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Mechanochemical Reduction of V_2O_5

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The reduction of V_2O_5 using Mg, Al, and Ti as reductants during mechanical milling in a ball mill has been studied. With all three reductants, a combustion reaction was observed after milling for a critical ignition time. Using Mg as the reductant, the ignition time was found to increase with decreasing collision energy. However, the combustion event could not be associated with a critical degree of microstructural refinement or a reduction of the ignition temperature. With both Mg and Al reductants TEM examination of the as-combusted powders showed the presence of nanoscale single crystal smoke particles, similar to those formed by gas evaporation techniques. © 1994 Academic Press, Inc.

INTRODUCTION

Recent studies (1–8) have shown that the mechanical alloying process provides a means to substantially increase the kinetics of solid state oxidation–reduction displacement reactions. The repeated fracture and welding of particles during mechanical milling ensures that the reactants are always in direct contact. As a consequence, the reaction rates are not determined by diffusion through product phases, but are dynamically maintained by the milling action. In addition to milling parameters such as collision rate and collision energy, the reaction enthalpy and particle and crystallite sizes have also been shown to influence reaction kinetics.

If the reaction enthalpy is sufficiently high, an unstable, self-propagating combustion reaction can be initiated by ball/powder collision events during milling. Such reactions are characterized by a critical milling time required for ignition, t_{ig} (4). It has been shown that t_{ig} is determined by the milling time required for the ignition temperature of the powder to be reduced through particle and crystallite refinement to the local particle temperatures reached during ball/powder collisions. Measurements of ignition temperature as a function of milling time indicate that collision temperatures of ~650 K can occur during high energy milling (4, 6). Such studies have also shown that combustion measurements provide an important method for characterizing the changes occurring during mechanical milling. In this paper we report the results of a study of the reduction of V_2O_5 using Mg, Al, and Ti as reductants.

EXPERIMENTAL PROCEDURES

The materials used in this study were V_2O_5 (99.9%, −30 mesh) and reducing elements Mg, Ti, and Al, all of 99.9% purity and −325 mesh. A total of 5 g of powder, including a 10% stoichiometric excess of reducing elements, unless otherwise specified, was used in all tests. The mixed powders were sealed in hardened steel vials with steel balls. A ball-to-powder mass ratio of 7 : 1 was used in all tests. Milling was carried out using a Spex 8000 mixer/mill. Loading and unloading of the vials were carried out in a high-purity argon glove box.

The vial temperature was monitored during the course of milling using a type-K thermocouple attached to its outer surface. Samples were taken at different stages of milling. The structures of the samples were analyzed by X-ray diffraction using a Siemens D5000 Diffractometer with CuK_α monochromatic radiation. The thermal behavior was studied by differential scanning calorimetry using a Perkin–Elmer DSC-4 Calorimeter. The morphology of the powder was examined in a JEOL 6400 scanning electron microscope (SEM) and a Philips EM430 transmission electron microscope (TEM). Both microscopes were equipped with EDAX 9900 energy dispersive spectroscopy (EDS) systems.

RESULTS

The reactions which were studied are given in Table I together with values of the enthalpy change and adiabatic temperature for each reaction. The adiabatic temperatures were estimated from the reaction enthalpy change and heat capacities of the product phases, taking into account any phase changes occurring to the product phases.

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TABLE 1
Enthalpy Changes and Adiabatic Temperatures of Reactions Studied

Reactions	ΔH (kJ)	T_{ad} (K)
$V_2O_5 + 5Mg \rightarrow 2V + 5MgO$	−1457	3354
$3V_2O_5 + 10Al \rightarrow 6V + 5Al_2O_3$	−3727	3468
$2V_2O_5 + 5Ti \rightarrow 4V + 5TiO_2$	−1623	2658

Mg/V_2O_5

The reduction of V_2O_5 with Mg was the most extensively studied of the three reactions examined. Measurements of the vial temperature showed an abrupt increase indicative of the onset of a combustion reaction after milling for only 4 sec with 9.5-mm-diameter balls. Measurements of the effect of ball size on the ignition time, t_{ig}, are shown in Fig. 1. Decreasing the ball size to 3.2 mm resulted in t_{ig} increasing to 570 sec.

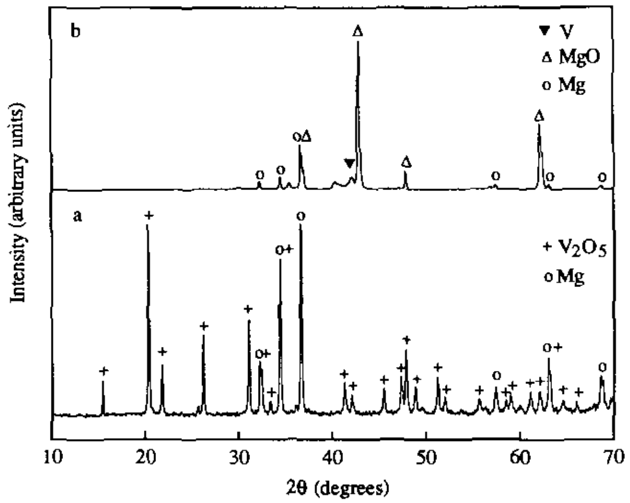

FIG. 2. XRD patterns of V_2O_5/Mg powder: (a) as-milled prior to combustion and (b) as-combusted.

X-ray diffraction patterns of powder milled with 3.2-mm-diameter balls prior to combustion (500 sec) and immediately after combustion are shown in Fig. 2. The phases present after combustion were V, MgO, and a minor amount of Mg. SEM analysis showed that the low intensity of the V diffraction peaks was due to the fact that the majority of the vanadium was embedded within large particles of MgO produced by the combustion reaction. No evidence of any reaction prior to combustion could be determined from the X-ray diffraction measurements, with only peaks corresponding to Mg and V_2O_5 being identified. X-ray diffraction measurements showed an increased line broadening and reduction in the peak intensities of the Mg peaks with increasing milling time prior to combustion; however, little change occurred in the V_2O_5 diffraction peaks. The effect of milling time on crystallite size, as estimated from the (101) diffraction peak of Mg and the (011) peak of V_2O_5 using the Sherrer method, is shown in Fig. 3.

Visual examination of the as-combusted samples showed that the powder consisted of nodules of a wide size distribution. A micrograph of a typical backscattered electron image of the polished surface of an as-combusted nodule is shown in Fig. 4a. The dark regions are MgO and the bright regions are V. Figure 4b shows a detailed view of a group of V particles in which a cellular type solidification structure is evident.

TEM examination of the as-combusted powder revealed two types of particles with different chemistry. In Fig. 5a a group of particles with well defined spherical or hexagonal shape of 150–200 nm in size is shown. Each of these particles is a single crystal as indicated by the electron diffraction studies. It is also evident in the micrograph that many of the spherical particles are joined together by necks. Detailed electron diffraction work, to-

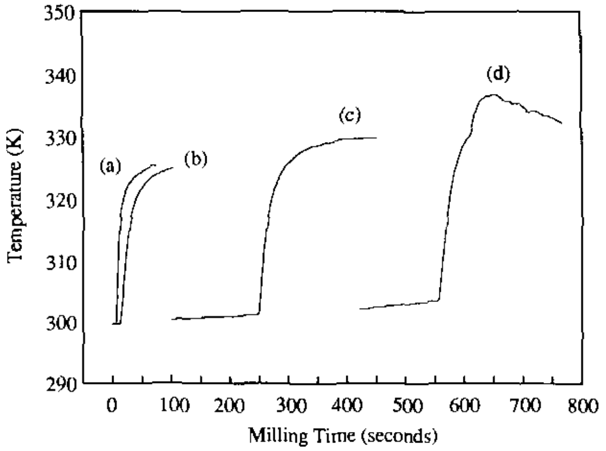

FIG. 1. Measurements of the vial temperature during milling of V_2O_5/Mg with different ball diameters: (1) 9.5, (b) 6.4, (c) 4.8, and (d) 3.2 mm.

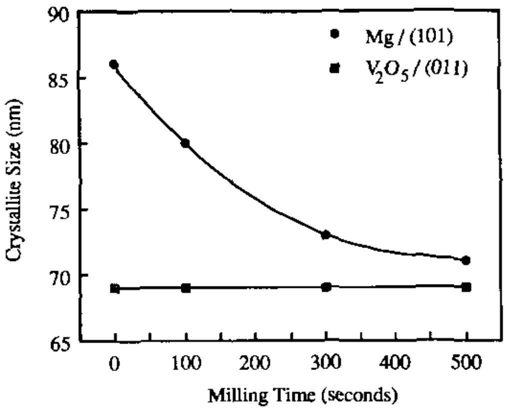

FIG. 3. Effect of mechanical milling on crystallite size for V_2O_5/Mg reaction.

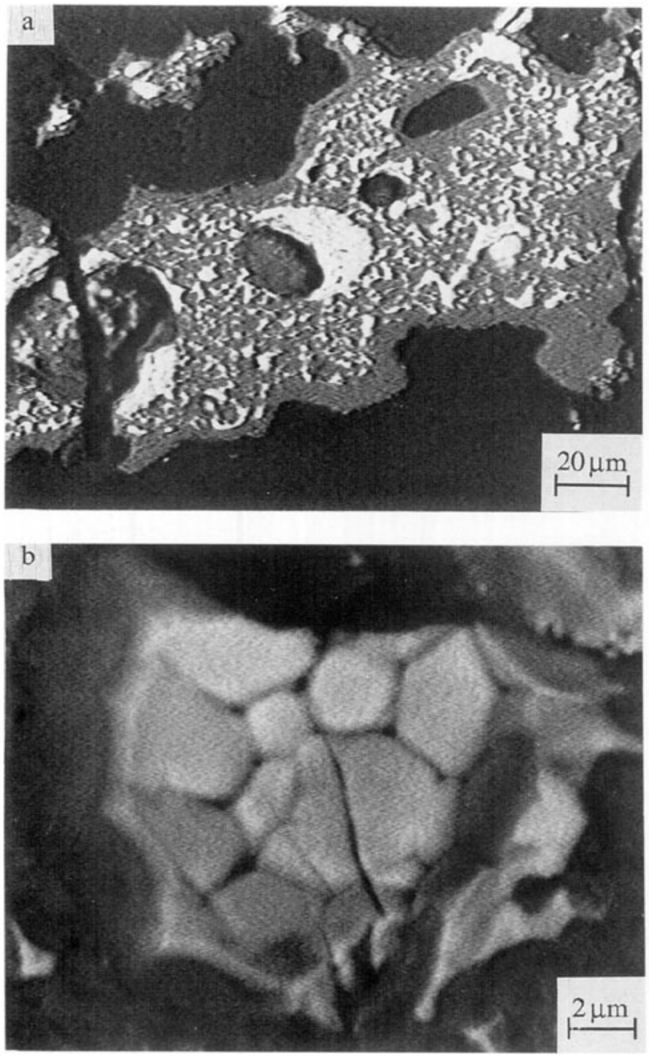

FIG. 4. SEM images of the as-combusted V_2O_5/Mg powder: (a) general view of a polished surface, and (b) cellular structure.

gether with EDS analysis, showed that these particles are pure Mg particles. The selected area diffraction pattern of an isolated hexagonally shaped particle is shown as an example in Fig. 5b, where the pattern is indexed to be zone (0001) diffraction of Mg. A rather different type of particle was also observed in the as-combusted powder, one of which is shown in Fig. 5c. The particles exhibited platelet morphologies and were too thick for the structure to be determined by electron diffraction. EDS analysis on the particles showed only the presence of V. Since the X-ray diffraction measurements did not show any V_2O_5 in the sample, the particles are tentatively identified as being pure vanadium. The majority of particles were found to contain both Mg and V. The relative amount of Mg and V varied from position to position within the particle. It is, therefore, believed that these particles contain a mixture of MgO and V. However, no detailed structure analysis was possible since the particles, due to their large size, were opaque to the electron beam.

DSC curves for samples milled for various periods of time prior to combustion using 3.2-mm-diameter balls are shown in Fig. 6. All samples exhibited a major exothermic peak on reaching a critical temperature. As shown in Fig. 6, the ignition temperature was equal to 740 K, independent of milling time.

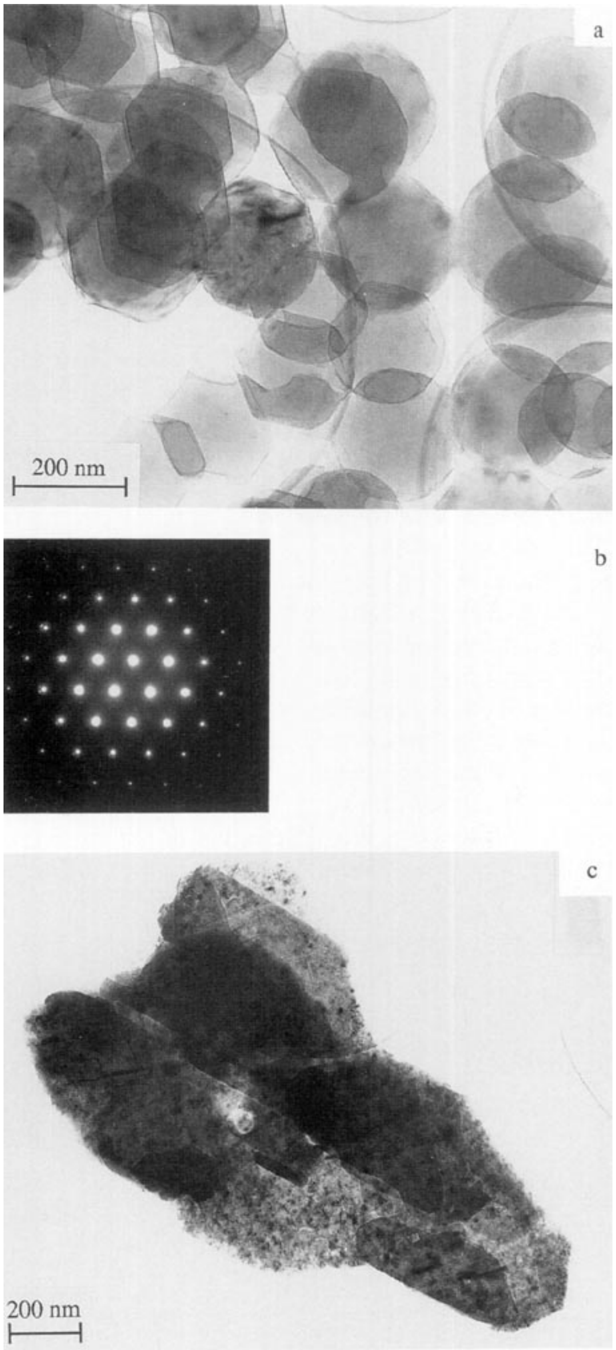

FIG. 5. TEM images of the as-combusted V_2O_5/Mg powder: (a) Mg smoke particles, (b) selected area diffraction pattern of smoke particle, and (c) vanadium particle.

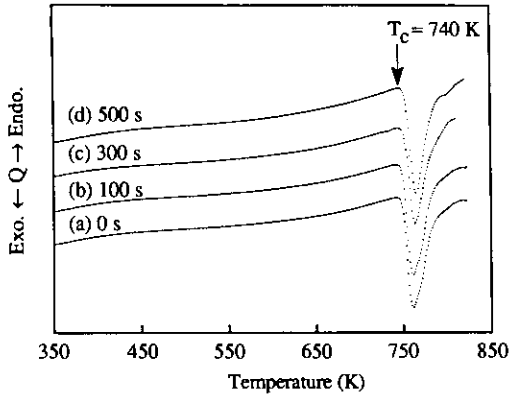

FIG. 6. DSC curves of V_2O_5/Mg powder samples milled for different times.

Al/V_2O_5

The milling of V_2O_5 and Al powders resulted in a combustion reaction after 400 sec using 9.5-mm balls. X-ray diffraction patterns of the as-combined powder showed the presence of α-Al_2O_3, V, and Al. SEM examination of the combusted powder showed clear evidence of the melting of both the Al_2O_3 and V phases as shown in Fig. 7. EDS analysis indicated that the top half of the particle is V (light area) and the bottom half is Al_2O_3 (dark area). The complete separation of V and Al_2O_3 as observed in Fig. 7 is consistent with the observation that pure metals and metal oxides are generally immiscible in the liquid state. TEM examination of the as-combusted powder showed spherical or hexagonal single crystalline particles as well as unusual spiral or zigzag filament type particles such as shown in Fig. 8. Detailed diffraction work and EDS analysis showed that these particles are γ-Al_2O_3, which has a cubic structure with a lattice parameter of 7.9 Å (see Fig. 8b inset). Pure V particles with a similar morphology as observed in the V_2O_5/Mg reaction (Fig. 5c) are also observed in the as-combusted powder. The

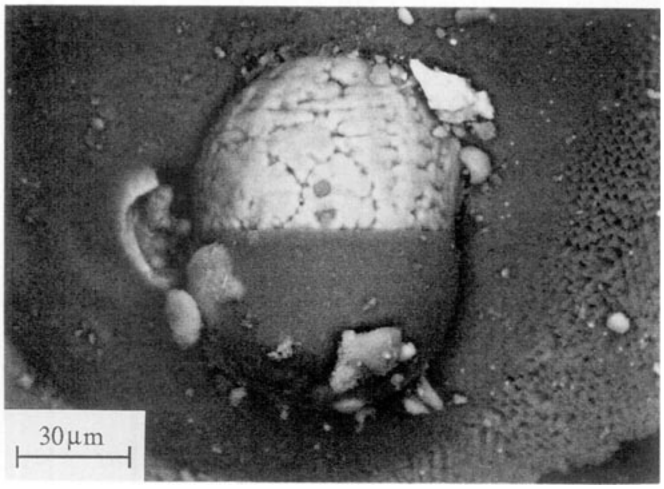

FIG. 7. SEM image of as-combusted Al particle.

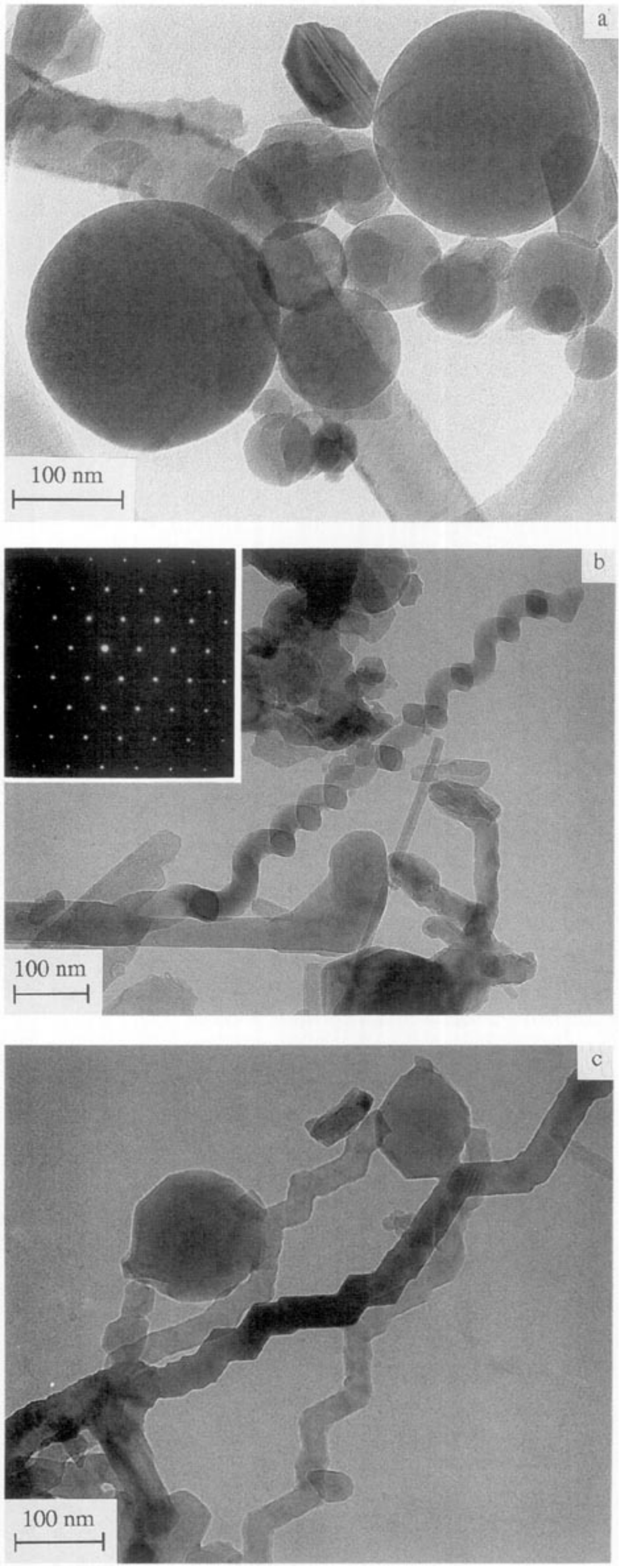

FIG. 8. TEM images of γ-Al_2O_3 particles formed during combustion.

ignition temperature of the starting V_2O_5/Al powders, as measured by DTA, was 963 K.

Ti/V_2O_5

The Ti and V_2O_5 powders also reacted in a combustion mode during milling, with $t_{ig} = 27$ sec using 9.5-mm balls. Using a 10% excess of Ti for the reaction $2V_2O_5 + 5Ti \rightarrow 5TiO_2 + 4V$ resulted in the formation of Ti_2O_3 rather than TiO_2. As shown in Fig. 9, diffraction peaks indexed to V and Ti_2O_3 were present in the as-combusted powder. In addition, several minor peaks were present which could not be indexed. In view of the formation of Ti_2O_3, two new compositions corresponding to the exact stoichiometric starting compositions to form TiO_2 and Ti_2O_3, respectively, were milled. With both compositions combustion reactions occurred and the resulting diffraction patterns were virtually identical to that shown in Fig. 9, indicating the formation of V and Ti_2O_3. A sample having the starting composition to form TiO_2 was milled for 10 hr more after combustion. The as-milled powder was compacted and annealed at 1173 K for 6 hr. The diffraction pattern of the annealed powder also showed peaks corresponding to V and Ti_2O_3. The ignition temperature for the Ti_2O_3 reaction was measured by DTA as 923 K.

DISCUSSION

With solid state reactions studied to date (1–8), combustion reactions have been observed only after the thermal ignition temperature measured using DTA has been significantly reduced during milling by particle and crystallite refinement. These measurements have been consistent with the ignition time being determined by the milling time required for T_{ig} to be reduced during milling to the value of the local temperature attained in ball/powder collision events. The local temperature rise experienced by the powder depends on milling conditions, such as ball size, and the physical and mechanical properties of the milling constituents. Previous measurements of T_{ig} and t_{ig} for the CuO/Fe (4) and ZnO/Mg (6) reactions using a Spex mill with 9.5-mm diameter balls indicate that temperatures as high as 650 K are reached during collision events, in agreement with collision temperatures estimated by computer modeling studies (9).

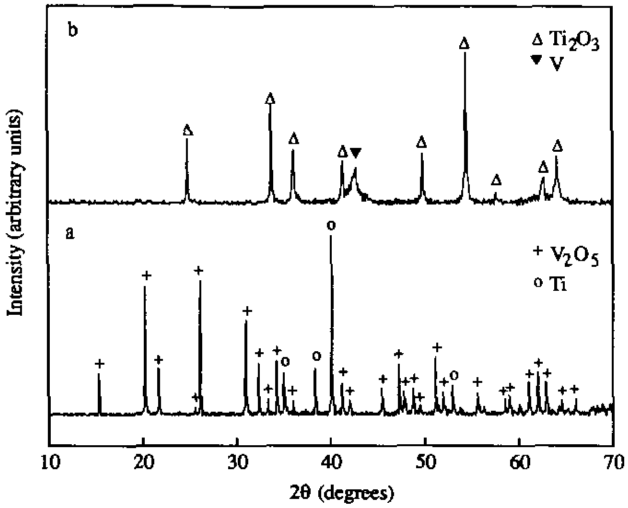

FIG. 9. XRD patterns of V_2O_5/Ti powder: (a) prior to milling and (b) as-combusted.

With the present measurements the ignition temperature was found to be independent of the milling time for samples milled with 3.2-mm-diameter balls. This result is consistent with the X-ray line broadening measurements which show that the V_2O_5 crystal size remains constant during milling. As a consequence, it is not possible to rationalize the occurrence of the ignition event as resulting from a decrease in T_{ig} during milling. In addition, the value of the ignition temperature measured by DTA (740 K) is clearly much higher than likely to be achieved by 3.2-mm balls during head-on collisions. With the larger ball sizes, the ignition times are too short for any significant microstructural refinement to occur. Modeling studies (9) have shown that the Spex mill is characterized by a wide spectrum of collision energies and angles. The present results indicate that the combustion condition is determined by the statistical probability of achieving a particular collision configuration, rather than by microstructural refinement. However, it is clear that further studies are required to fully understand mechanically induced combustion processes.

As shown in Table 1, the $V_2O_5 + 5Mg \rightarrow 2V + 5MgO$ reaction is highly exothermic, being characterized by an enthalpy change of −1457 kJ and an adiabatic temperature of 3354 K. The heat generated by the reaction is sufficient not only to cause melting of the V but also to vaporize the excess Mg ($T_m = 922$ K and $T_b = 1389$ K). The morphology of the single crystal Mg particles formed during the combustion reaction is similar to that of metal smoke particles produced by the gas-evaporation method (10). It is evident that the combusting reactants provide the source of Mg vapor which then condenses in the argon atmosphere of the vial.

Numerous studies of ultrafine metal or oxide smoke particles produced by gas evaporation have been carried out in recent years (10–13). These studies have shown that the size of the smoke particles depends mainly on the pressure of the inert gas atmosphere and the temperature of the evaporation source, with the particle size increasing with increasing gas pressure and source temperature. However, the particle size distribution is generally quite broad. Basically the smoke of a candle-flame shape consists of four zones, with the size and morphology of the particles varying from zone to zone (12). The particles are small and isometric in both the inner and vapor zones, large and isometric in the intermediate zone, and plates and rods in the outer zone. The exact shape of the particles depends on the crystal structure, rate of cooling and impurity content of the inert atmosphere. It has been suggested (10) that isometrically shaped particles, such as observed in the present study, are formed by the condensation of the vapor into a droplet, followed by crystallization into the particle. A spherical shape is likely to be the result of a high rate of cooling or surface oxidation, which tends to suppress the inherent anisotropy of the surface energy. The formation of plates or rod-shaped particles reflects particle growth by condensation of the vapor directly onto the solid.

The $3V_2O_5 + 10Al \rightarrow 6V + 5Al_2O_3$ reaction is also highly exothermic with an enthalpy change of −3727 kJ and an adiabatic temperature of 3468 K. The heat generated by the reaction is sufficient to cause melting and vaporization of Al_2O_3 ($T_m = 2288 \pm 15$ K and $T_b = 3253 \pm 60$ K). In addition to the spherical shapes the γ-Al_2O_3 single crystal particles exhibited an unusual filament morphology. The formation of ultrafine (20–100 nm) γ-Al_2O_3 smoke particles with spherical shapes by gas evaporation under high temperatures and gas pressure has been reported (13); however, filament smoke particles such as seen here have not been observed. The filament morphology probably reflects the fact that the source is in motion during combustion. Although the vial was stopped as soon as combustion was detected, several seconds were required for the mill to cease motion. The motion of the vial and its contents during this period is believed to be the main factor causing the unusual filament morphologies of the γ-Al_2O_3 particles.

Examination of the free energy data (Table 2) (14) shows that the free energy changes for the reactions, $10Ti + 3V_2O_5 \rightarrow 5Ti_2O_3 + 6V$ and $10Ti + 4V_2O_5 \rightarrow 10TiO_2 + 8V$, are similar. It was expected that whether TiO_2 and Ti_2O_3 formed would depend on the stoichiometry of the reaction. The formation of Ti_2O_3 from the reaction mixture having the TiO_2 stoichiometry is indicative of incomplete reduction of the V_2O_5. It could be argued that the formation of Ti_2O_3 is a consequence of kinetic factors rather than thermodynamics and further milling and heating should result in the reaction $5Ti_2O_3 + V_2O_5 \rightarrow 10TiO_2 + 2V$ ($\Delta G = -306$ kJ). However, as previously discussed, Ti_2O_3 and V were the only phases identified after further milling and annealing at 1173 K.

TABLE 2
Free Energy Changes of Possible V_2O_5/Ti Reactions

No.	Reaction	ΔG (kJ)
[1]	$10Ti + 3V_2O_5 \rightarrow 5Ti_2O_3 + 6V$	−2911
[2]	$10Ti + 4V_2O_5 \rightarrow 10TiO_2 + 8V$	−3217
[3]	$10Ti + 4V_2O_5 \rightarrow 5Ti_2O_3 + (11/2)V + (5/4)V_2O_4$	−3140
[4]	$10Ti + 4V_2O_5 \rightarrow 5Ti_2O_3 + (14/3)V + (5/3)V_2O_3$	−3390
[5]	$10Ti + 4V_2O_5 \rightarrow 5Ti_2O_3 + 3V + 5VO$	−3513

A number of intermediate oxides of vanadium, including V_2O_4, V_2O_3, and VO, also exist and the possibility of forming these oxide phases by partial reduction of V_2O_5 must also be considered. In Table 2 free energy changes associated with the formation of vanadium and several of the intermediate oxide phases are shown. The most negative free energy change is associated with the formation of Ti_2O_3, V, and VO (Reaction [5]). However, the unidentified minor peaks on the diffraction patterns could not be indexed to any of the known V_xO_y phases.

SUMMARY

The mechanochemical reduction reactions of V_2O_5 with Mg, Al, and Ti during mechanical milling all occur via combustion after a critical ignition time. Using Mg as the reductant, the ignition condition could not be associated with microstructural refinement or a reduction of the ignition temperature due to milling. Further measurements are required to characterize the combustion mechanism in this system.

Temperatures approaching T_{ad} are reached during combustion as evidenced by melting and vaporization of the reactant and product phases which result in the formation of nanocrystalline smoke particles similar to those formed by gas evaporation techniques. The Mg/V_2O_5 reaction resulted in the formation of spherical and isometric smoke particles of Mg, while in the Al/V_2O_5 reaction spherical and filamentous particles of γ-Al_2O_3 were formed.

The reduction of V_2O_5 with Ti resulted in the formation of Ti_2O_3 instead of TiO_2. This behavior appears to be associated with the formation of intermediate oxides of vanadium.

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