



Oxidation of differently prepared Al-Mg alloy powders in oxygen



Hongqi Nie, Mirko Schoenitz, Edward L. Dreizin*

New Jersey Institute of Technology, Newark, NJ 07103, USA

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ABSTRACT

Powders of both commercial atomized spherical Al-Mg alloy and mechanically alloyed Al-Mg were oxidized in oxygen using thermo-gravimetry (TG). For both powders, the Al/Mg mass ratio was equal to 1. Fully and partially reacted powders were recovered and characterized using scanning electron microscopy and x-ray diffraction. Voids grow within oxidized alloy particles for both atomized and mechanically alloyed powders. Results were interpreted accounting for the measured particle size distribution for the spherical powder and distributing the TG-measured weight gain among the individual particle size bins. The reaction interfaces were always located at the internal surface of the oxide shell as determined by matching the oxidation dynamics for particles with the same sizes but belonging to powders with different particle size distributions. Thus, the reaction is always rate limited by inward diffusion of oxygen ions through the growing oxide shell. Two oxidation stages were identified for both materials. Both Al and Mg oxidize during both observed oxidation stages. The second oxidation stage is caused by formation of the spinel phase, most likely occurring at a threshold temperature. In the present measurements, the step in the oxidation rate, or switch between the oxidation stages, occurs when the oxide shell grows above a certain thickness of approximately 1.5 μm . The apparent activation energy during the first oxidation stage energy changes during the first oxidation stage suggesting that more than one reaction occur in parallel, e.g., causing formation of MgO and amorphous alumina. For the second oxidation step, controlled by diffusion of oxygen through spinel layer, the activation energy remains nearly constant around 185 kJ/mol.

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1. Introduction

Various Al-Mg alloys find multiple applications in structural materials [1,2], for hydrogen storage [3], and as components of energetic formulations [4–6]. Most of the published work on oxidation of such alloys deal with compositions with small concentrations of Mg, varied from less than 1–5% [7–9]. For such materials, it was observed that the oxide includes different layers, with MgO typically observed on top of MgAl_2O_4 and/or Al_2O_3 . At the same time, alloys with much higher concentrations of Mg are of interest for propellants, explosives, and pyrotechnics [10–13]. Oxidation of such high-Mg content materials is not well understood. In Ref. [14], oxidation of an Al_3Mg_2 alloy was considered. The reaction was observed to proceed in three stages with three distinct rates: an MgO layer was reported to form initially; then MgAl_2O_4 oxide was produced, which finally cracked, leading to the third

oxidation stage. A general rule used to estimate the tendency of metals to continuously oxidize, the Pilling-Bedworth ratio [15] of the molar volumes of oxide and metal is close to unity for high-Mg aluminum alloys, and is therefore not expected to be particularly predictive for oxidation behavior. Further, kinetic details enabling the quantitative description of these reactions are not available. Such descriptions are important for reactive materials for prediction of both aging and ignition behaviors of the relevant compositions. Recently, thermo-analytical studies were used to clarify reaction mechanisms and describe them quantitatively for both Al [16,17] and Mg [18] powders. Here, a similar experimental approach and data processing techniques are applied to characterize high temperature oxidation in Al-Mg alloys with equal mass fractions of aluminum and magnesium. The objectives are to identify the interface for heterogeneous oxidation reactions and describe reaction mechanisms and rates quantitatively. The experiments performed with two types of Al-Mg alloys prepared by different techniques, and thus having distinct initial structures and morphologies.

* Corresponding author.

E-mail address: dreizin@njit.edu (E.L. Dreizin).

2. Experimental

2.1. Materials

Two Al-Mg alloy powders with Al/Mg mass ratio of 50:50 were used in thermo-gravimetric (TG) experiments. An atomized spherical alloy, –270 Mesh was provided by Valimet Inc. A mechanically alloyed powder was prepared at NJIT as described in detail elsewhere [19–21]. Briefly: starting materials for the mechanically alloyed powder were elemental powders of Al (Atlantic Equipment Engineers, 99.8% pure, –325 Mesh) and Mg (Alfa-Aesar, 99.8% pure, –325 Mesh). Mechanical alloying was performed using a Retsch PM-400 MA planetary mill operated at 350 rpm. Powder mass load was 30 g per vial; 9.5 mm-diameter hardened steel balls served as milling media. The ball to powder mass ratio was 10; the milling time was 2 h. Each vial was filled with 50 mg of hexane used as a process control agent.

Scanning electron microscope (SEM) images for both Al-Mg alloy powders are shown in Fig. 1. The particles have roughly spherical shapes for atomized Al-Mg alloys. Mechanically alloyed powder particles have characteristic angular shapes; they also are noticeably coarser than the atomized powders.

For detailed TG measurements described below, the spherical atomized alloy powder was split into two fractions with different but partially overlapping particle size distributions. The powder was passed through a 550 Mesh (25 μm opening) sieve. The particle size distributions for both obtained size fractions were measured using a Beckman-Coulter LS230 Enhanced Particle Analyzer as shown in Fig. 2. These measured particle size distributions were directly used to process the TG measurements for the atomized alloy powder. The TG measurements for the mechanically alloyed powder were interpreted qualitatively and did not rely on the particle size distribution measurements.

2.2. Oxidation experiments

Both Al-Mg powders were oxidized in an oxygen/argon mixture using a Netzsch STA409PC/PG thermal analyzer with a thermogravimetric sample carrier. The customized furnace used in experiments provided the oxidizer flow from the top of the furnace down to the sample. This flow pattern helped to oxidize and condense evaporating magnesium directly in the sample holder. Magnesium evaporation and deposition of the oxide elsewhere in the furnace presented a serious experimental problem in preliminary experiments, when a regular furnace was used, in which the oxidizing gas was rising from the bottom up.

In these experiments, argon was introduced as both a protective gas surrounding the thermobalance and as a carrier gas for oxygen/

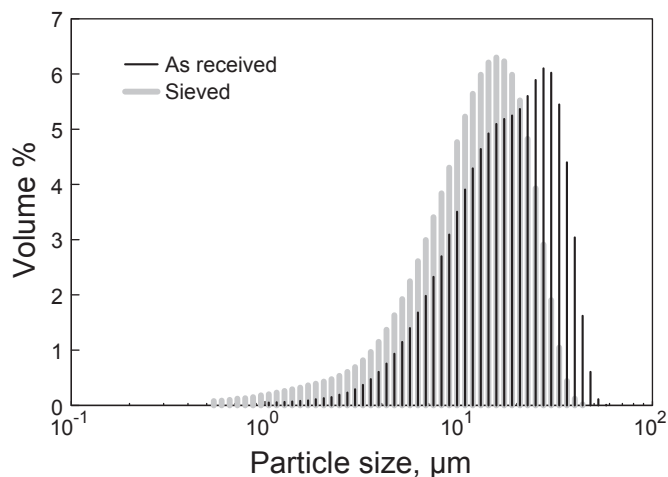


Fig. 2. Particle size distributions for coarse (as received) and fine (sieved) fractions of the spherical atomized Al-Mg alloy powder used in experiments.

argon oxidizing mixture; the respective flow rates of argon were 90 and 20 mL/min. The oxygen flow rate was 10 mL/min so that oxygen comprised 30% of gas supplied to the sample. The powders were held on a 17-mm diameter flat corundum sample holder and heated up to 800 °C. Heating rates varied from 2 to 20 °C/min in different experiments.

Fully and partially oxidized powders were recovered and examined using a scanning electron microscope (LEO 1530 Field Emission SEM); their compositions were characterized using x-ray diffraction (XRD) using a PANalytical Empyrean diffractometer. The diffractometer was operated at 45 kV and 40 mA using unfiltered Cu K α radiation ($\lambda = 1.5438 \text{ \AA}$).

3. Results and discussion

3.1. Phases and morphologies formed upon oxidation

Initial oxidation TG measurements were performed for both atomized and mechanically alloyed powders at a fixed heating rate of 5 °C/min. The resulting TG traces are shown in Fig. 3. A characteristic, two-stage oxidation pattern is observed for both materials. For the atomized powder, an appreciable oxidation begins above 350 °C. For mechanically alloyed powder, the mass increase becomes detectable above 400 °C. For both materials, reaction accelerates substantially around 500 °C. The second oxidation stage begins above ca. 530 °C, when the rate of oxidation becomes slower. It remains nearly constant for the mechanically alloyed powder at

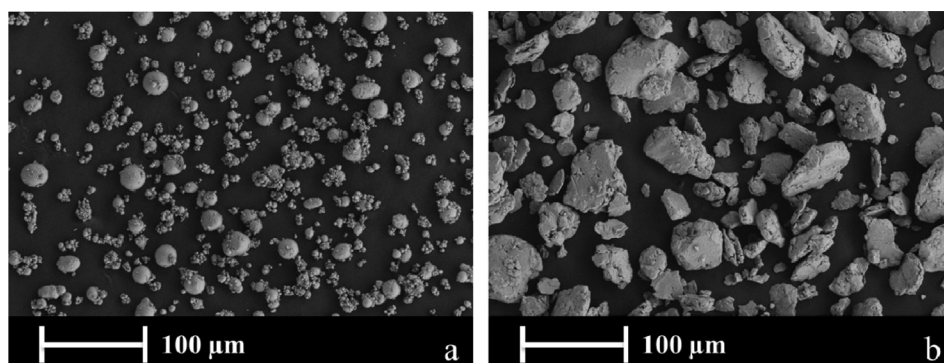


Fig. 1. Backscattered SEM images for Al-Mg powders: atomized spherical alloy (a) and mechanically alloyed powder (b).

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