Mechanochemical Treatment of Solid Mixtures – a Promising Way of Synthesizing Ceramic Precursors*

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Abstract

This report discusses the influence of mechanochemical treatment on solid state transformation and precursor formation from one- and two-component systems of interest to ceramic processing. The main focus is on "soft" mechanochemical reactions, *i. e.* processes in compounds containing water or hydroxyl groups.

INTRODUCTION

One of the defining features of traditional ceramics is their requirement for firing at high temperatures. The high-temperature processing of traditional ceramics is estimated to comprise ~40 % of the final cost. Decreasing the firing temperature can be achieved by either increasing the homogeneity of the mixtures or decreasing the particle size and increasing the defects in the batch constituents. Good homogeneity can be achieved by forming precursors in solution, as in sol-gel and co-precipitation processes. A decrease in particle size accompanied by increasing lattice defect concentrations is usually achieved by the grinding. Homogeneity can also be achieved by grinding if mechanochemical reaction occurs between the constituents.

Differences in precursor formation by solution chemistry and solid state reaction have been discussed in a previous report [1].

1. Solution process: starting raw materials ® dissolution ® chemical reaction in liquid state ® precursor.

2. Dry process: starting raw materials ® grinding (solid state reaction) ® precursor.

The preparation of ceramic precursors *via* solution chemistry methods has some disadvantages, such as:

– difficulty in producing a large amount of precursor in a single batch;

– expensive raw materials;

– necessity to utilize waste solutions.

As shown in the above scheme, precursor formation *via* the conventional solid state reaction can be achieved by mechanochemical treatment, with benefits in energy saving because of the absence of evaporation or melting, and dissolution occurring in liquid-state chemical reactions.

The mechanochemical reactions may involve mechanical stress. Mechanical treatment to increase the reactivity of solids has been known in the ceramics industry for a long time, as a method for generating new surfaces and various defects [2]. Although the mechanochemical method appears promising for the synthesis of ceramic precursors, it has some possible disadvantages:

– high energy consumption;

– possible contamination from the milling media;

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– less homogeneity than from solution chemistry methods.

If one of the reaction components contains water or hydroxyl groups, the mechanochemical reaction will occur more beneficially. The role of water or hydroxyl groups in mechanochemical reactions was systematically studied by M. Senna and his co-workers [3] and by E. Avvakumov and co-workers [4]. Such reactions were described by Senna as "soft", and by Avvakumov as "mild" mechanochemical reactions. The ease of complex formation was explained by E. Avvakumov et al. [5] on the basis that hydrated compounds are softer than anhydrous ones. M. Senna et al. [6] suggested that the effect was due to direct ion exchange. One of the first suggestions that direct ion exchange occurs between the powder mixture during grinding was made by Y. Arai et al. [7].

In this paper I will discuss the effect of mechanical stress on the thermal reaction sequences of the hydroxides and some aspects of "soft" mechanochemical reactions in ceramic precursor formation, illustrated by our previous results.

SOME FEATURES OF THE "SOFT" MECHANOCHEMICAL REACTION

Hydrothermal-like reaction

One of the interesting features of mechanochemical reactions in the presence of water is the operation of hydrothermal-like reactions. R. Kiriyama et al. [8] were among the first who drew attention to the similarity of the products of mechanochemical and hydrothermal reactions in the production of spinel ferrites. As it is well known, *hydrothermal reactions are those processes which occur under high temperature and pressure, in which mass transfer occurs through the liquid phase.* The question arises as to how high temperatures and pressures can be generated in the grinding vessel.

About three decades ago V. Boldyrev made to first theoretical analysis of energy transfer from the milling media to the reacting material in liquid-solid reaction systems [9]. If the reactant particles are considered as a porous matrix containing liquid, mechanical energy may be transferred to the reactant as a result of

adiabatic compression of the liquid present, especially if it contains gas bubbles, and as a result of liquid flow through the pores. Temperatures and pressures in such a system have been estimated to rise to 500–700 $°C$ and 500–600 atm, respectively, i. e., well into the range for hydrothermal reaction to occur via material transport in the liquid state. N. Kosova et al. [10] determined that the molar ratio of CaO/SiO_2 in mixtures of $Ca(OH)_2$ and $SiO_2 \times 0.5H_2O$ is an important factor in the hydrothermal reaction mechanism.

The importance of the optimal water content for the hydrothermal reaction mechanism was verified for the $Mg(OH)_2$ and $SiO_2 \times nH_2O$, and $Mg(OH)_2$ and silica gel mixtures [11]. After grinding, the XRD pattern of the mixtures showed new broad peaks corresponding to a poorly crystalline layered magnesium silicate. By contrast, magnesium hydroxide and silica gel mixtures did not form any new crystalline composition but the intensity of the $Mg(OH)_2$ peaks decreased. FTIR data also confirmed the formation of a layered magnesium silicate. Direct evidence for the structural similarity of the mechanochemical reaction product and hydrothermal products was however scarce.

Solid state MAS-NMR is well known to be an invaluable technique for determining the structure of inorganic compounds [12]. Figure 1 shows the ^{29}Si MAS NMR spectra of the original silicic acid and the product after mechanical treatment, together with the same mixtures treated hydrothermally with a small excess of water. The NMR peaks can be assigned to the Q^2 (–84 ppm) and Q^3 (–91 ppm) units of magnesium silicate, which correspond to chain and layered structures. Since the Q^3 peak does not correspond precisely to the known crystalline magnesium silicates, it may be suggested that it arises from a poorly crystalline phase.

However, it is impossible to predict whether grinding with the optimal water content will necessarily result in a hydrothermal reaction. When silicic acid was ground with $Al(OH)_3$, no crystalline phase was detected [13]. Moreover, the grinding efficiency of gibbsite was reduced because of agglomeration of particles arising from the presence of the hydrous silicic acid. On the other hand, the rates of mechanoche-
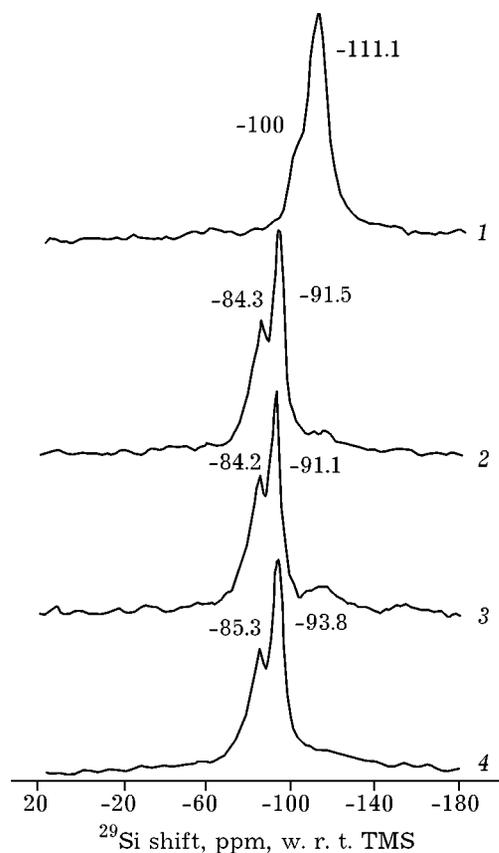
Fig. 1. ^{29}Si MAS NMR spectra of the starting materials and reaction products (after Temuujin *et al.* [11]): *1* – silicic acid (unground); *2* – Mg(OH)$_2$ + silicic acid (ground 20 h); *3* –MgO + silicic acid (ground 20 h); *4* – Mg(OH)$_2$ + silicic acid (hydrothermal).

mical reactions have been found to decrease in the order Al(OH)$_3$ > Ca(OH)$_2$ > Mg(OH)$_2$ [14]. Our result therefore appears to contradict the results of previous authors. These differences probably arise from differences in the raw materials (their silica source was fumed silica without excess water). Since magnesium hydroxide is a stronger base than aluminium hydroxide and silicic acid is a weak acid, the acid-base neutralization reaction occurs more efficiently in the former case. We believe that the possible reaction mechanism involves the release of excess water from the silicic acid which makes the surface of the magnesium hydroxide more alkaline. This should lead to the dissolution of silica at the contact points with precipitation of amorphous magnesium silicate. In the presence of water, the grinding system will create high temperatures and pressures, facilitating the nucleation of a layered magnesium silicate. Such reactions also occurred during the aging of

intimately mixed magnesium hydroxide and silicic acid [15].

Our observations do not necessarily suggest that the more hydrated forms of silica are more reactive, since precursor formation occurs more readily when a non-porous and less hydroxylated form of silica (fumed silica) was used [16]. Fumed silica particles have a size of several tens nanometers and because of the lack of porosity, fumed silica has no internal surface. Therefore, precursor formation occurs more readily between the silica surface and aluminium hydroxide. However, no crystalline phases were formed with aluminium hydroxide containing systems.

Mechanochemistry of aluminium hydroxides and the problem of "pentacoordinated" alumina

Mechanochemical effects in the various forms of aluminium hydroxides Al(OH)$_3$, g-AlOOH and g-Al$_2$O$_3$ have been studied in detail, revealing distortions in their long-range order [17–19]. The aim of this research was to study the thermal transformation of the ground aluminas to corundum. Grinding of gibbsite resulted in the formation of corundum at the temperature at least 400 °C lower than that for unground gibbsite [20] and about 200 °C lower in ground g-Al$_2$O$_3$ (O. Kirichenko *et al.* [21]). The transformation occurs without further heat treatment in ground boehmite [22]. One of the interesting features of ground aluminium hydroxide is appearance of the "pentacoordinated" alumina. As it is well known, aluminium hydroxide contains only octahedral Al. "Pentacoordinated" Al has previously been detected in mechanically treated hydroxyl-containing clay minerals such as kaolinite [23, 24], pyrophyllite [25], and ground gibbsite-silica gel mixtures [26] by ^{27}Al MAS NMR. This resonance at about 30 ppm in the ^{27}Al MAS NMR spectrum is often attributed to Al in five-fold coordination with oxygen [27] or alternatively to distorted tetrahedral sites in the vicinity of tricluster oxygen vacancies [28].

The interest in this resonance arises from the strong correlation between its presence and intensity and the homogeneity of the amorphous material, which in turn influences its crystallization temperature [29]. The same tech-
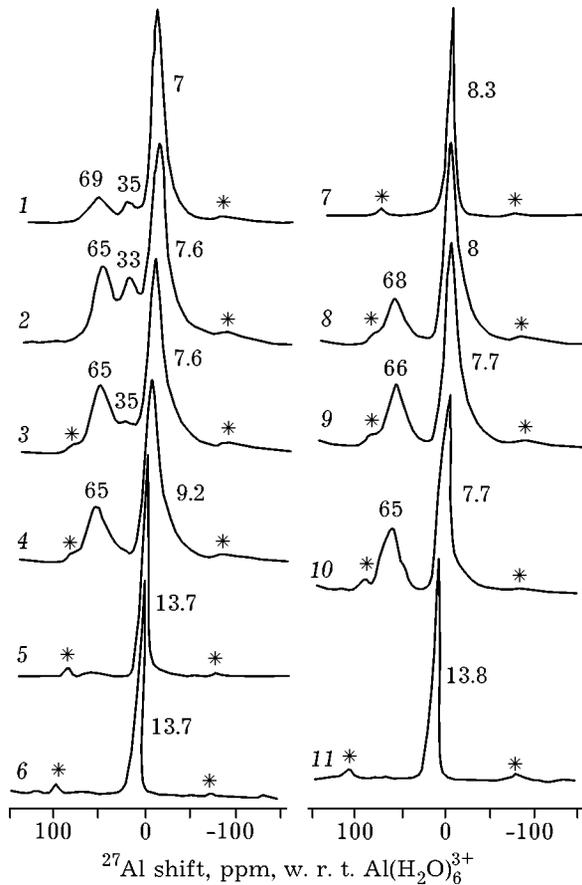
Fig. 2. 11.7 T ^{27}Al MAS NMR spectra of gibbsite heated for 15 mm at the indicated temperatures. After MacKenzie et al. [20]. Temperature, °C: 200 (1), 350 (2, 8), 700 (3), 800 (4, 9), 900–1000 (5), 1000–1200 (10), 1200 (6), 1350 (11), unheated (7); 1–6 – samples ground for 20 h, 7–11 – unground gibbsite.
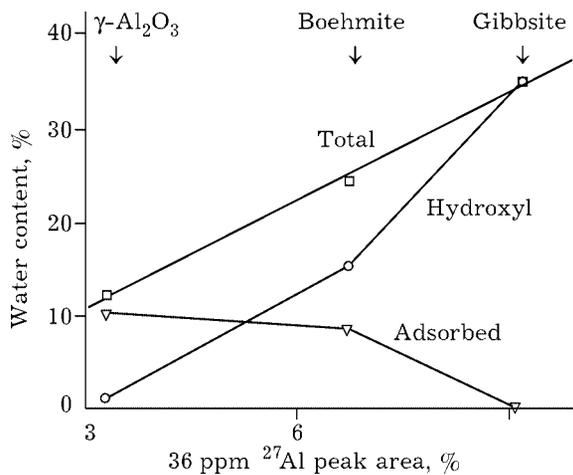

Fig. 3. Integrated area of the 36 ppm ^{27}Al MAS NMR peak area of aluminas as a function of their water contents. After K. MacKenzie et al. [32].

nique has revealed the appearance of "penta-coordinated" alumina in the ground gibbsite. The ^{27}Al MAS NMR spectra of unground and ground gibbsite heated to various temperatures are shown in Fig. 2. The unheated unground material (see Fig. 2, curve 7) shows a single octahedral resonance, but heating to just above the temperature of the endothermic water loss produces a new tetrahedral resonance at 68 ppm.

No "pentahedral" resonance was observed in this material. The ground gibbsite spectrum shows some similarity with r-Al$_2$O$_3$ [30], an XRD amorphous phase formed by the dehydration of gibbsite at 100–400 °C under reduced pressure [31] which contains 55 % octahedral Al, 20 % 34 ppm resonance and 25 % tetrahedral Al. In the present case, the 34 ppm peak shows less intensity, possibly due to the slower sample spinning speed (12 kHz) used in the present work.

The formation of "pentacoordinated" alumina was also observed in ground boehmite or g-alumina by K. MacKenzie et al. [32]. The hydroxyl contents of gibbsite and boehmite (with respect to Al$_2$O$_3$) are 34.6 and 15.0 wt. %, respectively, while the corresponding value for g-Al$_2$O$_3$ deduced from the TG results is 1.2 wt. %.

We have compared the peak area of the 36 ppm (pentacoordinated) resonance for the three different aluminas measured at 11.7 T and 12 kHz. The integrated intensities of all the three Al sites in the ground aluminas were plotted as a function of the hydroxyl water, adsorbed water and total water contents and are shown in Fig. 3.

From this relationship, the presence of hydroxyl water is seen to be a necessary and efficient condition for the formation of 36 ppm peak, which may arise from Al sites associated with and possibly stabilized by protons or structural water. This peak progressively decays to zero as the water is thermally removed.

THE ROLE OF THE "SOFT" MECHANOCHEMICAL REACTIONS IN CERAMIC PRECURSOR FORMATION
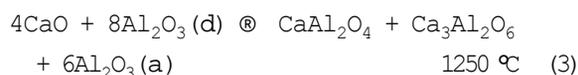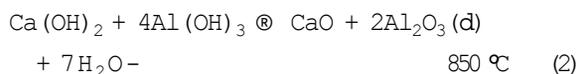
"Soft" mechanochemical synthesis is one of the interesting topics of mechanosynthesis. Detailed review papers have been published by M. Senna [3] and E. Avvakumov [4]. More recently, the effect of "soft" mechanochemical

reactions on the formation of ceramic precursors such as PZT [5], 0.9PMN-0.1PT [33], La_2SiO_5 [34], $CaAl_4O_7$ [35], $ZrSiO_4$ [36] and spinel ($MgAl_2O_4$) [37] have been reported. I will now show one example of a "soft" mechanochemical reaction.

The preparation of ceramics with low thermal expansion is one of research goals for the refractory ceramic industries, since failure due to thermal shock constitutes a major problem with many refractory ceramics. Recently, it was found that calcium dialuminate $CaAl_4O_7$, m.p. = 1750 °C) shows very low thermal expansion and can be used for refractory purposes [38]. The preparation of single-phase calcium dialuminate is complicated because the presence of other forms of calcium aluminate prior to formation of the dialuminate necessitates three firing steps at 1200, 1300 and 1450 °C [39]. We have prepared calcium dialuminate precursors by grinding $Al(OH)_3$ with $Ca(OH)_2$ or $CaCO_3$ [35]. Using different techniques we found that grinding forms a homogeneous precursor in which the constituents are intimately combined:

$$4Al(OH)_3 + Ca(OH)_2 \circledR CaO \times 2Al_2O_3 \times 7H_2O \quad (1)$$
$$\text{(amorphous)}$$

After heating at 850 °C, the ground mixture shows the major lines of $CaAl_4O_7$. Heating to 1050 °C completely transforms this sample into well-crystallised $CaAl_4O_7$ (Fig. 4). By contrast, the thermal reaction in the unground mixture follows the normal course of thermal decomposition of the reactants, which then undergo solid state reaction. The products of heating at 850 °C are CaO from the decomposition of $Ca(OH)_2$ and a mixture of transition aluminas (principally δ-alumina) from the decomposition of gibbsite. Heating at 1250 °C results in a mixture of α-alumina, $CaAl_2O_4$ and $Ca_3Al_2O_6$. These reactions may be written as:

$$Ca(OH)_2 + 4Al(OH)_3 \circledR CaO + 2Al_2O_3 (\delta)$$
$$+ 7H_2O - \qquad\qquad 850\text{ °C} \quad (2)$$

$$4CaO + 8Al_2O_3 (\delta) \circledR CaAl_2O_4 + Ca_3Al_2O_6$$
$$+ 6Al_2O_3 (\alpha) \qquad\qquad 1250\text{ °C} \quad (3)$$

By contrast with the ground mixture, no $CaAl_4O_7$ is formed in the unground sample even at 1250 °C, reflecting its considerably lower degree of homogeneity.
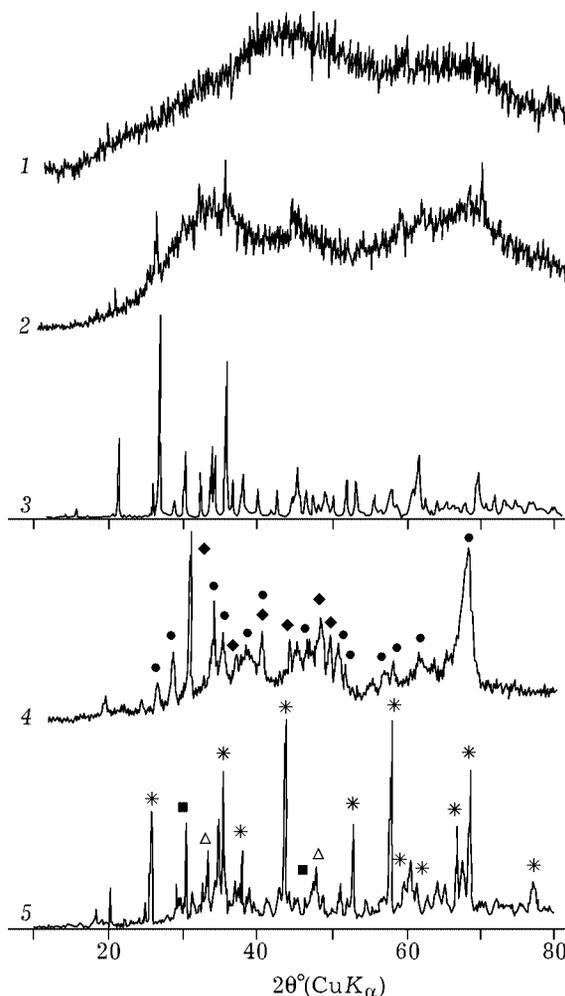

Fig. 4. XRD traces of ground and unground mixture, heated as indicated (after Teinuujin *et al.* [35]): *1* – ground, unheated; *2* – ground, 850 °C; *3* – ground, 1050 °C; *4* – unground, 850 °C; *5* – unground, 1250 °C. Key: ♦ CaO, ● δ-Al_2O_3, ✳ α~Al_2O_3, ■ $CaAl_2O_4$, △ $Ca_3Al_2O_6$, unmarked peaks correspond to $CaAl_4O_7$.

DIFFERENCES BETWEEN MECHANOCHEMICAL AND "SOFT" MECHANOCHEMICAL REACTIONS

The main difference between these reactions lies in the reaction rate. Mechanochemical reaction between two components requires high-energy milling. There are many examples, including the formation of magnesium aluminate spinel from an oxide mixture ground for 4 days and subsequently washed with acid to remove iron contamination from the milling media [40]. Another example is the formation of single-phase lead magnesium niobate, $Pb(Mg_{1/3}Nb_{2/3})O_3$ (PMN) from mixtures of PbO, MgO and Nb_2O_5 after high-energy shaker milling [41]. I. Wang *et al.* [41] have described the formation of nano-sized PMN powders without crystallization of

intermediate pyrochlore $Pb_3Nb_4O_{13}$ or $Pb_2Nb_2O_7$ phases. They suggested that nanocrystallites are formed in an amorphous oxide matrix by nucleation and subsequent growth mechanism. Although, they did not describe heterobridging bonding (HBB) between the oxide constituents, amorphous lead magnesium niobate apparently occurring in the mixtures contains Pb-O-Nb and Mg-O-Nb heterobridging bonds, potentially facilitating the nucleation of PMN from this amorphous precursor. This suggestion is supported by the research of these authors into the crystallization of perovskite lead zirconate titanate (PZT) from an amorphous lead zirconate titanate precursor [42].

On the other hand, solid-state reactions induced by the reactivity of newly exposed surfaces and stress relaxation have been postulated as the principal factor in the synthesis of new compounds during the grinding of powdered mixtures [43]. It therefore appears that two mechanisms exist for the formation of new compounds from oxide mixtures during the grinding:

– amorphization of the oxide constituents with the formation of amorphous precursors from which nanocrystallites nucleate and grow;

– crystallization of new compounds at the contact points of fresh surfaces between two particles under shear stress.

The reactions may also result in the complete formation of the desired ceramic phase, without further heat treatment. These results indicate that mechanochemical crystallization of new compounds requires high-energy milling, although "soft" mechanochemical reactions may not require very strong mechanical treatment. M. Senna [3] suggested that a relatively small shear stress would suffice to promote polarization and atomic exchange at the interparticle contact points, the solid-state surface reaction being accompanied by simultaneous dehydration of hydroxides. Such processes can involve the formation of heterobridging bonds between the oxide constituents, with the possible nucleation of new crystalline compounds from the heterobridging bonding in the amorphous mixture. T. Baek *et al.* [33] subjected mixtures of PbO, TiO_2, Nb_2O_5 and $Mg(OH)_2$ to mechanochemical treatment. They observed a minor amount of perovskite 0.9PMN-0.1PT phase and amorphous precursors after just 60min grinding. Although they did not grind the powder mixtures for more than 60 min, it is quite possible to increase the nucleation of perovskite by further treatment.

The advantages of "soft" mechanochemical reactions lie in their facilitation of complex formation between the oxide constituents. "Soft" mechanochemical syntheses are often stopped after precursor formation, but mechanosynthesis may also promote crystallization of the desired product.

These examples show that mechanochemical processing, especially "soft" mechanochemical reactions have considerable potential for the synthesis of ceramic precursors. However, this method is not often used in industrial production, possibly because of the large-sized equipment for mechanical activation, which is not always available to industrial companies. Most of the above examples were developed using laboratory scale mills. On the other hand, precursor formation by "soft" mechanochemical reaction does not necessarily require high-energy milling. This method could therefore find more extensive use by industrial plants in which good, continuously operating mills are available.

CONCLUSIONS

Precursor formation can readily be induced by moderate mechanical stress in mixtures containing water or hydroxyl groups. One of the interesting features of these "soft" mechanochemical reactions is the occurrence of hydrothermal-like reactions resulting in the crystallization of new compound from amorphous mixtures under hydrothermal conditions. One of the most promising prospects for "soft" mechanochemical reactions is in the preparation of desired crystalline compounds without further treatment.

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