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Oxidation kinetics of aluminum diboride

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ABSTRACT

The oxidation characteristics of aluminum diboride (AlB_2) and a physical mixture of its constituent elements (Al+2B) were studied in dry air and pure oxygen using thermal gravimetric analysis to obtain non-mechanistic kinetic parameters. Heating in air at a constant linear heating rate of 10 °C/min showed a marked difference between Al+2B and AlB_2 in the onset of oxidation and final conversion fraction, with AlB_2 beginning to oxidize at higher temperatures but reaching nearly complete conversion by 1500 °C. Kinetic parameters were obtained in both air and oxygen using a model-free isothermal method at temperatures between 500 and 1000 °C. Activation energies were found to decrease, in general, with increasing conversion for AlB_2 and Al+2B in both air and oxygen. AlB_2 exhibited O_2-pressure-independent oxidation behavior at low conversions, while the activation energies of Al+2B were higher in O_2 than in air. Differences in the composition and morphology between oxidized Al+2B and AlB_2 suggested that Al_2O_3–B_2O_3 interactions slowed Al+2B oxidation by converting Al_2O_3 on aluminum particles into a $Al_4B_2O_9$ shell, while the same $Al_4B_2O_9$ developed a needle-like morphology in AlB_2 that reduced oxygen diffusion distances and increased conversion. The model-free kinetic analysis was critical for interpreting the complex, multistep oxidation behavior for which a single mechanism could not be assigned. At low temperatures, moisture increased the oxidation rate of Al+2B and AlB_2, but both appear to be resistant to oxidation in cool, dry environments.

1. Introduction

Aluminum diboride (AlB_2) is a promising energetic fuel additive because of its high volumetric heat of combustion and favorable oxidation characteristics [1]. It may also be an important reaction intermediate in lithium aluminum hydride/lithium borohydride hydrogen storage systems [2]. Therefore, it is critical to understand the oxidation kinetics of AlB_2, in order to either exploit its rapid heat release as an energetic additive, or to prevent oxide formation and degradation during thermal cycling in hydrogen storage systems.

The oxidation characteristics of both aluminum and boron powders have been well studied. As boron particles react with oxygen, its diffusion towards the unreacted particle core is retarded by the formation of a thickening, molten, vitreous boron oxide (B_2O_3) layer [3,4]. Because B_2O_3 melts at 450 °C, but does not boil until 2067 °C [5], boron oxidation is generally slow and incomplete. Aluminum oxidation kinetics are initially controlled by a thin (2–4 nm) amorphous layer, which limits Al^{3+} diffusion from the melt. As this layer increases to 6–10 nm thickness, oxygen diffusion limits growth and crystallization proceeds through polymorphic transformations, which change growth rates [6,7].

In Al–B–O systems, the oxide interactions gain another level of complexity. Al_2O_3 and B_2O_3 will react to form $2Al_2O_3 \cdot B_2O_3$ ($Al_4B_2O_9$) at temperatures below 1035 °C, and decompose into $9Al_2O_3 \cdot 2B_2O_3$ ($Al_{18}B_4O_{33}$) at higher temperatures [8,9]. Because B_2O_3 melts at 450 °C, transport at high temperatures is generally sufficient for the two oxides to come into contact and react. Solid $Al_4B_2O_9$ acts to remove liquid B_2O_3 from particle surfaces in mixed systems, and may adopt a needle-like morphology [10], instead of a spherical shell.

The oxidation kinetics of Al–B mixed powder systems or AlB_2 have not been investigated to the authors' knowledge. The complex interactions between oxides, polymorphic phase transformations in Al_2O_3, reaction of unoxidized aluminum and boron, peritectic decomposition of AlB_2 or $Al_4B_2O_9$, vaporization of B_2O_3 and morphological changes make it exceedingly difficult to analyze this system with a single mechanistic model. Therefore, it is of interest to obtain kinetic parameters that account for all of the processes that occur as aluminum and boron co-oxidize and provide a quantitative description of oxidation rates and their temperature dependence unambiguously. A second purpose of this paper is to report on the resistance of AlB_2 to oxidation in moist environments at low temperatures.

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2. Experimental procedure

2.1. Powder preparation

AlB_2 powder with an average surface area of 2.0 m^2/g (d_{50} particle size of 5.7 μm) was purchased from ABCR (Karlsruhe, Germany). The powder (synthesized by H.C. Starck) had reported impurity concentrations of 1.9 wt% O, 0.2 wt% C, 0.1 wt% N and 0.1 wt% Fe, and also contained ~6% unreacted aluminum [11]. This powder was compared to a stoichiometric physical mixture of boron (H.C. Starck amorphous boron 95%, 10.9 m^2/g, 0.2 μm d_{50}) and aluminum (Valimet H3 aluminum 99.99% 1.4 m^2/g, 2.7 μm d_{50}). Aluminum and boron powders were mixed in a stainless steel mill using spherical WC-Co media and hexane to distribute particles and prevent oxidation [11], resulting in a surface area of 6.2 m^2/g and a d_{50} of 2.3 μm. X-ray diffraction patterns and scanning electron micrographs of representative Al+2B and AlB_2 samples are shown in Fig. 1.

2.2. Thermal gravimetric analysis

Thermal gravimetric analysis (TGA) was used to analyze the oxidation behavior of AlB_2, Al+2B, aluminum and boron. Isothermal studies were performed on 25 mg samples of Al+2B or AlB_2 powder using a Netzsch STA 409 in N_2–20%O_2 (referred to as air) or industrial grade O_2 flowing at a rate of 25 millimol $cm^{-2}\,s^{-1}$. For isothermal studies, samples were brought to temperature between 500 and 1000 °C as quickly as possible (~75 °C/min) and held at temperature for 5–7 h. Linear heating rate studies were conducted from room temperature to 1500 °C at a rate of 10 °C/min.

Analysis of isothermal data was conducted using the model-free formalism of Kujirai and Akahira [12]. This method was very useful for obtaining quantitative and comparable kinetic data for Al+2B and AlB_2 without assigning specific reaction mechanisms. The benefit of this approach is that it can provide activation energies and kinetic parameters for complex processes with multiple, interdependent and simultaneous phase transformations, diffusion, chemical reactions, and other activated processes. A series of isothermal reactions were performed, and the ratio of the weight gain at a time t_α to the maximum weight gain gave the extent of reaction, or conversion, α, for each temperature. The rate of the conversion can be written as [13]

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \tag{1}$$

where $f(\alpha)$ is the function that describes the oxidation process, and $k(T)$, the reaction rate constant, displays Arrhenius behavior as

$$k(T) = A\exp\left[-\frac{E}{RT}\right] \tag{2}$$

where E is the activation energy, R is the gas constant, T is absolute temperature, and A as the pre-exponential factor. Activation energies for specific conversions, E_α, can be found from plots of $\ln(1/t_\alpha)$ vs. $1/T$ since

$$t_\alpha = \frac{1}{A_\alpha \exp\left[-E_\alpha/RT\right]} \tag{3}$$

where A_α is the pre-exponential factor at a given conversion. These activation energies give a non-mechanistic activation energy for the global process at a specific value of conversion [14]. Kinetic data were then compared with X-ray diffraction (XRD) patterns and scanning electron micrsoscope (SEM) images to form a general qualitative description of oxidation in these systems.

2.3. Moisture sensitivity

The moisture sensitivity of the uncoated AlB_2 powder was measured at 20 or 40 °C for relative humidities of 10, 75, or 90%. Three silanes and an amine (see Table 1) were used to coat the AlB_2 powder in an attempt to improve its oxidation resistance. The silane treatments were prepared by making a constantly stirred solution of 95 vol% methanol–5 vol% distilled water, adjusting the pH to 4.5–5.5 with acetic acid, adding 35 g of AlB_2 powder to 100 cc of solution, and finally adding 2 g of the silane solution. The powders in solution were stirred for 30 min at 500 rpm, filtered, washed with methanol, rinsed with acetone, and dried at 110 °C for 15 min. The amine solution was made by adding 2.15 g of octadecylamine (Aldrich 305391) to 500 cc of hexane and heating to get into solution. The AlB_2 powder (35 g) was stirred for two hours and then filtered, rinsed with hexane, and dried at 110 °C for 15 min.

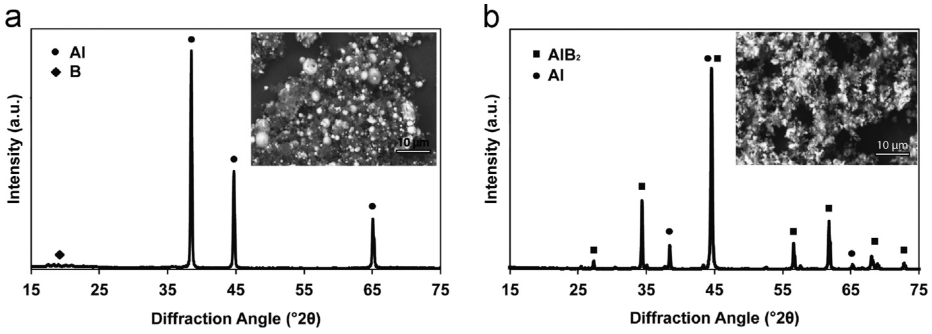

Fig. 1. XRD pattern of (a) Al+2B, showing mainly aluminum peaks, and (b) AlB_2, with only aluminum boride peaks. Inset: SEM backscattered electron images of Al+2B mixture and AlB_2 powder agglomerate. Markers are 10 μm.

Table 1
Kinetic parameters of oxidation in air and oxygen.

Material	Conversion Range (Δα)	ln A air (s^{-1})	ln A O_2 (s^{-1})	E air (kJ/mol)	E O_2 (kJ/mol)
Al+2B	0.15–0.50	11	$-43\alpha+42$	77	$-241\alpha+262$
AlB_2	0.15–0.50	$-83\alpha+58$	38	$-778\alpha+576$	396