Monte Carlo Simulations of Nano-Powders from Mechanical Milling

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ABSTRACT

In this study, we performed Monte Carlo simulations to model the nano-structure of the powder undergoing mechanical-milling processes as a function of milling time, milling intensity and milling frequency. Under the framework of the kinetic Ising model, the Monte Carlo simulation was performed on a square lattice. Based on the equipartition of energy theorem, the kinetic energy being obtained during the milling process gives rise to both mechanical-shearing work and the thermal energy which increases the diffusivity of atoms in the powder. The process of these actions determines the size of the powder. During the simulation, the size of the biggest powder at a particular milling time was recorded to investigate how parameters of the mechanical milling affect the powder size. From our results, it is found that the mechanical milling reduces the size of the powder, but the diffusivity caused by thermal energy (at low-enough temperatures) grows the powder up as the time passes by. When both the milling and diffusing were taken in action, the powder size was found to reduce sharply at the early milling stage and then slightly fluctuated around its mean size. Based on this phenomenon, it is clear that the powder size is controllable if a right set of milling parameters is chosen. As a result, the study can be concluded to successfully model the mechanical-milling method to obtain powders at nano-scale.

Key words: Nanostructure, Mechanical milling, Monte Carlo, Ising model, Kawasaki algorithm

INTRODUCTION

Being simple but functional, the mechanical milling is a sophisticated technique to synthesize powders in a non-equilibrium (dynamic) phase. Particularly, the mechanical activation can mix the immiscible elements even the considered system is currently in its thermodynamically-unstable state. This is from the fact that, during the milling process, the non-equilibrium phase is maintained as the effect of fracture, cold-welding and deformation of powders which allows the non-equilibrium phase to become dynamically-stable. As a result, some powders can be synthesized by the mechanical activation even at room temperature which offers another pathway to ceramics processing, besides the conventional solid-state reaction of mixed oxides. Furthermore, the mechanical activation can refine the powder into nano-scale structure to suit various applications (Jiang et al., 1997; Jiang et al., 1999; Tan, et al., 2004; Yadav, et al., 2004). This offers the possibility of synthesizing nano-composite ceramics by adjusting the temperature, milling time and the milling intensity. Consequently, the mechanical milling is of a great interest since nano-composite materials can strengthen the material hardness (Hellmig and Ferkel, 1999), and enhances the activity of material processing as well as lowers the sintering temperature (Xue et al., 1999; Wang et al., 2000). Therefore, the undesired pyrochlore phases which always occur in the conventional solid-state reaction can be minimized by the mechanical activation during the processing of relaxor ferroelectric which boosts up the dielectric properties in ferroelectric materials (Wang et al., 1999; Xue et al., 1999b).

However, the explanation underlying the mechanism of this mechanical milling is far from being well established. This is due to the complexity of the microstructure undergoing the competition between the mechanical shearing and the thermal diffusing during the milling process. For examples, fracturing and rewelding of grains during the milling process are sometimes followed by the transient phase transformations of different stage of milling, and always lead to lattice imperfections (microstructure parameters) of different kinds (Manik and Pradhan, 2004). Then, the general description of how temperature at collision points and the rate of shearing affect the powder size during the milling is not available in details.

On the other hand, there are a number of theoretical studies concentrating to explain such a phenomenon. However, most of them usually assume a long-time period of energy exchange between the system and its environment (Bellon and Averback, 1995; Wu et al., 2001; Gao et al., 2003). This can be implied that the systems from those studies are always in thermal equilibrium, and to believe in such the results from those studies may not be appropriate. This is due to that the milling mechanism happens intermediately fast and the container wall is often made of thermally- shielded material. Accordingly, the system should become a Joule's experiment-like that there is some conversion between the mechanical work and heat which increases the system temperature. Even the environment temperature is kept constant, the temperature in the milling system may increase as the time passes by. Consequently, to clarify this problem, in this study, we performed a Monte Carlo investigation to model the nano-structure of the powder undergoing the mechanical milling process as a function of milling time and milling intensity. During the milling process, the kinetic energy being obtained during the milling is assumed to transfer into both the mechanical work (which reduces powder size) and the thermal energy, which raises diffusivity in the system (and increases powder size). Then, by allowing the shearing and diffusivity effect, the competition between these two determines the sizes of the powders.

To outline, Monte Carlo simulations were performed on a rigid square lattice, containing a single powder. As the time passed, the kinetic of the mechanical milling (shearing) effect to the powders was assumed to raise the temperature and hence the diffusivity of the system. After that, the snap shots of the powder configurations were taken and the size of the biggest powder was recorded for analysis.

MATERIALS AND METHODS

In this study, we considered a planar system (i.e., 2D system) which its spatial dimension divided into an array of 2D square-lattice structure, consisting of 200x200 lattice points. The periodic boundary condition was taken on all edges of the 2D structure. Then, the simulation sample which is a single-grain particle (powder) was assumed to be consisting of atoms, and these atoms were allowed to reside only on the 2D square lattice point. The lattice point which was occupied by an atom of the powder was named the occupied point whereas the unoccupied point was name the vacant point. The distance between the adjacent lattice points was defined to be a unit of one lattice spacing. The Hamiltonian describing the interaction among atoms in the system was considered to take a form of Ising-like, that is

$$H = - \underset{<ij>}{} J_{ij} S_i S_j \qquad (1)$$

where $S_i = \{1,0\}$ referring to an occupied and a vacant point on the lattice point respectively. In the equation, the sum takes on only nearest-neighbor pair and $J_{ij} > 0$ is the interaction energy favoring like-atoms to form a cluster. In the simulation, J_{ij} was assumed direction-independent, i.e., $J_{ij} = J$. For convenience, J was considered to be the unit of energy, and then the unit of temperature T was defined to be J/k_B where k_B is the Boltzmann's constant. During the thermal diffusing process, simulations used the atom-vacancy exchange dynamic that the exchanging process consists of random atom-vacancy exchanges throughout the lattice. To describe, we made lists of occupied points and vacant points. Then, we randomly picked up one occupied point and one vacant point each from the lists. After that, we proposed the exchange between these two with the Metropolis probability

$$P = \exp\left[-\frac{H}{k_B T} \right] \tag{2}$$

where H is the energy difference between the before-exchange and after-exchange states. For a lattice with occupancy of N sites, the time unit was defined in terms of 1 Monte Carlo step (mcs) which is N trials of atom-vacancy exchanges.

Apart from the diffusing process, the mechanical shearing process was also taken into account. For every 1 mcs, the shearing action was taken on the system. One of the occupied point and one of the four <10> directions were randomly chosen. Then, starting from the chosen point, all occupied points in the same row (column) of the chosen point was shifted to the chosen direction for a random distance. The magnitude of this random distance was randomly chosen from 1 to $R_{\max}$ where the $R_{\max}$ is the maximum allowance of shifting, having a unit of lattice spacing. Then, the shearing procedure was repeated corresponding to the shearing frequency. For example, if the shearing frequency is set to be 10 times per mcs, this means that for every 1 mcs, the shearing action was taken ten times on the system.

On the other hand, since it is in general that some mechanical work loses and transforms to the thermal energy, this will more or less increase the temperature of the system. Hence, in the study, we assumed that for every 1 mcs, after the shearing action was taken on the system, the temperature of the system was raised with a magnitude of 0.000001 J/k_B. Then, when the time passes, the temperature of the system rises, and both the diffusing action (from thermal energy) and the shearing action (from mechanical work) determine the size of the powder. Starting from its initial state where all occupied points stay packed and form a cluster of 50x200 atoms in a single powder, the shearing and the diffusing action were taken on the powder. The shearing frequency ranges from 1 to 100 times per mcs and $R_{\max}$ ranges from 1 to 100 lattice spacing. All simulations, except the shearing-only and the diffusing-only tests, started at a fixed temperature of 0.1 J/k_B.

RESULTS AND DISCUSSION

In the simulations, we firstly considered the effect of the shearing process on the system at zero temperature. That means we did not take any diffusion into account. An example of this test is presented in Figure 1 which shows snap shots of the system undergoing shearing process with $R_{\max} = 20$ lattice spacing and the shearing frequency is 1 time per mcs. In Figure 1, the initial stage started with a single powder (particle) that all occupied sites stayed adjacent to each other. The white dots and the black dots refer to the occupied and the vacant points respectively. As can be seen, it is clear that the mechanical shearing broke the powder down into many smaller bits as the time passed by from 0 mcs to 50000 mcs. This shows nice evidence of how the mechanical milling reduces the size of the powder.

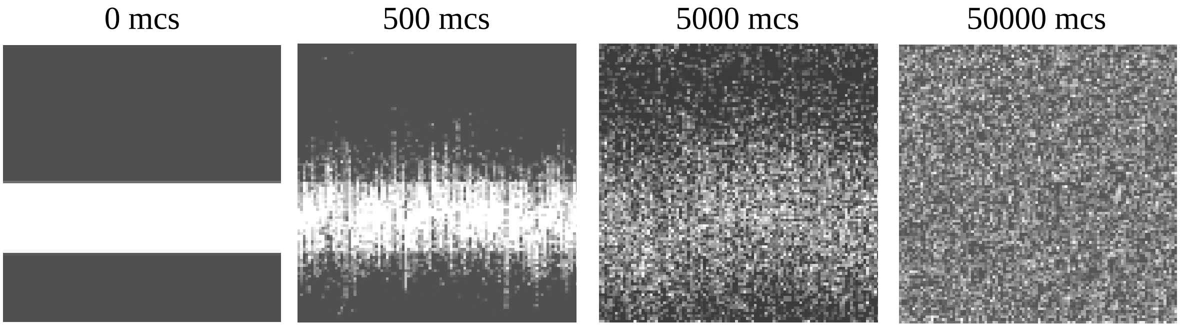

Figure 1. Snap shots of powder configurations under the effect of shearing only, at $R_{\max} = 20$ lattice spacing and the shearing frequency is 1 time per mcs, as a function of time. Black dots are the vacancy or the empty space whereas white dots refer to the powder.

On the other hand, we considered the effect of the thermal diffusion in a shearing-free environment. Speaking in another word, we discarded any shearing effect and chose a fixed temperature to investigation the thermal diffusing phenomena. Figure 2 shows an example of such a case. The system was started at a very high temperature where all atoms of the powder have a very high kinetic energy and distributed randomly throughout the system. Then, we suddenly cooled the system down to the temperature T = 0.1 J/k_B, and let the simulation started. From Figure 2, it is found that the occupied sites moved in such a way to form groups. This is due to that the system tries to reduce its energy by reducing the domain surfaces, and the forming groups grow bigger as the time passes by.

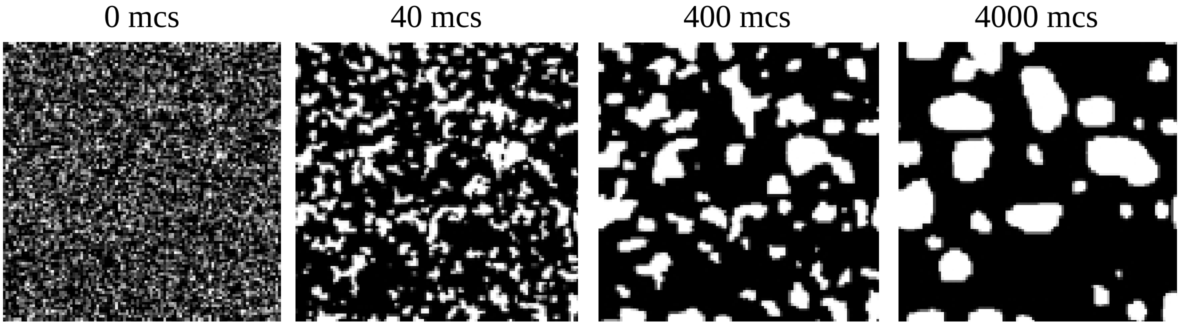

Figure 2. Snap shots of powder configurations under the effect of diffusing only at T = 1.0 J/k_B as a function of time. Black dots are the vacancy or the empty space whereas white dots refer to the powder.

However, when the temperature was raised, an opposite effect was found as presented in Figure 3. The figure represents snap shots of the system at the time t = 50000 mcs, based on a same procedure used in Figure 2 but at various temperatures. From the figure, at high temperatures, instead of a group forming, the atoms in the powder seem to diffuse freely which results in a smaller size of the powder. This is because an increase in temperature provides an increase in thermal energy to the system. Hence, the thermal fluctuations arising from this high energy, randomly distribute the occupied points out of the powder and the powder size gets decreasing.

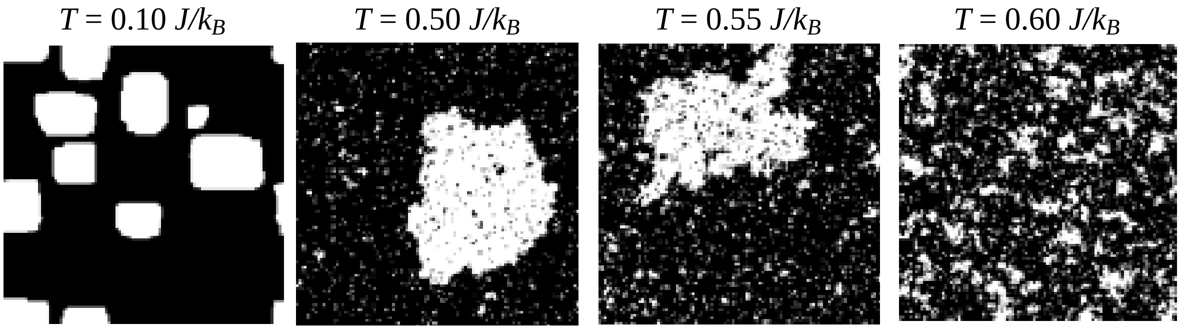

Figure 3. Snap shots of powder configurations under the effect of diffusing only at the simulation time = 50000 mcs with varying temperatures. Black dots are the vacancy or the empty space whereas white dots refer to the powder.

Therefore, from the shearing-only and the diffusing-only results, we can conclude that the mechanical shearing crushes the sample into smaller pieces but the thermal diffusion grows the sample up if the temperature is not too high. An example to summarize this behavior is given in Figure 4 which shows the biggest size of the sample (i.e. 10000 atoms) undergoing the shearing-only process (at R_{max} = 1 and the shearing frequency of 100 times per mcs) and the diffusing-only process (at $T = 0.1\ J/k_B$). The figure clearly shows that the competition between those two determines the size of the particles (powders).

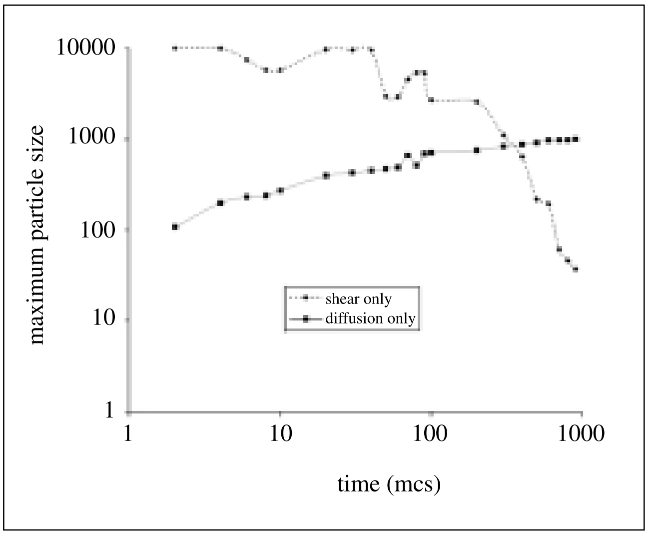

Figure 4. The size of the biggest powder (maximum particle size) as a function of simulation times. In the figure, -◆- refers to shearing-only process and -■- refers diffusing-only processes at R_{max} = 100 lattice spacing and the shearing frequency is 1 time per mcs.

Next, we investigated the effect of both shearing and diffusing on the sizes of the powders. For example, Figure 5 shows the maximum size of the powder simulated at an initial temperature $T = 0.1\ J/k_B$ and R_{max} = 50 lattice spacing with varying the shearing frequency from 1 time per mcs to 100 times per mcs. It is found that at low shearing frequency such as at 1 and 10 times per mcs, the size of the biggest powder is huge (covering almost all occupied sites). This is because the shearing effect is too small to break powder into pieces. However, at the late stage of the simulation (about 100000 mcs) the temperature at the considered point (which is raised by the mechanical work as the time passes) is high enough to cause a very strong thermal diffusion to the system. This results in a smaller size of the biggest powder. On the other hand, with increasing the shearing frequency, the maximum size of the biggest powder decreases very sharply at the early stage of the simulation. This is due to that the shearing magnitude is high enough to mill the powder. However, as the time goes by, the maximum size tends to fluctuate around a mean value. This is caused by the temperature of the system being raised to a high-enough level such that the thermal diffusing can play a significant role to the system. The competition between the diffusing and shearing results in the fluctuation of the size of the biggest powder as can be seen in Figure 5. However, a quantitative comparison of this behavior with experiments is difficult since the actual shearing rates during the mechanical milling can only be roughly estimated, and the non-equilibrium ordering of the system strongly depends on time, temperature, shearing rate, and microstructure. Nevertheless, to retrieve such a phenomenon as shown in Figure 5 is gratifying since it suggests a sophisticated way to control the particle size by controlling the magnitude and the frequency of the shearing (milling) at a particular temperature.

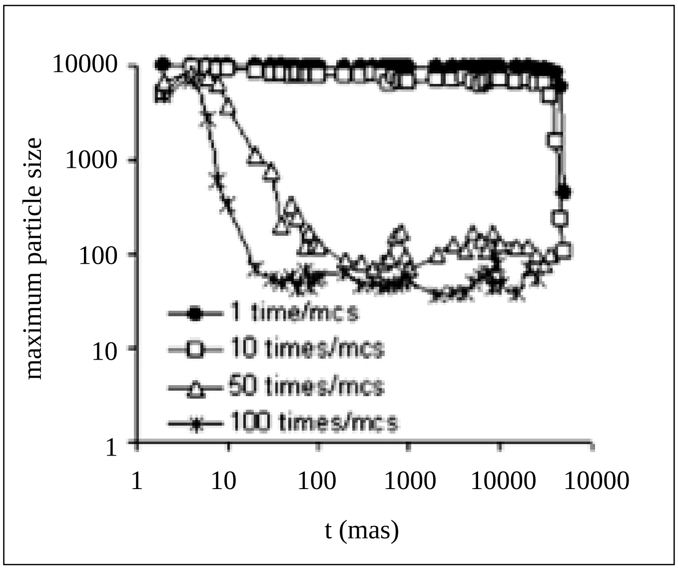

Figure 5. The size of the biggest powder (maximum particle size) as a function of simulation times *t* (mcs) at various shearing frequencies but fixed R_{max} = 50 lattice spacing.

CONCLUSION

In this study, we investigated the effect of mechanical milling on a size reduction of a powder from a micro-size to a nano-size via Monte Carlo simulations. We found evidence which confirms that the mechanical milling breaks the powder up into smaller pieces. On the other hand, if the temperature is not too high, the diffusivity tends to grow the powder up. The competition between the shearing and diffusing events determines the size of the powder as the time goes by. If a right set of conditions, i.e., the magnitude of shearing and the shearing frequency is chosen, the powder size can be controlled by the milling process. This provides a promising way to obtain the nano-sized powder for the benefit of the material processing and enhancing the material properties.

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