Study of energy-intensive mill lining during the grinding of silicon powder

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Abstract. Dynamics of silicon lining an energy-intensive planetary mill was studied using experimental methods and a developed mathematical model. The transformation of the silicon powder microstructure during its mechanical treatment was investigated. It was found that this changes the granulometric composition of the mixture, resulting in a constant reformation of silicon particles formed from the agglomerates, which are crushed and agglomerated into new particles. It is shown that with increasing mechanical treatment time there is an increase in the amount of material in the lining layer. The lining speed constant was determined from the solution of the inverse problem. The theoretical calculations were in good agreement with the experimental data.

1. Introduction

The relevance of studying mechanical activation is caused by the development of modern methods that use grinding devices [1–6]. Grinding contributes not only to the high dispersity of powders, but also in some cases changes the structural and physical and chemical characteristics of powder particles. For example, the accumulation of defects in particles during MA leads to a decrease in the activation energy for further chemical transformations of a substance. Mechanical activation is widely used as a preliminary stage for self-propagating high-temperature synthesis [6–14].

One of the problems of effective using mechanoactivators is that during MA the inner surface of the mill and the grinding bodies are lined with powder particles. As a result, in addition to the degradation of operating equipment performance, some amount of ground material is lost. Also, during the grinding of a multicomponent mixture, mill lining can lead to a change in a stoichiometric composition [7, 8]. Consideration of the above facts in the MA processes gives a possibility to obtain the required amount of a powder mixture with specified characteristics.

Mathematical models that evaluate the kinetic constants describing the grinding process and interpret the experimental results obtained can be used to optimize MA. In the works [15–16], an attempt was made to model mechanochemical processes during the lining of the operating surfaces of a mechanoreactor. In [16], a mathematical model was built and the kinetic speed constant of energy-intensive mill lining was determined for the grinding of a 2Fe + 5Al mixture.

It is worth noting that despite the relevance of studies aimed at reducing energy consumption and optimizing mechanical activation, the problem has not been solved yet. Existing modern concepts that explain many physical features of MA cannot be used to build reliable mathematical models.
describing the behavior of solids in an energy-intensive mill. The equations obtained by researchers, which determine the kinetics of MA, are phenomenological and based on experimental data. Such equations contain empirical constants.

In [13], a mathematical model was developed for mill lining during the mechanical treatment of a multicomponent mixture in an energy-intensive mill. The parameters of the mill and the time of mechanical treatment were shown to have a significant effect on the lining of the inner surface of the mechanical activator.

The rate of sedimentation of ground particles on the walls of the mill and grinding bodies was assumed to be proportional to the number of particles in the chamber, the size of the inner surface including the surface of the grinding bodies, and is inversely proportional to the internal volume that is not occupied by the grinding bodies.

Figure shows that the increase in the time of mechanical activation leads to the increase in the volume of the material used for mill lining. With the development the MA process the lining rate decreases. Figure demonstrates that long times of mechanical treatment and intensive operation of the mill contribute to the almost full adhering of ground substances on the walls of the chamber and the grinding bodies.

In this work, silicon lining of a planetary mill during MA of silicon powder is studied using experimental methods and a mathematical model proposed in [13]. Silicon was selected as an object of study due to its wide use in semiconductor manufacture and microelectronics, as well as in aviation, rocket engineering and nuclear industry. The MA method can be used to obtain finely dispersed silicides with high textural characteristics [17].

The structure of the paper is as follows. The second section contains a description of the experiment procedure. The third section analyzes the results of the experiments and provides the analytical ratio for calculating the volume fraction of the lining layer depending on the mechanical activation time. Using the experimental data and the analytical ratio, a speed constant for the lining of the working surfaces of the energy-stressed mill with silicon powder was found. Theoretical calculations are compared with experimental data. The main conclusions are summarized in the fourth section.

2. Experimental procedure

Mechanical activation of silicon powder with a purity of 99.7% was conducted in a planetary centrifugal mill with a power density of 60 g and water-cooled drums (Figure 1).

Figure 1. Appearance of high-tension planetary mill.

The ball-to-powder weight ratio was 20:1. The operation time of the mill ranged from 1 to 120 minutes. Balls (100Cr6) and steel drums (X38Cr13) were used in the experiments. The grinding of the
powder mixture was conducted in argon with a purity of 99.99%. The MA time was discrete: 5 min continuous activation was followed by the stop of the mill for 15 minutes necessary for cooling.

After the completion of MA, the mill was stopped and the mechanically activated mixture was weighted. The mass of the powder used for mill lining was determined by a difference between its initial amount and the amount after MA.

The particle size distribution of silicon powder before and after MA was studied using a sieve dispersion and calculating the grain size of agglomerates in SEM images (Philips SEM515). The iron content in mechanically activated silicon powder was chemically analyzed on an SF26 spectrophotometer.

3. Results
3.1 Experimental results
Figure 2 shows the microstructure of initial silicon powder. The picture demonstrates that particles have an angular shape with sharp faces. Figure 3 shows the microstructure of silicon powder subjected to 30 s mechanical activation. The size of the particles noticeably decreased and the particles lost their angular shape. Almost all large particles are round-shaped and surrounded with smaller particles of silicon. It seems that all particles of silicon were finely ground and formed layered agglomerates. However, the study of the microstructure of mechanically activated silicon powder subjected to further MA showed that this was not the case. In the picture (Fig. 4), it can be seen that after 1 min MA the small particles that surrounded a large silicon particle left it, and the irregular shapes of initial particle, the size of which decreased, were observed. Figure 5 shows the increase in the number of large irregular and smaller particles.
Analyzing these pictures, it can be concluded about the processes that occur at the initial stages of mechanical activation of silicon powder. In the first seconds of activation, the breaking of large particles occurs. The sharp corners and faces of large particles are broken and form a large number of small particles which surround the larger particles. This is seen in Fig. 3. In this case, part of the fine fraction goes to the walls of drums and grinding balls, and larger particles look like the initial ones, since they were surrounded with these small particles only on the surface, remaining inside the broken fragments of the initial particles, as can be seen in the picture during 1 min MA. Then, increasing the MA time, these processes are repeated. With a further increase in the MA time, small particles of silicon form layered agglomerates which consist approximately of uniform particles. In 15 minutes or more, the size of such agglomerates increases. Figure 6 shows a layered agglomerate formed during 60 min MA.

Figure 7 shows the relative mass of silicon powder used for mill lining as a function of MA time (curves 1–3). It is seen that all curves demonstrate a significant increase in the amount of the substance on the working surfaces of the mill for 20-30 min MA. During this time, more than half the mass of the ground mixture goes into the lining layer.

![Figure 6](image1.png)

**Figure 6.** Microstructure of silicon powder after 60 minutes of mechanical activation.

![Figure 7](image2.png)

**Figure 7.** Amount of silicon powder used for mill lining as a function of MA time, depending on the mass of the substance: 1 - 100 g, 2 - 30 g, 3 - 20 g.

Then a small increase in the amount of the substance in the lining layer and even its slight decrease at the time from 25 to 60 min MA are observed (curve 2). Probably, for the long mechanical activation time the lining process reaches saturation that is determined by the approximate equality between the amount of the substance adhered to the walls of the mill per unit time and that returned to the ground mixture. This fact was discussed in the work [9], the authors of which showed that during MA the surfaces of the mechanical activator were subjected to nonuniform lining and some amount of the lining material adhered to them returned to the ground mixture.

**Table 1.** Particle size characteristics of silicon powder.

| Size of agglomerate, μm | Proportion of fraction in the initial mixture, % | Proportion of fraction in the mixture after 15 min MA, % | Proportion of fraction in the mixture after 120 min MA, % |
|-------------------------|-----------------------------------------------|--------------------------------------------------------|--------------------------------------------------------|
| <300                    | 57                                            | 48                                                     | 27                                                     |
| 300 – 500               | 33                                            | 42                                                     | 15                                                     |
| 500 – 700               | 10                                            | 10                                                     | 57                                                     |
It is worth noting that during MA the particle size distribution of silicon powder changes constantly due to the rearrangement of agglomerate particles which during grinding break and immediately form new agglomerates. Table 1 shows that during MA the proportion of large agglomerates increases.

3.2 Theoretical assessments

Chemical analysis showed that the iron content in silicon powder did not exceed 0.3 - 2.8% after 1–120 min MA. In [13] a formula was obtained for estimating the amount of a substance used for mill lining during the grinding of a mixture, including a one-component mixture

\[ \mu_{\Phi} = 1 - e^{-\frac{S_{\Phi} t}{V}} \]  

(1)

where \( t \) is the time of mechanical activation; \( \mu_{\Phi} = \frac{m_{\Phi}}{m_{\Phi_{0}}} \) is the relative mass of the substance used for mill lining; \( m_{\Phi} \) is the mass of the powder in the lining layer; \( m_{\Phi_{0}} \) is the initial mass of the powder mixture; \( S = S_{M} + n S_{m} \) is the area of the working surface of the mill; \( S_{M} \) is the area of the inner surface of the mill; \( S_{m} \) is the surface area of the grinding body, \( n \) is the number of grinding bodies; \( V \) is the internal volume of the mill, not occupied by grinding bodies; \( K_{\Phi} \) is the mill lining speed constant. The parameter \( K_{\Phi} \) is assumed to linearly depend on the power of the energy-intensive mill \( W \) [15], therefore

\[ K_{\Phi} = k_{\Phi} W, \]  

(2)

where \( k_{\Phi} \) is the coefficient that considers the physical and chemical properties of the material to be ground (\( K_{\Phi} = \text{const} \)).

The parameter in (1) can be estimated by two methods. The first method is based on the transformation of relation (1) into the equation of straight line with the coordinates \( \ln(1 - \mu_{\Phi}) \):

\[ -\ln(1 - \mu_{\Phi}) = \frac{S}{V} K_{\Phi} t. \]  

(3)

Here, the value \( \frac{S}{V} \) is determined by the angle of inclination of a straight line (3) with respect to the X-axis using the experimental dependences \( \mu_{\Phi}(t) \).

The second method to calculate the lining speed constant includes the expansion of formula (1) in a Taylor series. Neglecting the terms with the degree at \( t \) greater than 1, the approximate equality \( e^{-\frac{S_{\Phi} t}{V}} \approx 1 - \frac{K_{\Phi} S_{\Phi} t}{V} \) is obtained, which will be met for small MA times. Substituting the above equality in (1), the relation is obtained as follows

\[ \frac{S}{V} K_{\Phi} = \frac{\mu_{\Phi}}{t}. \]  

(4)

Relation (4) geometrically determines the slope of the straight lines approximating the dependences \( \mu_{\Phi}(t) \) at the initial time of operation of the mill. The parameters \( S, V \) and \( W \) characterizing the mill in (3) and (4) are estimated to determine the lining speed constant \( K_{\Phi} \) and the coefficient \( k_{\Phi} \) that is included in (2).
Based on the experimental results, calculations obtained by the first (using the least squares method) and second methods showed the values of $\frac{K_p S}{V}$ as follows: $(\frac{K_p S}{V})_I = 0.0063^{+0.0003}_{-0.0002}$ min$^{-1}$, $(\frac{K_p S}{V})_II = 0.028^{+0.001}_{-0.001}$ min$^{-1}$. It is seen that $(\frac{K_p S}{V})_I < (\frac{K_p S}{V})_II$.

This inequality confirms that the value estimated by the 1st method with long MA times was several times smaller than that determined by the 2nd method (with small MA times). It can be concluded that the lining speed constant is not a constant value: apparently, with increasing the grinding time the rheological properties of the inner surface of the mill change due to the formation of a lining layer, resulting in a significant decrease in $K_p$.

It should be noted that the values obtained above are close to the values determined in [9] for a 2Fe + 5Al powder mixture: 0.008 min$^{-1}$ and 0.03 min$^{-1}$, respectively.

Figure 8 shows the experimental (curve 1 with a confidence interval) and calculated (curves 2 and 2') relative mass of silicon used in mill lining as a function of MA time.

**Figure 8.** Number of silicon powder used in mill lining as a function of MA time: 1 is the experiment; 2, 2' are theoretical calculations.

The theoretical dependences were calculated by formula (1) for $\frac{K_p S}{V} = (\frac{K_p S}{V})_I$, and $\frac{K_p S}{V} = (\frac{K_p S}{V})_II$, respectively. Calculations show that as the MA duration increases, the proportion of silicon powder in the lining layer increases and the higher the value of the $K_p$ constant. Figure 2 demonstrates that curve 2' well approximates the experimental line for small mill times ($t < 40$ min), and curve 2 for long grinding ($t > 70$ min).

4. Conclusion
Dynamics of silicon lining the energy-intensive planetary mill was experimentally studied and analytically estimated. It was shown that increasing the mechanoactivation time, the speed at which...
ground powder adhered to the surface of the mill reduced and the lining speed constant significantly decreased.

The speed constant for the silicon lining of the inner surface of the grinding mill was determined by the inverse method. The theoretical dependences well approximated the experimental data.

Appendices
MA - mechanical activation,
SHS - self-propagating high-temperature synthesis,
MPV - planetary centrifugal mill,
Balls (100Cr6) - steel grade balls,
Steel drums (X38Cr13) – steel grade drums,
SEM images - scanning electron microscope image,
Philips SEM515 - brand of the SEM device,
SF26 spectrophotometer - brand of the spectrophotometer device.

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