Mechanical activation of minerals – past, present and future?

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Abstract

Mechanical activation of materials, including minerals, has been an area of increasing interest in the past twenty years due to the unusual effects that can be obtained by extended milling. One apparent flaw in much of the research is the use of activation devices which are not available at the scale required for industrialization of production. A review of the effects of activation is made and a critical assessment of the requirements for commercialization of MA processes is made.

Key words : Mechanical Activation, Minerals, Materials

1.0 Introduction

Mechanical activation (MA) has been used for many thousands of years, one early example is the use of gold amalgam to gild artifacts in tombs of the Egyptian Pharoahs. The mercury in the amalgam was removed by rubbing to leave behind the gold, a form of mechanical dealloying. The Inca civilization manufactured articles containing 26-72% platinum, they did not have the technology to melt platinum (m.p. 1775°C) and could only have made such items by repeatedly hammering the metals together and then heating them.

The advent of gunpowder in China before 1350 and in Europe around 1500, resulted in the realization that the longer and more finely the components were ground the more rapidly the powder burned. This lead to the formation of greater pressures within the barrel thereby allowing projectile weapons to be used at longer ranges. The classic metallurgical textbook, de re Metallica by Agricola contains no evidence for mechanical activation.

In 1883, the first modern example of mechanical activation was described by Carey-Lee, adding mechanical energy to silver iodide resulted in it decomposing to silver and iodine. Fifty years later Tamman showed that grinding increased the rate of dissolution of metals and concluded that the accumulation of mechanical energy within the solid was responsible.

By 1970, MA was being used to disperse fine particles within metals resulting in composites unobtainable by conventional means. The use of MA on minerals was demonstrated in 1973 when chalcopyrite was shown to be substantially more soluble after MA. This was shortly followed by the first volume on "Tribochemistry" – the chemistry due to friction.

Since this volume there have been a number of non-english publication on the MA of minerals and most of the work reported was also unavailable in English. Consequently, MA remained a little known area of research until 1979 when the first English volume on MA of minerals was published. Since this time several other volumes have been published and the research into MA has widened. One reason for the increasing interest in MA is the resultant materials are often nanostructured and therefore have properties that are different from bulk materials.

This paper will now review what mechanical activation can actually achieve beyond crystallite size reduction or simple mixing of components. The examples are mostly taken from research concentrated on mineral systems.

2.0 What can MA actually do?

Extended grinding of the mineral ilmenite for up to 100 h in a laboratory mill was followed by leaching in strong hydrochloric acid. The graph below left shows the leaching rate normalized to the BET surface area, clearly, the longer the milling time the more rapid the dissolution. This increased dissolution has also been shown to occur in a range of other minerals.
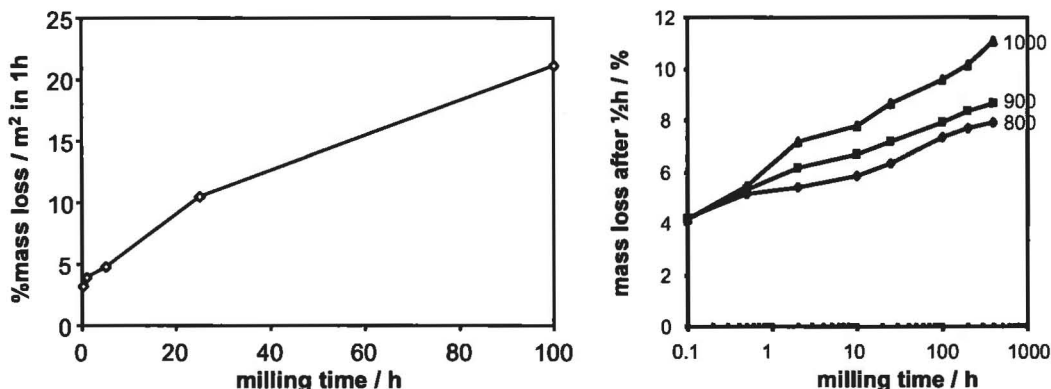

Figure 1. Grinding and milling of the mineral ilmenite

The same milled ilmenite was also heated at 800-1000°C in a hydrogen bearing atmosphere to induce reduction to Fe and TiO_2. The graph above right shows that increasing milling time results in increased reduction at all temperatures. Under otherwise identical conditions a near threefold increase in mass loss at 1000°C is evident compared to unmilled ilmenite.

For ilmenite, X-ray diffraction analysis indicates there was no phase change during grinding, but the crystallite size decreased as the lattice strain increased due to a slight compression of the unit cell. The combination of these factors resulted in a much more reactive surface than bulk ilmenite.

In the case of mixtures reactions can be induced to occur during milling, these can be either gradual with extent of reaction being a function of milling, or require a minimum amount of milling prior to a sudden, extremely rapid reaction. An example of the former type can be seen below left where $ZrSiO_4$ was milled with MgO to form $MgSiO_3$ and ZrO_2, clearly the reaction increases with milling time. The latter type is sometimes called a self-propagating high temperature synthesis (SHS) as the reaction involved is extremely exothermic after ignition and therefore as it heats itself up the reaction accelerates.

The X-ray diffraction traces below right show an example of SHS, the upper trace was the reactants milled for 12 h, the lower trace was for exactly the same materials milled for 13 h. There is a very dramatic change in the traces with the reactants being replaced by products. The narrow peaks of TiB_2 present can only indicate that the reaction occurred at high temperature – reactions at low temperature result in the much wider peaks which are indicative of low crystallite size.
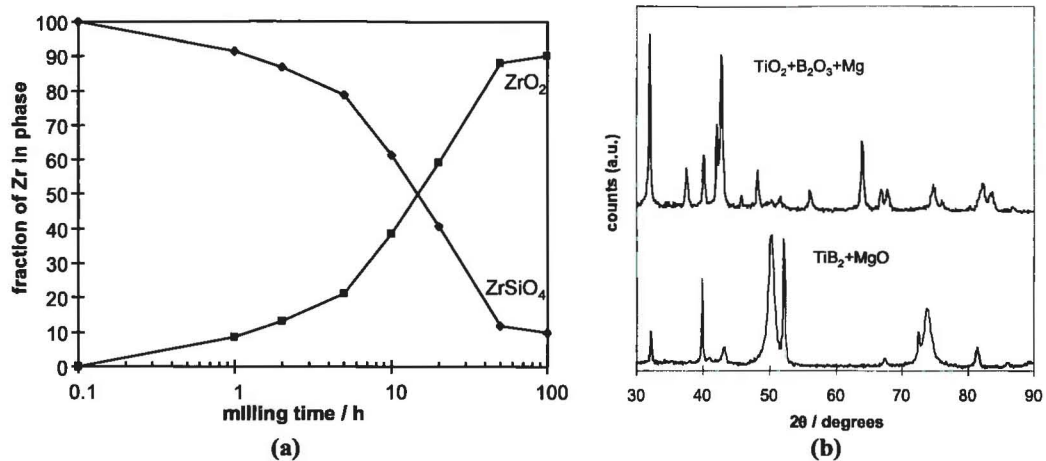
Figure 2. (a) Milling of $ZrSiO_4$ with MgO (b) The X-ray diffraction of TiB_2 at 12 h (upper trace) and 13 h (lower trace)

MA does not necessarily result in reaction during milling but the activated powder will have substantially different behaviour during subsequent processing. MA can result in a reaction occurring at either a lower temperature than a simple physical mixture or for the reaction to be more extensive than a less activated sample. One example is shown below left in which ilmenite has been milled with carbon for increasing times, the resultant powders were heated in a thermogravimetric analyzer with longer milling times showing a greater rate of reaction. This increase in rate of reaction can also lead to the formation of unusual phases due to separation of sequential reactions. This can be seen in the example below right where calcium tungstate was mixed with carbon and then either milled or simply mixed. Two features are evident in the traces, the reaction occurs at a much lower temperature in the milled sample, secondly, the milled sample clearly consists of two stages. The reaction sequence was determined to be

$$CaWO_4 => W_2C => WC$$

however, only in the milled samples was W_2C present as the major phase. Tungsten carbide, WC, is used for all hard material applications, however the hardness of W_2C is reportedly greater (3000 kg m^{-2}) than WC (2400 kg m^{-2}) but cannot be made by the conventional carburization of tungsten powder.
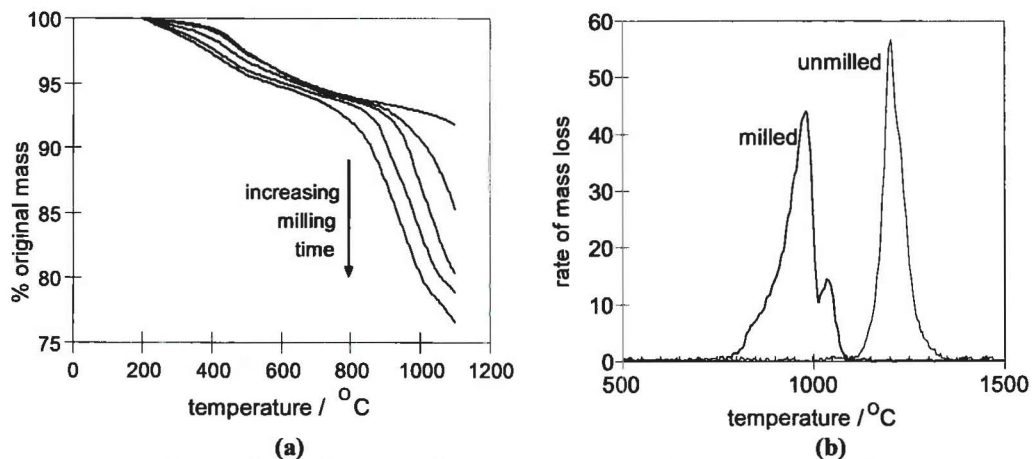

Figure 3. (a) Milling of ilmenite with carbon, (b) Milling of calcium tungstate with carbon

In spite of all of these advantages, there remain a number of things that MA cannot do. You cannot get a very narrow size distribution as this is statistically impossible due to the inability to remove particles of a specific size during processing. It is also very difficult to run a high purity system as the materials of milling device manufacture will abrade. Impurities can be reduced by ensuring the milling equipment is harder than the material being processed. Alternatively, impurities may need to be removed after activation. Despite a common misconception, MA cannot beat thermodynamics, the few examples where this appears to be the case are more likely due to large errors in the poorly determined free energies used in the calculations.

3.0 What is needed to commercialise MA?

Robert Cahn wrote "A common experience when exploring a field of research is to find that the community in question is split down the middle: the most common split is between scientists and engineers. When such a split develops, the two (or more) communities scarcely know of each other's existence, and they certainly don't learn from each other." One thing is clear. The people who design better mills for large-scale industrial usage and the materials scientists who research MA and nanocrystalline materials, pursue their respective careers separate from each other.

A simple example of this is of a researcher who developed a novel composite material with substantially enhanced wear properties compared with existing materials. The researcher decided to try to find a commercial partner to help them develop the material further. After finding a possible partner, the researcher was asked to supply 5 kg of the material so it could be evaluated before entering into a funding arrangement. Until this point the researcher had only produced a total of less than 1 kg of the material in the preceding six months. The researcher estimated the time required to produce 5 kg of composite using the same equipment as they had been using all along as around three months. The industrial partner then withdrew.

To progress MA on a large scale the needs of industry have to be considered. The primary consideration is scale, how many lab scale mills are required to produce a minimum 10 tonnes per annum? In reality, a much large scale of production is essential, for minerals a bulk processing capacity of >5000tpa would be the minimum. It is also vital to minimize the energy costs of MA, the simplest method is to minimise the grind time. It is important to realize that milling energy increases exponentially as the particle size get smaller. In minerals operations, the typical residence time for size reduction is ~20mins. The process has to have some advantages over current processes, such as a simpler route, fewer or less expensive reagents, reduced overall environmental impact and / or a more valuable product. Industry is intrinsically conservative and tends to avoid new processes, especially where a whole new production facility is required. Most industries want to be the first with proven technologies but do not wish to prove it themselves.

There are also equipment limitations, most notably that laboratory scale mills do not have equivalent mills available at a production scale. Additionally, few industrial mills can run controlled atmospheres, let alone atmospheres much above ambient unless they are batch processes. Laboratory scale mills will give little clue as to the true energy cost of a process. Researchers, usually also have little concept of the difficulties of scale up of a physical process.

The table below shows the potential of common laboratory type mills for use in large scale operations. Of these, only the stirred mill is used industrially for grinding below 10□m.

Mill type	Feasibility of large scale operation
Planetary	Maybe, forces too high, not continuous, 1tph Russian prototype
Tumbling ball	Yes, commonly in use, biggest 20MW, 2000 tph, low energy efficiency
Stirred ball	Yes, in use in both vertical and horizontal forms
Spex	No, lateral forces too high, not continuous
Vibratory	Yes, small size 5tph for size reduction, vertical ball motion

Stirred mills can be either vertical or horizontally oriented. Vertical stirred mills (tower mills, Vertimills etc) such as are used as pigment regrind mills and were used for concentrate regrinding at Stawell and Macraes gold mines. Commercial scale examples are available from several manufacturers. Horizontal mills are used extensively for fine grinding, the Isamill is a horizontal bead mill with ~40 installations with motor power of up to 3MW. There are twenty 1MW units in operation at Xstrata's George Fisher Mine to regrind finely dispersed PbS/ZnS ore to <7□m for flotation. Another unit is in operation at the Gidji roaster to regrind calcine to <5□m to liberate gold for cyanidation. Unusually, Netzsch offers a laboratory scale Isamill for which there is a clearly defined scale up to the 1MW units.

Some plants already have to grind extremely finely either to get a viable recovery of metal(s) during subsequent processing or to produce an extremely fine product (e.g. cement). Since we are putting in the energy to create a larger surface area and/or an activated mineral, why not add something during the grinding which will enhance the overall process. For example, can we grind in a controlled atmosphere? It has been shown that cement ground in CO_2 is slower setting and stronger than ground in air and that nickel sulphide wet ground in O_2 atmosphere showed 30% Ni solubility after milling. This leads to the proposition of grinding wet using leach solution? Preliminary work on copper sulphides indicate high extents of dissolution are possible, a nickel sulphide concentrate ground in a leach solution gave 40%Ni dissolution during milling + 20% more after.

4.0 Conclusions

Mechanical activation has a history stretching back to the ancient Egyptians. As a technique, it has only really been seriously studied in recent years due to the explosion of interest in nanomaterials. There are a number of things that MA can achieve by converting physical energy into chemical potential energy. Amongst these are increased dissolution, increased reaction rates and induction of reactions at reduced temperatures.

To use MA on a large scale requires scientists and engineers to collaborate to design MA devices capable of large scale operation. Some potentially useful devices are already produced but are not optimized for MA. If a large scale device capable of efficient MA is available, then MA may well play a role in the future of materials and minerals science.