

Article

Particle Size Refinement and Kinetic Modeling of Hercynite Powders Under Wet Mechanical Milling

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Abstract

The particle size refinement of hercynite (FeAl_2O_4) powders during wet high-energy mechanical milling was investigated through an integrated experimental and kinetic modeling approach. Hercynite powders were milled for different durations, and their microstructural, chemical, and particle size evolution was characterized using scanning electron microscopy, X-ray diffraction, semi-quantitative X-ray fluorescence analysis, and SEM–ImageJ-based particle size reconstruction. Particle size distributions were reconstructed from large particle populations, and the characteristic descriptors D_{10} , D_{50} , and D_{90} were determined from empirical cumulative distributions. The results revealed a pronounced reduction in median particle size from approximately 83.1 μm in the as-received powder to 0.422 μm after 8 h of milling. X-ray diffraction analysis showed progressive peak broadening and intensity reduction with increasing milling time, suggesting milling-induced structural disorder and possible crystallite refinement and/or lattice strain accumulation, while no additional crystalline phases associated with milling-induced decomposition were detected within the detection limit of XRD. Semi-quantitative chemical analysis indicated limited metallic transfer from the stainless-steel milling media under the applied wet milling conditions. The evolution of D_{50} with milling time exhibited a non-linear behavior characterized by rapid particle fragmentation at early stages, followed by a gradual transition toward a refinement-limited regime. This behavior was described using a first-order kinetic model with saturation behavior, yielding an asymptotic particle size of 0.443 μm and an effective milling rate constant of 1.539 h^{-1} . Overall, the proposed kinetic framework provides a descriptive and condition-specific quantitative basis for interpreting the competing fracture and agglomeration mechanisms governing particle size evolution during wet mechanical milling of refractory spinel powders.



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1. Introduction

Hercynite (FeAl_2O_4) is a spinel-type refractory material known for its excellent thermal stability, high melting point, and chemical resistance, which make it suitable for high-temperature industrial applications such as steelmaking and glass furnaces. From a fundamental perspective, its structural, electronic, and magnetic properties have been extensively investigated. Density functional theory studies have shown that hercynite exhibits a semiconducting antiferromagnetic normal spinel structure, in which Fe^{2+} ions occupy tetrahedral sites while Al^{3+} ions are located in octahedral coordination [1]. Despite these favorable characteristics, hercynite may undergo partial decomposition in oxidizing atmospheres at temperatures around 1000 °C, leading to the formation of alumina and iron oxides. This limitation can be mitigated through partial substitution of Fe with Mg, which stabilizes the spinel structure up to approximately 1200 °C by promoting the formation of magnesioferrite [2]. Beyond refractory applications, hercynite has also attracted increasing attention in heterogeneous catalysis and solar thermochemical processes, where its redox behavior and defect chemistry play a key role [3–5].

The microstructural characteristics of hercynite ceramics, particularly particle size and particle size distribution, are critical parameters governing densification behavior, sintering kinetics, and thermo-mechanical performance. Previous studies on related refractory systems have demonstrated that finer particle sizes enhance packing efficiency and promote improved sintering, resulting in significant increases in mechanical strength and hardness. For example, in magnesia–dolomite refractories, the incorporation of hercynite has been reported to improve mechanical strength and hardness by inducing favorable microstructural modifications [6]. Although direct studies addressing the influence of particle size in hercynite powders remain limited, investigations on ceramic and composite systems consistently indicate that particle size reduction improves mechanical performance and dimensional stability [7]. Consequently, controlling particle size distribution is essential for achieving homogeneous microstructures capable of withstanding severe thermal and chemical environments.

Mechanical milling is widely employed as an effective technique for particle size reduction and morphology modification; however, the process involves complex and inherently stochastic mechanisms, including particle fracture, agglomeration, and energy dissipation. Numerous studies have shown that mechanical milling typically produces a rapid decrease in particle size at early stages, followed by a reduction in refinement efficiency at longer milling times due to increased agglomeration and reduced impact effectiveness [8,9]. Microstructural characterization using scanning electron microscopy and particle size analysis has revealed that milling parameters such as milling time, ball-to-powder ratio, and milling media strongly influence the extent of particle size refinement and morphological homogeneity [10,11]. These observations have motivated the development of analytical and kinetic models to describe particle size evolution during mechanical milling, emphasizing the existence of saturation-type refinement behavior rather than linear size reduction trends [12].

Previous studies on hercynite powders have primarily focused on synthesis routes, phase formation, and microstructural characterization, while quantitative descriptions of particle size evolution during mechanical milling remain scarce. Although descriptive analyses reporting particle size changes with milling time are available, experimentally validated kinetic models specifically tailored to hercynite systems have not yet been reported. In contrast, physically motivated kinetic and stochastic models developed for other material systems have successfully described particle size refinement by capturing the balance between fracture-dominated and agglomeration-dominated regimes [13,14]. These approaches highlight the relevance of simple yet physically consistent formula-

tions for describing milling-induced particle size evolution when supported by reliable experimental descriptors.

In this work, a descriptive and condition-specific kinetic framework is proposed to describe particle size refinement in hercynite powders during wet mechanical milling. The approach integrates SEM-based statistical reconstruction of particle size distributions with a first-order kinetic model exhibiting saturation behavior to quantitatively describe the evolution of the median particle size (D_{50}) as a function of milling time. The proposed framework provides physically consistent insight into the refinement mechanisms governing hercynite powders and establishes a quantitative basis for process optimization under controlled milling conditions.

2. Experimental Procedure

Raw Materials

High-purity electrofused hercynite (FeAl_2O_4) powder supplied by RHI Magnesita was used as the starting material in this study. The as-received material presented a particle size smaller than $80\text{ }\mu\text{m}$ and was used without further chemical treatment prior to mechanical milling. The oxide chemical composition of the raw hercynite powder was determined by X-ray fluorescence (XRF) analysis, utilizing a PW2400 spectrometer (Philips, Eindhoven, The Netherlands), and is summarized in Table 1. The composition confirms the high purity of the material, with Al_2O_3 and Fe_2O_3 as the main constituents, along with minor amounts of MgO, CaO, and other trace oxides.

Table 1. Oxide composition (wt.%) of the raw hercynite powder.

Raw Material	MgO	CaO	Al_2O_3	Fe_2O_3	SiO_2	TiO_2	MnO	Others	LOI
Hercynite	4.29	0.14	46.32	46.45	1.02	0.15	0.49	1.13	0.01

Mechanical milling was carried out with the objective of reducing the particle size of hercynite powders to the submicrometric scale. The experiments were performed using a high-energy planetary ball mill (PM 100, Retsch GmbH, Haan, Germany) operating at room temperature. A cylindrical stainless-steel vial with a volume of 50 cm^3 was employed as the milling container, together with stainless-steel balls as the grinding media, which are commonly used for this type of high-energy milling experiments. Wet milling conditions were adopted using isopropyl alcohol as the milling medium in order to reduce excessive agglomeration and promote efficient particle size refinement. The abrasive charge consisted of ten stainless-steel balls with a diameter of 18.2 mm , corresponding to a constant ball-to-powder weight ratio (BPR) of 5:1. The milling speed was fixed at 450 rpm for all experiments. To investigate the effect of milling time on particle size evolution, milling durations of 2, 4, and 8 h were selected. After milling, the resulting slurry was dried to remove the solvent, and the powders were gently deagglomerated prior to characterization. These processing conditions were maintained constant throughout the experimental campaign to ensure reproducibility and enable a consistent evaluation of particle size refinement.

Phase identification and structural analysis of the hercynite powders after mechanical milling were performed by X-ray diffraction (XRD). Measurements were carried out using a (D8 ADVANCE X-ray diffractometer, Bruker AXS GmbH, Karlsruhe, Germany) equipped with $\text{Cu K}\alpha$ radiation ($\lambda = 1.5406\text{ }\text{\AA}$). Diffraction patterns were collected over a 2θ range of ($5\text{--}110^\circ$). The obtained diffraction patterns were analyzed to verify phase stability during milling, to detect any possible structural changes or secondary phase formation induced by the high-energy milling process, and to assess the potential presence of crystalline contamination phases, particularly iron-based species originating from the stainless-steel milling media. Morphological characterization and particle size analysis of the hercynite powders

milled for different durations were performed by scanning electron microscopy (SEM) using a field-emission scanning electron microscope (Nova NanoSEM 200, FEI Company, Hillsboro, OR, USA). The microscope was operated at an accelerating voltage of 10–15 kV, selected to achieve an adequate balance between spatial resolution and signal intensity for ceramic powder analysis. The SEM system was equipped with a scanning transmission electron microscopy (STEM) detector and an energy-dispersive X-ray spectroscopy (EDX) detector, enabling semiquantitative microchemical analysis. Elemental analysis was conducted using an Apollo XP 2930 energy-dispersive X-ray spectroscopy detector (EDAX Inc., Mahwah, NJ, USA) which was employed to assess the elemental distribution and to qualitatively evaluate potential contamination arising from the stainless-steel milling media.

SEM micrographs were acquired from multiple, randomly selected regions for each milling condition to ensure representative sampling. Quantitative particle size analysis was carried out by digital image processing of SEM micrographs using ImageJ software (version 1.54u7). For each milling condition, more than 400 individual particles with clearly distinguishable edges were manually segmented and measured to construct particle size histograms. Particle size was defined based on the equivalent circular diameter of the projected particle areas. From the reconstructed distributions, characteristic particle size descriptors were obtained, and the median particle size D_{50} was selected as the primary descriptor due to its robustness against distribution asymmetry. These experimentally reconstructed particle size descriptors served as the basis for the subsequent kinetic modeling and descriptive analysis of particle size evolution.

For each milling condition, three SEM micrographs were analyzed at a magnification of 1000 $\times$. Image calibration was performed in ImageJ using the scale bar embedded in each SEM micrograph prior to particle measurement. Particle segmentation was carried out manually based on grayscale contrast and particle boundary recognition. Only particles with clearly distinguishable boundaries were included in the analysis. Strongly overlapping particles, drying-induced dense agglomerates, and clusters without resolvable individual particle edges were excluded from the individual particle count. When agglomerated clusters could not be reliably separated into individual particles, they were not considered as primary particles for the calculation of the equivalent circular diameter.

It should be noted that the particle size statistics reported in this study correspond to image-level measurements obtained from SEM micrographs for each milling condition. Although more than 400 particles were analyzed per condition to improve the statistical representativeness of the reconstructed particle size distributions, independent milling replicates were not performed for each milling time. Therefore, the reported dispersion reflects intra-batch particle-population variability and image-analysis uncertainty, but it does not account for batch-to-batch variability associated with independent milling runs.

3. Results and Discussion

3.1. X-Ray Diffraction Analysis

Figure 1 shows the X-ray diffraction patterns of hercynite powders extracted at different mechanical milling times (0, 2, 4, and 8 h). All diffraction patterns exhibit the characteristic reflections of the hercynite spinel structure, indicating that no secondary crystalline phases were detected within the detection limit of XRD under the applied milling conditions. This suggests that no crystalline phase decomposition or phase transformation was detected within the detection limit of XRD under the applied milling conditions. However, amorphous or poorly crystalline phases cannot be excluded based solely on XRD analysis.

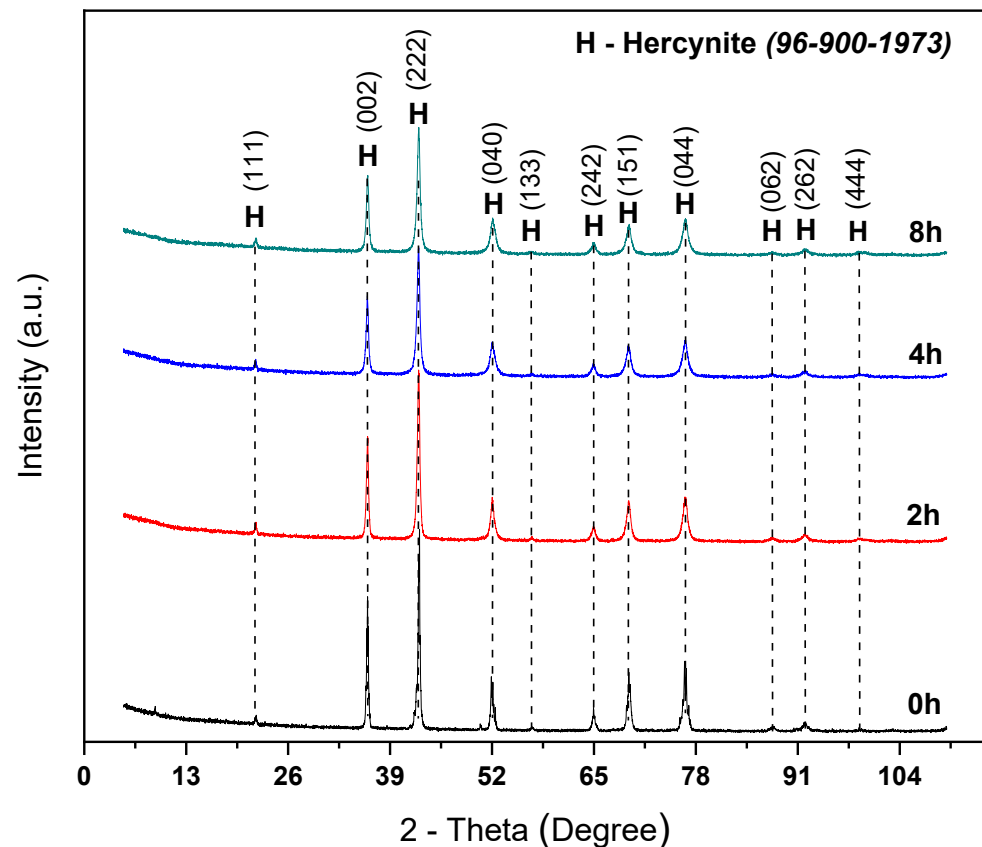


Figure 1. X-ray diffraction patterns of hercynite powders before and after wet mechanical milling for different milling times (0, 2, 4, and 8 h).

Despite the preservation of the spinel phase, a progressive decrease in peak intensity accompanied by a noticeable broadening of the diffraction peaks is observed as milling time increases. These effects become more pronounced for milling times of 4 and 8 h. This behavior is consistent with milling-induced structural disorder and possible crystallite refinement and/or lattice strain accumulation [15]. Previous studies on a wide range of alloy systems have shown that mechanical milling promotes grain refinement through mechanisms such as dynamic recrystallization, twinning, and the accumulation of dislocations, which collectively contribute to the formation of nanocrystalline or highly strained microstructures [16,17]. For instance, investigations on Ni-based alloys and Ti–Ni systems have demonstrated that mechanical milling leads to the development of nano-sized grains and increased microstrain, resulting in enhanced mechanical properties [18]. Consequently, the broadening of diffraction peaks observed in X-ray diffraction patterns is widely recognized as a characteristic signature of these microstructural changes, encompassing both reduced crystallite size and increased lattice strain associated with defects and dislocation networks [19].

3.2. Peak Broadening Analysis

To further illustrate the peak broadening phenomenon, selected diffraction peaks were analyzed in detail. Figure 2 presents enlarged views of representative reflections, where a clear increase in peak width with milling time can be observed.

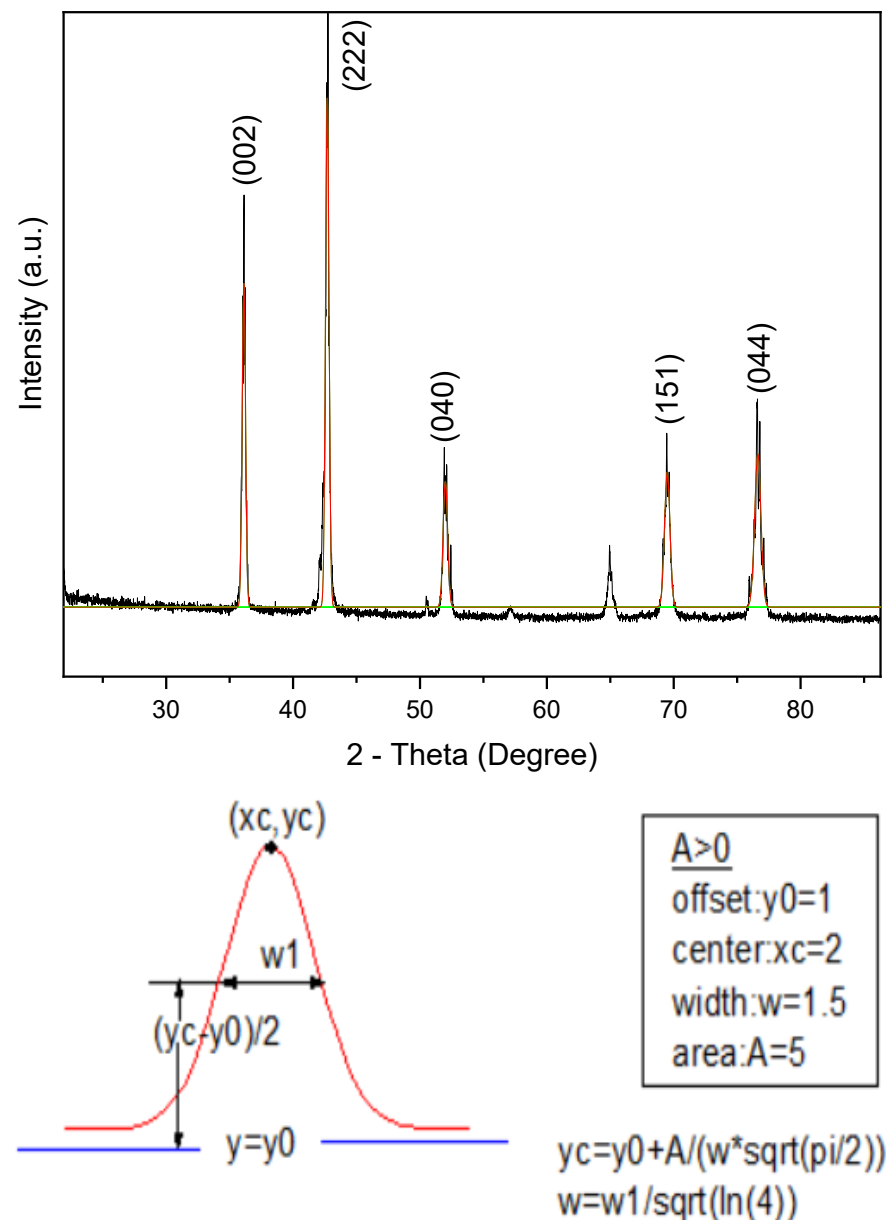


Figure 2. Peak fitting analysis of representative diffraction peaks in a diffractogram session.

To quantitatively support the peak broadening observed in the X-ray diffraction patterns, the full width at half maximum (FWHM) of several representative hercynite reflections was determined as a function of milling time. The selected crystallographic planes include both low- and high-intensity reflections, providing a comprehensive view of the structural refinement induced by mechanical milling.

As shown in Table 2, the FWHM values of the selected hercynite reflections increase progressively with milling time, confirming a systematic broadening of the diffraction peaks after wet mechanical milling. The relative increase in FWHM between 0 and 8 h was approximately 34.0% for the (002) reflection, 61.1% for (222), 77.1% for (040), 35.4% for (151), and 37.6% for (044). This trend indicates that peak broadening is not restricted to a single reflection, but occurs across several crystallographic planes, suggesting milling-induced structural disorder. The larger relative broadening observed for some reflections, particularly (040) and (222), may indicate that the structural response to milling is not completely uniform among crystallographic directions. However, because instrumental broadening correction, Williamson–Hall analysis, and Rietveld refinement were not performed

in the present study, crystallite size and microstrain were not independently quantified. Therefore, the observed peak broadening should be interpreted as qualitative evidence of possible crystallite refinement, lattice strain, and defect accumulation, rather than as a quantitative determination of crystallite size or anisotropic microstrain [20,21]. Future work should include instrumental broadening correction using a suitable standard, followed by Williamson–Hall or Rietveld refinement, to independently separate crystallite-size and microstrain contributions.

Table 2. Evolution of the full width at half maximum (FWHM) of selected hercynite diffraction peaks as a function of mechanical milling time.

Planes (hkl)	0 h	2 h	4 h	8 h
	FWHM (Degree)	FWHM (Degree)	FWHM (Degree)	FWHM (Degree)
(002)	0.26661	0.29829	0.34557	0.35724
(222)	0.27638	0.35891	0.43389	0.44524
(040)	0.35596	0.50173	0.62329	0.63023
(151)	0.43028	0.51936	0.53456	0.58258
(044)	0.49222	0.59369	0.66106	0.67743

3.3. Peak Intensity Evolution

Figure 3 illustrates the evolution of diffraction peak intensity as a function of milling time for a representative hercynite reflection. A clear decrease in maximum intensity is observed as milling time increases. This phenomenon is consistent with observations reported for other material systems, where high-energy mechanical milling disrupts intermediate- and extended-range structural ordering, leading to amorphization or reamorphization processes [22]. Mechanical milling progressively breaks down periodic atomic arrangements, resulting in the collapse of long-range crystalline order while, in some cases, preserving local bonding environments [23]. This structural disorder manifests as both broadening and reduction in intensity of diffraction peaks, reflecting increased lattice defects, microstrain, and fragmentation of ordered domains [24]. In several milled oxides and alloy systems, these effects are accompanied by slight shifts in diffraction peak positions and, in advanced stages, by the formation of partially or fully amorphous phases [25].

The combined effect of peak broadening and intensity reduction provides qualitative evidence of structural refinement and disordering processes occurring during mechanical milling. This process is commonly observed in a wide range of ceramic and alloy powders, where crystallite sizes progressively decrease to the nanometer scale while microstrain increases due to the accumulation of dislocations and lattice distortions [26]. Crystallite refinement enhances surface reactivity and can improve mechanical and functional properties, as reported for ferroelectric ceramics and WC-based composites, whereas the increase in microstrain reflects the build-up of internal stresses and defect structures within the lattice [27]. Furthermore, milling parameters such as milling time, milling media, and powder composition play a critical role in controlling the balance between crystallite size reduction and microstrain development, thereby influencing subsequent processing routes and the final material performance [28].

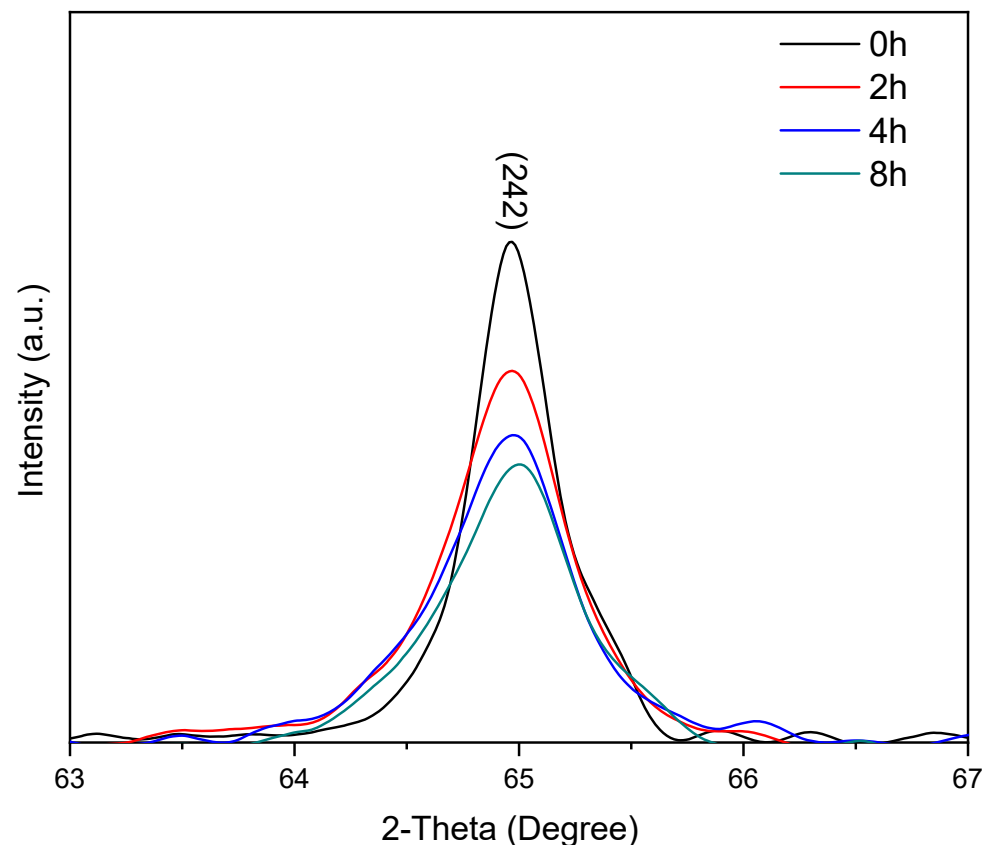


Figure 3. Evolution of the maximum diffraction peak intensity of a representative hercynite reflection as a function of milling time.

3.4. Assessment of Contamination During Mechanical Milling

In addition to the structural refinement evidenced by XRD analysis, the chemical stability of the hercynite powders during mechanical milling was also evaluated. The potential contamination introduced during mechanical milling was assessed by semi-quantitative chemical analysis using X-ray fluorescence spectroscopy (XRF). Table 3 summarizes the elemental composition of hercynite powders milled for different durations, allowing the identification of compositional variations associated with prolonged milling.

Table 3. Semi-quantitative elemental composition (wt.%) of hercynite powders at different mechanical milling times. The values are normalized to the detected elements, and oxygen was not quantified; therefore, the data should not be interpreted as oxide-normalized or stoichiometric FeAl_2O_4 compositions.

Sample	Fe	Al	Si	Mn	Co	Cu	Cr	Zr	Ti	S	P	Zn	Mo
FeAl_2O_4 (0 h)	87.51	9.08	1.33	0.81	0.30	0.21	0.21	0.16	0.13	0.11	0.09	0.03	0.02
FeAl_2O_4 (2 h)	90.18	5.75	1.76	0.79	0.35	0.21	—	0.14	0.12	—	—	—	0.03
FeAl_2O_4 (4 h)	90.65	5.17	0.63	0.81	0.35	0.20	1.90	0.12	0.11	—	—	—	0.01
FeAl_2O_4 (8 h)	92.58	3.41	0.53	0.57	0.36	0.20	1.96	0.13	0.11	—	0.05	—	0.03

It should be emphasized that Table 3 reports semi-quantitative elemental values normalized to the detected elements. Oxygen was not quantified in this analysis; therefore, the Fe and Al values are not oxide-normalized and should not be used to verify the stoichiometry of FeAl_2O_4 or as a direct bulk mass balance. Consequently, the apparent increase in Fe content and decrease in Al content with milling time should be interpreted cautiously, as these variations may be influenced by the semi-quantitative nature of the measurement, matrix effects, particle-size effects, surface heterogeneity, local compositional

heterogeneity, and the normalization procedure. Therefore, these variations are not used here as direct evidence of Fe–Al diffusion, alloying, or bulk chemical transformation.

The contamination assessment was therefore focused primarily on trace elements commonly associated with stainless-steel milling media, such as Cr, Mn, Co, Cu, and Mo. The detection of Cr after extended milling, particularly after 4 and 8 h, suggests some degree of material transfer from the stainless-steel vial and balls to the hercynite powders. This behavior is consistent with previous reports indicating that contamination during mechanical milling is affected by milling duration, media composition, media hardness, and the milling environment [29,30]. In the present case, the use of wet milling with isopropyl alcohol may have helped reduce excessive powder–media interaction compared with dry milling conditions; however, it did not completely suppress metallic transfer. Similar contamination effects have been reported in mechanochemical processing when metallic milling tools are used, even when the overall contamination level remains relatively low [31,32].

The relatively low concentrations of trace metallic elements suggest that metallic transfer from the stainless-steel media remained limited under the applied wet milling conditions. Nevertheless, these results should be interpreted as a qualitative and semi-quantitative indication of contamination rather than as a definitive assessment of chemical integrity. Previous studies have shown that contamination can be further reduced by using alternative milling media, such as ceramic or polymer-based materials, or by applying protective surface coatings to milling tools [33,34]. Therefore, a more rigorous evaluation of milling-induced contamination would require complementary analyses such as EDS elemental mapping, quantitative chemical analysis, or direct comparison with powders milled using ceramic media under equivalent conditions. These analyses were outside the scope of the present study but are recommended for future work to better distinguish true compositional changes from semi-quantitative normalization effects.

Regarding phase stability, the absence of additional reflections in the XRD patterns indicates that no secondary crystalline phases associated with contamination or milling-induced decomposition were detected within the detection limit of XRD. This observation is consistent with the absence of detectable crystalline transformation products under the applied wet milling conditions. However, it should not be interpreted as definitive proof of complete phase or chemical stability, because XRD may not detect amorphous species, nanocrystalline oxides, very low-level contamination phases, or phases present below the detection limit of the technique.

This consideration is particularly relevant in mechanically milled powders, where material transfer from milling tools may occur without necessarily producing crystalline secondary phases detectable by XRD. Previous studies have shown that contamination during mechanical milling depends on milling duration, milling environment, media hardness, and media composition [30–32]. Therefore, although the XRD patterns do not show additional crystalline phases, the semi-quantitative detection of trace metallic elements should still be interpreted as evidence of limited material transfer from the stainless-steel media rather than as proof of complete chemical invariance.

Complementary techniques such as XPS, TEM-SAED, Raman spectroscopy, or high-resolution EDS mapping would be required in future studies to further confirm the chemical and structural stability of the milled powders. In addition, comparison with powders milled under equivalent conditions using ceramic or polymer-based milling media would help distinguish true milling-induced compositional changes from contamination associated with stainless-steel tools [33,34].

3.5. SEM Morphology of Hercynite Powders

Figure 4 illustrates the morphological evolution of hercynite powders subjected to wet mechanical milling for different durations. The as-received powder (0 h, Figure 4a) is characterized by large, irregularly shaped particles with angular morphologies and sharp edges, which are typical of electrofused refractory materials [35]. The particle size distribution is broad, and the surfaces appear relatively smooth at the micrometer scale. After 2 h of mechanical milling, particle fragmentation occurs through repeated impact and shear forces, producing a mixture of coarse fragments and finer particles while largely preserving the angular morphology of the original powder. This behavior indicates that brittle fracture is the dominant size-reduction mechanism at this stage, where particles preferentially break along pre-existing cracks or structural flaws rather than undergoing plastic deformation [36]. Mechanical milling processes generally involve competing breakage mechanisms such as impact, attrition, and shear, with brittle fracture typically resulting in angular fragments with sharp edges [37]. The fragmentation rate and the resulting particle size distribution depend on factors such as milling energy, initial particle size distribution, and intrinsic material properties, which collectively govern particle breakage efficiency and the generation of fine particles [38]. Further milling to 4 h leads to a pronounced reduction in particle size and a more uniform particle morphology, characterized by a significant decrease in the fraction of coarse particles and the dominance of fine, irregularly shaped fragments. At this stage, partial agglomeration of fine particles is commonly observed, particularly in wet milling systems, due to the increase in surface energy and the action of capillary forces that promote particle clustering [8]. Agglomeration competes with particle breakage during mechanical milling, leading to a dynamic balance that can limit further particle size reduction beyond a critical milling duration [39]. Previous studies have shown that wet milling conditions enhance agglomeration through capillary forces and surface interactions between particles, which may influence powder flowability and surface reactivity [40]. The extent of agglomerate formation is strongly dependent on milling parameters such as milling time, rotational speed, and the use of additives or process control agents, which can mitigate cold welding and reduce excessive agglomeration [41]. After 8 h of mechanical milling, the powders exhibit a highly refined morphology dominated by fine particles with a comparatively narrower particle size distribution than those observed at earlier milling stages, indicating progressive morphological refinement with increasing milling time. Despite this refinement, small agglomerated clusters are still present, reflecting a dynamic balance between particle fracture and agglomeration during prolonged milling [10]. Previous studies have shown that extended milling promotes particle size reduction and morphological homogenization; however, agglomeration may occur as a consequence of increased surface energy and intensified particle–particle interactions, particularly in wet milling systems or nanocomposite powders [42]. In several material systems, mechanical properties such as hardness and tensile strength have been reported to reach optimal values at milling durations comparable to those employed in this study, which is commonly attributed to the refined and more uniform powder morphology [43]. Both experimental observations and modeling approaches confirm that the optimal milling time is material-dependent, with morphology evolution playing a critical role in governing powder behavior and the resulting properties of consolidated materials [44]. The SEM observations are consistent with typical high-energy milling processes, where continuous particle size reduction and morphological homogenization occur concurrently with agglomeration phenomena during extended milling.

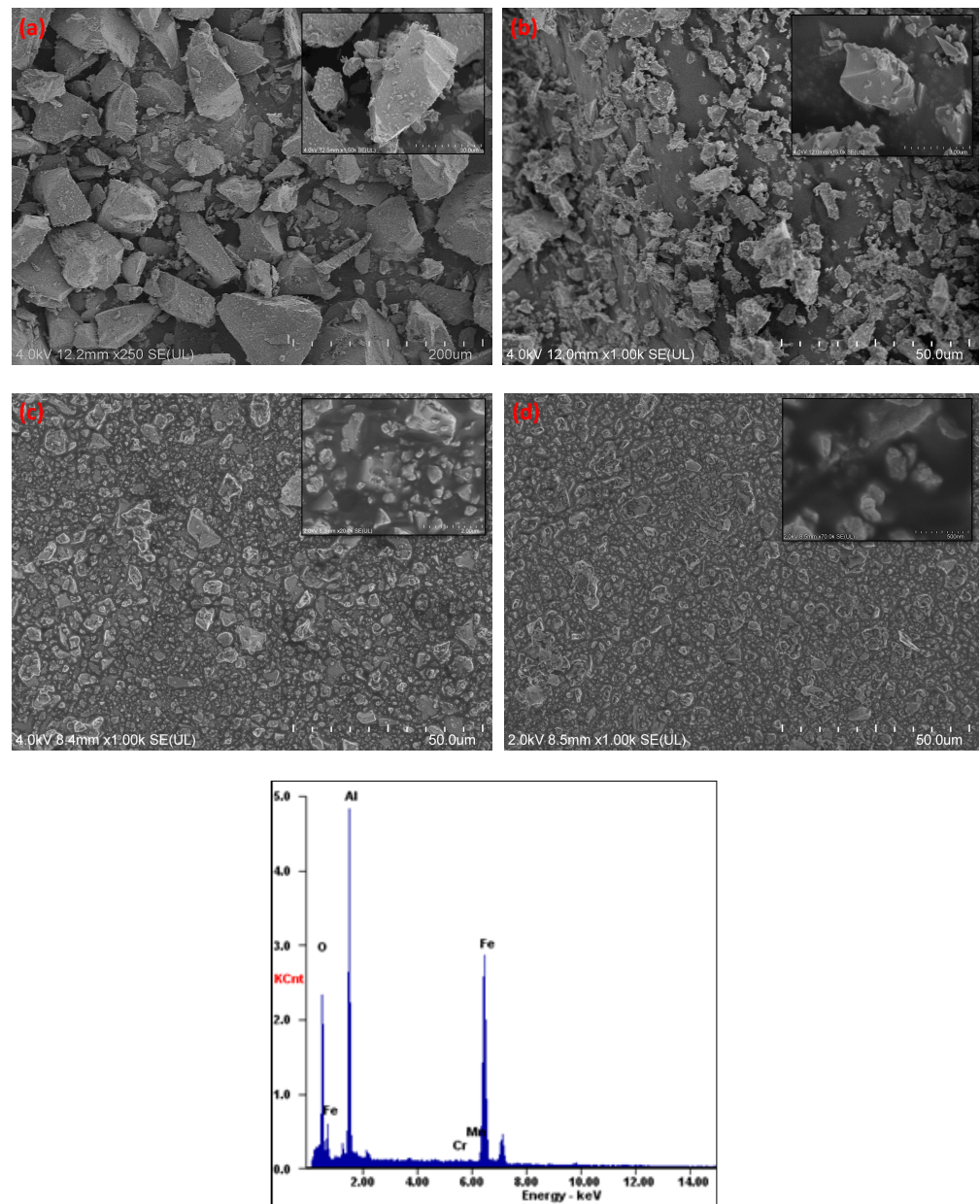


Figure 4. SEM micrographs of hercynite powders subjected to wet mechanical milling for different durations: (a) as-received powder (0 h), (b) 2 h, (c) 4 h, and (d) 8 h of milling. Insets show higher-magnification views highlighting particle fragmentation and morphological refinement. The EDX spectrum qualitatively indicates the dominant presence of Fe and Al in the analyzed region, consistent with the expected elemental constituents of hercynite.

3.6. Particle Size Analysis

During the mechanical milling process carried out under the previously described conditions, hercynite powder samples were extracted at selected milling times (0, 2, 4, and 8 h) in order to evaluate the evolution of particle size. As described in earlier sections, particle size analysis was performed using ImageJ software, which is based on image analysis through manual measurement of individual particle dimensions. Consequently, the acquisition of high-quality SEM micrographs with sufficient contrast and resolution was essential to ensure reliable particle delineation.

For each milling condition, SEM images were analyzed and particle size measurements were performed by manually identifying and measuring individual particles with clearly distinguishable edges. By analyzing multiple images for each condition, more than

400 particle measurements were obtained per milling time, ensuring adequate statistical representativeness of the particle size distributions.

Because particle size distributions are inherently non-negative and may become asymmetric after mechanical milling, the characteristic particle size descriptors were recalculated directly from the empirical cumulative distributions rather than assuming a normal distribution. The measured equivalent circular diameters were sorted in ascending order, and the cumulative frequency distribution was used to determine D_{10} , D_{50} , and D_{90} , corresponding to the particle diameters below which 10%, 50%, and 90% of the measured particles are located, respectively. This approach avoids the assumption that the fitted mean and median are equivalent and provides a physically meaningful description of the particle size distribution.

The resulting empirical percentile descriptors are summarized in Table 4. These values were subsequently used to describe the evolution of the particle size distribution with milling time and to update the D_{50} values employed in the kinetic modeling.

Table 4. Particle size descriptors obtained from empirical cumulative particle size distributions.

Milling Time (h)	D_{10} (μm)	D_{50} (μm)	D_{90} (μm)	Span, $(D_{90} - D_{10})/D_{50}$
0	58.217	83.092	131.218	0.879
2	2.575	4.247	6.943	1.029
4	0.300	0.643	1.157	1.334
8	0.290	0.422	0.654	0.863

To further evaluate the suitability of the distribution fitting approach, the experimental particle size distributions were fitted using normal, lognormal, Rosin–Rammler, and Weibull distribution functions. The normal distribution was included only as a comparative reference, whereas the lognormal, Rosin–Rammler, and Weibull models were considered because they are defined for non-negative particle sizes and are commonly used to describe skewed particle size distributions in comminution and powder processing. The goodness of fit was evaluated using the cumulative-distribution root mean square error (RMSE), as summarized in Table 5.

Table 5. Comparison of fitting models for the reconstructed particle size distributions using cumulative-distribution RMSE.

Milling Time (h)	Normal	Lognormal	Rosin–Rammler	Weibull	Best-Fit Model
0	0.0527	0.0186	0.0584	0.0534	Lognormal
2	0.0676	0.0218	0.0565	0.0569	Lognormal
4	0.0466	0.0233	0.0250	0.0256	Lognormal
8	0.0608	0.0209	0.0569	0.0624	Lognormal

As shown in Table 5, the lognormal model provided the lowest cumulative-distribution RMSE for all milling times, indicating that the reconstructed particle size distributions are better represented by a non-negative asymmetric distribution than by a normal distribution. Therefore, the normal fit was retained only as a comparative reference, while the particle size descriptors used for further analysis were obtained from empirical cumulative distributions.

The collected particle size data were subsequently processed through a differential statistical analysis, yielding particle size distributions commonly represented as frequency histograms. Figure 5 presents the SEM micrographs used for the analysis together with the corresponding particle size distribution histograms for each milling time.

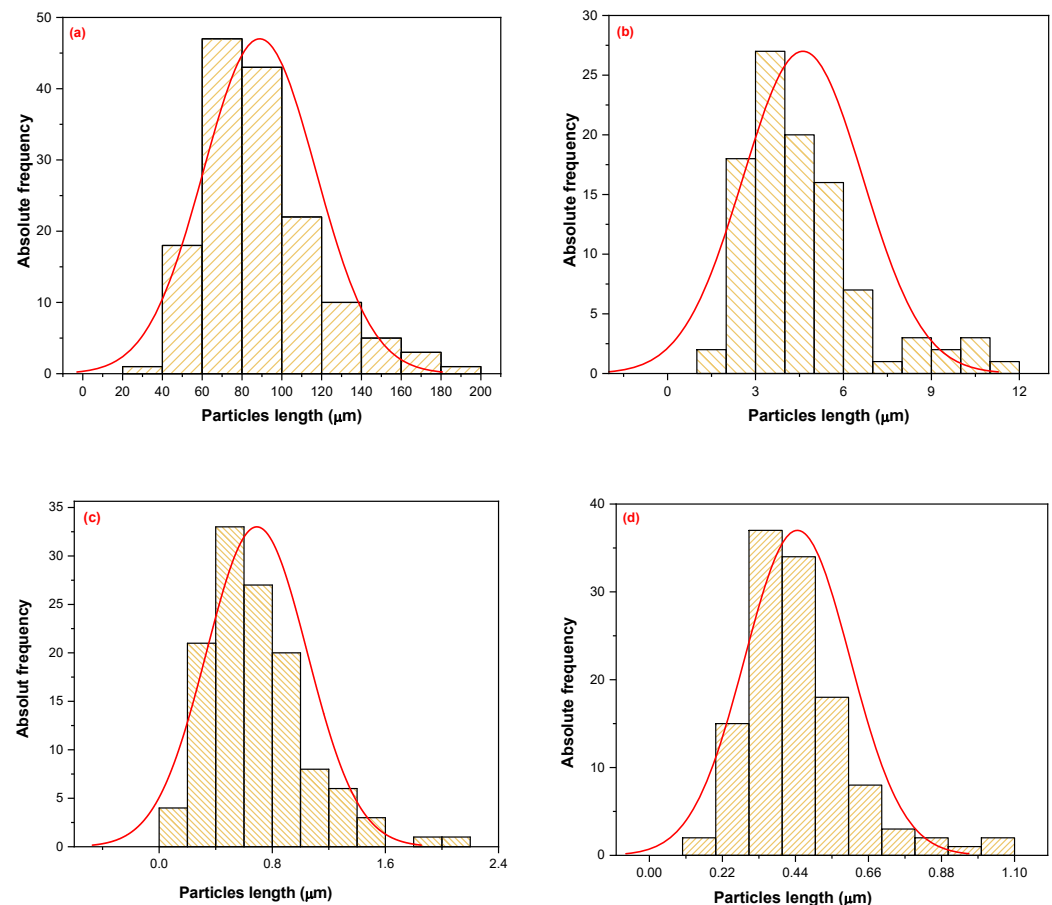


Figure 5. Particle size distribution histograms of hercynite powders obtained from SEM image analysis for milling times of (a) 0 h, (b) 2 h, (c) 4 h, and (d) 8 h.

The as-received hercynite powder (0 h) exhibits a broad particle size distribution characterized by large, angular particles predominantly in the tens of micrometers range. After 2 h of milling, a pronounced shift toward smaller particle sizes is observed, with the distribution centered in the micrometric regime, indicating that brittle fracture is the dominant size-reduction mechanism during the early stages of milling.

Further milling to 4 h results in a significant refinement of the particle size distribution into the submicrometric range. The distribution becomes narrower and more homogeneous, reflecting progressive fragmentation and partial homogenization of particle sizes. After 8 h of milling, the particle size distribution is dominated by fine submicrometric particles, with characteristic sizes on the order of a few hundred nanometers. Although minor agglomeration effects are still present, the overall distribution indicates that a stable refinement regime has been reached.

In addition to the empirical cumulative descriptors reported in Table 4, normal-distribution overlays were retained only as visual and comparative references for the reconstructed particle size histograms. These normal fits are shown in Figure 6 to illustrate the approximate central tendency and dispersion of each histogram. However, because the model comparison in Table 5 showed that the lognormal distribution provided a better description of the reconstructed particle size distributions than the normal distribution, the normal-fit parameters were not used to determine the D_{50} values employed in the kinetic model. The kinetic analysis was based exclusively on the empirical cumulative D_{50} values reported in Table 4.

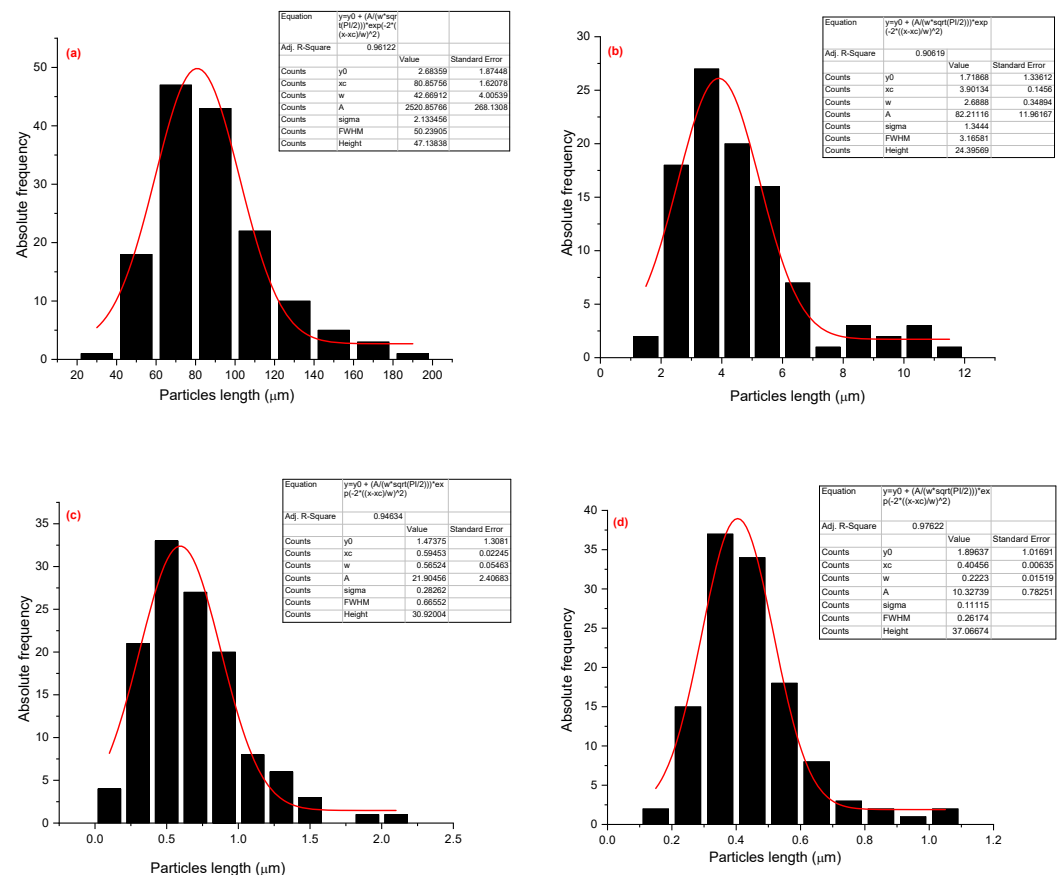


Figure 6. Normal-distribution overlays of the reconstructed particle size histograms of hercynite powders for milling times of (a) 0 h, (b) 2 h, (c) 4 h, and (d) 8 h.

The adjusted coefficients of determination of the normal overlays are reported only to describe the visual agreement between the fitted curves and the histogram shapes. These values should not be interpreted as evidence that the particle size distributions are normally distributed. As shown previously in Table 5, the lognormal model provides a better cumulative-distribution fit for all milling times. Therefore, the normal-fit centroids are reported only as comparative descriptors, whereas the empirical cumulative D_{50} values were used for all kinetic calculations. The comparison between the normal-fit centroids and the empirical D_{50} values is summarized in Table 6.

Table 6. Normal-fit centroid values retained as comparative descriptors of the particle size histograms. The empirical cumulative D_{50} values, not the normal-fit centroids, were used for kinetic modeling.

Milling Time (h)	Adjusted R^2	Normal-Fit Centroid, x_c (μm)	Empirical D_{50} (μm)	$x_c - D_{50}$ (μm)
0	0.96122	80.85756	83.092	−2.234
2	0.90619	3.90134	4.247	−0.346
4	0.94634	0.59453	0.643	−0.048
8	0.97622	0.40456	0.422	−0.017

As shown in Table 6, the normal-fit centroid values follow the same decreasing trend as the empirical D_{50} values, confirming the strong particle size refinement induced by wet mechanical milling. However, the deviations between x_c and the empirical D_{50} also confirm that the fitted normal centroid should not be assumed to be equivalent to the median particle size. Therefore, the empirical cumulative D_{50} values were retained as the quantitative descriptors for kinetic modeling.

3.7. Kinetic Modeling of D_{50} Evolution

The experimentally reconstructed median particle size (D_{50}), obtained from the statistical analysis of SEM–ImageJ particle size distributions, was selected as the characteristic descriptor to model the particle size evolution of hercynite powders during wet mechanical milling. The choice of D_{50} is justified by its robustness and its widespread adoption in comminution and powder processing studies as a representative particle size metric with reduced sensitivity to extreme values in the distribution tails [45–47].

The evolution of D_{50} with milling time demonstrates a pronounced reduction in characteristic particle size, transitioning from the micrometric scale in the as-received powder to the submicrometric regime after prolonged milling. These experimentally reconstructed descriptors form the basis for the kinetic modeling of particle size refinement. During mechanical milling, particle size evolution is governed by competing mechanisms, primarily particle fracture and agglomeration. At early milling stages, fracture dominates and leads to a rapid reduction in particle size, whereas at longer milling times the refinement rate decreases due to the increasing influence of agglomeration and energy dissipation [8]. As a result, particle size evolution typically exhibits a saturation-type behavior rather than a linear trend [12].

Table 7 compares representative milling investigations on hercynite-related systems, spinel-type materials, alumina, ferrites, and refractory oxides. The comparison includes the milling medium, solvent or milling environment, ball-to-powder ratio, rotational speed, milling time, final particle size, and kinetic or modeling approach when available.

Table 7. Comparison of representative milling studies on hercynite-related systems, spinels, alumina, ferrites, and refractory oxides. N.R.: not reported in the referenced study.

System	Milling Conditions	Final Particle Size	Kinetic/Modeling Approach	Ref.
FeAl ₂ O ₄ hercynite, present study	Stainless-steel vial and balls; isopropyl alcohol; BPR = 5:1; 450 rpm; 2–8 h	$D_{50} \approx 0.422 \mu\text{m}$ after 8 h	First-order saturation model for D_{50} evolution	This work
Plate-like Al ₂ O ₃	Wet and dry high-energy milling; BPR = 10:1 and 20:1; 4–32 h; speed N.R.	$\sim 0.29 \mu\text{m}$ at BPR = 20:1 under wet milling	No kinetic model reported	[48]
MgAl ₂ O ₄ spinel precursor mixture	Zirconia pot and balls; ethanol; 60–240 rpm; 1–7 h; BPR N.R.	9.00 μm at 240 rpm for 3 h; 11.69 μm at 120 rpm for 7 h	No kinetic model reported	[49]
α -Al ₂ O ₃ ceramics	Circulatory bead milling; 6, 15, and 20 h; solvent, BPR, and speed N.R.	$D_{50} \approx 170 \text{ nm}$ at 15 h	No kinetic model reported	[50]
α -Al ₂ O ₃	High-energy milling; 2–24 h; solvent, BPR, and speed N.R.	$\sim 10 \text{ nm}$ particle size distribution after 24 h	No kinetic model reported	[51]
CoCrFeNi oxide blend	High-energy ball milling; 2400 rpm; 5–30 h; solvent and BPR N.R.	60.74 nm at 5 h; 39.84 nm at 30 h	KAS reduction-kinetics model after milling; not a direct D_{50} milling-decay model	[52]
Refractory/oxide-rich natural materials	Agate tools and balls; aqueous suspension; optimized BPR and time, numerical values N.R.; speed N.R.	$d_{50} < 1.5 \mu\text{m}$, with target $d_{50} < 1 \mu\text{m}$	No kinetic model reported	[53]

As shown in Table 7, previous studies have reported particle size refinement in alumina, spinel-type oxides, ferrite-containing oxide blends, and refractory oxide-rich systems. However, the reported information is not homogeneous across studies, and parameters such as BPR, solvent, milling speed, and kinetic treatment are frequently omitted. Most of

the available studies focus on processing effects, densification, mechanical performance, phase transformation, or general particle-size refinement, while explicit saturation-type kinetic descriptions of D_{50} evolution are less commonly reported. Therefore, the contribution of the present work should be interpreted as a material-specific and condition-specific application of a first-order saturation model to wet-milled FeAl_2O_4 hercynite powders, rather than as the proposal of a fundamentally new comminution equation.

Consistent with this behavior, the experimental results show a rapid decrease in D_{50} at short milling times, followed by a gradual reduction in refinement efficiency as milling proceeds. This non-linear trend reflects the increasing contribution of particle–particle interactions and agglomeration phenomena as particle size decreases. To capture this behavior, the evolution of D_{50} with milling time (t) was described using a first-order kinetic model with saturation behavior, as shown in Equation (1).

$$D_{50}(t) = D_{\infty} + (D_0 - D_{\infty}) \exp(-kt) \quad (1)$$

where D_0 is the initial median particle size of the as-received powder, D_{∞} represents the asymptotic particle size reached at long milling times, and k is the effective milling rate constant. Similar formulations have been successfully employed to describe particle size refinement in mechanically milled ceramic and metallic systems [54,55].

To reduce the number of free fitted parameters, the initial particle size D_0 was fixed as the experimentally measured D_{50} value at 0 h, obtained from the empirical cumulative particle size distribution. Therefore, only D_{∞} and k were treated as fitted parameters in the nonlinear regression using the experimental D_{50} values corresponding to milling times of 0, 2, 4, and 8 h. Formal 95% confidence intervals were calculated from the nonlinear regression covariance matrix. However, because only four milling times were available, these confidence intervals should be interpreted cautiously and should not be considered a substitute for independent predictive validation.

With D_0 fixed as the empirical D_{50} value at 0 h, the fitted parameters yielded an asymptotic particle size of $D_{\infty} = 0.443 \mu\text{m}$ and an effective milling rate constant of $k = 1.539 \text{ h}^{-1}$. The corresponding formal 95% confidence intervals were 0.370–0.517 μm for D_{∞} and 1.523–1.556 h^{-1} for k . The quality of the fit was evaluated using the root mean square error (RMSE) and the coefficient of determination (R^2). The RMSE was 0.016 μm and the coefficient of determination remained above 0.999. Because the model was fitted using only four milling times, these values should be interpreted as indicators of fitting agreement rather than independent predictive validation. The fitted kinetic parameters and goodness-of-fit indicators are summarized in Table 8.

Table 8. Fitted kinetic parameters for the evolution of D_{50} during wet mechanical milling of hercynite powders.

Parameter	Estimated Value	95% Confidence Interval
Initial particle size, D_0 (μm)	83.092	Fixed from empirical D_{50} at 0 h
Asymptotic particle size, D_{∞} (μm)	0.443	0.370–0.517
Effective milling rate constant, k (h^{-1})	1.539	1.523–1.556
Root mean square error, RMSE (μm)	0.016	–
Coefficient of determination, R^2	>0.999	–

To evaluate whether the first-order saturation model provides a suitable description of the experimental trend, alternative kinetic expressions were also compared using the same empirical D_{50} values. The comparison included a shifted power-law model, a reciprocal saturation model used as a simplified comminution-energy-type surrogate, and a logistic/Hill-type model. Population-balance and full comminution-energy-based models

were not quantitatively fitted because they require additional size-class-resolved distributions, breakage and selection functions, or direct milling energy measurements. The results of this comparison are summarized in Table 9.

Table 9. Comparison of alternative kinetic descriptions for the evolution of D_{50} during wet mechanical milling.

Model	Expression	RMSE (μm)	Comment
First-order saturation	$D_{50} = D_{\infty} + (D_0 - D_{\infty}) \exp(-kt)$	0.016	Best balance between fit, parsimony, and physical interpretation
Shifted power law	$D_{50} = A(t + 1)^{-b}$	0.226	Does not explicitly represent an asymptotic refinement limit
Reciprocal saturation	$D_{50} = D_{\infty} + (D_0 - D_{\infty}) / (1 + at)$	0.725	Lower fitting agreement under the present conditions
Logistic/Hill-type	$D_{50} = D_{\infty} + (D_0 - D_{\infty}) / [1 + (t/t_c)^m]$	~ 0	Over-parameterized for four data points; not robustly identifiable
Population-balance model	Size-class-dependent breakage formulation	Not fitted	Requires time-resolved particle size classes and breakage functions
Comminution-energy-based model	Energy-specific breakage relationship	Not fitted	Requires direct milling energy or power-consumption data

As shown in Table 9, the first-order saturation model provided the lowest RMSE among the parsimonious models and preserved a physically meaningful asymptotic particle size. Although the logistic/Hill-type model could reproduce the four experimental values with very low residual error, it requires an additional fitted parameter and is therefore over-parameterized for the limited dataset. Consequently, the first-order saturation model was retained as a descriptive and condition-specific representation of the observed particle size evolution, rather than as a fully validated predictive model.

Although the proposed kinetic model showed good agreement with the experimental D_{50} values, the limited number of milling times restricts its predictive validation. Therefore, the fitted parameters should be interpreted as condition-specific descriptors of the observed refinement trend rather than universal kinetic constants. Additional intermediate and longer milling times are required to independently validate the estimated values of k and D_{∞} , and to assess whether the same kinetic behavior is maintained under different milling conditions.

Figure 7 presents the updated experimental D_{50} values, obtained from empirical cumulative particle size distributions, together with the fitted kinetic curve. The model reproduces the rapid particle size reduction observed at early milling stages and captures the subsequent transition toward a refinement-limited regime at longer milling times.

The existence of an asymptotic particle size suggests that, under the investigated milling conditions, further particle size reduction becomes increasingly limited due to reduced impact efficiency, enhanced energy dissipation, and the onset of agglomeration phenomena. Therefore, the proposed kinetic model provides a physically consistent framework to describe the experimentally observed particle size evolution and to estimate milling durations required to achieve targeted particle size ranges in hercynite powders. This limitation reinforces the need to interpret the fitted kinetic parameters as condition-specific descriptors of the wet milling behavior of hercynite powders, rather than as universal kinetic constants.

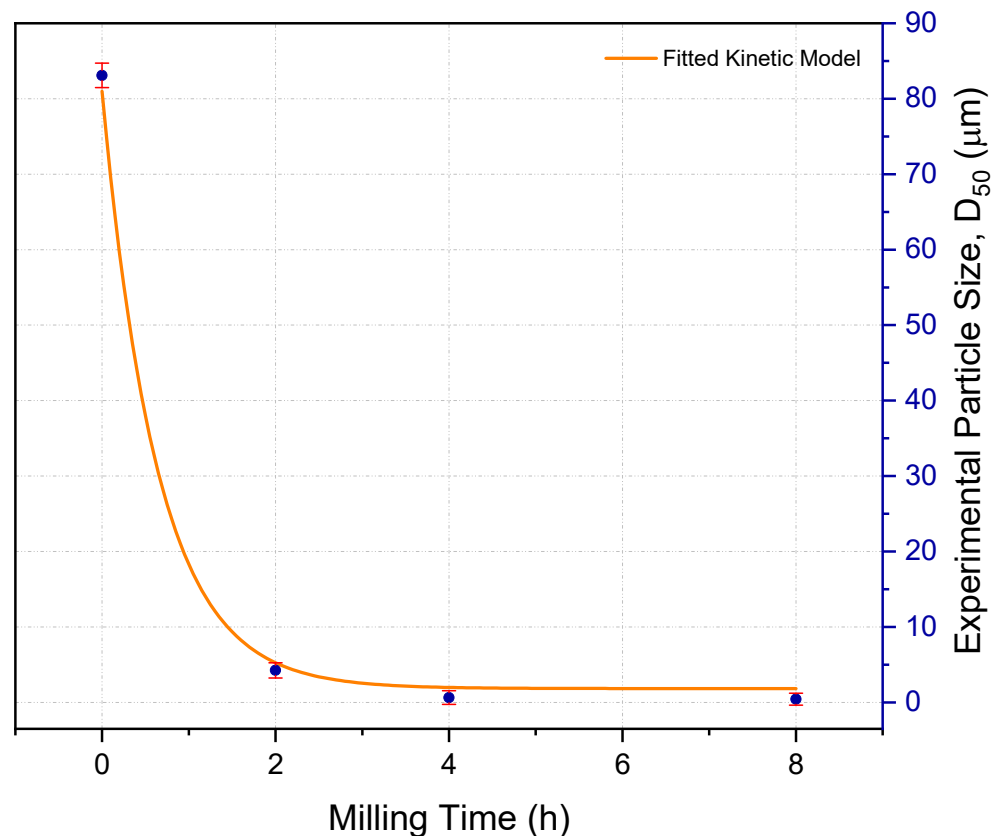


Figure 7. Experimental evolution of the median particle size (D_{50}), obtained from empirical cumulative particle size distributions, as a function of milling time, together with the fitted first-order saturation kinetic model.

3.8. Comparison Between Kinetic Model and Experimental D_{50} Values: Fitting Assessment and Limitations

To further evaluate the fitting precision of the proposed kinetic model, the experimentally obtained D_{50} values were directly compared with the corresponding values calculated from Equation (1) at each milling time. This comparison allows the deviations between the measured particle size descriptors and the model predictions to be quantified in terms of absolute residuals and relative error, as summarized in Table 10.

Table 10. Comparison between experimental and calculated D_{50} values obtained from the fitted kinetic model.

Milling Time (h)	Experimental D_{50} (μm)	Calculated D_{50} (μm)	Residual (μm)	Relative Error (%)
0	83.092	83.091	0.000	0.000
2	4.247	4.249	−0.002	0.052
4	0.643	0.618	0.024	3.759
8	0.422	0.443	−0.022	5.217

As shown in Table 10, the fitted kinetic model closely reproduces the experimentally reconstructed D_{50} values over the investigated milling-time range. The absolute residuals remained low, with relative errors ranging from 0 to approximately 5.2% for all milling conditions. These results support the fitting agreement between the saturation-type kinetic model and the experimental particle size evolution. However, considering the limited number of milling times, this comparison should be interpreted as an assessment of fitting precision rather than as an independent predictive validation.

Figure 7 shows that the fitted curve closely follows the experimental trend over the entire milling time range investigated. The agreement is particularly strong at early milling stages, where rapid particle fragmentation dominates the size reduction process. The relatively small deviations observed in Table 10 further support the suitability of the selected formulation to describe the particle size evolution under the investigated milling conditions. This close correspondence can be attributed to two main factors. First, the proposed exponential saturation model is physically consistent with the dominant mechanisms governing mechanical milling, namely rapid fracture at early stages followed by a gradual reduction in refinement efficiency due to agglomeration, reduced impact effectiveness, and energy dissipation. Second, the experimentally reconstructed D_{50} values are based on statistically significant particle populations and empirical cumulative particle size descriptors, providing a consistent representation of the particle size evolution.

Nevertheless, it should be emphasized that the present validation is based on a limited number of discrete milling times (0, 2, 4, and 8 h). As a consequence, the proposed kinetic model should be interpreted primarily as a descriptive and physically informed framework rather than a fully independent predictive tool. The limited number of experimental points constrains the assessment of model generalization and may contribute to the apparent close agreement between experimental data and fitted predictions. Despite these limitations, the model provides valuable quantitative insight into the particle size refinement behavior of hercynite powders during wet mechanical milling. In particular, the identification of an asymptotic particle size highlights the existence of a practical refinement limit under the applied milling conditions, beyond which further size reduction becomes increasingly inefficient. This information is relevant for process optimization, as it allows the identification of milling durations that balance particle size reduction against processing time and energy consumption.

In addition, because independent milling replicates were not performed, the uncertainty associated with the experimental D_{50} values and the fitted kinetic parameters should be interpreted as image-level and intra-batch uncertainty rather than full process-level variability. Therefore, future work should include at least three independent milling batches for each milling time to quantify batch-to-batch differences and strengthen the statistical robustness of the kinetic parameters. Additional intermediate milling times, alternative milling conditions, and independent validation datasets would also enable a more rigorous evaluation of the predictive capability of the proposed model.

Nevertheless, within the scope of the present study, the kinetic framework captures the dominant trends of particle size evolution and provides a useful basis for the quantitative interpretation and optimization of hercynite powder processing.

4. Conclusions

Wet high-energy mechanical milling reduced the median particle size, D_{50} , from approximately 83.1 μm in the as-received powder to about 0.42 μm after 8 h of milling, confirming the strong influence of milling time on particle size reduction and the feasibility of producing fine hercynite powders through controlled wet milling.

Quantitative particle size analysis based on SEM micrographs and ImageJ statistical reconstruction provided representative particle size distributions supported by the analysis of large particle populations. These descriptors enabled the evaluation of particle size evolution and provided a suitable experimental basis for kinetic modeling. The progressive decrease in particle size was accompanied by a narrowing of the particle size distribution, indicating increasing morphological refinement with milling time.

X-ray diffraction analysis revealed progressive peak broadening and intensity reduction with increasing milling time, suggesting milling-induced structural disorder and

possible crystallite refinement and/or lattice strain accumulation. No secondary crystalline phases associated with milling-induced decomposition were detected within the detection limit of XRD under the investigated conditions. However, amorphous phases, nanocrystalline oxides, or very low-level contamination phases cannot be completely excluded based solely on XRD. Complementary techniques such as XPS, TEM-SAED, or Raman spectroscopy would be useful in future studies to further support the phase-stability assessment.

The non-linear evolution of D_{50} with milling time was described using a first-order kinetic model with saturation behavior. The model captured the rapid particle size reduction at early milling stages and the subsequent transition toward a refinement-limited regime at longer milling times. The fitted parameters yielded an asymptotic particle size of approximately $0.443\ \mu\text{m}$ and an effective milling rate constant of $1.539\ \text{h}^{-1}$, providing quantitative insight into the refinement behavior of hercynite powders under the applied wet milling conditions.

Overall, the combined experimental and modeling approach provides a physically consistent framework for describing particle size refinement in hercynite powders and offers useful guidance for optimizing milling duration in refractory spinel systems. Nevertheless, because the kinetic model was fitted using four experimental milling times, it should be interpreted as a descriptive and physically informed framework rather than as a fully predictive model. Future studies incorporating additional intermediate milling times, longer milling durations, and alternative milling conditions would further strengthen the predictive capability and general applicability of the proposed kinetic approach.

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