The influence of collision energy and strain accumulation on the kinetics of mechanical alloying

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The kinetics of mechanical alloying have been investigated by examining the effect that ball mass has on the rate at which titanium carbide forms from the elements. By varying the ball density while keeping the ball diameter and the charge ratio constant, the collision energy was independently controlled. Grinding media with a density from 3.8 g cm^{-3} (agate) to 16.4 g cm^{-3} (tungsten carbide) were used. The reaction rate increases exponentially with ball mass until a critical level is reached, which is determined by the induced temperature rise. Above this level, collisions of higher energy have no advantage. It is also shown that the reaction rate increases exponentially with the rate at which strain accumulates in the reactants. It is suggested that the strain accumulation rate in mechanically induced reactions is analogous to temperature in thermally induced chemical reactions.

1. Introduction

Mechanical alloying is a complex process and a comprehensive model of the mechanism does not yet exist. Based on the early phenomenological model of ductile systems [1], mechanical alloying is generally believed to occur by the repeated fracture and welding of powder particles. Following the second wave of mechanical alloying research, triggered by the work on amorphization [2], a number of groups have examined the mechanics of mechanical alloying [3–14]. One result of that research is a computational model [5] which predicts the evolution of some physical characteristics of the powder. However, a detailed model at the atomic level is still lacking. Such a model is needed to, amongst other things, explain why mechanical alloying can induce chemical reactions at relatively low temperatures, whereas these reactions normally require elevated temperatures to proceed at reasonable rates. An atomistic model is also necessary to predict the reaction kinetics, which is important if the milling times are to be reduced significantly to allow wider industrial use. It has been suggested [15] that reaction rates in mechanical alloying are influenced by lattice strain and the rate at which it accumulates. It has been shown [16] that the reaction rate is diffusion controlled, that the diffusion pathway can change during the course of milling and that this may be dependent on lattice strain, which can include anisotropic atomic displacements [17] as well as crystal defects. The current work is an attempt to relate the reaction rate directly to the rate of strain accumulation and thereby provide a further contribution to the ultimate development of a comprehensive model of the mechanism of mechanical alloying.

A number of factors influence the rate at which mechanical alloying proceeds. These include the collision frequency (the frequency with which a powder particle is involved in an effective collision event) and the collision energy (the energy transferred from the grinding media to the powder particles). This energy transfer is believed to be a critical factor; indeed, mechanical alloying is often called a "high energy" ball milling technique, although "high" is never defined. The collision frequency is controlled by a number of factors, including the charge ratio (the ball to powder weight ratio). There is an inverse relationship between charge ratio and the time required to complete milling [18]. The collision frequency is also controlled by the quantity of powder involved in each collision event, which is controlled by the size of the milling balls. The ball size, though, also effects the collision energy. A number of investigators have examined these effects, but the collision energy has not been decoupled from the collision frequency. McCormick *et al.* [10] changed the collision energy by changing the angular velocity of a planetary mill, but this also changed the departure frequency of the balls and hence the collision frequency. A more common strategy [11, 18–21] is to change the size of the grinding media. The change in mass causes a corresponding change in the kinetic energy of the balls but the simultaneous increase in ball diameter also increases the collision volume and hence the collision frequency.

In the present work we investigated the role of collision energy in a systematic manner by using grinding balls of equal diameter but varying density, and this has been related to strain accumulation during the synthesis of titanium carbide.

2. Experimental procedure

Stoichiometric quantities of graphite ($< 100 \, \mu m$) and titanium powders ($< 45 \, \mu m$) were milled in a SPEX 8000 mixer/mill using a hardened steel vial. The vial was loaded and sealed in an argon glove box. All the grinding balls had a diameter of 10 mm and their densities ranged from $3.8–16.4 \, g \, cm^{-3}$. The details of the balls used are listed in Table I. New balls were used for each run in order to minimize the effects of wear. Charge ratios ranged from 5:1 to 40:1. Milling times ranged from 10 min to 3 h. The vial temperature was measured using a K-type thermocouple taped to its outside surface. A short series of confirmatory experiments were conducted in which cupric oxide was reduced by iron. These tests used tungsten carbide, zirconia and steel balls only.

The charge ratio is a critical factor which determines the rate at which mechanical alloying proceeds because it controls the quantity of powder involved in each collision and the number of effective collisions per unit time. The kinetics are dependent on the charge ratio, not on the absolute number of balls nor the mass of powder in the mill [18]. The charge ratio was held constant in these experiments when the ball mass was altered. This changed the number of balls in the mill. The amount of energy transferred to each powder particle during a collision is dependent on the kinetic energy of the balls prior to impact and the quantity of powder involved in each collision event. The former depends on the mass of the ball and the latter is dependent on the ball radius and the charge ratio only, not on the absolute number of balls. Therefore, if the charge ratio and the ball size are constant but the ball mass increases, the energy transferred to each powder particle during a collision will increase only because the kinetic energy of the balls increases.

The powders, both before milling and after a variety of milling times, were investigated using X-ray diffraction (XRD). To prevent oxidation of the components after milling, the vial was opened under argon and the contents were poured into silicone oil. The mixture was centrifuged and the excess oil decanted. XRD patterns of the oil-coated powders were collected using a Phillips PW1130 X-ray diffractometer with a graphite monochromator with CuK_α radiation, operating at 1600 W. The patterns were collected with a step size of $0.02° \, 2\theta$ at a speed of $0.2° \, min^{-1}$. Crystallite sizes (coherently diffracting domain sizes) and lattice strains were determined from integral Gaussian and Lorentzian XRD peak breadths using a spreadsheet [23] based on the methodology derived by

Langford *et al.* [24]. A strain-free line profile standard, LaB_6 Standard Reference Material (NBS 660), was used as a diffractometer calibrant. The patterns were also analysed using the commercial computer program μ-PDSM (release 4.3 from Fein-Marquart Associates), which uses peak intensities to calculate approximate atomic percentages of the phases in an XRD pattern.

3. Results and discussion

The synthesis of TiC from the elements was chosen as the system to study because it is highly exothermic, it is known to propagate as a combustion reaction [25] and because no intermediate phases form in the titanium–carbon system [26]. The reaction which occurs during milling is $Ti + C \rightarrow TiC$. With low-density grinding media (alumina and agate, effectively SiO_2) and a charge ratio of 40:1, the reaction proceeds gradually over time; combustion does not occur. The progression is apparent from the XRD patterns (Figs 1 and 2). With agate balls, the reaction remains incomplete after 3 h milling, the longest time examined.

It is apparent from these XRD patterns that the strain which develops in the powders during the course of milling is confined to the carbon. The titanium remains strain free. The reasons why this should occur and the influence it has on the reaction mechanism will be discussed elsewhere [27]. The amount of strain which accumulates in the carbon is plotted as a function of milling time in Fig. 3. Given that there is an exponential relationship between the amount of strain and the milling time, a plot of the natural logarithm of strain accumulation against time should yield a straight line, the slope of which is the strain accumulation rate (Fig. 4). There is then a linear relationship (Fig. 5) between the strain accumulation rate and the mass of the grinding balls. That is, the rate at which deformation is induced in the powder charge is dependent on the collision energy and it scales linearly with the kinetic energy of the balls. In a similar manner, the amount of product formed increases exponentially with the milling time (Fig. 6). The natural logarithm of the amount of powder which had reacted is plotted in Fig. 7 as a function of milling time. The slope of these straight lines is the reaction rate, which increases exponentially with ball mass (Fig. 8).

With a linear dependence of strain accumulation rate with ball mass and an exponential dependence of reaction rate with ball mass, there is necessarily an

TABLE I Properties of the grinding media [22] and calculated impact parameters

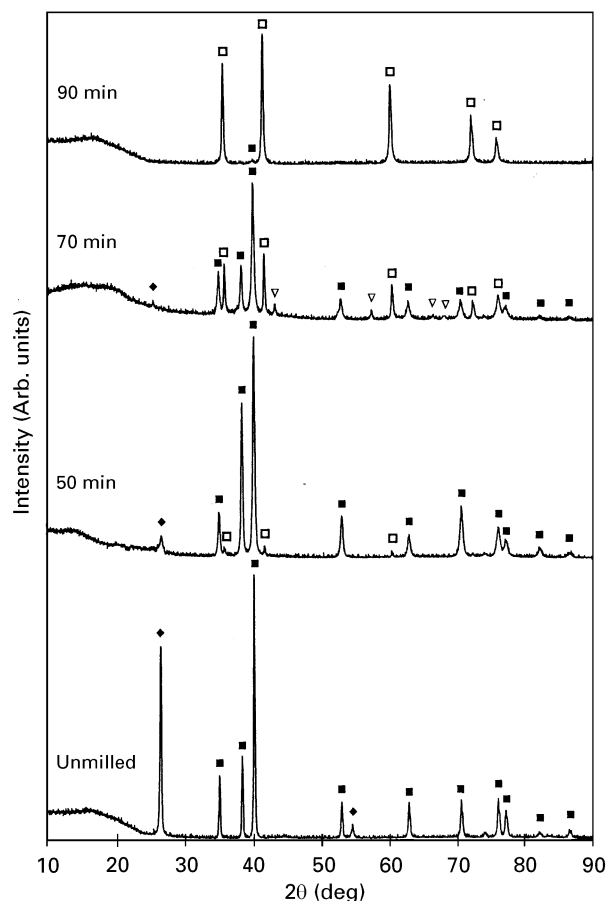| Ball	Density ($g \, cm^{-3}$)	Mass (g)	Elastic modulus (GPa)	Poisson's ratio	Kinetic energy (J)	Load (N)	Contact radius (μm)	Stress (MPa)	Stress life time (μs)	ΔT (K)
WC–Co	16.4	8.6	600	0.22	0.099	27.5	94	991	3.49	746
Steel	7.8	4.1	203	0.30	0.047	14.9	87	621	4.00	500
YTZ	5.7	3.0	205	0.31	0.034	12.4	82	588	3.51	444
Al_2O_3	4.2	2.2	340	0.25	0.025	11.2	74	649	2.54	417
SiO_2	3.8	2.0	71	0.17	0.023	7.3	87	306	4.57	264

Figure 1 XRD traces of titanium and carbon powder milled using alumina grinding media and a charge ratio of 40:1 showing that TiC forms without a combustion reaction. There has been some reaction after 50 min and the reaction is almost complete after 90 min (♦) C, (■) Ti, (□) TiC, (▽) Al$_2$O$_3$.
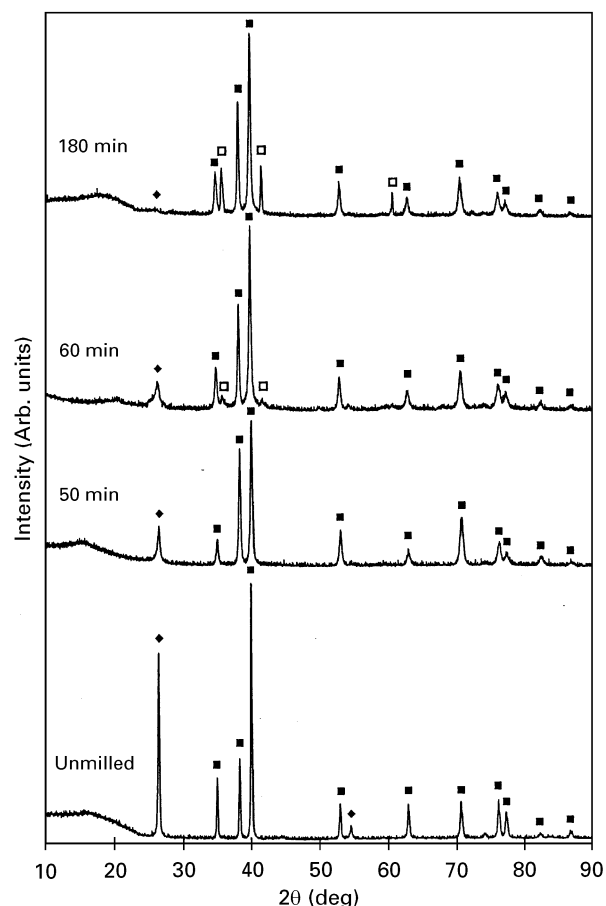

Figure 2 XRD traces of titanium and carbon powder milled with agate grinding media and a charge ratio of 40:1 showing that while TiC can form during low-energy collision events, the reaction remains incomplete after long times. (♦) C, (■) Ti, (□) TiC.

exponential relationship between reaction rate and the rate at which strain accumulates. This is shown in Fig. 9. In thermally induced chemical reactions, there is an exponential relationship between reaction rate and temperature, described by the Arrhenius equation. In an analogous manner, there is also an exponential relationship between the reaction rate and the rate at which strain accumulates in a mechanically induced reaction. Diffusion is the rate-controlling step in mechanically induced solid-state reactions and combustion occurs when short circuit diffusion paths are operative [16]. The reaction rate appears then to be controlled by the rate at which these short circuit diffusion paths are generated and hence on the strain accumulation rate.

With balls heavier than YTZ, the formation of TiC occurred by a combustion reaction. The ignition time, t_{ig}, defined as the milling time required to cause combustion, is simple to determine and is a measure of the reaction rate. Because the energy transferred to each powder particle during a collision depends on the kinetic energy of the grinding ball, which in turn scales with the mass, it might be expected that a plot of ignition time as a function of charge ratio would yield a series of parallel curves, displaced to shorter times for larger ball masses. However, this does not occur (Fig. 10). The inverse relationship between t_{ig} and
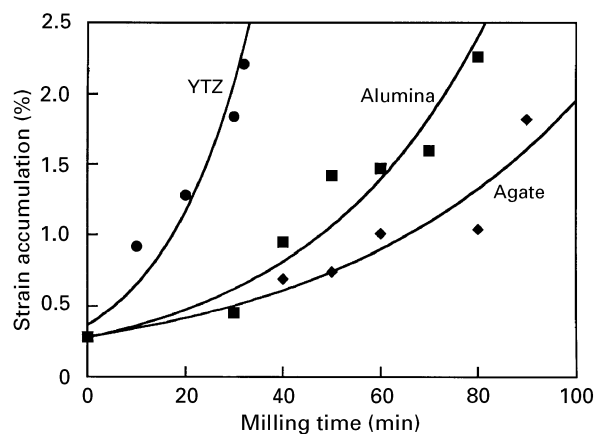

Figure 3 Strain accumulation in the graphite as a function of ball mass and milling time during the synthesis of TiC. The best fit for an exponential relationship between the amount of strain in the powder and the milling time.

charge ratio is independent of ball mass. The independence of reaction time and ball mass is not a specific feature of the carbide reaction; the results for a similar set of experiments for the reaction $5CuO + 4Fe \rightarrow 5Cu + Fe_3O_4 + FeO$ are shown in Fig. 11. Again, the time to combustion is independent
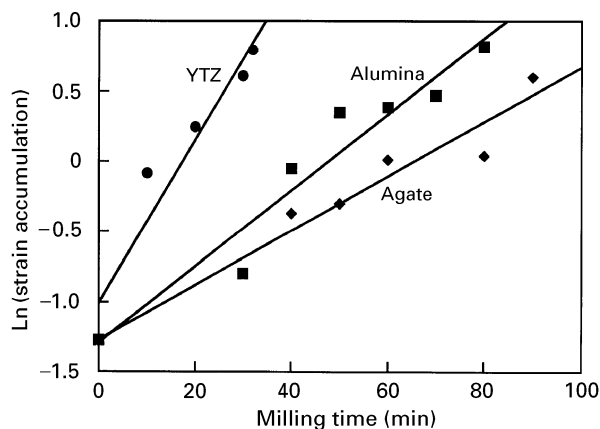
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Figure 4 The natural logarithm of the amount of strain which develops in the graphite as a function of ball mass and milling time during the synthesis of TiC. A linear relationship.
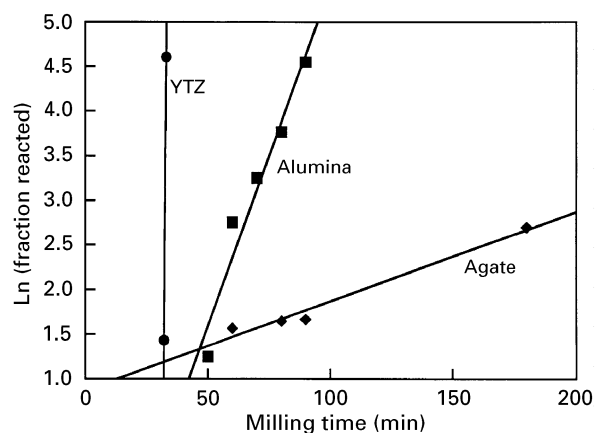

Figure 7 The natural logarithm of the fraction reacted as a function of ball mass and milling time during the synthesis of TiC. (——) A linear relationship between the concentration of TiC in the powder and the milling time.
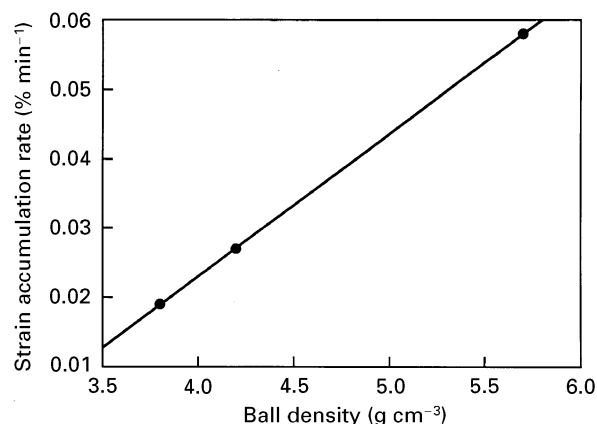

Figure 5 The strain accumulation rate of the carbon (the slope of the solid lines in Fig. 4) as a function of ball density, and hence collision energy, during the milling of Ti + C.
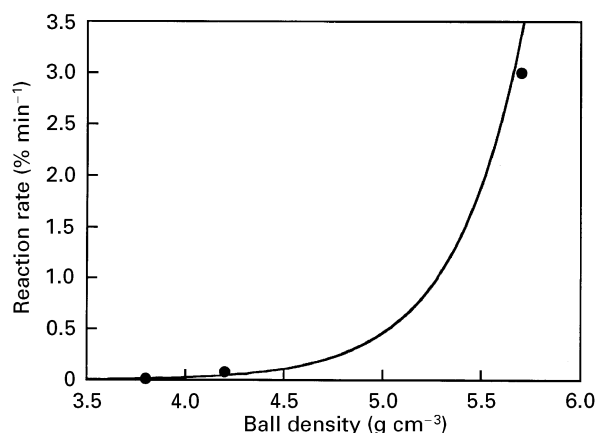

Figure 8 The reaction rate (the slope of the solid lines in Fig. 7) as a function of ball density, and hence collision energy, during the milling of Ti + C. (——) The best fit of the experimental data to an exponential relationship.
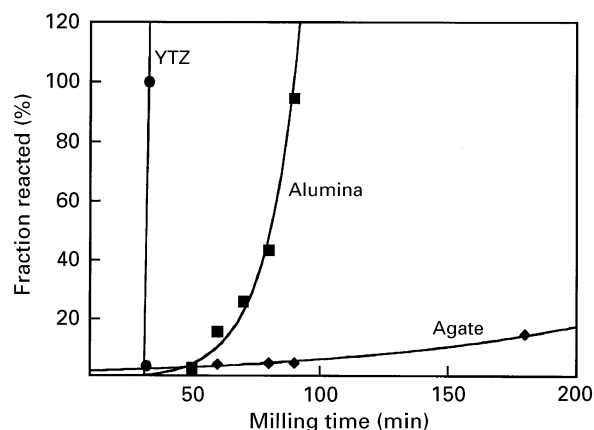

Figure 6 The quantity of product formed during the milling of Ti + C. (——) The best fit for the experimental data to an exponential relationship between the fraction reacted and the milling time.
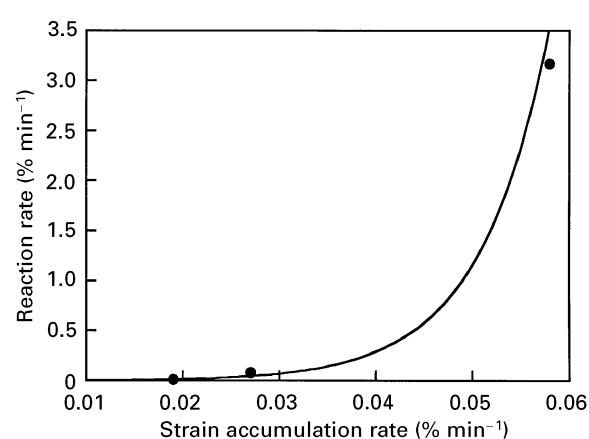

Figure 9 The reaction rate (from Fig. 8) as a function of the rate at which strain accumulates (from Fig. 5) in the graphite showing that reaction rate during mechanical alloying increases exponentially with the rate at which strain accumulates. (——) The best fit of the data to an exponential relationship; the regression coefficient is very close to 1.

of the ball mass. This implies that there is a rate-limiting step and simply increasing the collision energy does not always decrease milling times.

Given that the reaction rate is dependent on the rate at which strain accumulates, the rate-limiting step and

whether combustion occurs in the powders might be dependent on the quantity of short circuit diffusion paths which are generated. The minimum energy required to induce a reaction during mechanical
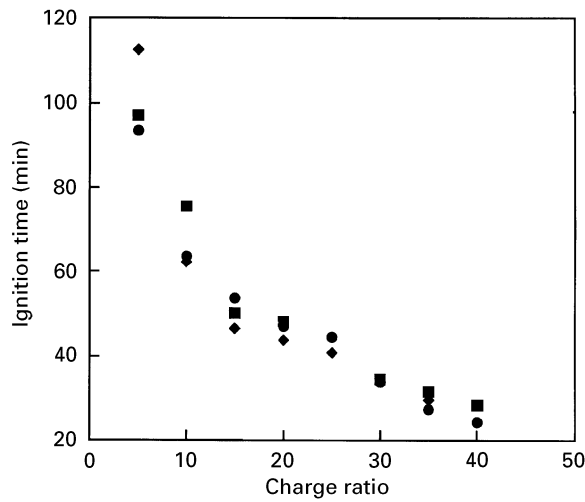
Figure 10 The effect of charge ratio on ignition time for the synthesis of TiC from the elements showing that the rate at which mechanical alloying develops is independent of ball mass in those systems where combustion occurs. (●) WC, (■) Fe, (◆) YTZ.
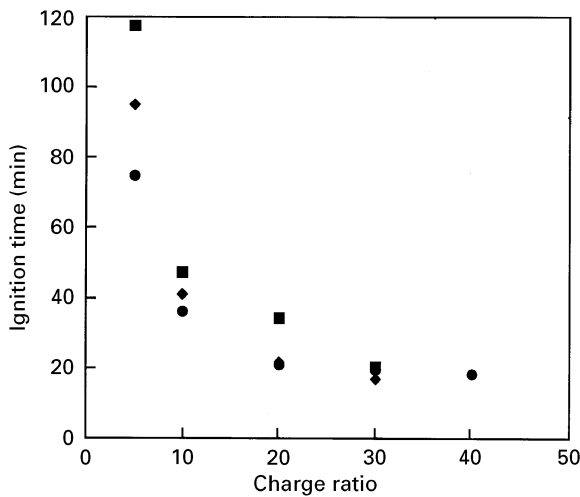

Figure 11 The effect of charge ratio on ignition time for the reduction of CuO by iron. This suggests that the independence of ignition time on ball mass in those systems where combustion occurs is system independent. (●) WC, (■) Fe, (◆) YTZ.

alloying may therefore be that which induces a stress in the charge which exceeds its yield strength. The reaction might then proceed fastest when the fracture strength is attained because short-circuit diffusion paths would be created at the maximum possible rate. To test this hypothesis, which would be valid if the strength of the graphite was intermediate between the stresses caused by collisions with alumina and zirconia, we examined the magnitude of the peak stresses in the powders.

It has been shown [28] that for a Hertzian collision between a sphere of radius R and a flat plate, the contact radius, r, is given by

$$r = (0.75kFR)^{1/3} \qquad (1)$$

where F is the impact load and

$$k = [(1 - \nu_b^2)/E_b] + [(1 - \nu_v^2)/E_v] \qquad (2)$$

where ν_b, E_b and ν_v, E_v are Poisson's ratios and the elastic moduli of the ball and the vial, respectively. We assume here that, because the radius of the vial is much greater than the radius of the ball, the vial can be approximated as a flat plate. For the purposes of this analysis, we further assume powderless collisions. This will be the most severe case; powder will act to dampen the collision. The impact load for powderless collisions is given by [28]

$$F = (5/3 \pi \rho_b)^{0.6} (3/4k)^{-0.4} V^{1.2} R^2 \qquad (3)$$

where ρ_b is the density of the sphere and V its impact velocity. The relative velocity between the balls and the vial have been determined for the Spex mill used here to be 4.79 m s^{-1} [29]. The stress during the collision is

$$\sigma = F/\pi r^2 \qquad (4)$$

The calculated loads, the contact radii and the stresses are shown in Table I. The stresses range from approximately 300 MPa (agate) to nearly 1 GPa (tungsten carbide). For even the smallest stress, this is significantly higher than the strength of graphite, which is in the 35–50 MPa range [22]. The maximum stress in the powder is clearly not the rate-limiting factor. It is also noteworthy that the stress is not directly proportional to the mass of the colliding ball. The stress caused by the alumina grinding media is second highest only to that caused by the WC–Co balls despite the low mass. This is a consequence of the relatively high modulus of Al_2O_3 which results in a small contact radius on impact. The kinetic energy of the balls is therefore not the only important factor controlling the reaction kinetics.

The deformation in the powder induces a temperature rise, ΔT. This was given by Schwarz and Koch [30] to be

$$\Delta T = \sigma V (2\tau/\pi \lambda C_p \rho_c)^{0.5} \qquad (5)$$

where λ, C_p and ρ_c are the thermal conductivity, the heat capacity and the density of the deforming species, respectively, and τ is the stress state life time [4]

$$\tau = V^{-0.2}(\rho_b/E_b)^{0.4} R \qquad (6)$$

For carbon, the thermal conductivity is $60 \text{ W m}^{-1} \text{ K}^{-1}$; the heat capacity is $750 \text{ J kg}^{-1} \text{ K}^{-1}$ and the density is 2 g cm^{-3} [22]. Using these values, the calculated parameters are collected in Table I. The stress state life time varies from 2.5 μs (Al_2O_3) to 4.6 μs (SiO_2) while the temperature rise ranges monotonically from 264 K (SiO_2) to 746 K (WC–Co). The temperature rise for alumina lies between that for glass and zirconia, i.e. it scales with the mass. The high stress caused by the alumina is more than compensated by the short stress life time: the stress is high but it is only applied for a short time.

The calculated temperature rise is of the order of the combustion temperature [31]. Because combustion occurs when the temperature rise exceeds the combustion temperature [32], the temperature rise may therefore be the rate-limiting step. If the impact stress exceeds the yield stress of the charge, short circuit diffusion paths will be created and the reaction rate

will accelerate. The reaction rate will increase with collision energy until the combusion temperature of the powder is attained. Combustion occurs at this point and no further advantage accrues when collisions of continuously higher energy are employed.

4. Conclusion

The rate of mechanical alloying scales exponentially with the rate at which the reactants accumulate strain, which is dependent on the kinetic energy of the grinding balls. This implies that the minimum requirement for mechanical alloying maybe that the collision stress needs to be greater than the yield stress of the powders. When the yield strength of the reactants is exceeded, the maximum reaction rate is determined by the collision-induced temperature rise. Ball masses and hence collision energies higher than that required to attain the combustion temperature are not advantageous.

Acknowledgement

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