Mechanochemical reaction at the interface between a metal plate and oxide powders

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A new geometry is proposed and explored for the investigation of mechanochemical reactions. Typical displacement reactions between an oxide (PbO, CuO, and WO$_3$) and Al as the reducing metal are studied, but instead of starting with a mixture of two powder reactants, Al is introduced in the form of a plate attached to the inside wall of the milling vial and only the oxide is milled in powder form. Consequently, the reaction takes place at the surface of the aluminium plate, where the microstructure can be investigated easily using SEM. The phase composition is followed by XRD. Of the three oxide components, the reaction is the fastest with PbO due to the intense ductile mixing at the interface. The current configuration can be utilized for the investigation of any mechanochemical or mechanical alloying process where at least one of the components can be prepared in the form of a ductile plate that is capable of withstanding the multiple impacts from the milling balls. © *2004 Kluwer Academic Publishers*

1. Introduction

Ball milling induces chemical reactions in reactive powder mixtures, providing the basis for the mechanochemical preparation of a variety of alloys, compounds, and composites, some of them amorphous or nanocrystalline [1–3]. Mechanochemical reactions are attractive because of their simplicity, flexibility, and the ability to prepare materials in the solid phase without solvents and at low temperature.
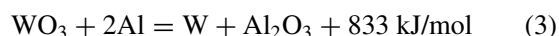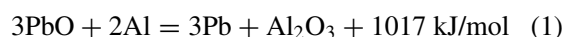
The details of how mechanical activation initiates and accelerates chemical reactions is the subject of intensive investigation. In contrast to the simplicity of their practical realisation, the theoretical description of ball milling-induced reactions is a difficult problem due to the complex combination of interrelated processes on several length and time scales [4, 5]. Although much empirical information has been collected, the microscopic mechanism of the process remains poorly understood. No general theory exists that could orient future investigations and the development of applications.

Ball milling is usually applied to powdered reactants, as they ensure large interface and consequently fast reaction kinetics. Fine powders are also convenient samples for the investigation of some important average properties—such as phase composition, thermal stability, and magnetic hysteresis [6, 7]. On the other hand, the use of powders complicates the investigation of the local reaction mechanism, as particles at different stages of the process are brought in contact stochastically. The local evolution of heat may turn a highly exothermic reaction into a self-sustaining thermal process, preventing further investigation of the effects of activation [8].

It is suggested that the microscopic mechanism of the reaction can be studied more efficiently, if the geometrical relationship between the reactants is better defined. In particular, instead of initiating the reaction between two powdered reactants, investigations are carried out with one of the reactants (a ductile metal) being in the form of a plate attached to the inner wall of the container and only the other component is milled as a powder. In this geometry, the reaction takes place at the surface of the metallic plate, rather than at various interfaces between the particles. The products form a coating layer over the metal plate that can be investigated easily by scanning electron microscopy (SEM) and X-ray diffraction (XRD).

The suggested "powder-plate" geometry was applied to displacement reactions between a 1-mm thick aluminum plate and the oxide powders PbO, CuO, and WO$_3$. The anticipated reactions are:

$$3PbO + 2Al = 3Pb + Al_2O_3 + 1017 \text{ kJ/mol} \quad (1)$$

$$3CuO + 2Al = 3Cu + Al_2O_3 + 1189 \text{ kJ/mol} \quad (2)$$

$$WO_3 + 2Al = W + Al_2O_3 + 833 \text{ kJ/mol} \quad (3)$$

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If both reactants were powders, ball milling would initiate mechanically induced self-sustaining reaction (MSR) in these systems [8, 9]. An MSR is not possible in the powder-plate geometry because of the much smaller interface area and the heat loss toward the thick metal plate. Consequently, the mechanical activation process is not interrupted by the ignition of MSR. The objective of this paper is to explore the utility of the controlled plate-powder geometry to the investigation of the microscopic mechanisms of reactions (1–3). The main experimental methods were XRD and SEM.

2. Experimental

The milling experiments were carried out using a SPEX 8000 Mixer Mill and a flat-ended hardened steel vial with 15 steel balls, 9.5 mm in diameter each. The Al plate was 99% pure and 1 mm in thickness. A rectangular piece of about 3×5 cm was bent into a cylinder and placed into the milling vial, followed by the balls and 30 mg of the powder component. Powders of WO_3 (99.0%), PbO (99.0%), and CuO (99.0%) were employed; all materials were obtained from Alfa Æsar. Milling was performed for 20 min with PbO and CuO and for 20 and 50 min with WO_3.

XRD measurements were carried out with a Philips X'Pert diffractometer in $\Theta-\Theta$ geometry, using Cu Kα radiation. The XRD lines were identified using the JCPDS data base.

The SEM investigations were performed on cross sections of the plates molded in epoxy, using a Jeol JSM-5600 instrument equipped with an Oxford Isis X-ray attachment. The samples were also inspected using a Nikon Optiphot-100 optical microscope.

3. Results and discussion

3.1. Macroscopic aspects of the process

In this experiments, the aluminum plate was placed against the cylindrical wall of the milling vial. Consequently, it was rarely hit head on by the milling balls. Instead, most collisions were at a small angle from the surface, providing more sheer and friction than compression. The oxide powder was delivered to the plate by the milling balls. At the beginning of the process, the powder is loose, but the balls can sweep together a few particles and press them into the surface. Later, the balls are coated with a layer of oxide particles and the collisions transfer the oxide particles from the surface of the balls to the Al plate, where it can mix into and react with the surface. The collisions can also remove material from the plate, including unreacted oxide, reaction products, even fragments of the Al plate itself. This dynamic transfer of material results in the roughening of the surface. After 20 min of milling, the peak to valley roughness is about 50 μm according to microscopy. The impacts of the balls also result in macroscopic deformation of the Al plate.

3.2. X-ray diffraction

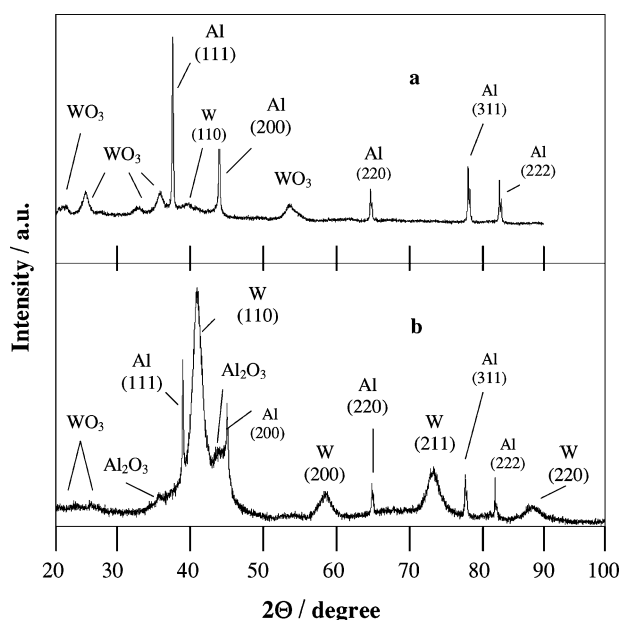The reaction between the Al plate and the oxide powder can be investigated by XRD (Figs 1 and 2). The patterns

Figure 1 XRD patterns of an Al plate milled with WO_3 for 20 min (a) and 50 min (b).
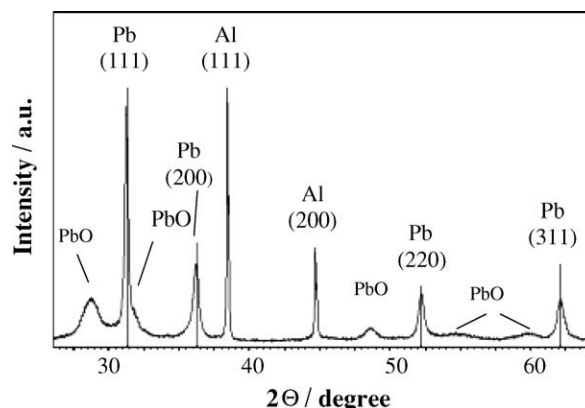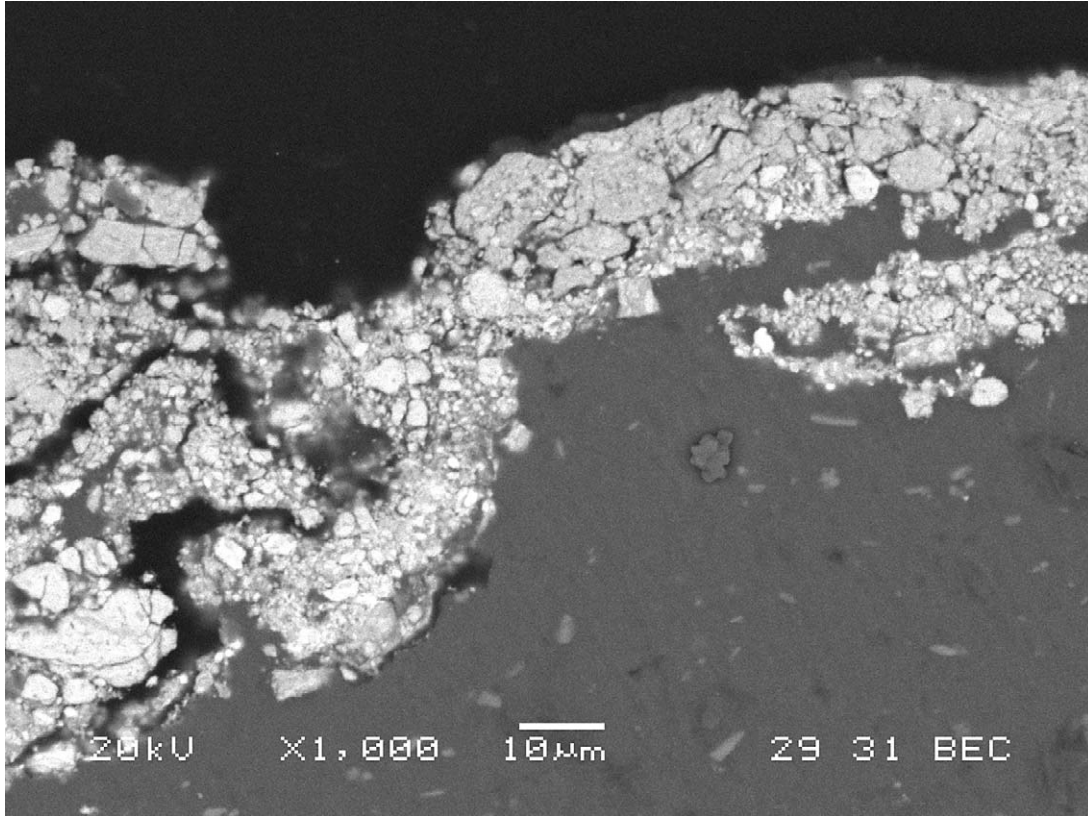

Figure 2 XRD pattern of an Al plate milled with PbO for 20 min.

reflect the deposition of the oxide powder onto the Al plate as well as its chemical interaction with the plate. Although XRD provides a clear qualitative picture, the quantitative interpretation of the intensity ratios is difficult due to the complicated nonuniform composition and morphology of the surface.

Fig. 1 shows XRD patterns of an Al plate milled with WO_3. After 20 min (Fig. 1a) the curve is dominated by the lines of the Al target. The relative intensity of the WO_3 lines is small, in spite of the large scattering amplitude of W, indicating that little oxide powder was deposited onto the Al plate and only a trace reacted with it chemically to form W metal. The situation is clearly different after 50 min of milling (Fig. 1b). The pattern is dominated by the lines of W metal, suggesting the delivery of more WO_3 and its quick reduction by the Al plate. Very small amounts of Al_2O_3 are visible due to its low crystallinity and low scattering amplitude. However, the lines of the Al plate are clearly present, probably from areas where the W-WO_3 coating was removed by a later impact of a milling ball. Similar results were obtained on Al plates milled with CuO powder.

The process is much faster when milling PbO powder with the Al plate (Fig. 2). The reason is probably the lower hardness of PbO and the low melting point of Pb. The reaction heats are quite similar, as shown by Equations 1 and 3. The lines of metallic Pb dominate and those of PbO are also clearly visible, suggesting efficient transport of the oxide powder to the Al plate by the milling balls, followed by chemical reaction with
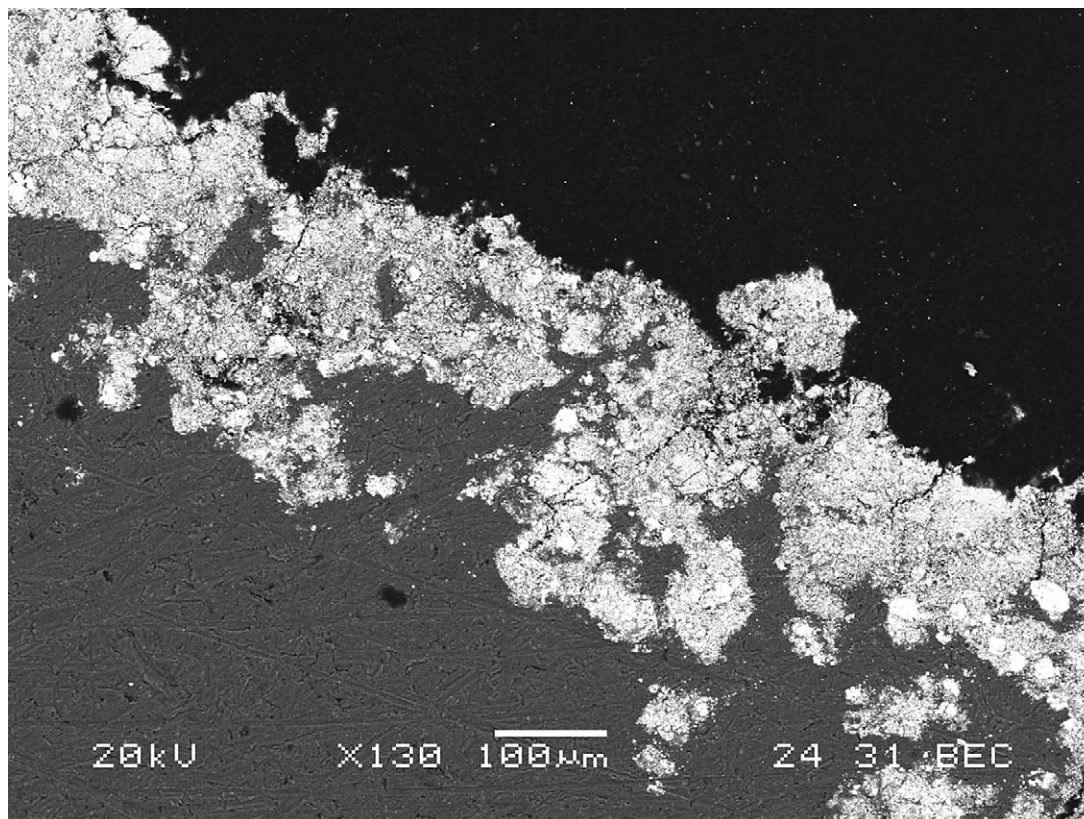

(a)
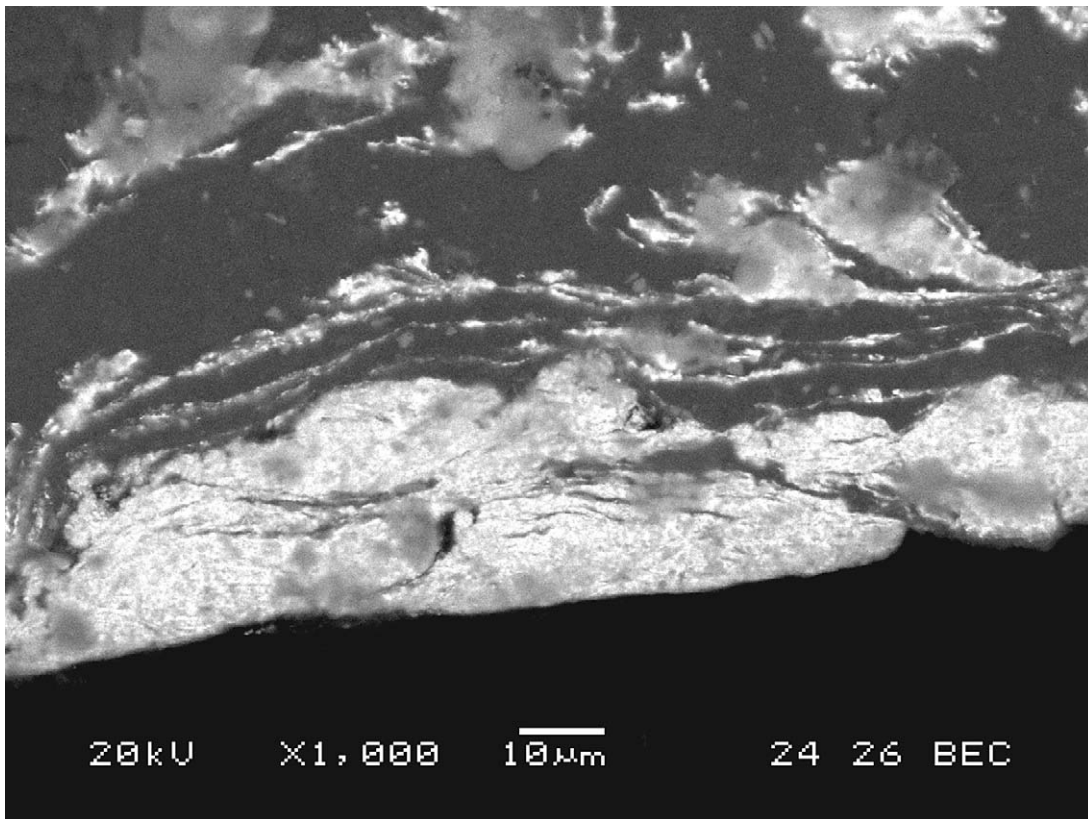
(b)

Figure 3 SEM backscattered electron image of the surface region of an Al plate milled with WO_3 (a) and PbO (b). The cross section was cut perpendicular to the surface of the plate.

the plate in most instances. The lines characteristic of the Al target are also present with significant intensity.

The roughness of the investigated surface, its chemical and morphological non-uniformity and the overlap between the lines from different phases preclude the detailed analysis of the line profiles and the separation of grain size and strain contributions to the line broadening. Nevertheless, it can be stated with reasonable

(a)
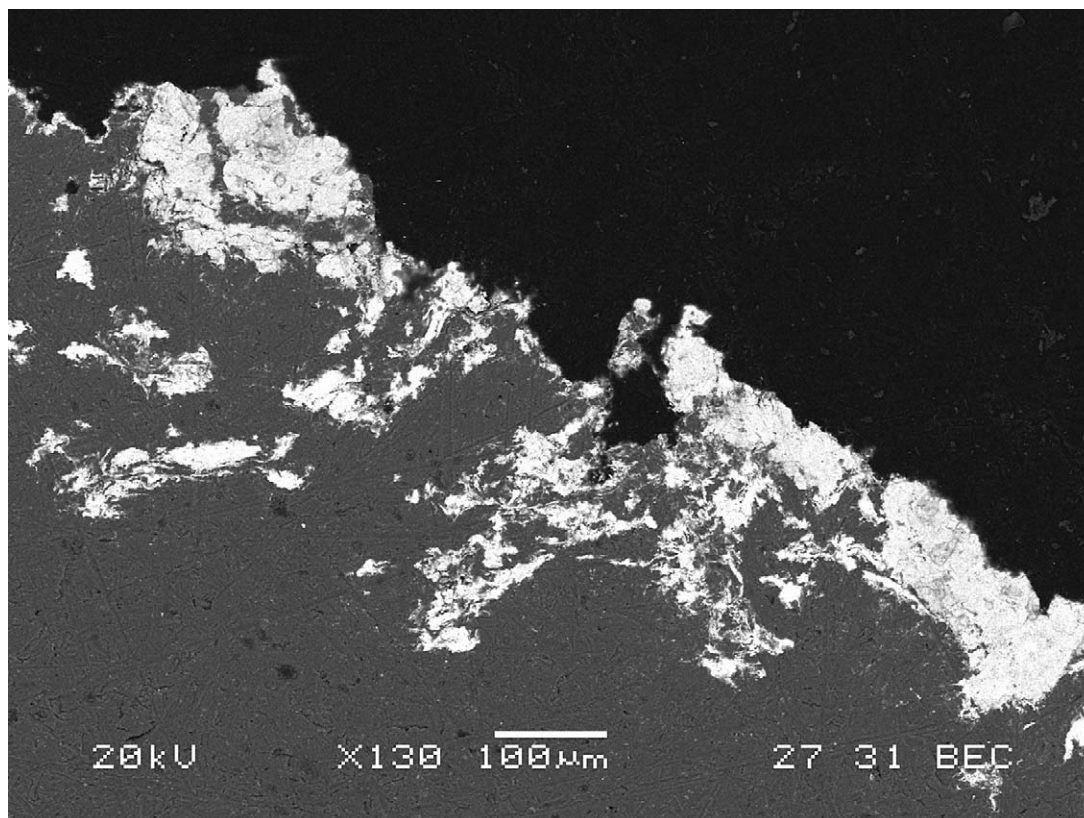
(b)

Figure 4 SEM backscattered electron image of the surface region of an Al plate milled with WO_3 (a) and PbO (b). The cross section was cut at an angle of $15°$ relative to the surface of the plate.

certainty that small grain size (about 6 nm) is the primary source of the line broadening in the case of W and lattice strain (about 0.3%) is the main contribution in the case of Pb.

3.3. Scanning electron microscopy

Although the macroscopic appearance of the "plate-powder" process described here is quite different from milling a mixture of powders, the elementary microscopic steps are probably very similar. Therefore, some conclusions derived from the morphological study of the plate-powder interface can be carried over to the conventional powder-powder interaction. This is especially useful, as the investigated reactions lead to MSR between powder reactants. Before ignition, only a rather undistinctive agglomerated powder can be seen by SEM and the morphology after the high temperature reaction contains no information about the mechanically activated state.

The surface of the Al plates has been investigated by SEM after milling with WO_3 (for 50 min) and with PbO powders (for 20 min). Fig. 3a and b compare the typical morphologies on perpendicular cross sections of the plates. The images were taken with backscattered electrons to emphasize contrast from compositional differences over details of the surface irregularities. Although the samples were coated with a thin layer of gold, some charging effects are visible at the more porous areas of the samples, especially in the case of PbO. In both samples, particles from the powder penetrated as deep as 50 μm into the surface of the Al plate. Moreover, the surface is quite nonuniform. The complexity of the structure suggests that the same area was hit by balls several times, depositing oxide powder, mixing it into the surface of the Al plate and initiating chemical reaction between the plate and the powder. Cracks develop and folding over pieces of the Al plate is evident. Matter is also removed from the surface occasionally, as suggested by the dent on the Al-WO_3 surface (Fig. 3a)

In spite of the similar reaction kinetics and the similar length scales of the morphologies, the WO_3 and PbO containing samples are very different. The WO_3 and the reduced W particles form agglomerates, they are rounded with sizes ranging from a few micrometers to well below 1 μm. The PbO and Pb particles are deformed into thin layers more easily (Fig. 3b), resembling features observed when milling a mixture of two ductile metals [1]. This is somewhat surprising as no flattening, folding, and cold welding of free particles is possible here, the morphology is developed by the repeated oblique collisions alone.

The same surfaces were also studied on cross sections cut at a sharp angle, so that the width of the region that is affected by the milling process is magnified about fourfold (Fig. 4a and b.) The advantage of this view is that a longer section of the surface can be viewed, without loosing much detail of the inner structure of the mixed volume. In the case of WO_3, the particles are rounded and this is reflected by the morphology correctly, independent of the direction of the cut relative to the surface (Fig. 4a). It is more difficult to interpret the structure in the case of PbO, as the layers clearly seen on a perpendicular cross section (Fig. 3b) are approximately parallel to the surface of the plate and this lamellar structure gets distorted when the sample is cut at an angle (Fig. 4b).

These results clearly show that milling can easily result in mixing to a depth of 50 μm, a distance comparable to the particle diameter in a typical fine powder. Therefore, thorough mixing on a size scale much smaller than the initial particle size can easily occur during ball milling of a mixture of powders. Also, the mixing process is very sensitive to the hardness of the components, agglomerates of rounded particles or layered structures can develop, similar to the case of milling ductile-ductile and ductile-brittle mixtures [1].

4. Conclusions

Although milled mixtures of powders lend themselves to the investigation of average macroscopic properties, it is difficult to study their microscopic details due to the random mixture of interfaces and the possibility of fast high-temperature reactions. In this study, one of the components (Al) was introduced in the form of a plate and only the other component (WO_3, PbO) was milled as a powder, using the collisions of the balls to both deliver the powder particles onto the plate and to initiate chemical interaction between the plate and the powder. This geometry lends itself to the detailed investigation of the local morphology.

The above method can be extended from the investigation of oxide-metal displacement reactions to other systems such as the formation of a carbide layer when milling graphite in the presence of a metal plate [10]. Similarly, sulfides can be prepared by milling sulfur in a container containing a plate of the metal component attached to the wall [11]. This arrangement may also lead to useful technologies for the mechanochemical preparation of coatings [12].

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