Application of Mechanical Alloying to Chemical Refining (Overview)

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Since its discovery the process of mechanical alloying has demonstrated significant potential for the synthesis of materials with novel structures and properties. In this paper recent studies of the application of mechanical alloying to solid state refining processes are reviewed. These studies show that mechanical alloying enables displacement reactions, which conventionally require high temperatures to be thermally activated, to be mechanically activated during milling in a ball mill at ambient temperatures. It is shown that mechanical alloying can provide the basis of a single stage process which combines the separate processes of refining, alloying and powder manufacture. Of particular interest is the application of the process to the synthesis of rare earth permanent magnet materials.

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I. Introduction

Mechanical alloying and mechanochemical synthesis techniques have attracted considerable scientific interest in recent years as a consequence of the unique structures and properties developed by the process. Since the process of mechanical alloying was first used by Benjamin⁽¹⁾⁽²⁾ for the production of oxide dispersion strengthened (ODS) superalloys, there has been a significant effort aimed at improving understanding of the process through kinetic and dynamic analyses of mechanical milling processes and in extending the range of materials that can be processed in this manner.

In addition to providing a means for solid state alloying, the mechanical alloying process can be used more generally to induce a wide variety of solid-solid and even liquid-solid chemical reactions, in particular, reactions used in chemical refining processes⁽³⁾⁻⁽¹¹⁾. With most solid state reactions the formation of product phases spatially separate the reactants, causing reaction kinetics to be dependent on product morphology and to be limited by diffusion rates through the product phases. As a consequence, although most refining reactions are thermodynamically favoured at room temperature, high temperatures are necessary if sufficiently high reaction rates are to be realised.

Our studies have demonstrated that the mechanical alloying process can provide the means to substantially increase the kinetics of solid state oxidation-reduction reactions. The repeated welding together of particles and fracture accompanying ball/powder collisions enable the reacting surfaces to be dynamically regenerated during milling. As a consequence, reactions which normally require high temperatures will occur at low temperatures during mechanical alloying without any externally ap-

plied heat. It has been shown that the kinetics of such mechanically activated reactions depend on milling parameters such as collision energy and frequency, as well as the thermodynamic properties of the reaction. Alternatively, the reduction of diffusion distances associated with microstructural refinement accompanying prior mechanical milling of reactants can be used to reduce reaction temperatures.

It has also been shown that self-propagating combustion reactions can be ignited during mechanical alloying, provided the reaction enthalpy is sufficiently high⁽⁴⁾⁻⁽⁷⁾. Such reactions require a critical milling time for the combustion reaction to be ignited. Measurements of the ignition time provide a useful means of characterizing structural and chemical evolution during mechanical alloying⁽⁸⁾.

A summary of reduction reactions induced by mechanical alloying is shown in Table 1. All of the reactions are characterized by a negative free energy change and are therefore thermodynamically possible. The occurrence of these reactions at ambient temperatures is thus limited by kinetic considerations. Also shown in Table 1 are the values of the enthalpy change accompanying the reactions.

In this paper recent studies of mechanically activated chemical reactions by the author and his co-workers are reviewed. In Sections II and III mechanically activated metal refining reactions and application to the synthesis of rare earth permanent magnets are discussed. Mechanically activated self-sustaining combustion reactions are reviewed in Section IV, and Section V gives a brief summary of recent measurements of reaction kinetics. While this paper is limited to oxidation-reduction reactions, it is emphasized that mechanical activation via mechanical milling processes can be applied to a wide range of chemical reactions and that the ball mill can now be considered

Table 1 Reactions studied.

Reaction	ΔH (kJ)	Reference
$\text{CuO} + \text{Ca} \rightarrow \text{Cu} + \text{CaO}$	-475	(3)(4)
$\text{CuO} + \text{Ni} \rightarrow \text{Cu} + \text{NiO}$	-83	(5)(43)
$2\text{CuO} + \text{C} \rightarrow 2\text{Cu} + \text{CO}_2$	-138	(9)
$2\text{CuO} + \text{Ti} \rightarrow 2\text{Cu} + \text{TiO}_2$	-633	(5)(6)
$3\text{CuO} + \text{Al} \rightarrow 3\text{Cu} + \text{Al}_2\text{O}_3$	-1197	(6)
$4\text{CuO} + 3\text{Fe} \rightarrow 4\text{Cu} + \text{Fe}_3\text{O}_4$	-502	(6)(8)
$\text{ZnO} + \text{Mg} \rightarrow \text{Zn} + \text{MgO}$	-248	(7)
$\text{ZnO} + \text{Ca} \rightarrow \text{Zn} + \text{CaO}$	-283	(3)
$2\text{ZnO} + \text{Ti} \rightarrow 2\text{Zn} + \text{TiO}_2$	-249	(40)
$\text{TiCl}_4 + 2\text{Mg} \rightarrow \text{Ti} + 2\text{MgCl}_2$	-447	(10)
$\text{ZrCl}_4 + 2\text{Mg} \rightarrow \text{Zr} + 2\text{MgCl}_2$	-293	(11)
$2\text{TaCl}_5 + 5\text{Mg} \rightarrow 2\text{Ta} + 5\text{MgCl}_2$	-1467	(11)
$2\text{GdCl}_3 + 3\text{Ca} \rightarrow 2\text{Gd} + 3\text{CaCl}_2$	-378	(13)
$2\text{ErCl}_3 + 3\text{Ca} \rightarrow 2\text{Er} + 3\text{CaCl}_2$	-407	(13)
$\text{SmCl}_3 + 3\text{Na} \rightarrow \text{Sm} + 3\text{NaCl}$	-202	(16)
$\text{V}_2\text{O}_5 + 5\text{Mg} \rightarrow 2\text{V} + 5\text{MgO}$	-1400	(42)
$3\text{V}_2\text{O}_5 + 10\text{Al} \rightarrow 6\text{V} + 5\text{Al}_2\text{O}_3$	-3653	(42)
$2\text{V}_2\text{O}_5 + 5\text{Ti} \rightarrow 4\text{V} + 5\text{TiO}_2$	-1608	(42)

to be an effective low temperature chemical reactor as well as a generator of non-equilibrium phases and microstructures.

II. Metal Refining Reactions

It is clear from Table 1 that most studies have been carried out on the reduction of metal oxides or chlorides to metals. While many of the reactions are only of academic interest, a number of the reactions are identical to that employed in high temperature thermal chemical refining processes. In particular, the reactions for producing copper, titanium, zirconium, tantalum and the rare earth metals have their high temperature analogs and are potential candidates for industrial application.

1. Copper

The initial studies carried out to demonstrate that chemical reduction reactions can be induced during mechanical alloying involved the reduction of copper oxide with calcium⁽⁵⁾⁽⁶⁾. As shown in Table 1 there is a large negative free energy change associated with the reaction (-475 kJ) which should ensure a large thermodynamic driving force. The reactants were milled with a Spex 8000 mixer mill in a sealed vial under a N_2 atmosphere, using anhydrous toluene as a milling lubricant. X-ray diffraction measurements showed initial formation of copper after milling for ~10 min, with the reaction being essentially completed after 100 min. Further experiments demonstrated the reduction of ZnO with Ca and the formation of β' brass by milling equal amounts of CuO and ZnO with Ca. It was also found⁽⁶⁾ that milling without a process lubricant resulted in a gasless combustion reaction as discussed in Section IV. The thermal reduction of copper oxide with carbon is a widely used process for the production of copper. This reaction is thermodynamically favored at room temperature, but will not occur for kinetic reasons. However, it

has been recently been shown that copper oxide is reduced with graphite during mechanical alloying⁽⁹⁾. The reduction of CuO was found to occur via a two-stage, $\text{CuO} \rightarrow \text{Cu}_2\text{O} \rightarrow \text{Cu}$, process. The effect of milling time on the phases present as determined from quantitative analysis of X-ray diffraction patterns is shown in Fig. 1. During the initial stage of milling the CuO reduction rate increased with milling, consistent with the effect of microstructural refinement on reaction kinetics⁽⁸⁾. The amount of Cu_2O reached a maximum of ~45% after 9 hours of milling and then decreased to zero after 24 hours. Examination of the powder using transmission electron microscopy (TEM) showed that the as-milled particles contained small Cu crystallites of 15–30 nm in size (Fig. 2).

Most solid-state mechanochemical reactions studied have been displacement reactions involving the formation of two or more solid product phases. The removal of unwanted reaction by-product phases can be difficult due to the high reactivity of the metal phase associated with

Fig. 1 Effect of milling time on the two stage reduction of CuO by C during mechanical alloying⁽⁹⁾.

Fig. 2 TEM micrograph of as-milled Cu particle⁽⁹⁾.

nanocrystalline grain sizes and inter-mixing of the phases induced by the mechanical milling process. The use of carbon as the reductant obviates the need to remove the reaction by-products, since gaseous CO_2 is formed by the reaction.

2. Titanium

Titanium is conventionally refined by the Kroll process, whereby molten Mg is reacted with TiCl_4 vapour at approximately 1000°C to form Ti and MgCl_2 . The reduction of TiCl_4 by Mg during mechanical alloying has been shown to occur at ambient temperature and at $-55^\circ\text{C}^{(10)}$. At room temperature TiCl_4 is a liquid and a liquid-solid reaction occurs during milling. In Fig. 3 the effect of the ball to powder mass ratio (charge ratio) on the milling time required to form Ti is shown. Cooling the milling vial to -55°C , below the freezing temperature of TiCl_4 , resulted in a reduction of the milling time required to form Ti by a factor of six, thus demonstrating the greater efficacy of solid-solid collision events during milling. The as-milled powder consisted of a mixture of Ti particles, 0.2–3 μm in diameter, embedded in MgCl_2 . The MgCl_2 and unreacted Mg could be removed by washing in dilute mineral acid or by conventional vacuum distillation. Figure 4 shows powder particles after vacuum distillation at 900°C for 24 h. The direct synthesis of TiAl and Ti_3Al by milling TiCl_4 , Al and Mg has also been demonstrated⁽¹⁰⁾. Similar results have also been obtained for the refining of Zr by milling ZrCl_4 with Mg⁽¹¹⁾.

3. Rare-earth metals

The rare earth oxides are amongst the most difficult materials to refine due to their low free energies. With the exception of Sm, Eu and Yb, the rare earth metals are conventionally refined by calciothermic reduction at temperatures exceeding $1000^\circ\text{C}^{(12)}$. Metallothermic reduction of Sm, Eu and Yb requires the use of La or mischmetal as the reductant due to the high stability of their respective divalent chlorides.

The reduction of ErCl_3 and GdCl_3 by Ca during

Fig. 3 Effect of charge ratio and milling temperature on time required to form titanium⁽¹⁰⁾.

Fig. 4 SEM micrograph of Ti powder after vacuum distillation⁽¹⁰⁾.

mechanical alloying has been demonstrated⁽¹³⁾. Milling for 24 h in a Spex mill with a charge ratio of 10:1 resulted in a fine mixture of metal crystallites in an amorphous CaCl_2 matrix. Crystallite sizes of 14 nm for Er and 9 nm for Gd were estimated from X-ray diffraction measurements. The as-milled powders were extremely reactive, making it necessary to use special handling procedures to avoid contamination. The reaction of rare earth metals with oxygen and nitrogen during milling can result in the formation of NaCl type phases⁽¹⁴⁾⁽¹⁵⁾.

(1) Samarium

The mechanochemical reduction of SmCl_3 using Na as the reductant provides an interesting example of a reaction that can be caused to occur at low temperatures by mechanical activation, which cannot occur at elevated temperatures due to unfavourable thermodynamics. As indicated previously, SmCl_3 cannot be reduced beyond the divalent state using calcium as the reductant because of the low free energy of SmCl_2 . However, examination of reaction free energies indicates that the reduction of SmCl_3 to Sm using sodium as the reducing agent is thermodynamically favoured at temperatures below 400 K.

The mechanical milling of SmCl_3 and Na has been shown to result in a nanoscale mixture of Sm and NaCl via the reaction $\text{SmCl}_3 + 3\text{Na} \rightarrow \text{Sm} + 3\text{NaCl}$ after a milling time of 16 h⁽¹⁶⁾. Vacuum annealing the as-milled powder at 575 K resulted in significant growth of the Sm crystals but no formation of SmCl_2 occurred as would be expected from free energy data. SmCl_2 was formed after annealing at 823 K. Although there is some doubt as to the value of the temperature below which Sm is stable, the formation of Sm by mechanical alloying is an important confirmation of the low temperature nature of the process. While it is impossible to directly measure particle temperatures reached during collision events, values of maximum collision temperatures inferred by combustion experiments and calculations (see Section IV) are estimated to be greater than 450 K. However, it is unlikely

that temperatures exceeding ~ 400 K would have been reached due to local melting of Na on reaching 371 K. The discovery of other low temperature reactions that can be uniquely induced by mechanical alloying, which for thermodynamic or other reasons will not occur at elevated temperatures, is an exciting prospect.

III. Synthesis of Rare Earth Permanent Magnet Alloys

The synthesis of permanent magnet materials is one of the most promising applications of mechanical alloying. A number of rare-earth alloys have been synthesized from metal powders, including $\text{Nd}_2\text{Fe}_{14}\text{B}$ ⁽¹⁷⁾, $\text{Sm}_2\text{Fe}_{17}\text{N}_{2.6}$ ⁽¹⁸⁾⁻⁽²⁰⁾, $\text{Sm}_2\text{Fe}_{14}\text{Ga}_3\text{C}_2$ ⁽²¹⁾, SmCo_5 ⁽²²⁾ $\text{Sm}_2\text{Co}_{17}$ ⁽²²⁾, SmFeTi ⁽²³⁾ and SmCoFe ⁽²⁴⁾⁻⁽²⁶⁾.

The synthesis of rare-earth permanent magnet alloys directly from rare-earth oxides or halides by milling with a suitable reductant has also been demonstrated. The reactions that have been studied are given in Table 2. Most work to date has been carried out on the synthesis of SmCo_5 from Sm_2O_3 , SmCl_3 or SmF_3 precursors by milling with Co and Ca. The as-milled structure consists of an amorphous SmCo phase and a reaction by-product, e.g. CaO. Subsequent heat treatment is required to crystallize the hard magnetic SmCo_5 phase. The ability of mechanochemical processing to combine refining, alloying and powder manufacture into a single, low temperature process provides significant potential for reducing the manufacturing costs of rare-earth permanent magnets.

1. Structure and properties

Most of the rare-earth transition metal alloys studied to date exhibit similar structures and properties in the as-milled condition. In alloys containing Fe the formation of a single phase does not occur during mechanical alloying. Instead, a two phase mixture consisting of crystallites of the transition metal phase, and a rare-earth rich amorphous phase is formed. For example, milling Fe, Nd and B in the ratio to form $\text{Nd}_2\text{Fe}_{14}\text{B}$ results in the formation of α -Fe and a Nd rich amorphous phase⁽¹⁷⁾. Typical as-milled microstructures consist of ~ 5 nm crystallites of α -Fe in the amorphous phase. Similarly the mechanical alloying of Sm and Fe to form $\text{Sm}_2\text{Fe}_{17}$ results in a mixture of α -Fe and a Sm-Fe amorphous phase. Recent Mössbauer measurements in as-milled $\text{Sm}_2\text{Fe}_{17}$ powders suggest that the composition of the

amorphous phase is approximately $\text{Sm}_{23}\text{Fe}_{77}$ ⁽³¹⁾.

The alloys which form two phase amorphous/crystalline mixtures during mechanical alloying are found to decompose when their respective intermetallic compounds are mechanically milled⁽³²⁾⁽³³⁾. Thus, nearly identical structures are found after milling, independent of the starting condition, suggesting the attainment of a steady-state, non-equilibrium structure. With SmCo_5 and $\text{Sm}_2\text{Co}_{17}$ the as-milled structure consists of a single amorphous phase⁽³⁴⁾.

It is necessary to crystallize the as-milled structure into a single hard magnetic phase (i.e. SmCo_5) by heat treatment at temperatures in the range of 600–800°C. Alloys which contain amorphous/crystalline phase mixtures after milling are found to exhibit multi-stage reactions on heating, with recrystallization of the crystalline phase preceding the crystallisation of the amorphous phase. In some alloys crystallisation of one or more non-equilibrium phases can precede formation of the equilibrium phases on heating. As shown in Fig. 5, the annealing of as-milled $\text{Sm}_{10.5}\text{Co}_{49.5}\text{Fe}_{40}$ initially results in recrystallization of α -Fe, followed by the crystallization of a $\text{Sm}_2(\text{Co}, \text{Fe})_7$ phase at low temperatures, with the formation of the equilibrium $\text{Sm}_2(\text{Co}, \text{Fe})_{17}$ phase occurring at high temperatures⁽³⁵⁾. With $\text{Sm}_2\text{Fe}_{17}$, crystallization must precede nitriding because of the instability of the $\text{Sm}_2\text{Fe}_{17}\text{N}_3$ phase at temperatures above 550°C.

A randomly oriented grain structure is formed by mechanical alloying and heat treatment. As a consequence, the magnetic properties are isotropic. Without further processing, e.g. die upsetting⁽³⁶⁾, the remanent magnetisation, M_r , and maximum energy product, $(BH)_{\text{max}}$, are limited to 0.5 and 0.25 respectively of the values achievable with full crystallographic alignment of the crystallites.

The process results in remarkably high values of coercivity. Samples of SmCo_5 synthesized from SmF_3 have exhibited coercivities in excess of 75 kOe. The high values of coercivity appear to be a consequence of the nanocrystalline grain structure which results in large

Table 2 Rare-earth alloy reduction reactions.

Reaction	Reference
$\text{Sm}_2\text{O}_3 + 3\text{Ca} + 10\text{Co} \rightarrow 2\text{SmCo}_5 + 3\text{CaO}$	(29)
$2\text{SmF}_3 + 3\text{Ca} + 10\text{Co} \rightarrow 2\text{SmCo}_5 + 3\text{CaF}_2$	(30)
$2\text{SmCl}_3 + 3\text{Ca} + 10\text{Co} \rightarrow 2\text{SmCo}_5 + 3\text{CaCl}_2$	(28)
$\text{Sm}_2\text{O}_3 + 3\text{Ca} + 17\text{Co} \rightarrow \text{Sm}_2\text{Co}_{17} + 3\text{CaO}$	(27)
$\text{Sm}_2\text{O}_3 + 3\text{Ca} + 17\text{Fe} \rightarrow \text{Sm}_2\text{Fe}_{17} + 3\text{CaO}$	(27)
$\text{Nd}_2\text{O}_3 + 3\text{Ca} + 14\text{Fe} + \text{B} \rightarrow \text{Nd}_2\text{Fe}_{14}\text{B} + 3\text{CaO}$	(27)

Fig. 5 X-ray diffraction patterns showing phases present after heat treatment of mechanically alloyed $\text{Sm}_{10.5}\text{Co}_{49.5}\text{Fe}_{40}$ powder; (a) as-milled, (b) annealed 120 min at 350°C, (c) annealed 10 min at 600°C, (d) annealed 10 min at 70°C⁽³⁵⁾.

Fig. 6 Magnetization curve for remanence enhanced α -Fe-Sm₂(Co, Fe)₁₇⁽³⁵⁾.

nucleation fields for magnetization reversal due to strong pinning of domain walls at grain boundaries and other defects.

2. Remanence enhancement

As discussed previously, the isotropic behaviour associated with the random crystallite alignment in each powder particle limits the magnetic properties of mechanically alloyed magnets. However, recent studies^{(35)(37)–(39)} have shown that mechanically alloyed and heat treated two-phase mixtures of a magnetically hard phase and a magnetically soft phase (such as α -Fe) exhibit significant remanence enhancement. Remanence enhancement requires a nano-scale grain structure and is associated with exchange coupling at interfaces between the hard and soft magnetic phases. As a consequence, the material, although crystallographically isotropic, can exhibit remanence values approaching that obtained in fully aligned materials without the necessity of crystallographic alignment. A typical magnetization curve for an exchange coupled, remanence magnetic material is shown in Fig. 6.

Ding *et al.*⁽³⁸⁾⁽³⁹⁾ first reported remanence enhancement in mechanically alloyed two-phase α -Fe/Sm₂Fe₁₇N_{2.6} alloys containing 5–11 at%Sm prepared by mechanical alloying and heat treatment. The as-milled structures consisted of two-phase mixtures of α -Fe and an amorphous phase. Crystallization at temperatures above 500°C resulted in two phase α -Fe/Sm₂Fe₁₇ mixtures which were nitrided at 400°C to convert the Sm₂Fe₁₇ phase to Sm₂Fe₁₇N_{2.6}. The resulting crystallite size was ~15–20 nm. The crystallite size is a key parameter influencing the degree of remanence enhancement and coercivity. In Fig. 7 the effect of annealing temperature on the coercivity and remanence is shown. Both H_c and M_r decreased with increasing temperature above 600°C due to the increase in crystallite size, and two phase magnetic behaviour was observed in samples annealed above 800°C⁽³⁸⁾.

Values of M_r/M_s exceeding ~0.75 have been subsequently reported in several two-phase systems (Table 3). Such values of M_s/M_r generally require crystallite sizes less than 20 nm. Figure 8 shows a typical microstructure of a remanence enhanced magnetic alloy⁽³⁵⁾.

Fig. 7 Effect of annealing temperature on H_c and M_r for α -Fe-Sm₂Fe₁₇N_{2.6}⁽³⁹⁾.

Fig. 8 Nanocrystalline structure of remanence enhanced Sm_{10.5}Co_{49.5}Fe₄₀ powder⁽³⁵⁾.

IV. Combustion Reactions

The efficacy of the mechanical alloying process is such that for many oxidation/reduction reactions self-sustaining combustion reactions are initiated on milling for a critical time, defined as the ignition time, t_{ig} . These reactions exhibit relatively large enthalpy changes (Table 1) and as a consequence will also undergo a thermal combustion reaction if heated to above a critical ignition temperature, T_{ig} .

Table 3 Properties of remanence enhanced magnet alloys.

Alloy	M_r/M_s	H_c (kOe)	Reference
Sm ₉ Fe ₉₁ N _{2.6}	.76	7.1	(38)
Sm _{14.4} Co _{85.6} Fe ₂₀	.74	9.1	(28)
Sm ₁₁ Co ₈₉	.77	2.2	(37)

1. Ignition condition

It has been postulated⁽⁴⁰⁾ that t_{ig} is equal to the milling time required for the ignition temperature to decrease to the temperature, T_c , attained during ball/powder collision events. The variation of T_{ig} and T_c during milling is shown schematically in Fig. 9. The ignition temperature is a function of the reaction enthalpy and microstructural parameters, such as particle and crystallite sizes, which influence reaction kinetics. In Figs. 10 and 11 measurements of crystallite size and T_{ig} (from DTA measurements) are shown as a function of milling time for the ZnO/Mg reaction⁽⁷⁾. The ignition temperature decreases with milling time, with the refinement of microstructure during milling being the major factor causing this decrease. The collision temperature increases with milling time due to the increase in the background temperature resulting from energy dissipation in the mill, until a steady state value is reached.

By assuming that combustion occurs during milling

Fig. 9 Schematic variation of T_{ig} and T_c during milling⁽⁴⁰⁾.

Fig. 10 Effect of milling time on crystallite size for ZnO/Mg reaction⁽⁷⁾.

Fig. 11 Effect of milling time on T_{ig} for ZnO/Mg reaction⁽⁷⁾.

when T_{ig} decreases to the value of the collision temperature, values of T_c can be estimated by extrapolating the values of T_{ig} , such as shown in Fig. 11, to the ignition time. Values of T_c obtained in this manner using a Spex 8000 mixer mill and 12 mm diameter balls have been found to equal 640 K in the ZnO/Mg reaction and 400 K for the CuO/Fe reaction. These values are consistent with values calculated from modelling studies⁽⁴¹⁾. However, recent measurements of combustion in the V_2O_5 /Mg reaction indicated that the initiation of combustion could not be associated with a reduction of the ignition temperature during milling⁽⁴²⁾.

From Fig. 9 it is evident that combustion should only occur if T_c exceeds the minimum value of T_{ig} . The value of T_c is dependent on a number of factors, including the collision energy and the work dissipated during the collision event. The collision energy can be controlled by varying milling parameters such as collision frequency and ball size. With the CuO/Fe reaction it has been shown that combustion requires a ball size 12 mm or greater⁽⁸⁾. With smaller ball sizes the measurements of T_{ig} were found to decrease to a minimum and then increase with further milling as the reaction occurs in a steady-state manner.

2. Combustion products

The examination of powders immediately after combustion has revealed a rich variety of structures which reflect the high temperatures reached during the combustion event⁽⁴⁾⁻⁽⁷⁾⁽⁴²⁾. Estimates of adiabatic temperature rises are in the range of 3000–5000 K and structures consistent with melting and vaporisation of the constituents are observed.

In general the as-combusted powders consist of heterogeneous mixtures of varying size from nodules as large as 1–5 mm down to particles 100 nm in diameter. Figures 12 and 13 show two morphologies of combustion products. Figure 12 shows a cellular pattern on the sur-

Fig. 12 Cellular structure on surface of nodule formed during combustion of $V_2O_5 + Mg^{(42)}$.

Fig. 13 Powder particles formed during combustion of $CuO + Ti^{(5)}$.

Fig. 14 Composite particle formed during combustion reaction of V_2O_5 and $Al^{(42)}$.

face of a nodule formed during the V_2O_5/Mg combustion reaction⁽⁴²⁾, while Fig. 13 shows an aggregate of 1–5 μm Cu spheres formed during the reaction between CuO and $Ti^{(5)}$. In Fig. 14 a composite particle formed during

Fig. 15 TEM images of $\gamma-Al_2O_3$ smoke particles formed during combustion reaction of V_2O_5 and $Al^{(42)}$.

the combustion of V_2O_5 and Al is shown⁽⁴²⁾. The left side of the particle is V (light area) and the right side is Al_2O_3 , and it is clear that both phases have melted and re-solidified. The separation of the two phases is consistent with the observation that pure metals and oxides are generally immiscible in the liquid phase.

TEM examination of fine powder formed during the V_2O_5/Al reaction revealed spherical and hexagonal single crystalline particles, as well as unusual filamentary particles (Fig. 15)⁽⁴²⁾. Electron diffraction and EDS analyses showed that these particles are $\gamma-Al_2O_3$. Such particle morphologies are similar to ultrafine metal and oxide smoke particles formed by gas phase condensation and thus indicate that vaporization of Al_2O_3 occurred during combustion. As shown in Table 1, the $3V_2O_5 + 10Al \rightarrow 6V + 5Al_2O_3$ reaction is characterised by a reaction enthalpy change of -3727 kJ. The adiabatic temperature for this reaction is 3468 K, which is greater than both the melting (2288 K) and boiling (3253 K) temperatures of Al_2O_3 . It is thus clear that temperatures approaching the adiabatic reaction temperature are reached during mechanically activated combustion.

V. Reaction Kinetics

To date few studies aimed at establishing reaction kinetics and delineating the factors controlling reaction rates have been carried out. While dynamic models can be constructed to evaluate collision frequencies, impact energies and other quantities, the characterization of different types of mills and process optimization requires accurate assessment of the effect of various milling parameters on reaction kinetics. For such studies it is necessary to be able to quantitatively measure the progress of a particular reaction during milling under a certain set of conditions.

Recent quantitative measurements of the effect of milling parameters on reaction kinetics have been carried out using the CuO/Ni displacement reaction, $\text{CuO} + \text{Ni} \rightarrow \text{NiO} + \text{Cu}$ ⁽⁴³⁾. Nickel is the only ferromagnetic phase present in the reaction and thus the progress of the reaction during milling can be established from measurements of saturation magnetization, M_s , as a function of milling time.

Measurements of the effect of milling time and milling speed on the fraction of Ni, f_{Ni} , present in tests carried

Fig. 16 Effect of milling time on progress of $\text{CuO} + \text{Ni} \rightarrow \text{Cu} + \text{Ni}$ reaction⁽⁴³⁾.

Fig. 17 Effect of collision energy on reaction kinetics of $\text{CuO} + \text{Ni} \rightarrow \text{Cu} + \text{Ni}$ reaction⁽⁴³⁾.

out on a planetary mill are shown in Fig. 16⁽⁴³⁾. The inverted 's' shape of the curve may be rationalized on the basis of microstructure refinement during the early stage of reaction and dilution effects at the completion of the reaction. By varying the milling speed it was possible to vary the collision energy and frequency without varying the ball trajectory and impact angle, thus enabling the effect of collision energy on reaction kinetics to be established. The collision energy was found to significantly influence reaction kinetics (Fig. 17). However, further studies are needed to establish the relative importance of collision temperature and the processes of plastic deformation, interparticle welding and fracture on the reaction kinetics.

VI. Summary

The application of mechanical alloying to chemical refining enables the direct synthesis of metals and alloys without the need for heating. Three processes, refining, alloying and powder manufacture can be carried out in a single stage, low temperature process. The production of alloy powder by low temperature processing in a sealed, inert environment minimises the sources of oxidation inherent in conventional processes. However, attention must be given to the handling and further processing of highly reactive as-milled powders and the removal of reaction by-products.

Mechanical alloying provides significant advantages for the processing of rare earth permanent magnets. The nanocrystalline grain structures obtained after mechanical alloying and heat treatment result in near optimum magnetic properties. In particular, the nanocrystalline microstructures inherently developed by the mechanical alloying process appear to be ideally suited to the synthesis of remanence enhanced magnetic materials. Since with remanence enhancement there is no need for an alignment process, significant potential exists for achieving cost savings and simplification of the manufacturing process.

Studies of chemical reactions during mechanical alloying provide important methods for assessing the effect of milling parameters on reaction kinetics. Of particular value are reactions which include a single ferromagnetic phase, enabling quantitative analysis via magnetization measurements. Such measurements are of vital importance for the optimization of the mechanical alloying process.

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