Studies on activity and oxide shell thickness of micron-sized Mg-Al alloy powder

Yang Liu[1, a], **Hui Ren**[2, b, *]

1. The Civil-Military Integration Institute, China Center for Information Industry Development, Beijing 100091, China
2. The state key labortary of explosive science and technology, School of Machatronical Engineering, Beijing Institute of Technology, Beijing 100081, China
a. liuyang@ccidthinktank.com b. renhui@bit.edu.cn
***corresponding author**

Abstract: The empirical formula of average oxide thickness of atomized micron-sized aluminum - magnesium alloy powder was proposed. At the same time, the influence of particle size and the ratio of magnesium on samples' activity was studied. The phase composition, morphology, and oxidation process of the alloy powders were studied by x-ray diffraction, scanning electron microscope/energy-dispersive x-ray, respectively. Study on the change of powder activity was achieved by standard gas volumn method. The results show that the oxide thickness of the atomized micron-sized aluminum - magnesium alloy powder is positively correlated with the particle size, and the activity decreases with the increase of the particle size and the magnesium content.

Key word: atomized Al-Mg alloy powder, thickness of oxide shell, active Al-Mg, size distribution

1. Introduction

Micron and nanometer scale metallic powders, serving as combustion components, can enhance the calorific value of energetic materials while reducing reaction temperatures, presenting significant potential for development and application [1]. Among these, micron and nanometer scale aluminum powder is the most widely used. However, due to the presence of a dense oxide layer in its natural state, issues such as ignition delay are observed during combustion [2]. Therefore, developing new materials that capitalize on the advantages of metallic fuels to address these issues holds great practical application value [3, 4].

A common approach to increase the reactivity of metal additives is to substitute aluminum powder with aluminum-magnesium alloy powder. Magnesium, being more chemically active, rapidly participates in oxidation during reactions and can also reduce the uneven agglomeration of aluminum in reactions. Aluminum-magnesium alloy powders are known for their high combustion enthalpy, controllable density, high energy density, and shorter ignition delay periods. According to existing research, different preparation methods and ratios of aluminum to magnesium in the alloy yield properties distinct from micron-sized aluminum powder [5, 6]. Liang Zeng conducted studies on the particle size and reactivity of atomized micron-sized aluminum powder [7], and the oxidation properties of aluminum-magnesium alloy powders prepared by different methods [8]. Research by E.L. Dreizin found that atomized aluminum-magnesium alloy powders exhibit a better thermal response effect compared to those prepared by ball milling [9]. The shell-core structure and reactivity relationship of atomized micron-sized aluminum-magnesium alloy powders are among the primary factors affecting reactions in energetic materials. Moreover, the oxidation-reduction behavior at low temperatures is also significant for further exploring the properties of atomized micron-sized aluminum-magnesium alloy powders, an area which remains unexplored.

Due to the typical shell-core structure of micron and nanometer scale aluminum-magnesium alloy powders, reactivity has a significant impact on the material's oxidation properties. This study further explores the oxidation process of micron-sized aluminum-magnesium alloy powders prepared by atomization, establishing a relationship between oxide layer thickness and reactivity. Additionally, using standard reactivity testing methods, this paper explores the relationship between particle size, aluminum-magnesium ratio, and reactivity changes of aluminum-magnesium alloy powders stored at 71℃ over an extended period.

2. Samples and Experiment

2.1. Samples and Instruments

Samples: The experimental samples were spherical micron-sized aluminum-magnesium alloy powders prepared by atomization. The magnesium content was controlled by adjusting the aluminum-magnesium feed ratio during preparation, with aluminum-magnesium molar ratios of 8:1, 3.6:1, and 0.88:1, each with four particle sizes. The samples were purchased from Tangshan Weihao Magnesium Powder Co., Ltd.

Instruments: A Hitachi S4700 scanning electron microscope (SEM) and its equipped energy-dispersive X-ray spectroscope (EDS) were used for micro-morphology and elemental distribution characterization of the samples. Particle size analysis was conducted using a Malvern Mastersizer 2000 laser particle size analyzer.

2.2. Reactivity Experiment of Atomized Micron-Sized Aluminum-Magnesium Alloy Powder

For each particle size and aluminum-magnesium ratio, 10g of aluminum-magnesium alloy powder was spread in a dish and heated in a drying oven at 71℃ for 1 hour, 2 hours, 24 hours, and 144 hours, respectively. The aluminum-magnesium alloy powders treated at different times were collected. Following the national standard GB3169.1-82, the active aluminum-magnesium content of atomized aluminum-magnesium alloy powder was determined using the gas volumetric method. The setup for reactivity testing is shown in Fig.1.

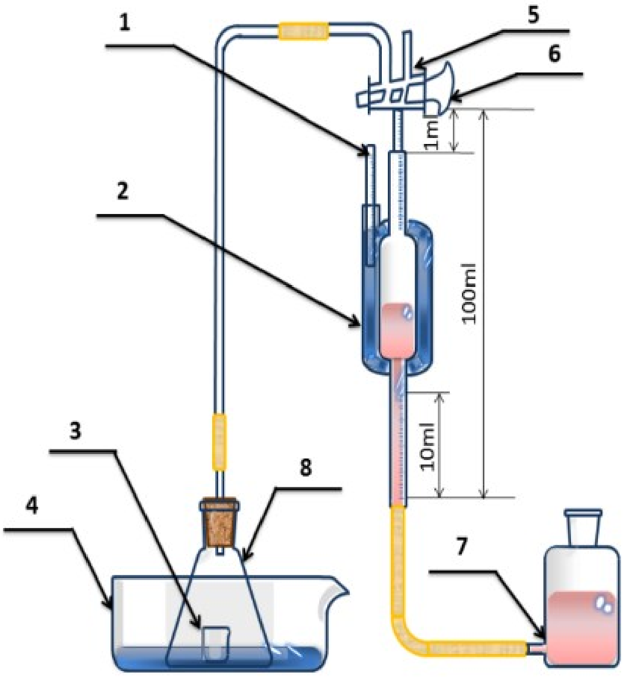

Fig.1 Schematic diagram of the standard gasometric method for determining active aluminum-magnesium content

1. Thermometer; 2. Trachea; 3. Sample tube; 4. Sink; 5. Exhaust hole; 6. Airway piston; 7. Standard bottle; 8.Reaction bottle

The percentage content of active magnesium or active aluminum-magnesium in the powder was calculated according to the following formula:

$$\text{Active Aluminum} - \text{Magnesium}(\%) = \frac{(P_1 - P_2 - P_3)V \cdot K}{(273+t)m} \times 100 \tag{1}$$

Where P_1 is the barometer reading in mmHg; P_2 is the corrected barometer reading, obtained from meteorological tables; P_3 is the saturated water vapor pressure at temperature t in mmHg; V is the volume of hydrogen gas produced, in mL; t is the temperature of the gas measuring tube in degrees Celsius; K is the conversion factor for hydrogen to active aluminum-magnesium; m_0 is the mass of the sample in grams.

3. experimental data

3.1. Physicochemical Properties of Atomized Micron-Sized Aluminum-Magnesium Alloy Powder

3.1.1. Activity and Particle Size Characterization

Characterization of the particle size distribution of the samples yielded the median particle size (D50). A statistical analysis of the particle size distribution revealed that the atomized micron-sized aluminum-magnesium alloy powder conforms to a log-normal distribution, as illustrated by Equation (2) and partially depicted in Figure 2. The composition of the raw micron-sized aluminum-magnesium alloy powder was determined, with results presented in Table 1, showing that the aluminum-magnesium content ratio of the atomized powder is consistent with the ratio used during preparation.

$$\text{Percentage} = y_0 + \frac{A}{\sqrt{2\pi}\sigma D} \cdot e^{-\frac{(\ln D-\mu)^2}{2\sigma^2}} \tag{2}$$

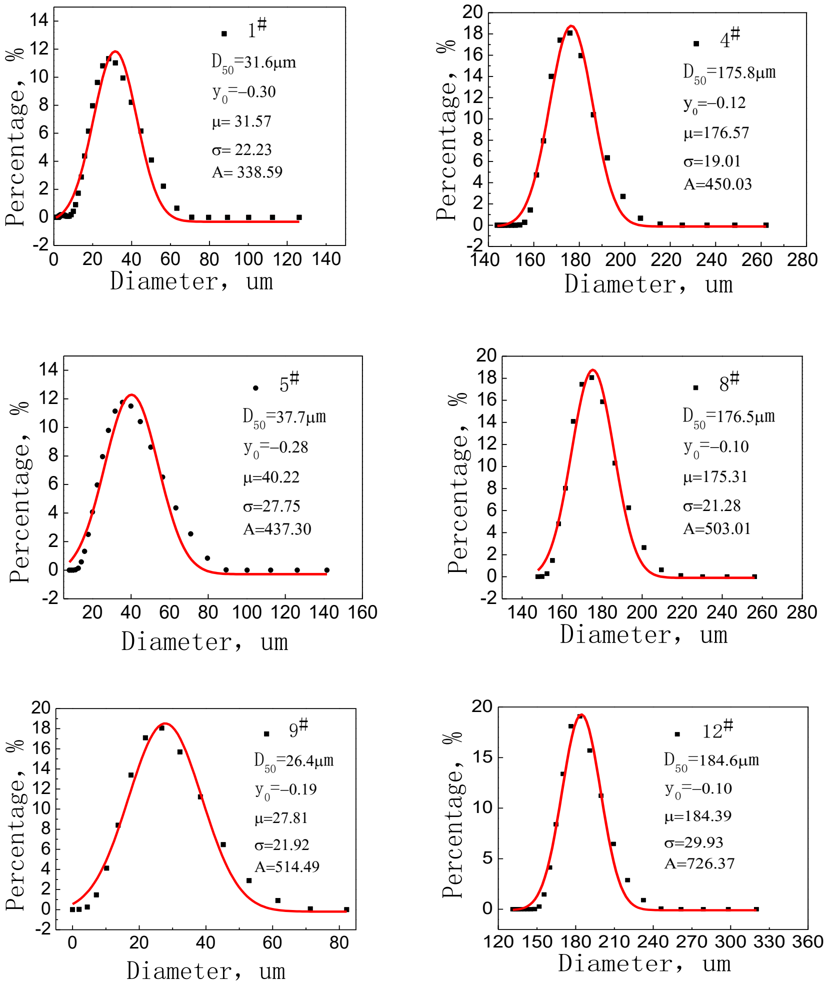

Figure 2: SEM Photo of Magnesium-Aluminum Alloy, Particle Size Distribution, and Fitting Curve

Table 1: Sample Parameters and Active Aluminum Content

Sample	Size, μm	Content	Ratio
		Active Al-Mg, %	Al:Mg
$1^{\#}$	31.6	98.56	88.64
$2^{\#}$	45.8	98.28	88.64
$3^{\#}$	65.4	98.48	88.64
$4^{\#}$	175.8		
$5^{\#}$	37.7	98.73	80.86
$6^{\#}$	46.5	98.56	79.66
$7^{\#}$	64.6	98.86	81.79
$8^{\#}$	176.5		
$9^{\#}$	26.4		
$10^{\#}$	44.9		
$11^{\#}$	70.1		
$12^{\#}$	184.6		

3.1.2. SEM Characterization

SEM characterization of the apparent morphology of atomized micron-sized aluminum-magnesium alloy powder revealed standard spherical shapes with good sphericity, complete particles, and smooth oxide layer coverage, as shown in some SEM photos in Figure 3.

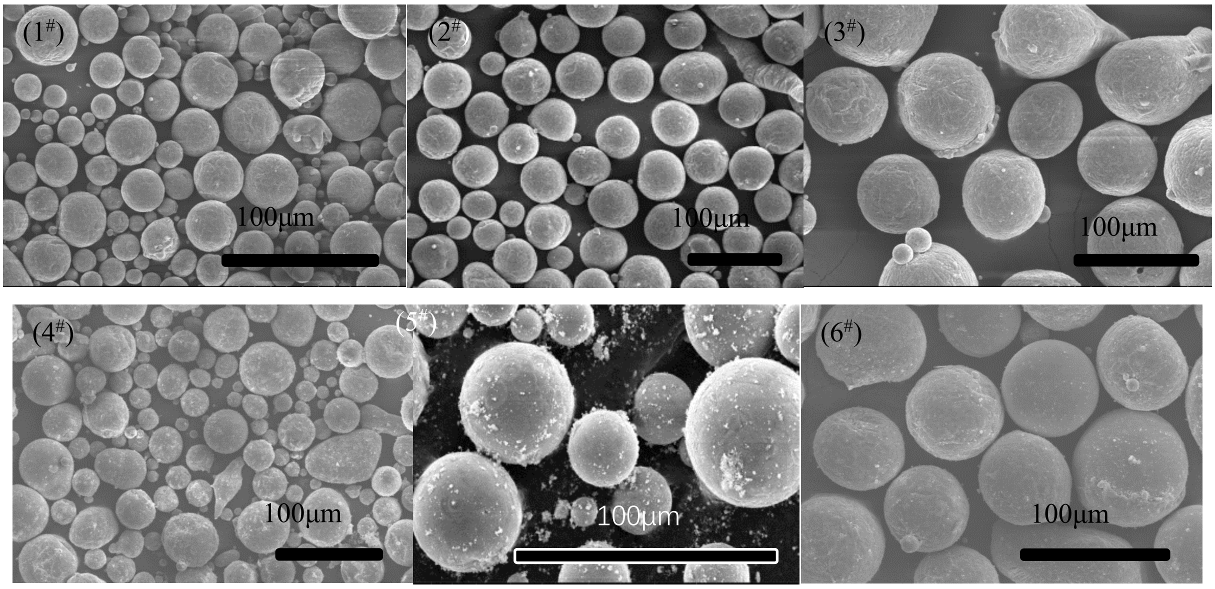

Figure 3: SEM Photos of Atomized Micron-Sized Aluminum-Magnesium Alloy Powder

3.1.3. Elemental Composition Analysis

Surface scanning of the atomized aluminum-magnesium alloy powder for elemental distribution is shown in Figure 4. Green represents aluminum atoms, yellow represents magnesium atoms, and red represents oxygen atoms. The surface distribution of aluminum, magnesium, and oxygen in the atomized micron-sized aluminum-magnesium alloy powder is uniform. Based on the density of elemental distribution, it can be roughly inferred that the aluminum and magnesium content is higher than the oxygen content. According to the phase diagram of magnesium oxide and aluminum oxide, the oxide on the particle surface exists in the form of aluminum oxide and magnesium oxide.

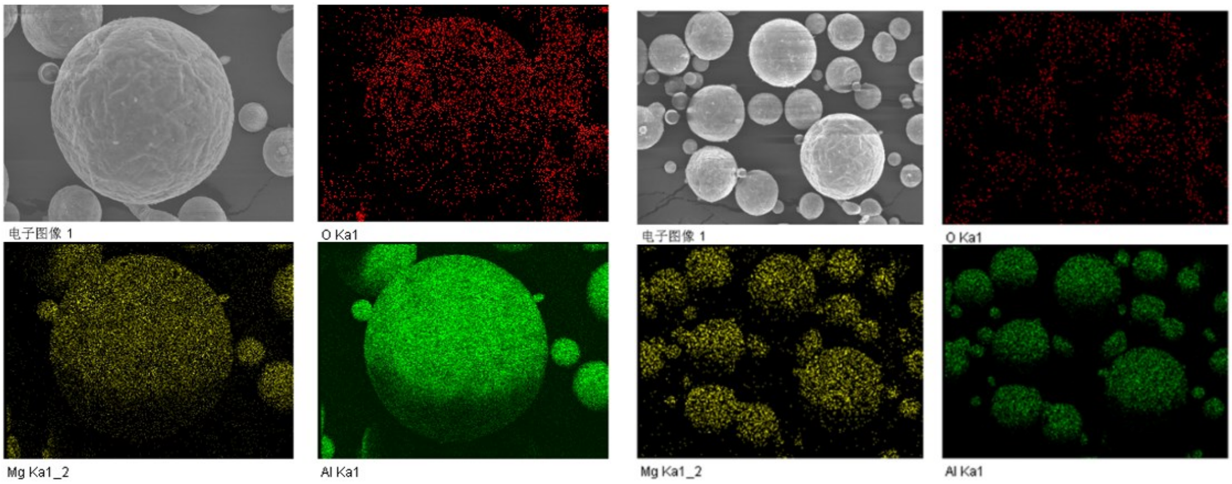

Figure 4: Elemental Surface Scan of Aluminum and Magnesium in Atomized Aluminum-Magnesium Alloy Powders 1# and 9#

3.2. Physicochemical Properties of Atomized Micron-Sized Aluminum-Magnesium Alloy Powder

3.2.1. Activity

The activity of atomized micron-sized aluminum-magnesium alloy powder treated at 71°C for 1h, 2h, 24h, and 144h was characterized, revealing the remaining active aluminum-magnesium content over different durations, as shown in Table 2.

Table 2: Activity of Atomized Micron-Sized Aluminum-Magnesium Alloy Powder after 71°C Treatment

Sample	Active Al-Mg after 1 hour, %	Active Al-Mg after 2 hours, %	Active Al-Mg after 24 hours, %	Active Al-Mg after 144 hours, %
1#	97.89	97.75	96.15	96.70
2#	98.09	96.68	96.83	96.63
3#	98.10	97.14	96.78	96.40
4#				
5#	97.88	97.51	95.84	95.88
6#	97.90	97.09	96.75	96.42
7#	97.81	97.00	96.06	96.08

3.2.2. Activity Change with Particle Size

Activity change curves for different particle sizes (Figure) indicate a slight decrease in aluminum-magnesium activity with increased storage time at 71°C.

3.2.3. Activity Change with Aluminum-Magnesium Content

To compare experimental results, the activity of pure aluminum powder and pure magnesium powder with the same particle size distribution was characterized after treatment at 71°C for different durations. The activity change curve for samples of the same particle size level and the aluminum-magnesium content ratio (Figure) suggests that the magnesium-aluminum content ratio affects the sample's activity.

3.2.4. Activity Change Over Time of Atomized Aluminum-Magnesium Alloy Powder

Using a modified Arrhenius equation, the storage time at room temperature (21°C) was inferred from the experimental duration at high temperature (71°C).

$$t_0 = \tau t_1 \tag{3}$$

Where t_0 is the storage time at room temperature, τt_1 is the experimental time at high temperature, and τ is the acceleration coefficient.

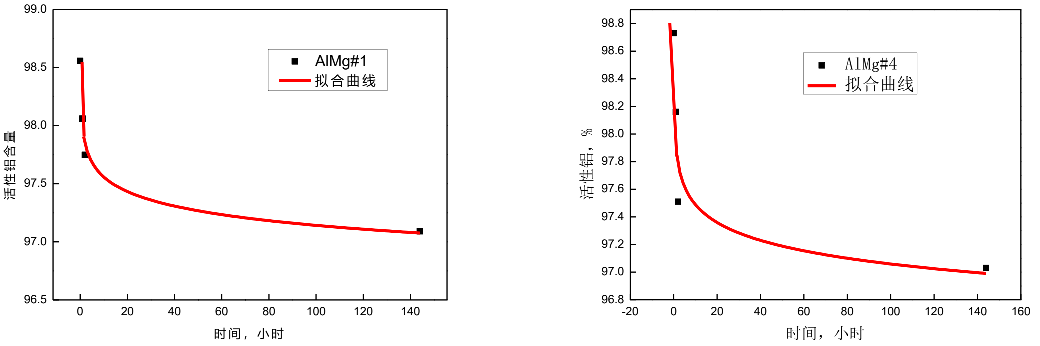

Figure 4: Change in Activity of AlMg#1 and AlMg#4 Over Time

Activity decrease was fitted using Origin 8.0, following a logarithmic distribution, with the fitting curve shown in Figure 5. The fitted parameters are presented in Table 4.8.

$$y = a - b\ln(x + c) \tag{5}$$

Table: Fitting Parameters for Activity

Parameter	AlMg#1	AlMg#4
a	*97.974*	*97.91924*
b	*0.18068*	*0.18678*
c	*0*	*0*

Fitting results for activity changes of three different particle sizes and aluminum-magnesium ratios indicate that the typical storage time for samples is 28, 56, and 84 days. The activity of magnesium-aluminum alloy samples remains above 96.5%, and the rate of deactivation decreases over time, eventually reaching equilibrium. Long-term storage at 71℃ does not continuously decrease activity, which can remain stable under certain temperature conditions.

The passivation layer on the surface of the micron-sized aluminum-magnesium powder is composed of a compound of aluminum oxide, magnesium oxide, and their alloy. The relatively low oxide content to some extent weakens the passivation effect of the oxide layer on the micron-sized aluminum-magnesium alloy samples compared to micron-sized aluminum powder. The slow heating reaction of micron alloy powder samples is more likely to occur. Due to the large compositional differences between the two components, the alloy samples may also exhibit uneven element distribution, which cannot be quantitatively determined by EDS. This is partly due to the limited characterization area of EDS and also related to the binding mode of aluminum and magnesium.

Table: Activity Calculation for AlMg Alloy Powder

Passivation Environment	Activity Calculation Results (%)	Passivation Environment	Calculation Results (%)
71℃28d	96.80	71℃28d	96.70
71℃56d	96.67	71℃56d	96.57
71℃84d	96.60	71℃84d	96.50

4. Results

4.1. Calculation of Oxide Layer Thickness for Atomized Micron-Sized Aluminum-Magnesium Alloy Powder

4.1.1. Mechanism of Oxide Layer Thickening

Mott assumed that a very thin layer of oxide already exists on the metal surface, with the movement of cations and electrons through the layer being independent. At lower temperatures, thermal energy alone is insufficient for diffusion through the thin film. However, electrons can transfer via thermal emission or tunneling effect, adhering to hydrogen atoms on the oxide film surface, enabling timely electron acquisition by oxygen on the film surface to form oxygen ions. As a result, a cationic region is formed at the metal/oxide interface, an anionic region at the oxide/gas interface, and a space charge region within the oxide film, creating a potential difference across the oxide layer. For instance, a 1V potential difference across a few nanometers thick oxide layer can generate an electric field strength of about 107 V/cm, facilitating the migration of metal ions outward or oxygen ions inward, even in weak thermal diffusion. However, the strong electric field inhibits the outward movement of electrons. Thus, ion migration in a thin oxide layer primarily depends on the potential difference across the oxide layer, not the chemical potential difference, which contrasts with thicker films.

4.1.2. Calculation of Oxide Layer Thickness

Based on the binary phase equilibrium of oxidized magnesium and aluminum, the external oxide layer of magnesium and aluminum consists of a mixture of magnesium oxide and aluminum oxide. Based on the proportion of atomized aluminum-magnesium alloy powder, to establish a relationship between oxide layer thickness and reactivity, a shell-core structural model for aluminum-magnesium alloy powder is proposed, with the following simplified spherical assumptions:

1. The atomized micron-sized aluminum-magnesium alloy powder has a shell-core structure with good sphericity and uniform shell thickness;
2. The particle's oxide layer is composed of aluminum oxide and magnesium oxide in the same ratio as the aluminum to magnesium ratio;
3. The particles have a very low impurity content, existing within the metal core, not affecting the calculation of the oxide layer.

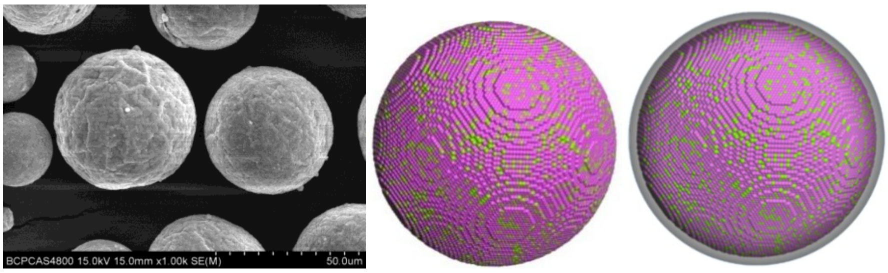

Figure: Schematic Diagram of Aluminum-Magnesium Alloy Particle Shell-Core Structure, with pink representing aluminum atoms and green representing magnesium atoms

With these assumptions and the shell-core structural model of aluminum powder, active aluminum content refers to the ratio of the core's mass to the total particle mass. Converting this ratio from mass to volume using the densities of the aluminum core and aluminum oxide, and then using the calculated average particle size, the average thickness of the aluminum powder's oxide layer can be calculated using the following equations:

$$A = \frac{d'^3 \cdot \overline{\rho_1}}{d'^3\left(\overline{\rho_1} - \overline{\rho_2}\right) + d'^3 \cdot \overline{\rho_2}} \tag{2}$$

$$\overline{\delta} = \frac{d}{2} \cdot \left(1 - \sqrt[3]{\frac{A \cdot \overline{\rho_2}}{(1 - A) \cdot \overline{\rho_1} + A \cdot \overline{\rho_2}}}\right) \tag{3}$$

Where ***A*** is the active aluminum-magnesium content; ***d*** is the D_{50} of the aluminum-magnesium alloy; d' is the diameter of the active aluminum core; $\overline{\rho_1}$ is the average density of aluminum-magnesium; $\overline{\rho_2}$ is the average density of the aluminum and magnesium oxide layer, calculated based on the determined aluminum-magnesium ratio. The calculated thickness of the aluminum oxide layer is shown in Table 4, increasing with particle size.

Table 4: Calculation of Oxide Layer Thickness for Aluminum-Magnesium Alloy

Sample	Thickness of oxide shell,nm	Sample	Thickness of oxide shell,nm	Sample	Thickness of oxide shell,nm
1#	47.01	5#	47.01	9#	47.01
2#	88.21	6#	88.21	10#	88.21
3#	111.19	7#	111.19	11#	111.19
4#	64.15	8#	64.15	12#	64.15

4.2. Effect of Particle Size of Atomized Micron-Sized Aluminum-Magnesium Alloy Powder on Reactivity

According to low-temperature metal oxidation theory, the thicker the oxide layer, the greater the potential difference between the metal's outer oxide layer and the metal interface, making the oxidation process less likely. The oxide layer thickness of metal powder samples increases with particle size.

4.3. Effect of Magnesium Content in Atomized Micron-Sized Aluminum-Magnesium Alloy Powder on Reactivity

The activity of the samples treated at 71°C decreased by about 1%. The decrease in activity was relatively lower for larger particle sizes. At 200°C, the deactivation of aluminum-magnesium alloy powder was more evident, but not lower than 95%.

Comparing the activity of pure aluminum powder and pure magnesium powder with alloy powder of the same particle size, the activity remained intact. The alloy samples were stable in the system, without any significant impact on the deactivation of the energetic system. Therefore, micron-sized magnesium-aluminum alloy can still maintain a certain degree of activity and temperature insensitivity with a lower surface oxygen content, ensuring quality in energetic system applications.

The oxidation of metals is mainly controlled by the migration of ionic vacancies and interstitial ions in the crystal. Altering the defect concentration in the oxide film by adding appropriate foreign ions can change the metal's oxidation rate. This follows the Wagner-Hauffe semiconductor valence rule. For P-type oxide films in electron-conducting oxides, when the valence state of the foreign cation is lower than that of the base metal forming the oxide, the concentration of ionic defects decreases.

The addition of magnesium reduces the concentration of cationic vacancies in the aluminum/aluminum oxide system, thereby decreasing the oxidation rate. The oxidation rate of the alloy decreases after alloying, possibly due to the formation of complex compounds (such as Al12Mg17), changing the ion migration number, as the alloy structure is denser than pure aluminum oxide and magnesium oxide, enhancing the protective properties of the oxide film.

When a small amount of alloy component with a greater affinity for oxygen than the matrix metal is added, and when the oxide of the alloy component and the oxide of the matrix metal are almost insoluble in each other, a new oxide layer may form, providing better protection to the body.

5. Conclusion

The study on the activity and shell-core structure of micron-sized aluminum-magnesium alloy powder prepared by atomization shows that under the shell-core structure model assumption, the element distribution and sphericity of magnesium-aluminum alloy powder samples are uniform, with particle size distribution following a logarithmic normal distribution. The samples have a protective oxide layer on the surface, but overall, compared to pure aluminum particles, the oxygen content is lower, and the oxide layer's density is weaker, with a naturally thicker oxide layer. The relationship between the active aluminum content and the oxide layer thickness of the powder is directly proportional. With a 10%-15% magnesium content, the increase in magnesium content reduces the oxide layer thickness.

A deactivation study of magnesium-aluminum alloy powder using the 71°C reactivity test method found that the deactivation characteristics of magnesium-aluminum alloy follow a logarithmic distribution, decreasing rapidly in the first two hours and gradually reaching equilibrium with extended thermal treatment. Under long-term storage conditions, the reactivity of magnesium-aluminum alloy powder remained above 96%, with long-term stability fitting a logarithmic distribution with time.

6. References

[1] Moussa, R.B., et al., Physical mechanisms involved into the flame propagation process through aluminum dust-air clouds: A review. Journal of Loss Prevention in the Process Industries, 2017. 45: p. 9-28.
[2] Pisharath, S., F. Zhang, and H.G. Ang, Influence of passivation on ageing of nano-aluminum: Heat flux calorimetry and microstructural studies. Thermochimica Acta, 2016. 635: p. 59-69.
[3] Starik, A.M., A.M. Savel'ev, and N.S. Titova, Specific features of ignition and combustion of composite fuels containing aluminum nanoparticles (Review). Combustion, Explosion, and Shock Waves, 2015. 51(2): p. 197-222.
[4] Schreiber, S., G. Theodossiadis, and M. Zaeh. Combustion synthesis of reactive nickel-aluminum particles as an innovative approach for thermal joining applications. in IOP Conference Series: Materials Science and Engineering. 2017. IOP Publishing.
[5] Xie, G., et al., Behavior of Oxide Film at Interface between Particles of Al-Mg Alloy Powder Compacts Prepared by Pulse Electric Current Sintering. Japanese Journal of Applied Physics, 2003. 42(42): p. 4725-4728.
[6] Xie, G., et al., Reduction mechanism of surface oxide films and characterization of formations on pulse electric-current sintered Al–Mg alloy powders. Applied Surface Science, 2005. 241(1–2): p. 102-106.
[7] 曾亮, et al., 微米铝粉活性及氧化膜厚度研究 [J]. 北京理工大学学报, 2012. 2: p. 020.
[8] Aly, Y. and E.L. Dreizin, Ignition and combustion of Al·Mg alloy powders prepared by different techniques. Combustion & Flame, 2015. 162(4): p. 1440-1447.
[9] Nie, H., M. Schoenitz, and E.L. Dreizin, Oxidation of differently prepared Al-Mg alloy powders in oxygen. Journal of Alloys & Compounds, 2016. 685: p. 402-410.