Reaction kinetics of magnesium subjected to hygrothermal aging under oxygen-rich conditions

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1 Introduction

Fossil fuels have abundant energy and are widely used in the world. However, they have the fatal disadvantages that having limited reservs and accelerating global warming by emitting CO_2. As a result, many comprehensive studies have been conducted to find the alternative to fossil fuels. Among them, metal fuels are being studied as they have abundant enrgy and can be used without emitting CO_2 through oxidation-reduction reaction [1, 2]. Julien *et al.* [1] identified seven metals (i.e. Ti, Zn, B, Al, Mg, Fe, and Si) by considering various constraints. Trowell *et al.* [2] suggested that aluminum could be a good alternative to fossil fuels, subject to several constraints.

In particular, among various metal fuels, magnesium is also widely used in various fields such as lithium-ion batteries, additives in propellant, and energy storage due to its good energy density and low price. Many studies have been conducted on Mg, Mg mixtures, and Mg compounds [3-7]. Nie *et al.* [3] studied the oxidation properties according to the particle size and found that the finer the particle size, the faster the oxidation reaction occurs. Yuan *et al.* [4] investigated the oxidation characteristics of magnesium according to the nitrogen/oxygen ratio and found that the reaction shifted to higher temperatures as the nitrogen ratio increased. Juyoung *et al.* [5] investigated the change in the thermal properties of Mg with aging and found that the oxide film formed during the aging process caused the performance degradation of Mg. Liu *et al.* [6] studied the combustion and thermal properties of Mg alloys (AZ31, ZE10, WE43). They found that ZE10 had a highest activation energy amongall. Soltani *et al.* [7] investigated the information on the oxidation of Al-Mg powder. They showed that the activation energy calculated by Starink and Friedman methods decreases as the oxidation proceeds.

However, the oxidation mechanism of Mg and the change in reaction kinetics according to oxygen flow rate have not been clarified yet. In this study, the aging mechanism of Mg was investigated through morphological and thermochemical analysis. In addition, by applying two different oxygen flow rate condtions, Mg oxidation efficiency was studied. As a result, as aging period was prolonged, oxide film completely surrounded magnesium surface. Then, long-term aged samples had a peculiar propety that only core oxidation occurred due to sufficient oxide film. In addition, as hygrothermal aging progressed, more magnesium hydroxide, which accelerated the oxidation reaction, was formed. And it made activation energy increase under oxygen-rich condition. Thus, this study provide the insight into the effect of oxygen flow rate to hygrothermal aged magnesium.

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2 Methods

2.1 Samples

All magnesium used in this study are provided by US Research Nanomaterials Inc. They have a purity of 99.9% and a size of 40 μm. Table 1 summarizes the serial numbers and aging conditions used in the experiment. All aging samples were stored in an oven at 71 ℃ for accelerated aging by referring to the 'Criteria for explosive systems and devices on space launch vehicles' [8]. Accelerated aging is a technique that can identify the effects of aging in a short period by storing metals in a high temperature environment [5, 9]. In addition, during aging, the relative humidity was maintained at about 50-60%. The aging period was set to 3, 5, and 25 weeks.

Table 1: Serial number and aging conditions of mg powder

Serial number #	Aging condition		Aging type
	Temperature	Aging duration	
#0	71 ℃	-	Pristine
#1		3 weeks	Hygrothermal aging
#2		5 weeks	
#3		25 weeks	

2.2 Morphological analysis

All samples were taken with scanning electron microscope (SEM) image using field emission-scanning electron microscope (FE-SEM), which analyzes the components of the samples using electrons and X-rays generated when accelerated electrons irradiate the sample surface. FE-SEM used in this study was JSM-7800F Prime (JEOL Ltd, Japan), which equipped with energy-dispersive X-ray spectroscopy (EDS) to analyze the composition of the sample. The resolution range of FE-SEM is 0.7-3.0 nm.

2.3 Thermal analysis

To examine the thermal behavior of Mg, differential scanning calorimetry (DSC) was employed according to the standard of International Confederation for Thermal Analysis and Calorimetry (ICTAC) [10]. DSC is a device that measures the difference in heat flow between a sample pan and a reference pan, and has a temperature range of 30-640 ℃. In this study, DSC-3+ (Mettler Toledo) were used. Heating rates of 1, 2, 3, 4, and 5 ℃/min were applied. Also, oxygen flow rates of 50 ml/min and 100 ml/min were used to examine the magnesium oxidation efficiency according to oxygen flow rate. About 0.3-0.5 mg of sample was placed in a standard 40 μL aluminum crucible and sealed with a 0.5 mm diameter lid with a hole for DSC experiments.

In DSC results, a baseline was formed by drawing a sigmoidal tangential type line between the start and end point of exothermic reaction. Heat of reaction was calculated by integrating the area between the baseline and exothermic reaction peak. In addition, peak separation based on the Frazer-Suzuki function was performed.

2.4 Calculation of reaction kinetics

Reaction kinetics calculation was carried out according to the standard of ICTAC, and Friedman method, which is the most widely used differential isoconverstional method [10, 11]. Friedman method is a differential model-free method that calculates activation energy (E_α) and pre-exponential factor (A_α) according to reaction progress (α), and can be expressed as the following equations.

Equation (1) is a rate equation, and Eq. (2) can be obtained by applying the isoconversional principle. Here, with a constant heating rate, Eq. (2) can be replaced with Eq. (3). Since a constant heating rate is used in this study, Friedman method in the form of Eq. (3) was used. Activation energy and pre-exponential factor were calculated from the slope and y-intercept of the graph in the plane of *1/T* vs ln*(dα/dt)*.

$$\frac{d\alpha}{dt} = A_\alpha \exp(-\frac{E_\alpha}{RT}) f(\alpha) \tag{1}$$

$$\ln(\frac{d\alpha}{dt})_{\alpha,i} = \ln[f(\alpha)A_\alpha] - \frac{E_\alpha}{RT_{\alpha,i}} \tag{2}$$

$$\ln[\beta_i(\frac{d\alpha}{dT})_{\alpha,i}] = \ln[f(\alpha)A_\alpha] - \frac{E_\alpha}{RT_{\alpha,i}} \tag{3}$$

3 Results

3.1 Morphological and atomic analysis

Figure 1 shows the surface of pristine and aged magnesium powders by SEM. The surface of pristine sample was smooth while that of aged samples became increasingly rough. In particular, long-term aged sample changed the original magnesium shape beyond recognition. As presented in Eq. (4) - (6), Mg reacts with oxygen and moisture in the surrounding atmosphere during aging process to form an oxide film composed of magnesium oxide (MgO) and magnesium hydroxide ($Mg(OH)_2$).

$$2Mg_{(s)} + O_2 \rightarrow 2MgO_{(s)} \tag{4}$$

$$Mg_{(s)} + 2H_2O \rightarrow Mg(OH)_{2\,(s)} + H_{2\,(s)} \tag{5}$$

$$MgO_{(s)} + H_2O \rightarrow Mg(OH)_{2\,(s)} \tag{6}$$

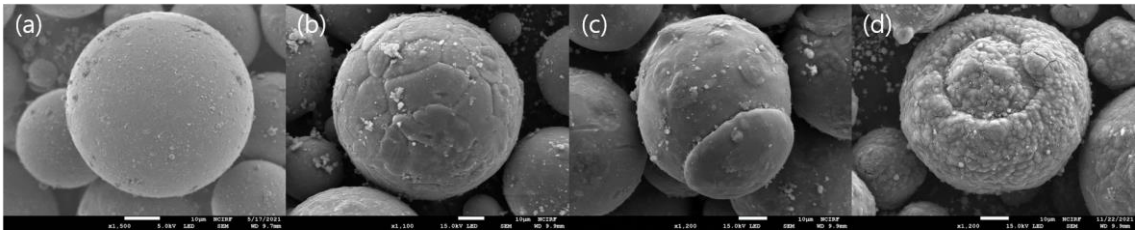

Figure 1: The surface of magnesium powder (a) Pristine (b) 3 weeks aged (c) 5 weeks aged (d) 25 weeks aged

The components of each sample through EDS is shown in Fig. 2. As short-term aging proceeded, magnesium ratio decreased and oxygen ratio increased by about two times. In addition, with long-term aging, oxygen ratio increased more than before. Here, since an increase in oxygen ratio indicates an increase of MgO, which means that a large amount of oxide film is formed as aging progresses.

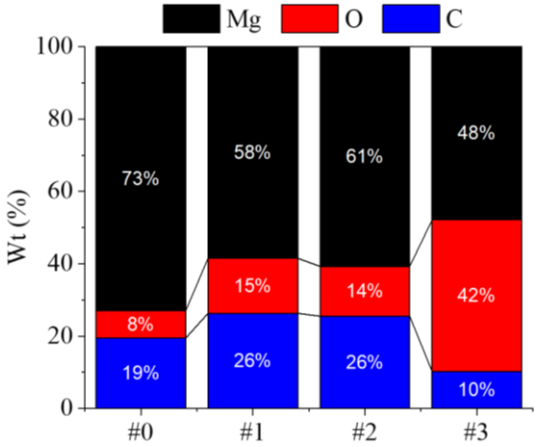

Figure 2: Composition of pristine and aged samples

3.2 Thermal analysis

Figure 3 (a) show the peak seperation result of pristine sample at oxygen flow rate of 50 ml/min. Magnesium oxidation reaction appears as a complex exothermic reaction, which consists of surface oxidation and core oxidation [12]. Surface oxidation occurred gradually at about 550 ℃, whereas core oxidation occurred with a steep slope at relatively higher temperature of about 580 ℃.

Figure 3 (b) and (c) show the DSC results at oxygen flow rates of 50 ml/min and 100 ml/min, respectively. Pristine samples showed little change with increasing oxygen flow rate, but some differences can be observed in aged samples. First, the heat flow tended to increase as oxygen flow rate increased. This is because the remaining intermediates, which failed to react with oxygen at 50 ml/min, proceeded to react at 100 ml/min. In addition, as aging progresses, the peak temperature shifts to a lower temperature due to oxide film, as can be seen in Fig. 3 (c). Finally, at all oxygen flow rates, short-term aged samples started oxidation gradually at a relatively low temperature, similar to pristine samples. However, in long-term aged samples, an oxidation reaction ocurred with a steep slope at a relatively high temperature, similar to core oxidation. As aging was prolonged, a sufficient oxide film was formed to cover the entire magnesium surface, which resulted in the skip of surface oxidation.

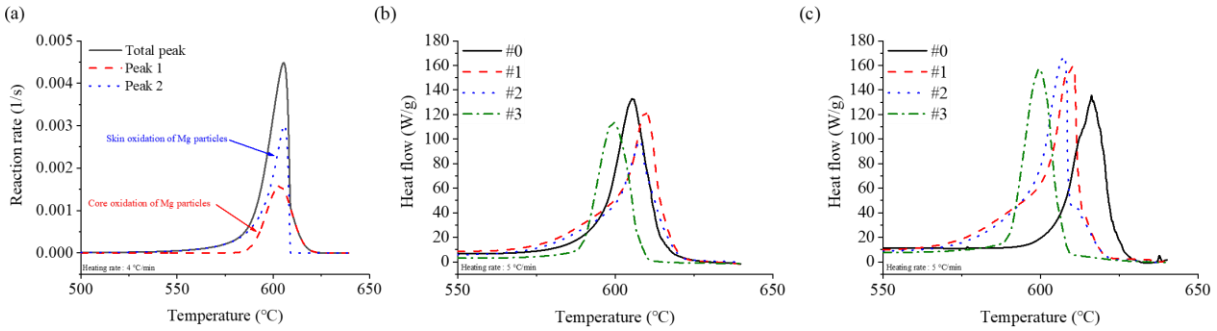

Figure 3: DSC results (a) Peak seperation of pristine mg particle at 4 ℃/min (b) 5 ℃/min and 50 ml/min (c) 5 ℃/min and 100 ml/min

3.3 Reaction kinetics

Kinetics used in this study were calculated by applying Friedman method to DSC data. Since experimental errors occur a lot when α is outside the rage of 0.05-0.95, only data in the range of 0.05-

0.95 were considered [11]. Figure 4 (a) shows the kinetics of pristine sample at 50 ml/min. Activation energy and pre-exponential factor had a similar trend due to the 'kinetic compensation effect' [13], which can be expressed as Eq. (7).

$$\log A_\alpha = aE_\alpha + b \tag{7}$$

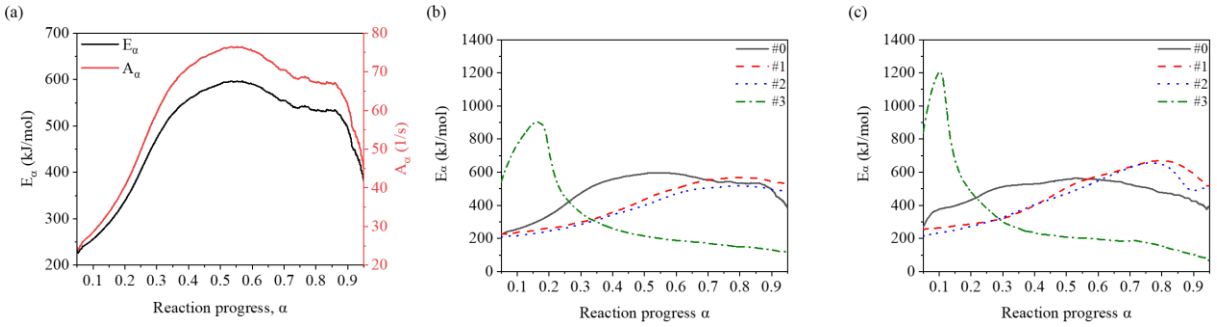

Figure 4: Activation energy and pre-exponential factor of pristine magnesium at oxygen flow rate of 50ml/min

Figure 4 (b) and (c) shows activation energy according to α. Regardless to oxygen flow rate, short-term aged samples reached a peak at higher α than pristine samples. This is because the oxide film formed by aging disturbs the oxidation reaction. In addition, the long-term aged samples had a high activation energy at low α as only core oxidation occurred.

Table 2: The calculated activation energy at different oxygen flow rates

Serial number #	Activation energy (kJ/mol)		Aging type
	50 ml/min	100 ml/min	
#0	596.45	563.79	Pristine
#1	569.09	669.13	Hygrothermal aging
#2	517.03	657.71	
#3	835.47	1147.88	

Mg oxidation reaction can be divided into oxygen-lean and oxygen-rich conditions according to oxygen flow rate. $Mg(OH)_2$ accelerates the oxidation reaction at high temperature, whereas MgO disturbs the reaction. Table 2 shows the peak activation energy of each sample. In pristine samples, an increase in oxygen flow resulted in a decrease in activation energy. However, the aged samples in which sufficient $Mg(OH)_2$ was produced showed a tendency to increase activation energy from oxygen-lean to oxygen-rich. This is because the reaction of $Mg(OH)_2$ with residual oxygen involves the formation and decomposition of various intermediates.

4 Conclusion

This study provides insight into the changes in the magnesium-oxygen reaction according to aging and oxygen flow rate. Mg was exposed to hygrothermal aging for 3, 5, and 25 weeks to investigate the effect of aging. The thermal behavior was investigated through non-isothermal thermal analysis such as DSC and TGA, and kinetic parameters were calculated by applying the differential isoconversional method to the thermal analysis data. It was confirmed that as aging period increased, an oxide film was formed on the surface and activation energy decreased. When short-term aged samples were changed from oxygen-lean to oxygen-rich, $Mg(OH)_2$ reacted with residual oxygen to generate and decompose various intermediates, resulting in an increase in activation energy. In addition, long-term aged sample skipped surface oxidation and only core oxidation occurred. This decrease in activation energy indicates that an ignition reaction can easily occur during storage, which eventually causes safety hazards.

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