Oxidation mechanism of micron-sized aluminum particles in Al-CO$_2$ gradually heating system

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Abstract. Micron-sized aluminum powders were heated in carbon dioxide atmosphere through differential scanning calorimetry (DSC) method in this work. Aluminum powders were oxidized into four distinct stages from room temperature to 1500 ℃. Stage I, amorphous alumina shell turns to γ-Al$_2$O$_3$ phase from room temperature to 620 ℃. Stage II, accompany with the aluminum core melting, alumina shell becomes thicker and fragile at the temperature around 667 ℃ which is the melting point of aluminum. Stage III, in the temperature range of 690-1150 ℃, alumina shell was broken partially because of the inside pressure. Liquid aluminum spurts out through the weak point which becomes cracks on the surface just like volcano eruption and then oxidized by CO$_2$ while the temperature increased from 700 ℃ to 900 ℃. Stage IV, alumina changes to stable α-Al$_2$O$_3$. From what was presented above, a mechanism of micron-sized aluminum particle oxidation in CO$_2$ under gradually increasing temperature condition was proposed as “eruption model”.

1. Introduction

Because of its several practical applications in energetic materials, metal combustion process, especially the aluminum combustion process is a continuing interest of a lot of researchers. Materials that can store large amounts of chemical energy, and are characterized by a high rate of energy release are termed “energetic materials”. Micron-sized aluminum powders are often added into various energetic materials, including pyrotechnics, explosives, and rocket propellants. It is because that the performance of energetic materials can be highly improved such as the oxidation enthalpy and the combustion temperature, especially the motor acoustic stability [1-4]. In recent several decades, basic understanding of aluminum combustion mechanisms has been improved significantly in experimental and theoretical investigations [5-9]. However, it is difficult to determine the accurate reactive mechanism because the different properties of aluminum powders, for instance, the specific surface area, particle size and distribution, different synthetic methods, environment condition, core@shell structure of aluminum powder [10, 11] will eventually influence the oxidation mechanism of aluminum.

Carbon dioxide is one of the gas products in solid rocket engines, for this reason, it is meaningful to find out the oxidation behavior of aluminum powders in CO$_2$. Aluminum powder is typical core@shell structure. Although there is a strong thermodynamic driving force for the reaction between aluminum and oxidizers, they can’t contact directly because of the alumina oxide shell outside each particle [12]. Several literatures [13, 14] show an idea that the ignition temperature of aluminum particles is in the vicinity of Al$_2$O$_3$ melting point (2054 ℃), however, some others prove that the ignition temperature
range of different micron-sized aluminum powders is from 650°C to 2000°C [13, 15-18]. Therefore, the oxidation mechanism of micron-sized aluminum particles in CO₂ is not that clear.

Thermal analysis method is mature enough in the study of oxidation kinetics of aluminum powders. Thermogravimetric-Differential Scanning Calorimetry (TG-DSC) was employed to observe the mass and thermal behavior of prepared material during the heating process. TG-DSC can provide useful information on phase transitions through exothermic and endothermic reactions in the studies of aluminum powders [19-23]. Prof. M. A. Trunov [24] presented a characteristic thermo-gravimetric analysis (TGA) curve of oxidizing aluminum powder and sequence of changes of alumina shell. In order to find out the characteristics of micro-sized aluminum in CO₂ under gradually increasing temperature, further studies were done and new mechanism is put forward in this work.

2. Experimental approach

2.1 Materials and apparatus

Aluminum powders in six different sizes numbered from Al#1 to Al#6 which were synthesized through wire electrical explosion (WEE) by Angang Group Aluminum Powder Co., Ltd were investigated in this Al/CO₂ system. Particle size distributions were analyzed by MASTERSIZER2000 Laser particle size analyzer. The experimental setup utilized in this research consists of a combination of Thermo-Gravimetric Analyzer coupled with NETZSCH STA449F3 - DSC200F3 Differential Scanning Calorimeter (TG-DSC) and Hitachi S-4700 field emission gun scanning electron microscopy (FEG-SEM). The corresponding chemical changes are analyzed by Philips PW1710 powder X-ray Diffraction (XRD). The composition of all the samples, including the impurities and their content were analyzed by ELEMENT GD glow discharge mass spectrometer, at the meantime, the specific surface areas of the three samples were calculated by the BET (Brunauer, Emmett and Teller) equation. These facilities can closely simulate the residence time, temperature histories a chemical environment of various combustion units allowing for a variety of solid-solid, solid-gas interactions.

2.2 Experiment procedure

All the six samples were heated from room temperature to 1450°C in the first group. The balance and furnace were purged with argon at 10 and 20mL/min respectively. Heating rate was 20°C/min which was appropriate to ensure high resolution of mass and energy variations as a function of temperature and an ignorable measurement error. The reaction chamber was vacuumed prior to introducing research grade CO₂ with a steady flow rate of 1.2L/h which can ensure aluminum powders completely reacted.

According to the results of TG-DSC curves got in the first round of heating process, experimental conditions will be changed appropriately. (1) Add extra constant high temperature process to special samples. (2) Stop heating process at different temperature and collect the samples. (3) Reheat the samples in a certain condition and compare the different oxidation mechanism. The intermediate and final products will be collected and do further analysis. In order to recover intermediate products without any other impact, samples were cooled down in argon.

3. Results

3.1 Characterization of Al powders

The properties of all the samples are given in table 1. According to the statistical analysis, size distribution of all the samples fully complies with lognormal distribution which is given as equation 1. Figure 1 exhibits the size distribution and fitting curve of Al#3 and Al#6 as examples.
Table 1. Properties of all six aluminum samples used in the experiments.

| Sample | Specific surface area (m²/g) | Active aluminum (%) | D₅₀ (μm) | Fe (%) | Si (%) | Cu (%) | H₂O (%) |
|--------|----------------------------|--------------------|-----------|--------|--------|--------|--------|
| Al#1   | 1.35                       | 98.21              | 1.89      | 0.080  | 0.067  | 0.002  | 0.025  |
| Al#2   | 1.01                       | 98.43              | 2.51      | 0.081  | 0.062  | 0.002  | 0.023  |
| Al#3   | 0.45                       | 99.01              | 5.24      | 0.082  | 0.061  | 0.002  | 0.022  |
| Al#4   | 0.17                       | 99.32              | 13.35     | 0.079  | 0.065  | 0.002  | 0.020  |
| Al#5   | 0.10                       | 99.37              | 24.02     | 0.082  | 0.062  | 0.002  | 0.021  |
| Al#6   | 0.06                       | 99.35              | 40.05     | 0.080  | 0.063  | 0.002  | 0.019  |

Figure 1. Size distribution and fitting curves of two samples. (a) Al#3, (b) Al#6.

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f(x) = \frac{A}{\sqrt{2\pi}u} \cdot \exp\left(-\frac{(\ln x - \mu)^2}{2\sigma^2}\right), \quad x \in [a, b]
\]  

Figure 2 is the SEM pictures of four different sized particles. The surface of the particles is not that smooth (see the inset of figure 2 (b)), some cracks can be seen clearly.

Figure 2. SEM characterization of aluminum powders (1) Al#2 is roughly equiaxial. (2) Al#3 particle size distribution is in the range of 2-8μm. (3) Al#4 slightly agglomerate together. (4) Al#6 contains a wider range of size distribution from 4μm to 50μm.

3.2 Thermal behavior of aluminum powders

Assuming that alumina was the only solid product of the reaction, the mass increasing can be calculated easily according to the chemical reaction equation. Under ideal condition, mass increase should be 88.89%, however, all the aluminum powders utilized in the experiment consist several kinds of impurities (table 1). Therefore, even though the active aluminum was oxidized completely, the mass increase is less than 87.30%. In order to keep it clear enough to read, TG curves of Al#2, Al#3, Al#4 and Al#6 were demonstrated in figure 3, the changing tendency of all six samples is highly related to the particle sizes. In figure 3 (a), the DSC records in the range from 300°C to 1450°C are presented (there are no mass changes before 300°C). The mass increase of the aluminum samples doesn’t stop except the ones which are smaller than 2μm. Then the second round of DSC experiments is designed as follows, heating process starts from room temperature to 1500°C and kept in 1500°C for additional
15 minutes. Under this condition, figure 3 (b) presents clearly that the particles smaller than 5μm could be oxidized completely and kept in a constant mass eventually, particles larger than that still stayed in a relatively low reaction rate. Therefore, sample Al#3 are chosen as a representative in the following discussion.

The entire oxidation process can be divided into four stages. Oxidizing reaction of micron-sized aluminum particles observed in this work could be divided into 4 stage. Stage I, from room temperature to 620℃, the weight of the samples changed little, but DSC curve had a small exothermic peak at the end of this stage, amorphous alumina changed its phase to γ-Al₂O₃. Stage II, TG curve increased a little and an obvious endothermic process was observed at the same time. This stage happened from 620℃ to 690℃, aluminum reach its melting point (667℃) during this stage. Stage III, vigorous oxidation reaction was happened from 690℃ to 1150℃, peak C corresponded to the increasing of weight. Stage IV, from the beginning of 1150℃, oxidation processes went on and all the alumina turned to α- Al₂O₃.

Figure 3. TG curves of four different sizes aluminum samples. (a) Samples heated to 1450℃, (b) Samples heated to 1500℃ and kept in 1500℃ for another 15 minutes.

Figure 4. TG, DTG and DSC curves of Al#3 from 300℃ to 1450℃. Stage I, from room temperature to 620℃. Stage II, 620-690℃. Stage III, 690-1150℃.

In the whole heating process according to figure 4, there are two steps of mass increasing which is presented by DTG curve. The first step (peak 1) begins around 660℃ and the accurate value of mass increasing which is considered as a thickness increasing of the alumina shell is measured for 4%. The second step (peak 2) emerges in the vicinity of 800-930℃, the mass changes quite obviously and reaches 150% of the original weight. DSC curve presents three peaks which are marked by A, B and C. Peak A and C are exothermic process which are known to be respectively associated with a phase transformation alumina and with ensuing thermally activated oxidation, peak B is an endothermic process which is considered to be the melting of aluminum core.
3.3 Characterization of intermediate products

How the samples changed in the previous system could not be determined just by DSC experiments, therefore XRD and SEM are required as support. Figure 5 shows the X-ray patterns of samples. Strong peaks of metallic aluminum of the raw particles are observed.

![XRD patterns of Al#3 sample. The observed XRD peaks are identified for different polymorphs of Al₂O₃. (a) as-prepared; (b) after calorimetric measurements in the 20–620 °C temperature range; (c) after Calorimetric measurement in the 20–1150 °C temperature range.](image)

SEM pictures of Al#3 after calorimetric measurement in different temperature are presented in figure 6, in general, the stable oxide exterior shells still kept the initial sphere shape. Empty shell structure could be seen clearly and the size of the particle is as big as the initial aluminum particles. The thickness of the shell was measured in SEM pictures which increased to almost 0.1μm. Figure 7 describes the monograph of particles that heated from room temperature to 1450 °C. Small particles could be oxidized completely; the reaction products consist of fragment of alumina shell and empty shells of the aluminum particles. When it comes to the larger sized powders (>10μm), the sphere particles with a few cracks on the surface could be seen instead of empty shell structure. What was more, compared with the initial particles, the size did not change as well.

![Monograph of Al#3 heated to different temperature. (a) 620 °C. (b) 1150 °C.](image)
4. Discussions

4.1 Oxidation process of aluminum powders
For the recovered samples that only heated to 620°C, weak peaks of γ-Al₂O₃ are observed. For the XRD patterns of 1150°C heated samples, the peaks of α-Al₂O₃ become comparatively strong and the peaks of γ-Al₂O₃ disappeared. According to the XRD patterns, during the entire gradually heating process, the alumina shell changed its phase stages by stages. The whole process includes a history of amorphous → γ→ α-Al₂O₃. γ-phase alumina can be synthesized industrially with the temperature of 500-750°C, 800-1050°C, 900-1100°C respectively, which is accordance with the phenomenon in the experiment. α-Al₂O₃ is the most stable and hard kind of alumina phase. In the present results of XRD pattern, γ- and α-Al₂O₃ could be seen clearly at the end of the first stage and the fourth stage respectively.

SEM observations after DSC scans show that the granular structure of the powder was modified by the thermal treatment. It is noted that if the molten aluminum is pushed into these cracks by the high internal pressure characteristic of the stress field, its surface, where reaction occurs, could be fractal in nature and affect the fundamental nature of the burning law.

4.2 Comparation of oxidation behavior in different heating process
Firstly, all the samples were heated in CO₂ atmosphere from room temperature to 620°C which is the point of the second stage, then cooled down to room temperature in argon. After the first preheated process, the samples experienced another whole DSC test from room temperature to 1450°C again. Mass increase of 53% is observed on one-time heated process from figure 8, whereas only a value of 0.37% is recorded for the reheated Al#3 sample. In figure 8, there is only one endothermic peak at the melting point of aluminum. Because of consumption of aluminum in the first heated process, the endothermic peak is smaller than the one-time heated samples. It is shown that, whatever is the size of particles, the thermal expansion of the metallic core is not affected by an alumina shell with a 3 ± 2 nm thickness which is the normal value. In contrast, when the thickness of the crystalline alumina shell exceeds 20 nm, strong strain effects are evidenced. This different results between the two round of DSC test demonstrate that the thickness increase of alumina shells do causes apparent restriction of the oxidation of aluminum particles.
Figure 8. TG-DSC scanning curves of Al#3 samples in one-time heated and reheated process respectively. Comparison of TG (1) and DSC (2) between two different heating processes.

4.3 Oxidation mechanism of aluminum particles

In the first stage, from room temperature to 620 ℃, XRD patterns showed that alumina shell changed from amorphous phase to γ- Al₂O₃, this process was corresponded to the small exothermic peak A in DSC curve. The microscopic morphology of aluminum powders changed little; therefore, the main difference between the aluminum heated to 620 ℃ and the initial ones was that the γ- Al₂O₃ replaced the amorphous alumina.

The thickness of metal-substrate crystalline-oxide film will increase with the growing of temperature, a significant increase in the metal’s reactivity leads to the fracture of the protective oxide film. The thermal expansion coefficient of aluminum is approximately ten times larger than that of γ- Al₂O₃. Then the pressure in the oxide shell increased and the overwhelming force formed between aluminum core and alumina film was becoming larger and larger. Alumina shell was in the stretch state, and its counterpart aluminum core, was in the compression state. This kind of internal stress was increasing with the elevating temperature. The influence of mechanical stresses is quantitatively described, arising due to phase and polymorphic transformations of the metal, and also of the difference in the thermal-expansion coefficients and densities of the metal and its oxide. The smaller the particle sizes were, the higher radius of curvature of particle surface had. With the existing of inner stress, alumina shell was kinetically unstable and the tendency of forming cracks on the alumina shell was large enough. In addition, γ- Al₂O₃ was not the same dense and stable as the amorphous alumina as well. The cracks were a kind of passageway for gas; oxidizing gas could go through the passageway and reacted with the aluminum in the shell. So the early oxidation reaction is happened around the melting point of aluminum. When the particle is immersed in a hot atmosphere containing oxygen atom, dissociative adsorption occurs and then the O atoms at the surface diffuse inwards towards the aluminum surface which can be expressed as equation 2.

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2\text{Al} + 3\text{O} = \text{Al}_2\text{O}_3
\] (2)

Stage III, from 690 ℃ to 1150 ℃, when the samples were heated up to the melting point of aluminum, the solid aluminum core melted and its volume was becoming larger. Because of the cracks on the shells as well as the impurity content of the samples, defects existed on the surface of the particle inevitably. When the inside pressure became large enough to break the defect, liquid phased aluminum came out. When aluminum powders was larger than 10μm, the alumina shell was thicker than the small particles, the melting aluminum could not erupt easily, the liquid aluminum flowed from the cracks and reacted with the CO₂. With the reaction of the aluminum, the alumina deposit formed on the particle surface. At last, the volume of aluminum inside the shell was too weak to flow out. Therefore, larger aluminum powders did not react completely. During heating, the interference, caused by the difference of thermal expansion coefficients between aluminum core and its oxide shell, can be calculated. Even though the particle sizes are different, the increment caused by increasing of
the temperature in the radial direction is unchanged. Therefore, from the microcosmic point of view, the oxide films of smaller particles that owe larger radius of curvature are more likely to break. So the smaller the particles are, the more completely of the oxidation processes happen. And the big peak C of DSC curve appeared at the same period that stands for the degree of the reaction.

Stage IV, from 1150°C to a higher degree, the specific processes responsible for the individual oxidation stages of aluminum powders must be understood in order to accurately model aluminum ignition. XRD patterns show that α-Al₂O₃ is the main product and the structure of different sized powders changed differently. The oxidation stages observed in this work are generally consistent with previous reports on aluminum powder oxidation.

The mechanism influenced by particle sizes were firstly take into consideration, figure 9 shows the whole history of the oxizide process of aluminum particles.

![Figure 9](image)

**Figure 9.** The whole history of oxidation processes about micro-sized Aluminum particles.

5. Conclusion

By integrating sophisticated experimental and testing methods, history of slow heating reaction and changing of single aluminum particle were characterized. An “eruption model” which is accounted for multiple processes occurring in aluminum combustion and is not expected to be limited to quasi-steady description of the single micron-sized aluminum particle oxidizing process in gradually heated oxidizing atmosphere was developed. Also, the present conclusion makes an emphasis on the relationship between different steps of oxidation processes and the change of the particle sizes. During the heterogeneous oxidation of metallic particles in a gaseous oxidant, an oxide film usually separates the metal and oxidant, so the rate of reaction is governed by the protective properties of that film. Reaction history of the micron-sized aluminum particles on the gradually heating environment includes 4 stages. The whole process can be summarized to be an eruption model; also, the particle sizes are taken into consideration. For the aluminum powders that the impurities are less than 2% of the total weight, this conclusion can be referred in practical application.

6. References

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