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Combustion Reaction of Zinc Oxide with Magnesium during Mechanical Milling

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Combustion in the solid-state displacement reaction between zinc oxide and magnesium during mechanical milling was investigated using X-ray powder diffraction, electron microscopy, and thermal analysis. It was found that mechanical milling decreases the critical reaction temperature at which the combustion reaction occurs. Under the milling conditions employed in this study, the temperature of the powder mixture during ball/powder collisions is estimated to reach a value of 640 K before combustion.

Introduction

New methods of materials synthesis have received increased attention in recent years. Of particular interest are low-temperature techniques, such as mechanical alloying, which offer the possibility of forming structures exhibiting new and unusual properties. Mechanical alloying is a high-energy ball-milling process which is capable of causing both alloy formation (*1, 2*) and disproportionation (*2–4*), and inducing chemical reactions (*5–8*). Recent studies have shown that a number of metals and alloys, including titanium (*7*), tantalum (*9*), and rare earth permanent magnet alloys (*10, 11*), can be synthesized by the reduction of the respective oxides or halides during mechanical milling with strong reducing elements such as Ca and Mg. Depending upon the value of the adiabatic temperature of the reaction and milling conditions, the reaction may occur in a steady-state manner during milling or by unstable thermal combustion of the reactants (*12–15*). It has been shown that combustion occurs during milling if the temperature rise during ball/powder collision events exceeds the ignition temperature of the reactant mixture (*14*). In this paper, we report the study of a combustion reaction between zinc oxide and magnesium during mechanical milling.

Experimental Procedures

The starting materials used for milling were ZnO (AJAX Chemicals, ≥ 97%) and Mg (CERAC, 99.9%, −325 mesh) powders. A total of 5 g of powder, including a 10% stoichiometric excess of Mg, and a ball-to-powder mass ratio of 7 : 1 were used. A Spex 8000 mixer/mill with a hardened steel vial and balls (Ø 9.5 mm) was used for milling. The vial was loaded and sealed under high-purity argon in a controlled-atmosphere glove box. The reaction was followed by monitoring the vial temperature during the course of milling using a type-K thermocouple attached to its outer surface. Samples were taken from the vial at different stages of milling and the structures were analysed by X-ray diffraction (XRD) using a Siemens D5000 Diffractometer with Cu$K\alpha$ monochromatic radiation. The morphology of the

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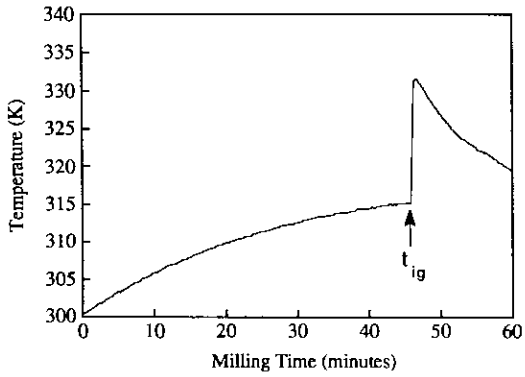

FIG. 1. Variation of vial temperature with milling time.

powder was examined in a JEOL 6400 scanning electron microscope (SEM) and a Philips EM430 transmission electron microscope (TEM), each with an EDAX 9900 energy dispersive spectrometry (EDS) system attached. Thermal behavior was studied by differential scanning calorimetry (DSC) using a Perkin–Elmer DSC-4.

Results and Discussion

The variation of the vial temperature monitored during the mechanical milling of ZnO/Mg mixture is shown in Fig. 1. An initial increase in temperature with milling time was observed as the result of mechanical energy dissipated in the mill. At a milling time of ~45 min, an abrupt temperature rise of ~18 K within seconds was recorded. After the abrupt increase, the temperature gradually decreased to its previous steady-state value. The sudden increase of the temperature is an indication of the rapid release of a large amount of heat associated with a combustion reaction between ZnO and Mg. The reaction was confirmed by XRD analysis as shown in Fig. 2. Curve (a) is the XRD pattern of a sample taken from the vial after milling for 40 min (prior to combustion). The pattern is composed of diffraction peaks associated only with the reactants ZnO and Mg, with no evidence of the reaction products Zn or MgO. Due to the similarity in crystal structure between ZnO and Mg, the diffraction peaks of the two phases are virtually overlapped. However, with an enlarged 2θ scale, it was found that each apparent diffraction peak in the figure is actually composed of two diffraction peaks corresponding to ZnO and Mg, respectively. The XRD pattern of the powder removed immediately after the combustion event showed only the product phases of Zn and MgO (curve (b)).

TEM examination of a powder sample (as-milled for 40 min prior to combustion) revealed an intimate mixture of the two milling constituents of ZnO and Mg. In Fig. 3, a dark-field TEM image of a typical particle of the powder is shown. The dark regions in the micrograph are Mg whereas the surrounding bright areas are ZnO, as determined by both the EDS analysis and the previous XRD results.

The milling was interrupted immediately after the combustion, to preserve the morphology of the combusted powder particles. Visual examination showed that the combusted powder consisted of homogeneous fine particles, unlike those other reactions where nodules and flakes with significant

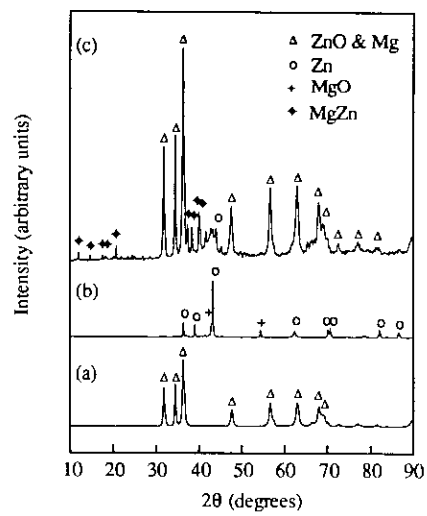

FIG. 2. XRD patterns of samples: (a) as-milled for 40 min, (b) as-combusted (45 min), and (c) as-milled for 40 min, followed by annealing at 573 K for 3 hr.

FIG. 3. Dark-field image of as-milled powder prior to combustion.

size variation are commonly obtained after combustion (*16*). Shown in Fig. 4 is a SEM micrograph of a combined secondary and back-scattered electron image of the as-combusted powder. Based on both EDS and XRD analysis, the light particles are zinc and the dark regions are MgO.

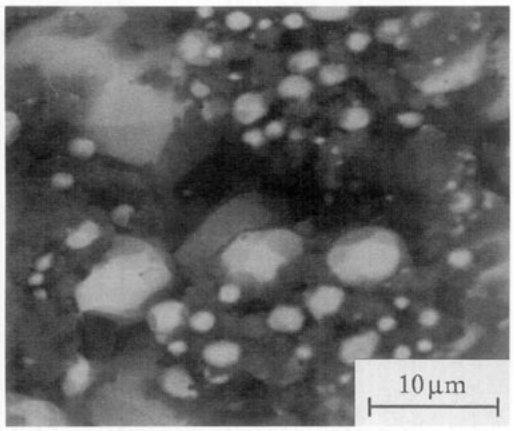

FIG. 4. SEM micrograph of as-combusted powder.

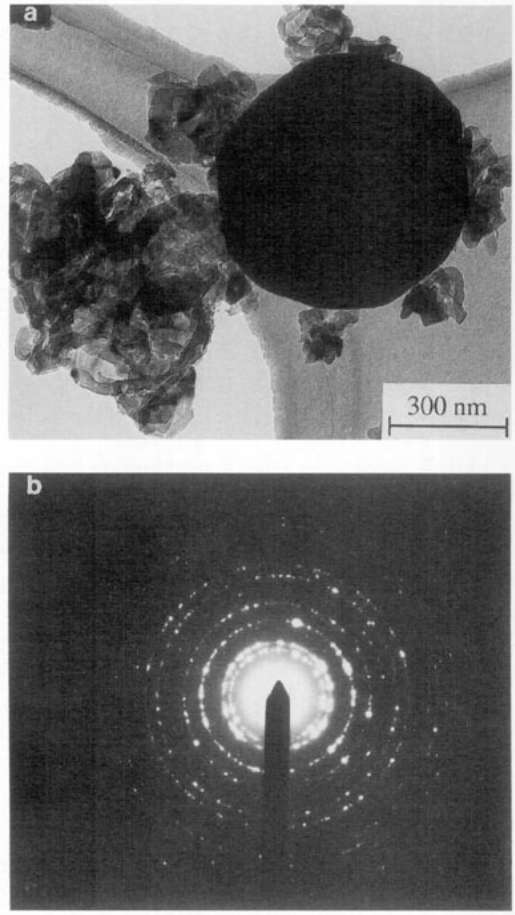

FIG. 5. TEM micrograph of the as-combusted powder: (a) general view and (b) SAD of MgO agglomerates.

A typical TEM bright-field image of the combusted powder is shown in Fig. 5a, in which two types of particles are clearly distinguished. The large dark particle of ~700 nm is a Zn particle. The polygonal shape of this Zn particle is consistent with the faceted morphology of Zn observed by SEM. No detailed structure could be observed due to the thickness of the particle, suggesting that the particle is equiaxed. However, electron diffraction using a convergent beam at the edge of the particle revealed clear Kikuchi lines, indicating that the particle is crystalline. The porous particle agglomerates consist of small crystallites of 50–80 nm; EDS

detected only Mg in these agglomerates. Figure 5b shows a selected area diffraction pattern of the Mg-rich regions. The pattern is indexed to a fcc structure with a lattice parameter of 4.22 Å, corresponding well with the structure of MgO.

The reaction of ZnO + Mg → Zn + MgO is characterized by an enthalpy change of −253 kJ and an adiabatic temperature of 2006 K. The adiabatic temperature is well above the melting and even the boiling temperature of Zn metal, T_m = 693 K and T_b = 1180 K. In addition, the vapor pressure of pure zinc is rather high, reaching 1 atm at 907 K (*17*). The morphology studies suggest that the heat generated by the combustion reaction is enough to cause not only the melting of the Zn, but also vaporization. Toward the end of the combustion reaction, Zn vapor condenses to form solid zinc particles and/or a Zn coating on MgO particles.

To study the effect of premilling on the ZnO + Mg → Zn + MgO reaction, the milling was interrupted at different time intervals prior to the combustion and samples were removed for analyses. XRD measurements showed a progressive line broadening and a reduction in peak intensity with milling time. The effect of milling time on the crystallite size, estimated from the (100) diffraction peak of ZnO based on the Scherrer equation (*18*), is shown in Fig. 6. A progressive reduction in crystallite size is clearly evident with increasing milling time.

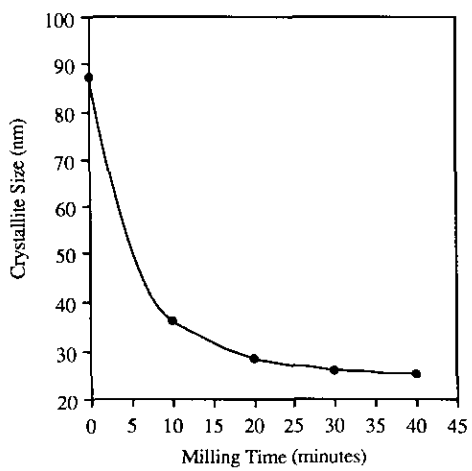

FIG. 6. Effect of mechanical milling on crystallite size.

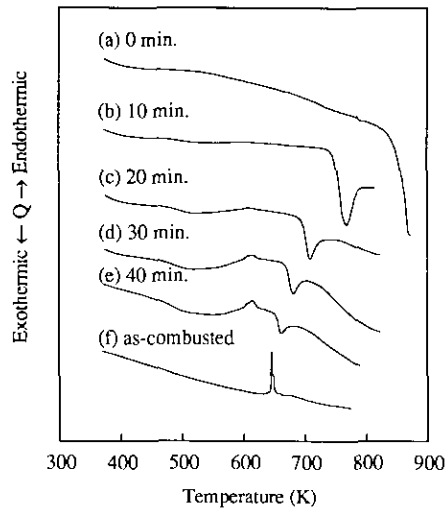

FIG. 7. DSC curves of powder samples milled for different times.

DSC curves of samples milled for different periods of time are shown in Fig. 7. As a reference, the DSC curve of a ZnO/Mg mixture not subjected to mechanical milling is also included in the figure. Three thermal events can be seen in the DSC curves of the premilled samples, most clearly shown in curve (e). An exothermic reaction was first observed in a temperature range of 480–580 K. This reaction was followed by an endothermic event occurring at ~625 K. The third exothermic reaction, which corresponds to the only one observed in the reference sample (curve (a)), occured at the highest temperature. It is seen that the heats of the first two reactions increased with milling time, whereas the heat and the critical temperature associated with the third reaction decreased as milling time increased. The reaction temperatures of this reaction taken as the temperature of maximum heat flow are shown in Fig. 8 as a function of milling time. It is seen that the reaction temperature decreases from a high value of 850 K before

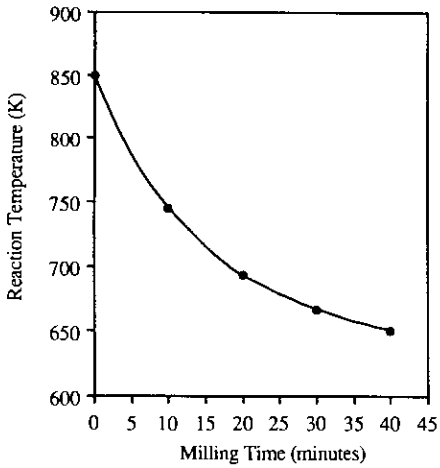

FIG. 8. Effect of mechanical milling on critical reaction temperature.

the start of milling to 650 K after milling for 45 min. The DSC trace for the as-combusted sample (curve (g)) showed a single sharp peak commencing at 642 K. Reference to the Zn–Mg phase diagram shows that this peak corresponds to the eutectic temperature of a Zn–8% Mg alloy. This result indicates that complete reduction of ZnO occurred during combustion, with the excess Mg combining with the Zn to form a Zn-rich alloy.

To study the three reactions involved in the heating process of premilled powder samples, a sample milled for 40 min was annealed at 573 K for 3 hr in an argon atmosphere and then examined by X-ray diffraction. As shown in Fig. 2, curve (c), a number of new diffraction peaks appeared as a result of the isothermal treatment, although the main diffraction peaks remained the same as those without thermal treatment (the scale of the curve (c) is enlarged relative to that of curves (a) and (b) to show the peaks corresponding to the minor phase). Most of the new diffraction peaks were indexed to the MgZn phase which has a rhombohedral structure. In addition, a small peak consistent with the {101} reflection for Zn is also present.

The presence of MgZn in the heat treated powder indicates that the exothermic event which started at 480 K is the reduction of some of the ZnO by Mg and the subsequent alloying between the Zn and Mg to form the MgZn intermetallic. According to the equilibrium phase diagram of Mg–Zn (*19*), MgZn melts peritectically at 627 K. This reaction is believed to be responsible for the small endothermic peak observed in the DSC measurements. The exothermic reaction occurring at higher temperatures corresponds to the reduction of the remaining ZnO by Mg to form Zn and MgO.

For displacement reactions, such as that studied here, self-sustaining thermal combustion reactions occur when the reactant mixture reaches a critical ignition temperature (*20*). It has been shown that a similar combustion condition applies during mechanical milling and it may be characterized as the milling time for the temperature required to ignite the combustion reaction, T_{ig}, to decrease to the particle collision temperature, T_c (*14*). The ignition temperature is a function of the enthalpy change and microstructural parameters such as particle and crystallite size. Combustion does not occur at the start of milling when $T_{ig} > T_c$. The refinement in microstructure during milling progressively reduces T_{ig} (Fig. 8), resulting in combustion when $T_{ig} = T_c$. Approximating T_{ig} with the value of the reaction temperature from DSC measurements, the particle collision temperature of the reactant mixture immediately prior to the combustion can be estimated by extrapolating the reaction temperature measurements to the ignition time (t_{ig} = 45 min). The value of 640 K obtained is in good agreement with the value observed in other reactions under similar milling conditions (*14*) and values estimated from computer modeling (*21*).

Acknowledgment

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