Reaction mechanism of micron-sized aluminum powders in O_2 and CO_2 gradually heated environment

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Abstract: The behavior of aluminum powders in specific oxidized environment is different from each other obviously. Thermal behaviors of micron-sized aluminum powders in different oxygenated and gradually heating environments were discussed in order to find out the oxidation mechanism. Particular attention is paid to the reaction mechanism of oxygen and carbon dioxide atmosphere. Thermogravimetric analysis and related characterization methods are used and the results demonstrated that under the certain condition, reaction process of micron-sized aluminum powders can be divided into four stages. General routes for the oxidation of micron-sized aluminum in general heating system are the same, however, itis different among the extent of reaction at the third stage in different kinds of oxidizing gas atmospheres. Gas phased products were detected during the main reaction stage under carbon dioxide by combining thermal analysis and mass spectrometry which contributes to the rupture of alumina shell and further reaction of micron-sized aluminum powders. Consequently, rapider and more complete reaction process was achieved. The increasing thickness of original alumina shell can restrict the reaction rate of aluminum powders harder at the same time.

Keywords: micron-sized aluminum powder, oxidized environment, thermogravimetric analysis, oxidation mechanism

1. Introduction

Aluminum powders are widely used as an addictive in energetic system such as propellant, explosives and thermite [1, 2]. As an ingredient of solid rocket propellants, the specific impulse can be highly increased because of the large amount of heat generated during the aluminum oxidation reaction [3]. In solid propellants, aluminum powders are used in quantities of 10%-20% by mass, and the particles are typically 20μm - 30μm in diameter. The particles may melt and coalesce into larger agglomerates, ranging from 100μm to 200μm in size after being heated. Basic understanding on combustion and oxidation mechanism of aluminum particles in different conditions has been improved significantly by experimental and theoretical investigations in recent several decades [4-7]. There is a strong thermodynamic driving force for the reaction of aluminum with various oxidizers such as air, water vapor and carbon dioxide, but aluminum ignition difficulties and application limitations occur as a result of the initial oxide layer that coats each particle, separating the metal from the oxidizing gases[8]. When aluminum burns in a composite solid propellant, it typically reacts with combustion products of the energetic oxidizer and binder, such as CO_2 and H_2O[9, 10]. Carbon dioxide is one of the gas products in solid rocket engines, for this reason, it is meaningful to investigate the oxidation behavior of aluminum powders in CO_2[11, 12]. The thermodynamically predicted benefits of aluminum combustion are rarely achieved because of extended ignition delays associated with protective alumina layer, which is always present on the aluminum surface[13]. Although a series of oxidation mechanism has been built by the researchers about the changing of aluminum oxide layers in different conditions, the oxidation mechanism of aluminum powders is still not that clear. Metal oxidation processes crucial for accurate modeling of metallized energetic materials remain poorly understood. To extend this model, one needs to understand how the change in the gaseous oxidizer affects processes of oxidation for aluminum powder.

In this paper, oxidation mechanism is investigated about micron-sized spherical aluminum powders that are coated with natural amorphous aluminum oxide. Based on the previously published related thermogravimetric analysis – differential scanning calorimetry TGA-DSC experimental studies [14] and the combination of TGA-DSC and Mass spectrometry MS analyzing, an oxidation history which is accounted for multiple processes occurring in aluminum oxidation is not expected to be limited to quasi-steady description of the single aluminum particle oxidizing process in gradually heated oxidizing atmosphere was developed. Also, the presented conclusions make an emphasis on the relationship between different steps of oxidation processes and the interface products generated from the reaction. In order to establish correlations between the structural parameters and the reactivity of the powders, it is also important to identify the mechanisms at the scale of a single particle and to understand the alumina layers' growth evolution[15]. Therefore, the thickness of alumina film was changed in different ways in this study and the influence caused by the alumina layers in the oxidation process was proved.

2. Experiment

2.1. Powder characterization

All the micron-sized aluminum powders were provided by Angang Group Aluminum Powder Co.,Ltd. which are named from sample 1 to sample 4 according to the increasing of particle sizes. The morphology of samples was observed by Hitachi S2700 scanning electron microscope (SEM). The SEM micrographs(Fig. 1)show a comparison between four samples. Particles appear mainly spherical and the external surface has no defects. There is no agglomeration for the original powders as well.

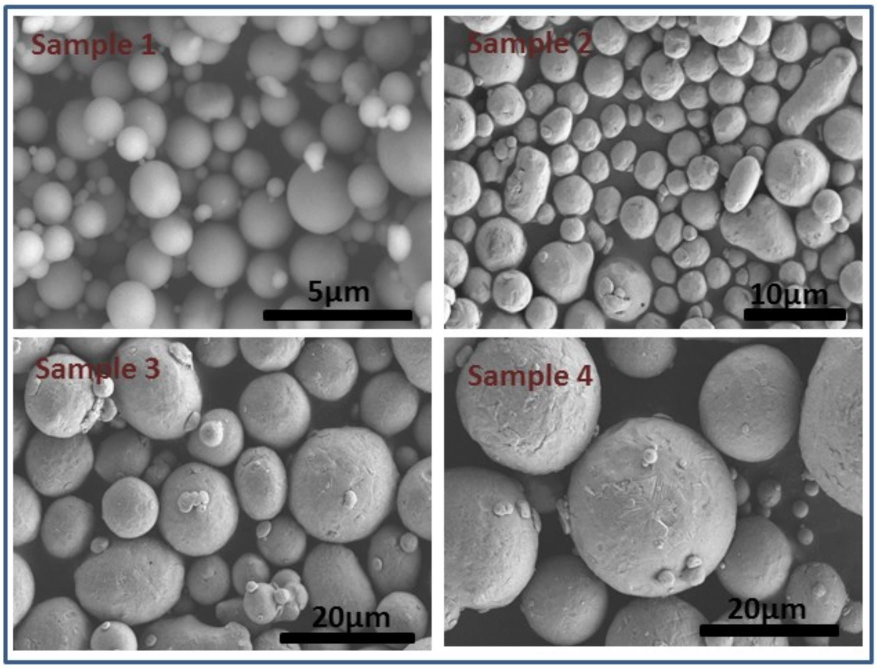


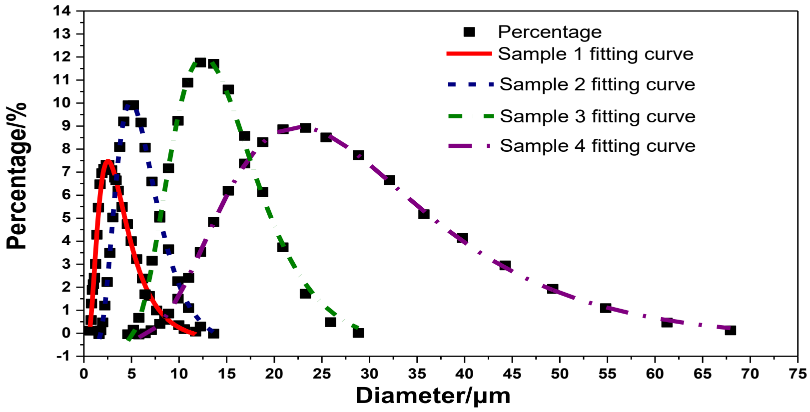
Fig. 1. SEM images of aluminum powder samples showing the morphology and surface structures.

The size and distribution of all the samples was measured by means of Malvern Mastersizer 2000 laser particle size analyzer for further characterization. The median diameter (D50)of four samples and the fitting curves of size distribution computing by statistical methods are reported in Table 1. The particle size distribution of aluminum samples is in line with the lognormal distribution according to Kolmogorov test curve fitting test which has a correlation better than 96%.

$$f(x) = \frac{A}{\sqrt{2\pi}\sigma x} \cdot e^{-\frac{(\ln x-\mu)^2}{2\sigma^2}}, \qquad x \in [a, b] \tag{1}$$

Table 1 Size distribution and fitting curves of aluminum samples.

Sample	D50/um	Sample	D50/um
Sample 1	1.76	**Sample 2**	5.24
Sample 3	13.35	**Sample 4**	24.02



2.2. Methodology

2.2.1. Experimental Method

The thermal effects of aluminum particles' reactivity on oxidation were analyzed by means of TG-DSC in oxygen and carbon dioxide. All instrument used in the study was calibrated and standardized in advance to ensure the accuracy. Mass change and heat flow of the reaction in gradually increasing temperature system at certain gas environment can be real time captured. Useful information on phase transitions and chemical reactions was obtained through endothermic and exothermic reactions [16]. The solid state reactions such as precipitation, solid-gas and solid-liquid reactions, incipient melting and solidification are elucidated based on the increase and decrease of the mass. Gas phased products of aluminum powder during reaction were examined using a TG-DSC equipped with an MS, whereas their solid phased counterpart was analyzed using (1) Philips PW1710 X-ray diffraction (XRD) and (2) Hitachi S-4700 scanning electron microscope (SEM). Fig. 2 demonstrates the outline of research process.

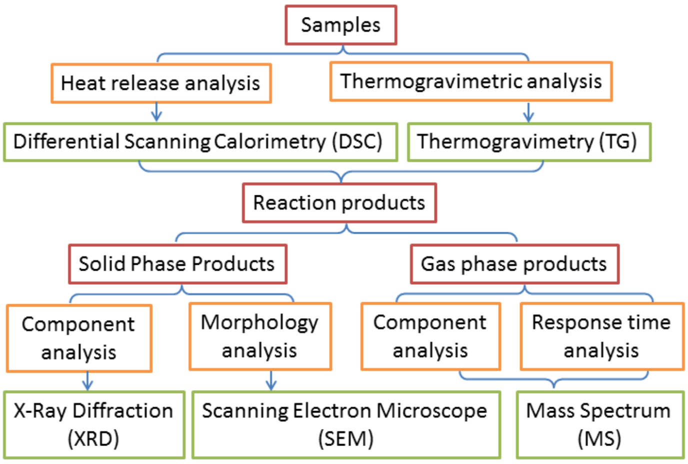


Fig. 2. The outline of experimental study of aluminum powders in oxidized gradually heated environment.

Intermediate products of the reaction in different stages were recovered and more accurate analysis of their characterization and oxidation mechanism is operated in order to explore corresponding reactions in different temperature ranges. The heating process was interrupted at different temperatures by controlling the reaction temperature program state to obtain the intermediate products. Heating scan was from the beginning to specific predetermined temperature then cooled to room temperature again along with changing the reaction environment to argon protection during the cooling process.

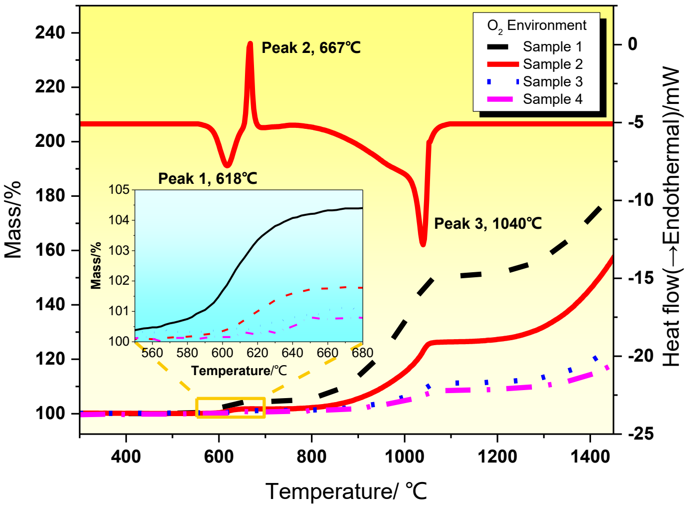
2.2.2. Experimental conditions

Samples are placed in the vacuum drying oven at 40℃ for 24 hours before being scan in TG-DSC to eliminate the influence of volatile component such as water. In producing repeatable calorimetry data on aluminum powders, sample preparation, reproducibility and baseline drift need to be considered in detail. The heating rate is 20℃•min^{-1} which can ensure the change of mass and heat flow function to temperature in a high resolution. Temperature range is from room temperature to 1400℃ which is within the safe scale of the equipment. Samples were heated in pure oxygen and carbon dioxide respectively with identical flow rate of 30ml•min^{-1} which can keep the sample chamber a constant pressure at the same time. The amount of aluminum powders in each heating cycle was around 5mg and all evenly distributed inside the standard alumina crucible. In order that the experiments were repeatable and accidental error was eliminated, all experiments were repeated three times.

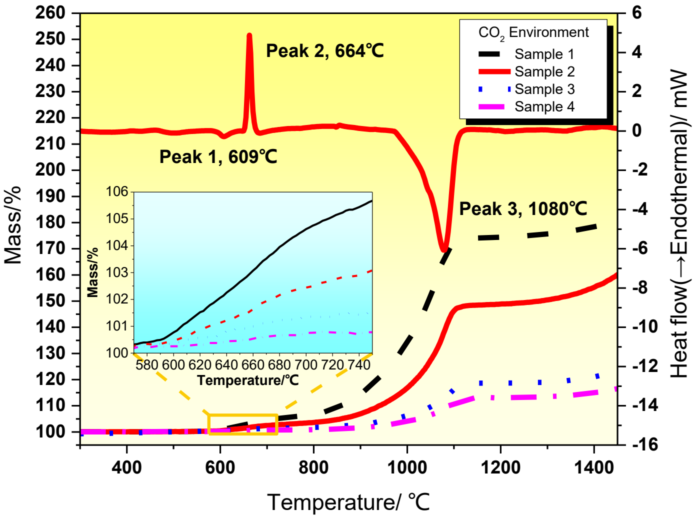
3. Results

3.1. Variation of mass and heat flow

The TG curves which present the reaction of aluminum powders in O_2 and CO_2 are demonstrated in Fig. 3 (1) and (2) respectively. As representatives, the DSC scans of sample 2 in different systems are given in Fig. 3 as well. Samples of different grain size increased slightly from 1% to 4.5% by weight from 580℃ to 630℃ according to the insert curves, the smaller the particle size is, the greater the weight gains. The first mass increase stair corresponds to exothermic peak 1 which is relatively small. DSC curves have clear endothermic peaks (peak 2) when the temperature increased to 660℃ which is close to the melting point of aluminum. This process indicated that the inside core part of core-shell structural aluminum powders is melting at this time. Aluminum core experienced a solid phase to liquid phase conversion. The reaction rate increased markedly when heating temperature was raised to the range from 770℃ to around 1050℃. The maximum weight gain comes to sample 1 which achieved to about 80%. The DSC curve which corresponds to this reaction stage is Peak 3 and the heat release increased significantly. Although the temperature reached to almost the highest quality equipment, the mass gain of sample 3 and sample 4 is less than 20%. The oxidizing of large aluminum particles are not completely in the experiment.



(1)TG curves of four aluminum samples and DSC curve of sample 2 in oxygen environment



(2)TG curves of four aluminum samples and DSC curve of sample 2 in carbon dioxide environment.
Fig. 3. TG and DSC curves of samples using in the experinments.

In order to describe the heating process clearly, it is divided into four stages which is presented in Fig. 4 according to the results and previous study [17, 18]. When micron-sized aluminum powders were slowly heated in oxygen and carbon dioxide, the whole process can be described as follows, (1) first stage of the reaction is from room temperature to about 580°C, (2) the second stage contains a an exothermic peak after a slight endothermic peak from 580°C to 700°C, (3) the main reaction stage starts from 700°C, to the temperature of 1050°C(O_2) - 1130°C(CO_2) which is slightly different in two atmospheres, (4) the last stage is sample subsequent reaction stage from the end of third stage to the maximum temperature scale of the instrument.

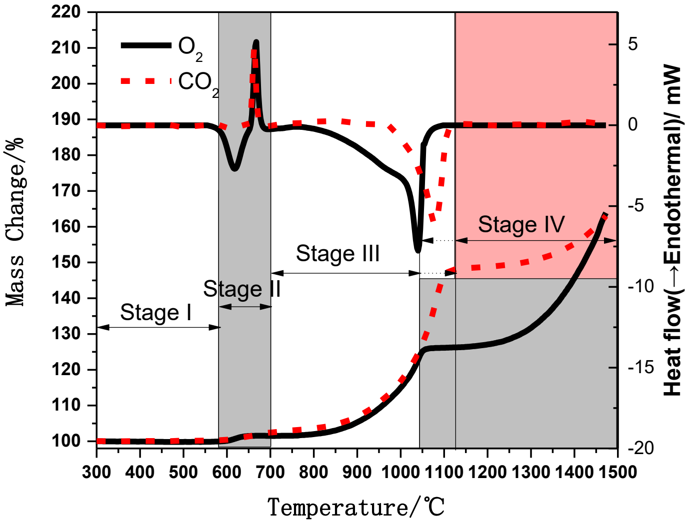


Fig. 4.Reaction process divided according to TG and DSC curves of sample 2 heated in O_2 and CO_2 environments.

Samples heated in carbon dioxide and oxygen environment start to be oxidized at almost the same time in both atmosphere but exothermic peak in oxygen environment is lager, while the lasting time of exothermic history is longer and the reaction carried out more complete in their carbon dioxide counterpart. Mass increase in carbon dioxide is 20% more than that in oxygen at the end of the third stage which showed a significant difference in both gas environments.

3.2. Solid phased products

Solid intermediate products are collected at specific temperature. These heating temperature was terminated at (1) 620℃ which is the end of the first stage and the beginning of the second stage, (2) 950℃ which is the most dramatic weight increasing temperature in the third stage, (3) 1350℃ at which the reaction is substantially complete. Three different intermediate solid reaction products were characterized by XRD and SEM respectively which are shown in Fig. 5 and Fig. 6. XRD patterns showed thatγ-Al_2O_3 appeared at temperatures around 620℃ which demonstrated that the phase change of alumina happened. The nature crystal structure of the aluminum oxide layer, thickness and density change when the alumina changed from amorphous phase toγ-Al_2O_3. SEM images of samples collected from this temperature illustrated that the sample powders remains spherical and the surface didn't change obviously. When the temperature rises to 950℃, peaks stand for crystal type ofθ-Al_2O_3 appeared whereas the peak intensity of aluminum reduced accordingly at the same time. Empty shell structure has been found in the SEM images which also showed that parts of the particles are stick with the others. In the last stage when the sample is heated to 1350℃, the XRD spectra shows that all of the alumina turned to α-Al_2O_3. A large area of adhesion appeared between particles. Empty spherical shell structures remains in the SEM images.

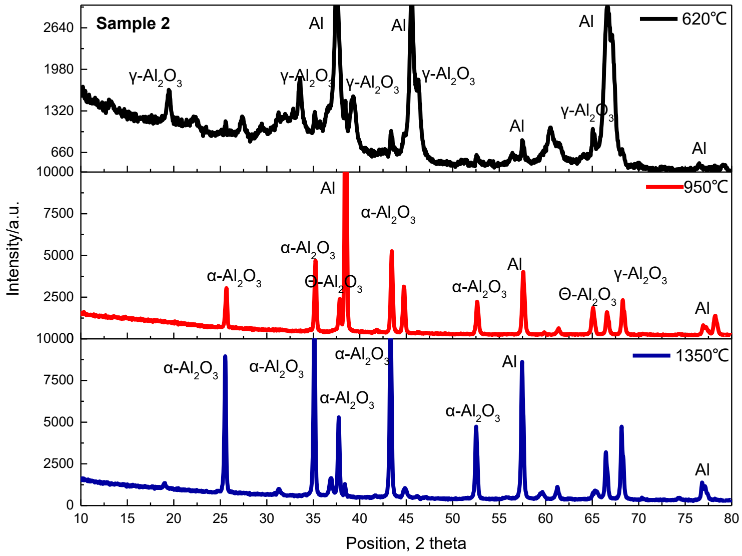


Fig. 5. XRD patterns of sample 2 intermediate products collected in different temperature.

In addition to intermediate products, final products of different samples during the heating reaction were also taken by SEM (Fig. 6). The images show that it's easier for smaller samples (Sample 1, Sample 2) to form empty shell structure which is also representing a relatively complete reaction. The larger samples (sample 3, sample 4) are roughly spherical structure and clear cracks exist on the surface of the samples. Because the oxidation reaction product of aluminum is solid phase, the mass increase can be easily calculated. The bigger sized of the samples, the harder to fully react according to the results of TG curves. Aluminum inside the core overflowed to form aluminum oxide on the surface and cause a certain degree of adhesions between sample particles.

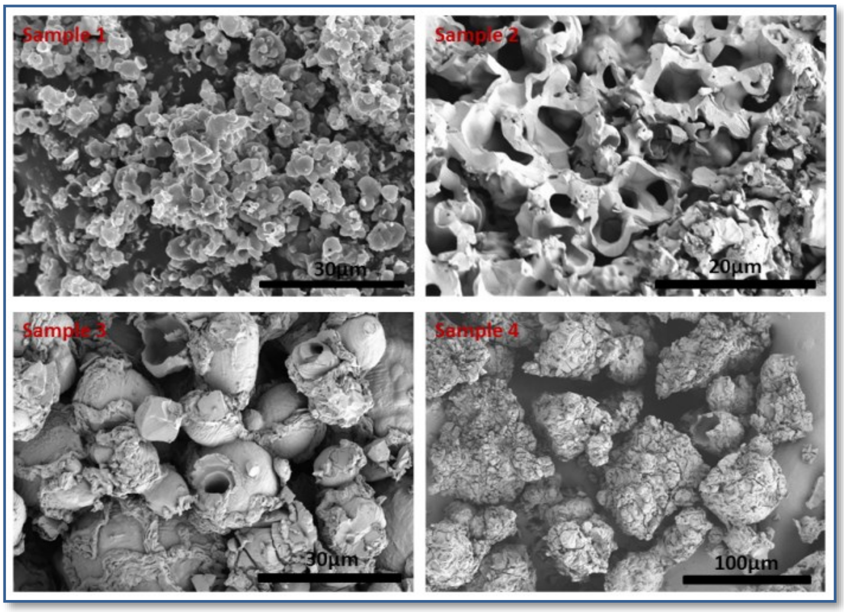


Fig. 6. SEM images of final products of four samples in oxygen environment.

3.3. Gas phased products

To further explore the different reaction between two oxidizing system, possible gas phased products were tested through MS. No gas products signal was observed in oxygen environment, therefore, the following study is focused on relatively complex reaction products in carbon dioxide. Ignore the fluctuations of airflow instability and unchanging signal detected by MS, the results was given in Fig. 7. Carbon dioxide and carbon monoxide gas ion intensity corresponding to differential of mass gain (DTG) was compared. A clear generation of carbon monoxide and consumption of carbon dioxide process was demonstrated in the third reaction stage.

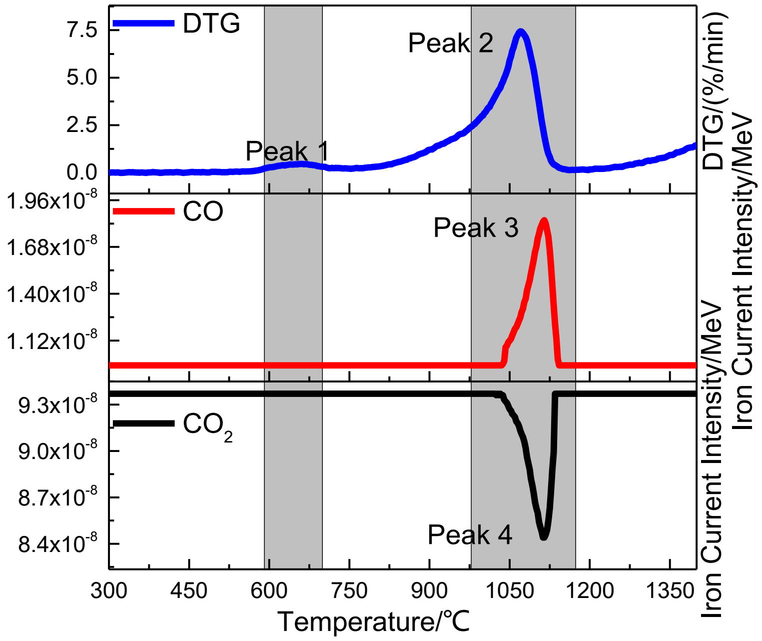


Fig. 7. DTG curve of sample 3 and the corresponding iron current of detected gas products.

4. Discussion

4.1. Reaction process and intermediate products

The whole heating process and detail of the reaction with the increasing of temperature can be deduced on the basis of TG-DSC-MS, XRD and SEM analysis. The first stage of the reaction starts from room temperature and end at 580°C. Aluminum particles oxide shell gradually transited crystal phase from amorphous to γ-Al_2O_3 which can lead to the change of density and certain defect of the oxide shell. The structural modification on the surface of sample powders make the penetration between the gas oxidizer and the liquid aluminum inside the shell more effective when the temperature increased to 700°C (beyond the melting point of aluminum). The mass gain and spherical particle structure under this temperature indicated the aluminum was partially oxidized and the oxide shell becomes thicker. The amount of materials exchanged between alumina shells which can lead to oxidation of aluminum was very limited because of the relatively low temperature. Exothermic peak of related DSC curves indicate the ongoing of the reaction and the endothermic peak stand for the melting of aluminum powders. Starting from 700°C until 1050°C to 1130°C which is different in different atmosphere, the reaction proceeded to the third stage. The phase of alumina shell continued to change in a certain degree, the process has deeper impact on the density of the oxide layer, compactness, etc. with the increasing of temperature. The activity of liquid aluminum and gaseous O_2/CO_2 was increasing at the same time. Alumina shell is broken because of thermal expansion effects and the oxidation of aluminum core which can lead to violently release of heat flow. The third stage of the reaction occurs at the same time between carbon dioxide and oxygen under basic environmental but the process of carbon dioxide last longer. Reaction was substantially complete after the breaking of alumina shells which was followed by the conversion of other phased alumina to α-Al_2O_3 under high temperature atmosphere.

Fig. 4 demonstrates the TG curves of original micron-sized aluminum particles at two different heating processes. At the temperature below 620°C, the oxidation was relatively slow. One to four percent of mass increase was observed in a temperature range from 650°C to 750°C which includes the melting point of aluminum (around 670°C). When the temperature was up to about 1000 to 1100°C, significant increasing of samples' mass was observed. While the temperature was above 1100°C, the oxidation rate was decreased again and only Al#1 gained to about 85%, then other samples were not oxidized completely until 1450°C. Limited by the equipment, all the samples were heating from room temperature to 1500°C and keeping in this degree for 15min in the second round of experiments. The results indicated that all the samples reacted to a higher degree. Al#2 which was not oxidized completely before was completely oxidized this time. Because of the special different results, the following explanation was mainly took Al#2 as an example.

4.2. Reaction mechanism in carbon dioxide.

Aluminum powders are naturally covered by an oxide layer in oxygen-containing environment. The passivation shell exists as an obstacle to reactivity and a strong shield against further degradation by the oxidized atmosphere as well [19]. This phenomenon causes that the oxidation of small aluminum powders is difficult to directly analyze in the available oxidized gas system such as CO_2 which is one of the major oxidizing species produced from a typical burning solid propellant.

$$4\mathrm{Al} + 3\mathrm{CO_2} = 2\mathrm{Al_2O_3} + 3\mathrm{C}, \ \Delta\mathrm{H} = -2170.9\ \mathrm{kJ/mol} \quad (2)$$

$$2\mathrm{Al} + 3\mathrm{CO_2} = \mathrm{Al_2O_3} + 3\mathrm{CO}, \ \Delta\mathrm{H} = -826.7\ \mathrm{kJ/mol} \quad (3)$$

$$\mathrm{C} + \mathrm{CO_2} = 2\mathrm{CO} \quad (4)$$

According to the reactant, equation 3, 4, 5 are inferred to be the simplified possible chemical reaction equations. Carbon dioxide was consumed and at carbon monoxide was generated at the same time. The results obtained by MS which can capture the gaseous products real timely in the process demonstrated that the generation of carbon monoxide occurs in the third stage. The generation of gas product can help the shell of aluminum particle break into piece in a certain extent. This behavior makes oxidation process between the active aluminum interior of the shell and oxidized environment more complete.

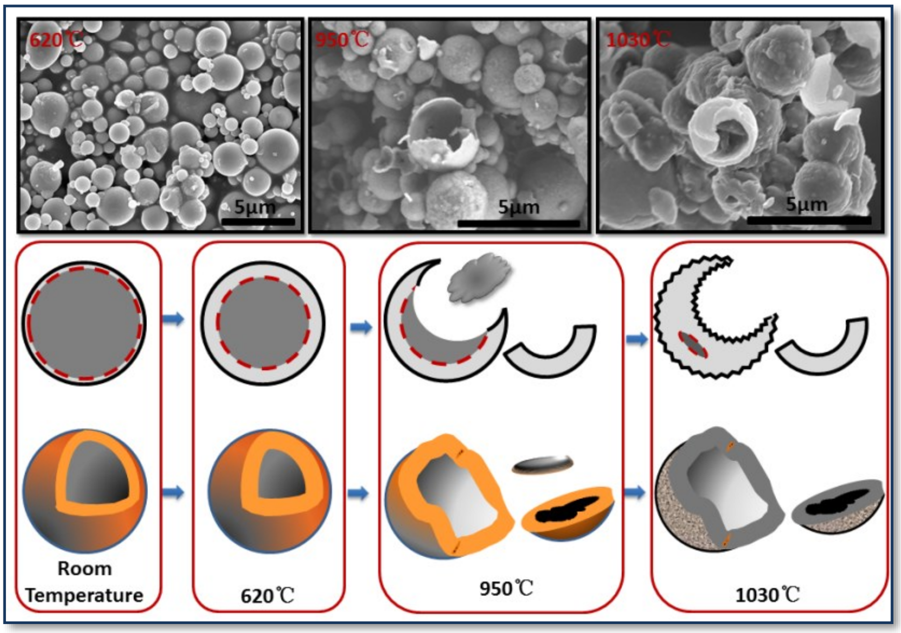


Fig. 8. Intermediate products of sample 2 collected from different temperature in carbon dioxide environment.

Since the reaction process of aluminum powders involves complex physical processes such as phase transformation, product proliferation, so domestic and foreign scholars normally use macroscopic reaction mechanism explain the chemical reaction of aluminum powder [17, 20].

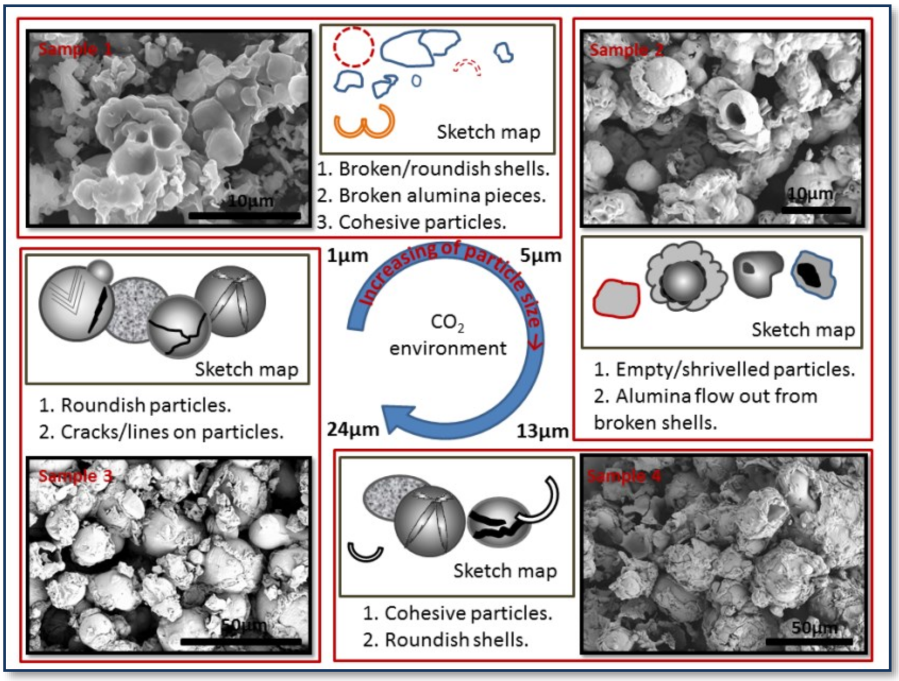


Fig. 9.Final products after the whole DSC heating processes in CO_2 environment.

Reaction mechanism in oxygen.

$$4\mathrm{Al} + 3\mathrm{O}_2 = 2\mathrm{Al}_2\mathrm{O}_3, \Delta\mathrm{H} = -3351.4\ \mathrm{kJ/mol} \tag{5}$$

Assuming that alumina was the only solid product in the whole reaction. The mass increasing can be calculated easily according to the chemical reaction equation which should be 88.89% under ideal condition, however, all the aluminum powders utilized in the experiment consist of impurities. Therefore, even though the active aluminum was oxidized completely, the increasing of mass is less than 87.30%. The main reason is that the reaction does not generate gaseous products in the third stage of the reaction and no further promotion to break alumina shell. With the increasing of sample size, the final mass gain decreased. On the micron scale, the thickness of passive layer alumina coated on the external of aluminum powder can limit the reaction obviously.

4.3. Thermal reaction mechanism of micron-aluminum powders in different environments.

Compare the TG curves of same sized particles under different oxidizing environment, mass gain is almost same in both atmospheres from beginning to the first part of third stage of the reaction. The reaction of carbon dioxide last longer from the second half of the third stage to the fourth stage of the reaction. The oxidation process was speculated the reaction is started by the diffusion, the influence of the reaction gas is not, as the temperature rises, broken shell react intermediate gaseous reaction products formed environment more severe, then the dominant dynamics control.

The first half of the first two phases and the third phase is controlled by diffusion, 1050 ℃ (different particle size is slightly different), the first i.e. after the three-stage segment, kinetically controlled reactions, the reaction of carbon dioxide environment faster.Experimental research on aluminum in both environments reaction process is different, especially in the third stage of the reaction, the reaction conditions under two different atmospheres third phase are significant differences, the stage is broken aluminum shell stage reaction, oxygen in the weight gain is relatively small with respect to the environment of carbon dioxide, the carbon dioxide in the environment, significant weight aluminum, an increase of more than about 20% oxygen atmosphere. According to [17] reported that in a steam environment aluminum reacts violently, the conclusion may be inferred from the above, the water vapor will react with the aluminum powder to generate a certain amount of gas, such as reaction (5).

Thus, when the environment is water vapor, carbon dioxide and the reaction will be basically the same, there is a certain amount of intermediate gaseous products generated. This is also one reason why aluminum reacts with water more quickly.

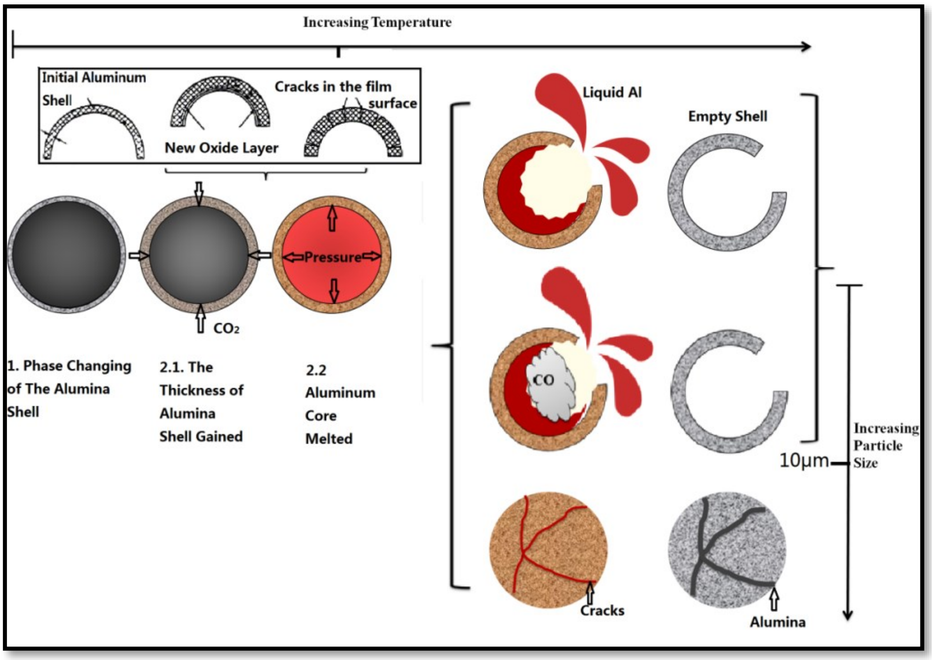


Fig. 10. Sketch map of reaction mechanism of micron-sized aluminum particles.

5. Conclusions

There are four stages of the reaction of aluminum powder. The first stage, from room temperature to about 600°C, alumina aluminum shell phase transition occurs from the initial amorphous transformed into γ-Al_2O_3. The second stage occurs in the vicinity of 660°C, alumina, aluminum shell thickness increases while nuclear liquefaction. The third stage, 700°C began to about 1050°C, the liquid aluminum and the environment in an atmosphere of violent reaction. Fourth stage, the high temperature section to 1050 deg.] C, the phase transformation of alumina, the final product of α- Al_2O_3.

6. Acknowledgements

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7. References

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