

Mechanical alloying of MoSi_2 with ternary alloying elements. Part 2 computer simulation

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Abstract

A computer model of the mechanical alloying process has been developed to simulate phase formation during the mechanical alloying of Mo and Si elemental powders with a ternary addition of Al, Mg, Ti or Zr. Using the Arrhenius equation, the model balances the formation rates of the competing reactions that are observed during milling. These reactions include the formation of tetragonal C11_b MoSi_2 (t - MoSi_2) by combustion, the formation of the hexagonal C40 MoSi_2 polymorph (h - MoSi_2), the transformation of the tetragonal to the hexagonal form, and the recovery of t - MoSi_2 from h - MoSi_2 and deformed t - MoSi_2 . The addition of the ternary additions changes the free energy of formation of the associated MoSi_2 alloys, i.e. $\text{Mo}(\text{Si}, \text{Al})_2$, $\text{Mo}(\text{Mg}, \text{Al})_2$, $(\text{Mo}, \text{Ti})\text{Si}_2$, $(\text{Mo}, \text{Zr})\text{Si}_2$ and $(\text{Mo}, \text{Fe})\text{Si}_2$, respectively. Variation of the energy of formation alone is sufficient for the simulation to accurately model the observed phase formation.

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1. Introduction

Numerous methods have been developed to model the mechanical alloying process. The models developed to date may be classified into three broad categories. The first may be referred to as “mechanistic models”, which focus on the motion of balls, calculations of velocities and impact energy probabilities, and on the macro segregation of powder within the mill [1–9]. This subset of models have been termed “global models”, since they are specific to the mill device used. A related subset, referred to as “local models”, examine the ball–powder interaction, including deformation, fracture and diffusion processes; and with consideration of the material properties, predict the effect on the powder morphologies. The second set of models predicts phase formation and evolution during mechanical alloying by under-

standing the thermodynamic variations. The Miedema model [10] for example, which can predict amorphous phase formation and heats of mixing of metastable phases, provides insight into the formation of amorphous materials using MA. These models usually contain no information on the rate of phase formation. A final set of models can be termed “kinetic models” [1,11–16]. These models use chemical reaction rates to understand the influence of processing parameters, such as charge ratio, collision frequency, collision energy or ball mass.

Here we present the development of a computer simulation that, from basic physical premises, attempts to quantify the increase in the free energy of the milled compounds during mechanical alloying. The model is optimised using an adaptive simulated annealing algorithm. The results from [17] are used as inputs into the model to yield estimates of the energy of formation of several metastable compounds and to validate the model. The model is derived in full in the thesis by Heron [18], which also contains the complete simulation code.

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2. The model

The total powder charge is simulated by an arbitrary number of powder regions or “packets”, n , which are considered to contain exactly 1 mol of Mo atoms and 2 mols of Si and/or Al atoms. After the initialisation of the variables, the alloy content is randomly distributed throughout the n packets. For each of the packets in turn, the mechanical alloying process is performed over the time step dt . The deformation incurred is modelled as an increase in the effective processing temperature for each packet, $dT_{i,t}$.

Five reactions, shown in Table 1, dominate the phase formation observed during mechanical alloying. The reaction rates, r_Z (where $Z = \text{comb, trans, t2h, h2t, and rec}$), are calculated using Arrhenius equations of the form:

$$r_{Z,i,t} = A_Z e^{-\frac{Q_{Z,i,t}}{RT_{i,t}}} \quad (1)$$

where $r_{Z,i,t}$ is the reaction rate, A_Z is the reaction rate constant, $Q_{Z,i,t}$ is the activation energy, $T_{i,t}$ is the effective reaction temperature and R is the gas constant. Both A_Z and $Q_{Z,i,t}$ are determined by comparison and optimisation against the observed result from the mills containing Al additions. The following convention is adopted to identify variables in this model. The subscript Z is the reaction designation, i is the packet designation, t is the time step designation and Φ is the phase designation. If one or more of these subscripts are not associated with a particular variable, then that variable is constant with respect to that subscript designation.

The activation energy for each reaction at time step t is modified from its equilibrium values, $Q_{Z,o}$, by two parameters: the change in energy due to alloying additions, $dE_{\Phi,i,t,\text{alloy}}$, and the change due to the introduction of vacancies from deformation, $dE_{\Phi,i,t,\text{def}}$ (where Φ , represents the phases $t\text{-MoSi}_2$, $h\text{-MoSi}_2$ or the elemental powder). The set of allowable reactions depends on whether each packet contains predominantly elemental powder or intermetallic MoSi_2 , and also depends on which of the MoSi_2 polymorph is the most energetically favourable. If the combustion of Mo and Si to form $t\text{-MoSi}_2$ occurs within a packet, the temperature of that packet is increased by the combus-

tion temperature, T_{comb} . In order to reflect the propagation of the spontaneous high-temperature synthesis reaction, the temperature of the surrounding packets is increased by an amount governed by the heat transfer rate, t_{heat} . The phase proportions within each packet is updated by;

$$f_{\Phi,i,t} = f_{\Phi,i,t-1} + r_{Z,i,t} \Delta t \quad (2)$$

where $f_{\Phi,i,t}$ and $f_{\Phi,i,t-1}$ are the phase proportion of the Φ phase within the i th packet at time steps t and $(t-1)$, respectively. The sum of the phase proportions with each packet always equals one. Once updated, the phase proportions are compared with determine the predominant phase for the next time step. If there is a change in the principal phase, the effective reaction temperature is reset to zero in order to simulate the recovery of the internal strain.

The mechanical alloying event is applied sequentially to each packet of powder. After each packet has experienced a milling process for the current time step t , the phase proportions across the entire mill is then calculated as the average of the phase proportions over all n packets. The final routine for each time step is to diffuse the alloy additions between neighbouring packets, using a finite difference model. The time step is advanced by Δt and the mechanical alloying process is repeated across all the n packets, until the maximum alloying time, t_{max} , is reached. The structure of the model is shown in Fig. 1.

The activation energies for each packet at each time step, $Q_{Z,i,t}$, is calculated from the base activation energy for the Z reaction, $Q_{o,Z}$, less the change in energy due to alloying addition, $\Delta E_{\Phi,i,t,\text{alloy}}$, and mechanical deformation, $\Delta E_{\Phi,i,t,\text{def}}$, as shown in Equation (5).

$$Q_{\text{comb},i,t} = Q_{o,\text{comb}} - \Delta E_{e,i,t,\text{def}}$$

$$Q_{\text{trans},i,t} = Q_{o,\text{trans}} - \Delta E_{e,i,t,\text{def}}$$

$$Q_{\text{t2h},i,t} = Q_{o,\text{t2h}} - \Delta E_{t,i,t,\text{def}} - \Delta E_{t,i,t,\text{alloy}}$$

$$Q_{\text{h2t},i,t} = Q_{o,\text{h2t}} - \Delta Q_{\text{h2t}} - \Delta E_{h,i,t,\text{def}} - \Delta E_{h,i,t,\text{alloy}}$$

$$Q_{\text{rec},i,t} = Q_{o,\text{rec}} - \Delta E_{t,i,t,\text{def}} - \Delta E_{t,i,t,\text{alloy}} \quad (3)$$

where ΔQ_{h2t} is the difference in free energy between pure $t\text{-MoSi}_2$ and $h\text{-MoSi}_2$ at the base milling temperature.

Table 1
The reactions simulated during the mechanical alloying of Mo and Si

Reaction	Description	Equation	Designation (Z)
1	The combustion reaction of Mo and Si to form $t\text{-MoSi}_2$	$\text{Mo} + \text{Si} \rightarrow t\text{-MoSi}_2$	comb
2	The transformation of Mo and Si to form $h\text{-MoSi}_2$	$\text{Mo} + \text{Si} \rightarrow h\text{-MoSi}_2$	trans
3	The transformation of $t\text{-MoSi}_2$ to $h\text{-MoSi}_2$	$t\text{-MoSi}_2 \rightarrow h\text{-MoSi}_2$	t2h
4	The recovery of $h\text{-MoSi}_2$ to form $t\text{-MoSi}_2$	$h\text{-MoSi}_2 \rightarrow t\text{-MoSi}_2$	h2t
5	The recovery of $t\text{-MoSi}_2$ to form strain free $t\text{-MoSi}_2$	$t\text{-MoSi}_2 \rightarrow t\text{-MoSi}_2 (\text{rec})$	rec

The change in the activation energy due to deformation, $\Delta E_{\Phi,i,t,def}$, may be calculated from the number of vacancies (v_{Φ}) present at the effective reaction temperature of the i th packet, $T_{i,t}$. The equilibrium number of vacancies at the milling temperature T_{mill} , which may be considered to be room temperature, is given by Cottrell [19]:

$$E_{\Phi,i,t,def} = W_{\Phi}v_{\Phi,i,t} - RT_t[(1 + v_{\Phi,i,t})\ln(1 + v_{\Phi,i,t}) - v_{\Phi,i,t} \ln v_{\Phi,i,t}] \quad (4)$$

where W_{Φ} is the formation energy for a mole of vacancies. Therefore, the increase in free energy due to deformation is given by:

$$\begin{aligned} \Delta E_{\Phi,i,t,def} &= E_{\Phi,i,t=0,def} - E_{\Phi,i,t,def} \\ &= W_{\Phi}(v_{\Phi,t=0} - v_{\Phi,i,t}) \\ &\quad - RT_t[(1 - v_{\Phi,i,t})\ln(1 - v_{\Phi,i,t}) - v_{\Phi,i,t} \ln v_{\Phi,i,t}] \\ &\quad + RT_{mill}[(1 - v_{\Phi,t=0})\ln(1 - v_{\Phi,t=0}) - v_{\Phi,t=0} \ln v_{\Phi,t=0}] \quad (5) \end{aligned}$$

The increase in the free energy due to alloying addition is given by:

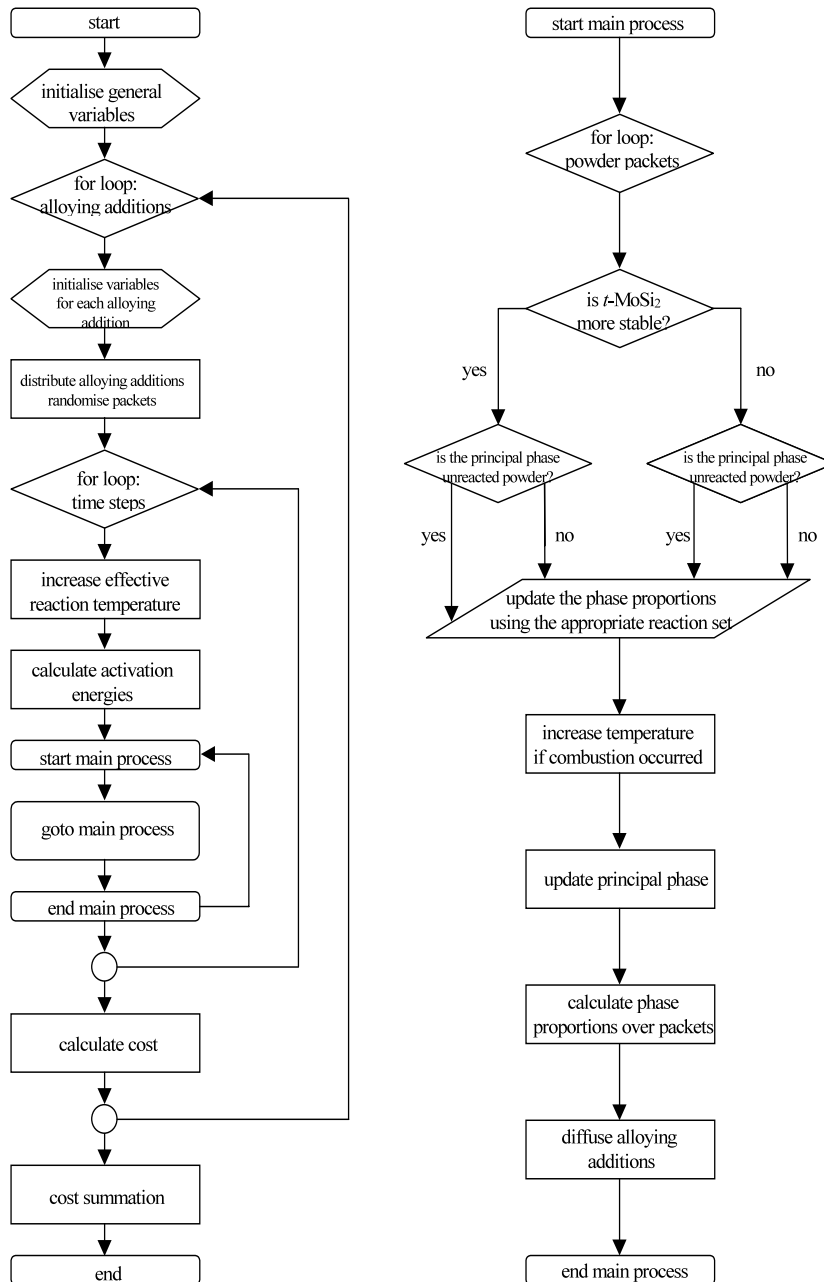


Fig. 1. Flow chart for the computer simulation.

$$\Delta E_{\Phi,i,t,\text{alloy}} = G_{\Phi,\text{Mo:Si}} - G_{\Phi,i,t,\text{alloy}} \quad (6)$$

The alloy distribution sets up a monotonically increasing function from a_{min} in the first packet to some maximum value in the n th packet. Therefore, the packets are subsequently randomly rearranged to form a one-dimension string. During the t th time step, the change in the alloy concentration of the i th packet, $\Delta a_{i,t}$, may be determined as:

$$\frac{\Delta a_{i,t}}{\Delta t} = D_{i,t} \cdot \frac{\partial^2 a_{i,t}}{\partial x^2} \quad (7)$$

where $D_{i,t}$ is the local diffusivity for the i th packet during the time step t .

The flow of heat takes the form of Laplace's potential equation:

$$\frac{\Delta T_{i,t}}{\Delta t} = h_{\text{trans}} \cdot \frac{\partial^2 T_{i,t}}{\partial x^2} \quad (8)$$

where h_{trans} is the heat transfer constant. The $\frac{\partial^2 a_{i,t}}{\partial x^2}$ and $\frac{\partial^2 T_{i,t}}{\partial x^2}$ terms were modelled using a finite difference model.

The unknown factors may be estimated by optimising the model against the cost function in Equation (9). A cost function is a user defined function to indicate that level of fidelity between the simulation and the experimental results. The cost function may be solved for every combination of the parameters within predefined bounds. The parameter set with the minimum cost is considered the optimal solution. One method of finding the optimal solution is to choose the parameter set at random, and then use the simulation to calculate its cost. The cost is stored for that particular parameter set. A new parameter set is randomly chosen and the cost for it similarly calculated and compared with the cost for the first parameter set. The process is continued across the entire parameter search space with the cost stored for each iteration. The parameter set with the minimum cost is considered the optimal estimation.

This approach would be computationally intensive and a cost effective search and optimisation algorithm must, therefore, be employed. Adaptive simulated annealing (ASA) is well suited to this type of problem [20]. The algorithm may be visualised simply as geographical terrain. In this case, the cost function, height, depends on only two parameters; distance in the North ordinate and distance in the East direction. The ASA approach to this problem is similar to using a randomly bouncing ball that initially has a large amount of energy and can bounce over mountains from valley to valley. The ball's energy, or temperature, allows the ball to bounce very high such that, given enough bounces it can access every valley (or minima) within the search space.

With consecutive iterations, the temperature becomes colder and the ball eventually becomes trapped within a local minima. The cost value (height) of this minima is stored for later comparison with other local minima to find the global minima. The ball may then be "re-annealed" and allowed to find another local minima.

After several iterations, the algorithm uses statistical analysis to determine the probability that a lower value of cost than the minima already found may still exist within the search space. If this probability is less than a user defined level, the algorithm is exited and the lowest minima found is considered the global minima. The interface between the MATLAB development environment and the ASA core code that is used in the present study was developed by Drack and Wharington [21]. The cost function is used to determine how well the results from the extended mechanical alloying model match the observed results. For the present problem, the cost for a single ternary alloying species (i.e. Al, Mg, Ti or Zr) is the sum over all the alloying concentrations, from 0 to 16.7%. The cost for each alloying concentration may be defined as the sum across the milling times (from 0 to 50 h) and across the phases (Mo, Si, X, t -MoSi₂ and h -MoSi₂ where X represents the ternary alloying addition) of the squared residual or difference between the observed and calculated phase proportions.

$$C_{\text{Total}} = \sum_{\text{alloy additions}} C_{\text{alloy}} \quad (9)$$

$$C_{\text{alloy}} = W \sum_t \sum_{\Phi} (f_{\Phi,t,\text{calc}} - f_{\Phi,t,\text{obs}})^2 \quad (10)$$

where C_{alloy} is the cost for each alloying addition (alloy = 0, 1, 4.8, 9.1 and 16.7% Al), and C_{Total} the cost of the model as a whole. The phases Φ that are summed across are t -MoSi₂, h -MoSi₂, Mo, Si and Al, and, for alloy concentrations greater than 0, the times that are summed across are 0, 2, 5, 10, 20, 50 h. If alloy = 0 the times used are 2.6, 5, 10, 15, 22, 42 and 50 h.

The relative importance of error between the calculated and observed phase proportions may be represented using a weighting matrix, \mathbf{W} . As the proportion of a particular phase decreases, the peaks found by X-ray diffraction begin to merge with the background radiation and thereby become more difficult to distinguish using Rietveld analysis. Since less confidence can be placed on the values of the phase proportions found using the Rietveld method as the phase proportions decrease, a weighting was given to each of the residuals proportional to the observed phase proportions. Also, since the formation of the two MoSi₂ polymorphs are of particular interest, the residuals for these two phases were given weighting of 4, relative to the weighting for the elemental phases of 1. These values were chosen arbitrarily to improve the correlation between the

calculated and observed phase proportions for the proposed mechanical alloying simulation.

The cost function for each alloying concentration is additionally augmented by the difference between the calculated and observed cross-over times, which is the time at which the relative proportions of the *t* and *h* phases are equal. This squared difference is multiplied by a cross-over weighting, $w_{cr}=0.1$, to bring it to a comparable order of magnitude as the phase residual. Therefore, the cost for a given alloying concentration is given by:

$$C_{\text{alloy}} = w_{cr}(t_{cr,calc} - t_{cr,obs})^2 + \mathbf{W} \sum_t \sum_{\Phi} (f_{\Phi,t,calc} - f_{\Phi,t,obs})^2 \quad (11)$$

3. Comparison of observed and simulated results

The model was tested using the milling experiments from Part 1 [17]. The simulation containing Al ternary additions was used to “calibrate” the parameters in the mechanical alloying simulation using the estimates for the free energies of the tetragonal and hexagonal forms of MoSi_2 and MoAl_2 available from Costa e Silva and Kaufman [22]. The values of the parameters developed for the Al series were then applied without change to the Mg, Ti and Zr series. The comparison of the observed and simulated phase proportions at 16.7% for these additions are shown in Figs. 2–4.

In general, the model fits the results closely. The combustion reaction to form *t*- MoSi_2 during the early stages of milling is accounted for, as is the formation of

t- MoSi_2 as milling progresses. The amount of *t*- MoSi_2 that forms immediately after combustion is shown to decrease in proportion to the amount of the third element added, as observed experimentally. There is, however, some variation between the observed and simulated data, particularly for the mills containing Zr. These variations may be due to the difficulties in determining the relative phase proportions from broad low intensity patterns during Rietveld analysis. The extensive broadening of the diffraction patterns may also indicate that some of the material may be converted into an amorphous phase. Since Rietveld analysis cannot estimate the amount of amorphous phase, such as SiO_2 , and the results presented are relative phase proportions of observable material, the proportions of both *t*- and *h*- MoSi_2 may be overestimated for these series.

4. Discussion

There are several parameters that control the behaviour and operation of the model, such as the activation energies and reaction rate constants for the competing reactions, the activation energy for vacancy formation within the various phases and the free energy of the fully alloyed metastable compounds. Given the change in free energy with the addition of aluminium, the other unknown parameters can be determined using the adaptive simulation annealing algorithm. For the most part, the simulation parameters follow expected trends. For instance, the activation energy for the combustion reaction is less than for the transformation reaction; the vacancy formation energy is lower for the low density, high temperature, hexagonal MoSi_2 form than it is for

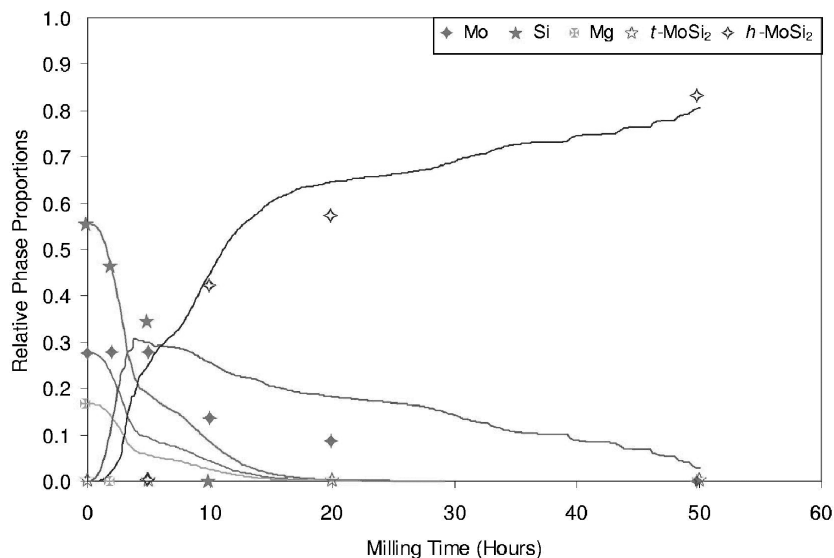


Fig. 2. Comparison of simulated with experimentally determined phase proportions for the mechanical alloying of Mo and Si with 16.7% Mg. The solid lines show the simulated phase proportions while the symbols show the experimentally observed values.

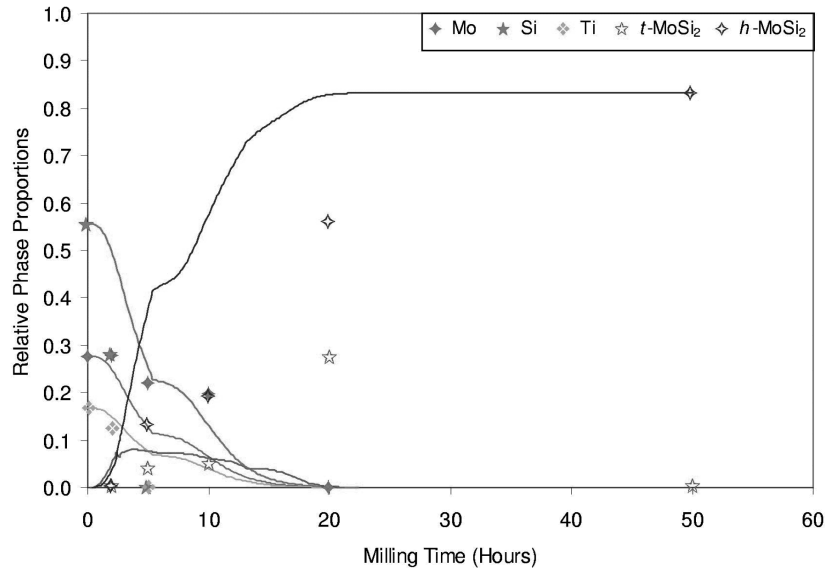


Fig. 3. Comparison of simulated with experimentally determined phase proportions for the mechanical alloying of Mo and Si with 16.7% Ti. The solid lines show the simulated phase proportions while the symbols show the experimentally observed values.

the tetragonal form; and the reaction rate constant is low for the transformation reaction, yet high for the combustion and the tetragonal to hexagonal reactions. Thus the variation of the free energy of the preferred metastable phase alone was sufficient to simulate the phase evolutions observed for the various alloying additions. This indicates that the methodology may be valid for other systems and given that the thermodynamics of the metastable phases are known, it may be used to predict the phase evolution during mechanical alloying.

5. Conclusions

A simulation describing the mechanical alloying process was developed that models the rate of phase evolution using the Arrhenius equation and is dependent on the reaction rate constant, the activation energy and the effective reaction temperature. A simulated annealing algorithm is used to optimise the unknown parameters, which are calibrated against a well characterised system. The model, which balances the competing reactions, which occur during mechanical alloying, has

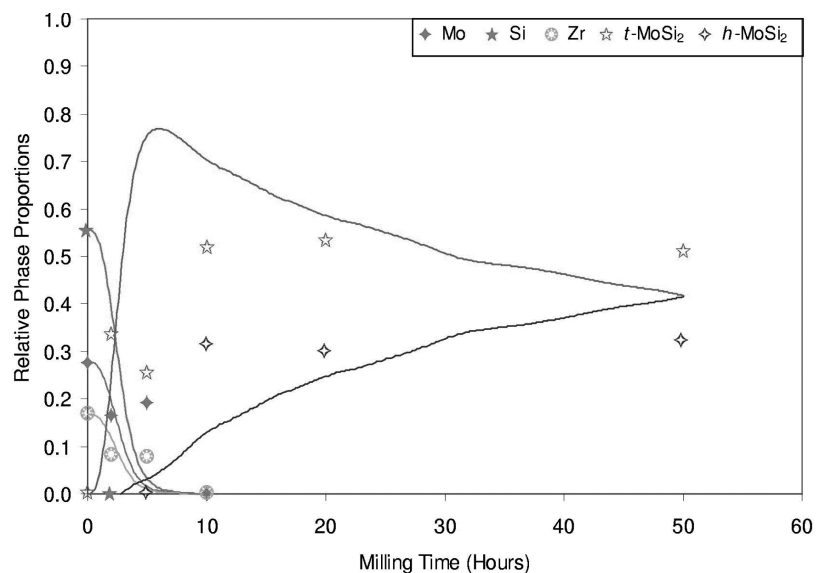


Fig. 4. Comparison of simulated with experimentally determined phase proportions for the mechanical alloying of Mo and Si with 16.7% Zr. The solid lines show the simulated phase proportions while the symbols show the experimentally observed values.

been applied to the milling of Mo and Si to form MoSi₂, alloyed with Al, Mg, Ti or Zr. The calculated phase proportions, as a function of alloying addition and milling time, closely match the observed results.

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