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PROCESS MODELING OF THE MECHANICS OF MECHANICAL ALLOYING

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Introduction

Readers of this overview set will appreciate the versatility and robustness of mechanical alloying (MA). MA can be used to synthesize dispersion strengthened superalloys, nanocrystalline structures, intermetallics, and ceramics. It accomplishes this through the myriad events which transpire when powder particles are milled in high energy mills. Powder particles, trapped between colliding workpieces, are subjected to deformation, to cold welding and to fracture. And they also may engage in chemical reactions.

It would be of value to have an approximate idea of the frequencies of fragmentation and cold-welding, as these control particle size and alloying kinetics. Clearly, these events are functions of the frequency of "effective" collisions the powders experience and the deformation they are subjected to during each such collision. Knowledge of these parameters offers the possibility of developing models having predictive capabilities. This article attempts to summarize efforts at modeling the "mechanics" of MA. Successful modeling of this facet of MA is necessary precursor for modeling "chemical" effects that take place in MA; the issue is addressed near the article end.

It is important to appreciate what can be expected of even the most successful efforts of this kind. "Absolute" predictions are unlikely; this is exacerbated in the case of MA by its inherently stochastic nature. In addition, models require input "data"; material properties (often not known to precision, particularly at the high strain levels to which powder is often subjected during MA) and process characteristics (collision frequency and velocity, also seldomly known *a priori*). Thus, realistic goals of process modeling are to correctly predict general trends, and perhaps even to predict resulting properties/dimensions within an order of magnitude. The benefits of successful models lie not in their abilities to predict outcomes, but in that they help to identify critical process and material variables, and reduce the amount of testing needed for process optimization.

We have (somewhat arbitrarily) divided MA modeling into two categories; local modeling and global modeling. Local modeling considers a "typical" collision taking place in a specific device with stipulated process characteristics; impact velocity and frequency, media size and charge ratio (CR = grinding media mass/powder mass). Determination of the extent to which powder particles deform, and the frequency with which they cold-weld and fracture, in a single collision is sought. These events depend on mill charac-

teristics and powder material properties (hardness, fracture toughness etc.). During a single collision, and as a result of deformation, fracture and cold-welding, powder hardness, size and shape are altered. Thus a temporal description of MA requires incorporation of local modeling into a computational scheme.

Aspects of global modeling are important to render local modeling technologically useful. Such aspects include media impact frequency, angle, and velocity. Many impacts (ball sliding in an attritor, glancing impacts in a SPEX mill) are ineffective for achieving significant powder deformation, fracture or cold-welding. Global modeling seeks to specify the frequency of *effective* media impacts (much less than the actual impact frequency) and the corresponding velocity in a specific device. In addition, global modeling considers other heterogeneities associated with milling; e.g. powder segregation in an attritor.

Local Modeling

Maurice and Courtney (MC) [1] were the first to attempt to model a collision involving powder entrapped between grinding media. This treatment has been superseded by a more refined one, but it is worthwhile to briefly review the initial treatment for it contains much of the essential mechanics of MA. MC viewed a collision between grinding balls coated with powder as similar to a Hertzian collision between uncoated balls. They reasoned that the powder coating only mildly perturbs such a collision; that is, the work performed on the powder during impact is much less than the pre-collision media kinetic energy.

The powder "collision volume" is a cylinder, having a radius equal to the Hertz radius, the same contact radius found in a collision absent a powder coating on the ball. The Hertz radius scales with the grinding media radius and also varies as $v^{0.4}$ where v is the impact velocity. The assumed contact radius is a maximum one; i.e., if the powder work involved in a collision is comparable to the pre-collision kinetic energy, less of the energy goes into elastic deformation of the colliding balls and this is manifested by a reduced contact radius. The collision volume also scales with the cylinder height, h. MC estimated h using a simple geometrical model and found h to vary with CR^{-1} (i.e., h increases linearly with powder charge). Their calculations suggested the cylinder height is typically on the order of 10^{-4}m, a value consistent with previous empirical estimates of powder coating thickness, and borne out by simple experiment.

Since the Hertz radius is much less than the grinding media radius, the collision is analogous to upsetting. The powder strain per collision is calculated by considering the charge to be compressed for a period equal to half the collision time; the latter also estimated as the collision duration absent powder. Denoting this time as 2τ, the strain per collision (ε) equals $v\tau/2h$ (for the usual case where $v\tau << 2h$). In an extension of this model [2], required processing times (t_p) were estimated on the assumption that t_p is linked to a critical amount of total powder deformation. If this strain is E, then E/ε is the number of effective collisions needed for alloying. The time between collisions varies as v^{-1}. In addition, only a certain fraction of the powder "associated" with an individual grinding ball is impacted in a single collision. Taking these factors into account, t_p is found to vary with $v^{-2.6}$ (when $v\tau/2h << 1$).

There have been other simple treatments of this nature. Benjamin [3] modeled a single collision based on the material response of the powder, which was treated as one or more particles of 100μm height and diameter. His calculated collision times are comparable to those of [1]. Bhattacharya and Artz (BA) [4] followed an alternate approach, modeling the response of a porous compact (using a configuration similar to the more sophisticated MC model described below). BA predict the change in powder dislocation density as a function of time and milling intensity.

The models described above treat powder deformation, and not powder fragmentation and coalescence. Moreover, these "snapshots" of a single collision shed little light on the temporal evolution of powder during MA. Maurice and Courtney considered such factors in their later analysis of the process.

First, a more serious treatment of the mechanics of a single collision is made [5]. The material response to the imposed deformation imparted to the powder by the colliding balls is considered. The maximum

stress is along a line contacting the ball centers. When the stress attains the powder yield stress, powder plastic deformation commences at the contact point and then spreads radially outward. The analysis defines a "plastic contact zone" radius (which does not deviate significantly from the Hertz radius). While the average strain estimated by this method does not differ substantially from the estimated via the simpler model, the more sophisticated method does incorporate the effects of work-hardening and hence processing time. In addition, the treatment enables the tracking of the behavior of more than one species.

Second, cold-welding and fragmentation criteria are developed. The cold-welding criteria are based on previous treatments of the phenomena. In effect, the particle surfaces make metal-metal contact over a fraction of the mating area between them. If the resulting bond is sufficient to withstand the separation force associated with load release, a cold-weld is formed. The fracture criteria stipulate a critical fracture initiation strain and a crack propagation criterion based on the J integral approach. Powder shape can also be determined (shape changes during a collision due to deformation, fracture and cold-welding).

The deformation, fracture and cold-welding criteria are incorporated into a computational scheme from which particle size, shape, hardness and microstructural scale are predicted as a function of process time [6]. The scheme predicts the several stages of the MA process described originally by Benjamin [7]; particle flattening, cold-welding dominance, equiaxed particle formation and an eventual "pseudosteady" state. Predicted particle sizes follow this scenario and are in reasonable accord with measured sizes (Fig. 1). It is of interest that better than order-of-magnitude agreement between observations and predictions is found, particularly since "guesses" with respect to collision velocity and frequency had to be made and macroscopic material properties (perhaps not pertinent to microscopic deformation/fracture) were used in the computation. One model deficiency is that it apparently underestimates the rate at which the powder charge is deformed.

Since predicted and empirical trends are in agreement, predictive capabilities are possible by use of empirical parameters to appropriately "adjust" the model. Beyond that, it can be used to investigate the effect of process variables in an approximately realistic way. We have used it so to investigate how collision velocity and initial material properties should affect process time (Fig. 2). In this case, process time

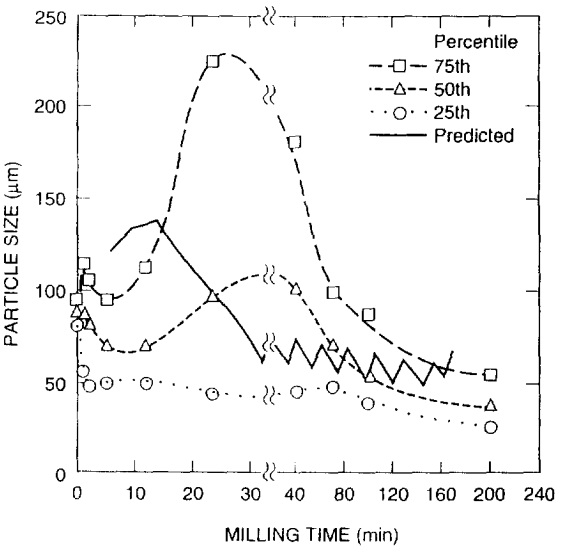

Figure 1. Measured [8] and predicted powder particle sizes for SPEX mill processed Fe-Cr alloys. The model predicts a slightly larger size than the median size measured. And the model predicts the maximum size should be found after 12 min of processing whereas it is observed after 30 min.

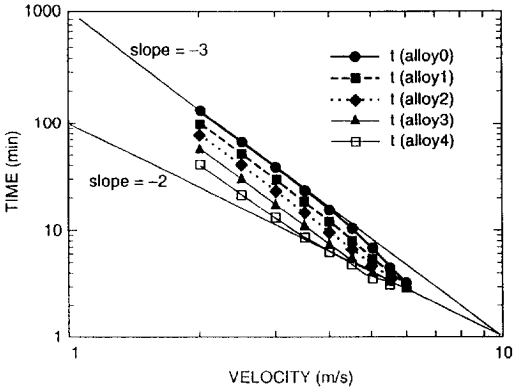

Figure 2. Time required to alloy powders as a function of collision velocity. The different alloys represent materials with different initial material properties: alloy 0 is composed of elements with the most disparate properties; alloy 4 with the least.

is the time needed to blend elemental powders into alloy particles. The properties of the constituents were varied systematically; i.e., for alloy 0 of Fig. 2, the starting elemental hardnesses differed by almost a factor of 3, their fracture initiations strains by about 30% and their fracture toughnesses by about 10%. For the alloy sequence 1–4, the properties of the constituents are made increasingly similar; e.g., for the alloy 4, the starting hardnesses differ by only 20%, the fracture initiation strains by 7% and the fracture toughnesses by 2%. As expected, the lower the collision velocity or the greater the differences in starting properties, the longer the process time. Two lines corresponding to process time varying as v^{-3} or v^{-2} are drawn in Fig. 2. Most of the "data" are intermediate to these limits; recall that the initial MA model predicted process time to vary with $v^{-2.6}$.

Global Modeling

Global modeling attempts to describe the motions and distributions of media and powder during milling. While device specific, the findings of global modeling impact local modeling. Even single impact models are based upon an assumed form of media-powder interaction. The computational scheme described above tacitly assumes only a certain fraction of media collisions is effective in MA, and thus the velocity and frequency used in the simulations are those appropriate to such collisions. Successful coupling of local and global modeling is required to establish useful predictive capabilities.

Empirical studies often involve observation, photographic recording and analysis of media action in a transparent mill (Davis et al [9], Rydin et al [10], McCormick et al [11], Henley [12]). Courtney and Maurice physically modeled a SPEX mill [2]; their predictions (for a specific vial geometry) on the distribution of impact angles and collision energies are shown in Figs. 3 along with the impact angle distribution observed by Davis et al and the energy distribution deduced from the Davis et al results. It is clear that most ball-ball collisions are glancing ones which do not result in appreciable kinetic energy loss. Conversely, only a small fraction of collisions are near head-on. If these types of collisions are most responsible for MA, the time between them is much greater than the time between the average collision. Thus a SPEX mill is inefficient, even though the media velocities (estimated as ca. 5 m/s) in the mill are relatively high.

An attritor, a lower energy device, is inefficient both in terms of the relative number of impacts effecting MA and because the distribution of powder within the mill is heterogenous. Rydin et al found that

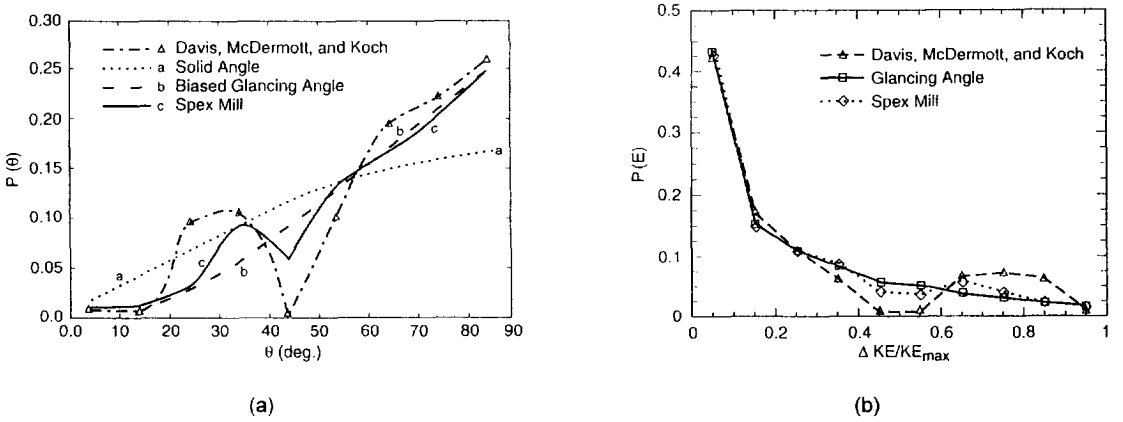

Figure 3. (a) Distribution in frequency of impact angles in a SPEX mill. The experimental distribution of impact angles (Davis et al) is compared with ones calculated [2] for glancing impacts in a SPEX mill (ball-ball collisions) and for collisions between ball and the vial walls and ends (curve denoted as SPEX mill). (b) Comparable distribution in kinetic energy loss per collision for inelastic balls with a coefficient of restitution of 0.7 (as measured by Davis et al).

the vast majority of interactions between balls is of a sliding (glancing) nature. Head-on collisions take place primarily in the attritor core where little powder is present; instead powder segregates to the outer edge of the attritor bottom where the "impact velocity" is next to nil and the impact frequency is low.

There have been several noteworthy efforts to globally model a planetary ball mill (PBM). Abdellaou and Gaffet [13] find that in a PBM containing one ball, collision energy is almost a parabolic function of plate rotational velocity (as expected) but is much less sensitive to vial rotational velocity. Analogously, collision frequency increases about linearly with plate velocity, but is less sensitive to vial velocity. Details of the relationships depend on the specific PBM geometry (e.g., the relative radii of the plate and the vial). Burgio et al [14] treated a PBM somewhat similarly, but considered ball-ball interactions. They deduce that with the use of additional balls the energy per collision is reduced by a factor which is essentially the fraction of vial space occupied by the balls. LeBrum et al [15] combined theoretical and empirical methods and deduced that there are three modes of milling in a PBM (impact, friction-impact and friction), depending upon the ratio of the vial and plate rotational velocities. They conclude that in a PBM, MA should be described in terms of attrition and wear, not impact. (If so, then a PBM and an attritor have some similarities.) McCormick et al [11] examined the effect of ball slippage (relative motion between the balls and the vial wall). They define a slip factor (f_s) which ranges from 0 (when the balls and the vial have the same rotational velocity) to 1 (when the balls are dormant). For the mill they used, $f_s = 0.8$. This results in ball tumbling, rather than cascading, and leads to a reduction in collision energy; by about 1/3 when f_s increases from 0 to 0.8.

MA is also conducted in horizontal rotary mills. For such a mill, Henley [12] has found that, in distinction to conventional views of such mills, balls circulate parallel to the mill central axis as well as about this axis. This considerably enhances ball circulation.

These studies indicate the difficulties in obtaining appropriate values of process parameters for use in local modeling, as well as the necessity of linking global to local modeling to make the latter of most use.

Synthesis Modeling

MA is used widely for materials synthesis. It would be useful to extend ideas derived from mechanical modeling of MA to synthesis. Although daunting, such an effort has potential to develop some funda-

mental understanding of phenomena which until now have been considered only in an *ad hoc*, empirical way.

There have been several attempts at correlating synthesis with process parameters. Burgio et al [14] and Gaffet [16] correlated structures of milled Ni-Zr and Fe-Zr powders to milling parameters. Processing diagrams, having axes of collision energy (or rotational velocity) and frequency (or power), were constructed and areas within the diagrams correlate to different resulting structures; e.g., amorphous, nanocrystalline, intermetallic. Schaffer and McCormick [17–19] correlated the kinetics of a number of redox reactions with various milling parameters (CR, ball size, impact number). In addition, they relate milling conditions to the occurrence of spontaneous combustion. Kosmac et al [20] analyzed the kinetics of Ni_3S_2 synthesis in a SPEX mill using a variant of the MC local model. Effects of mill atmosphere and initial Ni powder hardness on kinetics could be semi-quantitatively explained with the model.

Diffusion taking place in MA can be qualitatively described . In Fig. 4 the interlamellar spacing (l) of two malleable constituents is sketched vs. process time. Decreases in l occur at intervals τ_c (the time between effective impacts). During impact the powder is temporarily heated (over the impact time, τ_1) and cooled (over τ_2; τ_1 and t_2 are estimated $<< \tau_c$). Alloying (over a distance x_D) is assumed to take place during each temperature excursion, and is considered complete when the accumulated diffusion distance equals the interlamellar spacing. The scheme predicts an acceleration in alloying kinetics with milling time, as has been observed in Ni_3S_2 synthesis and in alloying of Si-Ge (although the microstructure of milled Si-Ge is not lamellar). The idea has been developed semiquantitatively [21]. The time to alloy an elemental mixture depends upon the several times described above, the strain per effective collision, the initial interlamellar spacing (which can be taken as the initial particle size), the "equilibrium" concentration (e.g., = 0.5 for a 50 at.% mixture of completely soluble elements) and the average diffusion coefficient during the heating interval. The approach could be extended to other types of synthesis; e.g., intermetallic formation could be approached in the manner that Kosmac et al [20] used for Ni_3S_2 synthesis.

Criteria for self-sustaining reactions might be developed. These occur when the exothermic heat generated per unit volume is sufficient to sustain reaction completion. Self-sustaining reactions ought to take place when reaction kinetics are inherently slow. That is, if a reaction product is formed early on during processing, the amount of interfacial reaction area per unit volume developed by successive collisions is reduced relative to that which would form if no early reaction took place. Thus, for self-sustaining reaction to occur the required diffusion distance (l, Fig. 4) must decrease relatively more rapidly than the accomplished diffusion distance (x_D) increases.

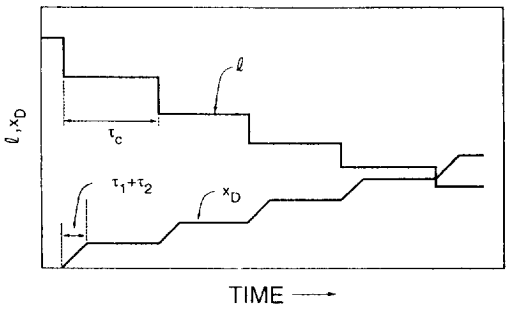

Figure 4. During milling of two different elements the interlamellar spacing (l) within a particle decreases with each effective impact. During the associated thermal excursion a certain amount of diffusion takes place over the distance x_D. Alloying is considered complete when the interlamellar and the diffusion distances are equal.

These ideas are difficult to implement. Available kinetic data are sparse. In addition, the often nanocrystalline nature of milled powders suggests their diffusivities are likely to be quite different from bulk diffusivities. And the diffusion coefficient is averaged over time and temperature and must also take into account exothermic heat. (Bharracharya and Arzt [4] have attempted to incorporate factors like this in a recent treatment.) Thus, initial attempts at modeling synthesis are likely to be even more qualitative than are MA mechanical models. On the other hand, synthesis modeling also offers the possibility of more clearly delineating salient material and process variables.

Summary

We have tried to provide an overview of recent efforts at modeling mechanical aspects of MA. Predictions emanating from models and their computational implementations are qualitatively accurate. Empirical refinement and model improvements may make them more useful for predictive use. In closing, it should be reemphasized that since modeling of complex processes like MA is a "hazardous" venture, the most that can be reasonably hoped for from such efforts is identification of trends imparted by changes in material and process variables, and order-of-magnitude estimates of alloying kinetics, powder size, morphology, microstructural scale and properties.

Acknowledgments

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