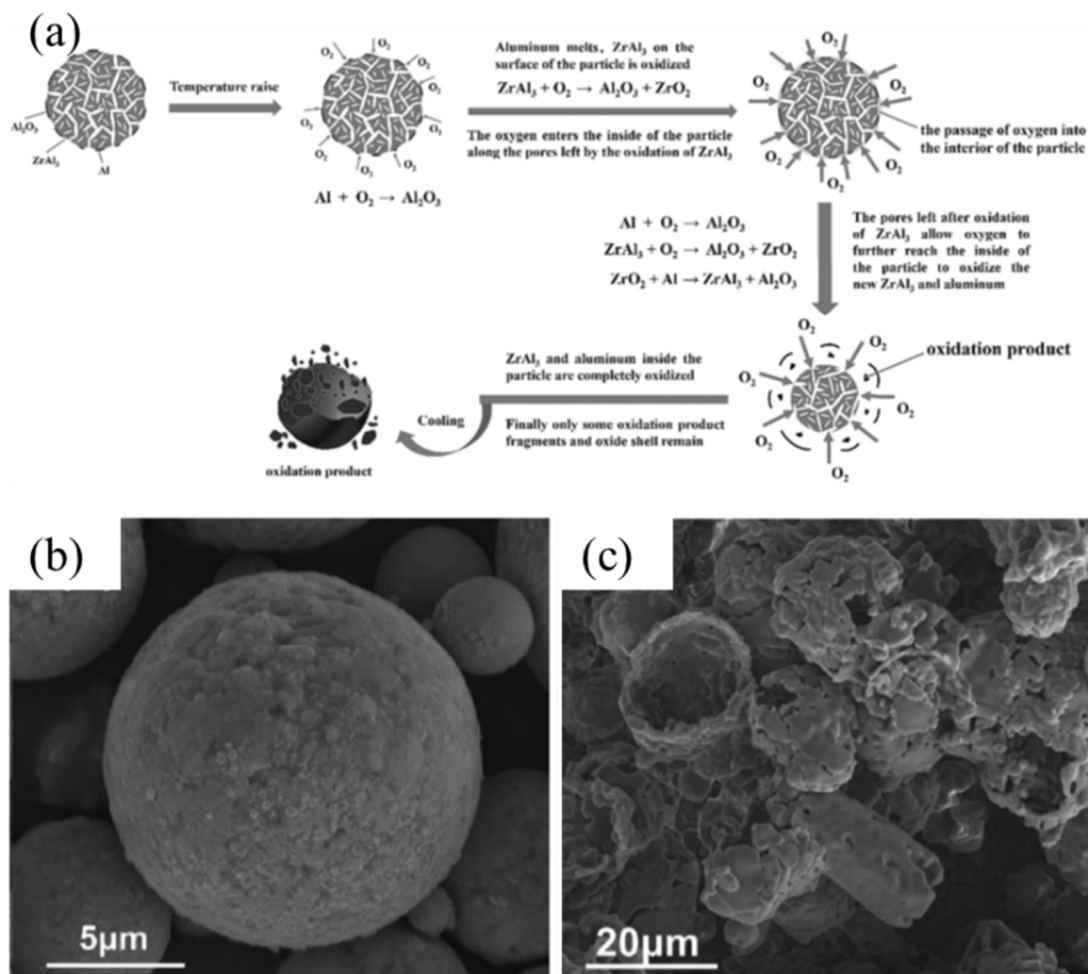


Figure 9. The oxidation process of Al-Zr alloy (a), Al-W alloy (b) and Al-W alloy after combustion (c), reprinted/adapted with permission from Refs. [53,54]. 2019 and 2021, Ai-min Pang and Shuizhou Cai.

3.3. Accelerating the Melting of the inside Active Al

The composite made of high thermal conductivity material and Al can increase the rate of Al absorbing heat, which can accelerate the melting of active Al inside and break through the limitation of Al_2O_3 shell. Consequently, the inside active Al can make contact with the oxidant and the reactivity of Al will be improved. However, as with MICs, how to achieve an efficient, safe and low cost batch preparation is the key problem when it is used in PBXs and propellants.

Jinpeng Shen [101] investigated the effects of nano-Ag on the combustion wave behavior of Al/CuO. The experimental observations confirm that the presence of nano-Ag particles improves the heat transfer efficiency, and the first exothermic peak temperature decreases from 607.8 °C to 567.6 °C.

Ahmed Fahd [77] compared and analyzed the thermal behavior of different nanothermite tertiary compositions based on Al, graphene oxide (GO), and various salt and metallic oxidizers. The addition of GO enhances the reactivity of nanothermites with both salt and metallic oxidizers by reducing the reaction onset temperature, activation energy and increasing the heat release.

4. New Trend of Improving Reactivity of Aluminum Powder

With the deepening of research on the Al oxidation process, various factors restricting Al oxidation have been found, gradually. The methods of improving the reactivity of Al have been integrated, which can simultaneously change multiple conditions

in the oxidation process of aluminum powder to improve the properties of Al from multiple perspectives.

Jena McCollum [102] investigated the reactivity of Al/MoO₃@perfluoropolyethers (PFPE) and Al/CuO@PFPE. As shown in Table 3, fluorine–Al-based surface reaction can improve the reactivity of Al/MoO₃. However, the reactivity of CuO reduces when the PFPE concentration is increased. Lei Xiao [47] successfully assembled Al/CuO/PVDF/RDX, and the combustion properties of microspheres is mainly affected by the content of RDX. Aifeng Jiang [72] prepared Fe₂O₃/nano Al and FeF₃/nano Al@vinyltrimethoxysilane by ball milling. The initial combustion temperature of Fe₂O₃/nano is about 600 °C. FeF₃/nano Al@vinyltrimethoxysilane had a large specific surface area (26.33 m²/g) and could be well-preserved from air atmosphere and water. Furthermore, the maximum heat release of FeF₃/nano Al@vinyltrimethoxysilane can go up to 12,852 J/g.

Table 3. The data DSC of Al/MoO₃@PFPE and Al/CuO@PFPE, reprinted/adapted with permission from Ref. [102]. 2015, Michelle L. Pantoya.

Sample	PIR Onset Temperature °C	PIR Heat Release J/g	Thermite Reaction Onset Temperature °C	Thermite Heat Release J/g
Al@PFPE	315	19.80	561	133
Al/MoO ₃	-	-	508	2078
Al/MoO ₃ @5%PFPE	298	21.79	534	1370
Al/MoO ₃ @10%PFPE	301	35.17	541	1672
Al/MoO ₃ @20%PFPE	305	103.1	566	1889
Al/CuO	-	-	517	763
Al/CuO@PFPE	298	19.56	569	1658
Al/CuO@10%PFPE	299	29.70	581	1305
Al/CuO@20%PFPE	303	51.37	583	843

In the meantime, the safety of Al during storage, transport and usage also should be addressed when improving the properties of Al. The design and preparation of Al composites with high stability during storage and transportation, and high reactivity during usage, will become a research focus in the future.

DeQi Wang [56] designed flake Al/TiC, with TiC embedded on the surface of flake Al, which retains the Al₂O₃ shell to keep Al stable during storage and transportation, and cracks the Al₂O₃ shell to improve the reaction activity and combustion efficiency by the reaction of Al₂O₃ and TiC before 633 °C. In addition, the heat release of flake Al/TiC is 21,419 J/g at 985.6 °C.

5. Summary and Prospect

With increasing research, the oxidation process of Al has been gradually revealed, which is closely related to the reaction conditions. The oxidation process of nano Al (large specific surface area) is mainly restricted by oxidant diffusion under a slow heating rate, and conforms to a three-step oxidation process, proposed by Zachariah. The Al₂O₃ shell has the greatest influence on the micron Al oxidation process and Al₂O₃ shell transformation, and the growth mechanism can well explain this process, which was proposed by Trunov under the slow heating rate. The melting and dispersion of the internal active Al has a great impact on the oxidation process of nano Al under a fast heating rate, which can be described by the melting diffusion mechanism proposed by Levitas.

Therefore, to improve the properties of Al, the key influencing factors of the Al oxidation process need to be changed. MICs, flake Al and nano Al can improve the diffusion efficiency of the oxidant during Al oxidation, which can influence the properties of Al under a slow heating rate. Since the Al₂O₃ shell can be cracked by fluorine, TiC, and alloy, the properties of Al under a fast heating rate can be changed by them. Those materials with good thermal conductivity can increase the heat transferred to the internal

active Al, so the properties of Al under a fast heating rate can be improved by good thermal conductivity materials modification.

In order to improve the properties of Al more comprehensively, an integration of different modification methods has been employed, such as fluoride coated nano Al-based MICs, flake Al/TiC, various material-covered Al and so on. Furthermore, the safety of Al during storage, transport and usage also needs to be addressed when improving the properties of Al. The design and preparation of Al composites with high stability during storage and transportation, and high reactivity during usage, will become a research focus in the future.

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