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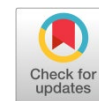
Synthesis and Sintering

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Research article

On the synthesis and sintering behavior of a novel Mg-Ca alloy, Part I: Mechanical alloying



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ABSTRACT

A novel Mg-0.7Ca alloy was prepared by the mechanical alloying (MA) process. Different variables were examined in order to obtain the optimum sample with the best milling behavior and potential sinterability. The structural studies were carried out using X-ray Diffractometer (XRD) and scanning electron microscopy (SEM). Crystallite size and lattice strain of the milled samples were examined by Scherrer and Williamson-Hall methods in order to finalize the investigation. The optimum milling time was found to be 60 minutes. In addition, a starch-containing sample with a fraction of 2.5 weight percent seemed to have the best microstructural properties, based on SEM observations and crystallite size assessments. Due discussions about the effective phenomena during the mechanical alloying were also included.

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KEYWORDS

Mechanical alloying
Magnesium
Crystallite size
Morphology
Phase analysis



1. Introduction

As the lightest structural metals, magnesium and Mg-based alloys have been widely attended by researchers and engineers, mostly due to the growing global tendency toward lightweight structures during the last decades. Hence, a wide range of potential applications, including automotive and aerospace to medical and pyrotechnics have been developed based on the magical combination of properties provided by magnesium. However, besides its attractive low density, high dimensional stability, biocompatibility, and exceptional machinability [1, 2], magnesium encounters poor mechanical strength and high corrosion rate, which challenge its industrial applications. Therefore, strategies have been historically followed to enhance the mechanical properties of Magnesium; most of them are focused on alloying the metal with other metallic and non-metallic elements. Although alloying has its own issues such as consequent intensified and heterogeneous corrosion behavior [3], the strategy is the most common method to enhance the mechanical properties of Mg-based materials.

Alloying is usually conducted through routine melting and casting processes. The process then may be followed by the shape casting and/or further forming processes to obtain the final components. However, the high oxidation rate of Mg-based alloys which may even result in the ignition of the molten metal, as well as the defects derived from the melting and casting processes, promotes the development of other manufacturing processes [4] such as powder metallurgy (PM). The method seems to be one of the most efficient processes to achieve near-net-shape metallic products with tailored mechanical properties [5].

Shaping and densification in temperatures lower than the melting point of the Mg-based alloys eliminate many drawbacks of the casting processes and then introduce the PM process as a promising method to develop advanced magnesium components. More specifically, it has been recently applied in manufacturing biodegradable Mg-based implants [6].

While applying the alloyed raw powders in the PM method, the alloying process can also be carried out through mechanical alloying

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(MA), a solid-state and mechanically-activated solution process [7]. The MA process includes simultaneous mixing and dissolution of the alloying elements and matrix powders, using the kinetic energy provided by ball-milling. Therefore, a homogenous solid-state solution will be formed through a repeated weld-fracture–reweld (WFR) phenomenon on the powder particles [8]. Balancing the welding/fracture phenomenon has been introduced as an essential factor in achieving a well-distributed solid solution structure through the MA process. Hence, process control agents (PCA) such as stearic acid are usually used to prevent excessive cold welding of the powder particles, particularly in ductile metallic powders [9]. Besides the solid solution formation, MA also promotes the formation of nano-scale and/or amorphous structures [10].

MA process also provides advantages in homogenous distribution of the reinforcement phases in Mg-based alloys, as well as the alloying elements with low solubility in Mg [11]. Achieving homogenous, highly activated, and semi-alloyed powder mixtures through the MA process directly affects the later sintering and densification process and consequently, the properties of the sintered components [12].

The conventional sintering processes such as pressure-less sintering (PS) and even pressurized methods such as hot-pressing (HP), commonly provide favorable conditions to the mass transfer through the atomic diffusion mechanism and promote sintering. The relatively long dwelling time of the mentioned processes, however, intensifies the unfavorable grain growth [13]. Hence, modern fast sintering methods such as spark plasma sintering (SPS) have been developed which shortens the sintering time and prevents undesired grain growth [14]. However, the atomic diffusion-based dissolution of the alloying elements is restricted in these fast sintering methods. Therefore, the MA process plays a key role to achieve the homogenous solid solution and consequently mechanical properties in the components sintered through the mentioned fast sintering techniques.

Despite its advantages, mechanical alloying of Mg-based powders has its own issues, including powder contamination, oxidation, and even ignition (due to the high oxidation rate of activated g powder particles). Using a protective atmosphere (vacuum or inert gas) to prevent any contact of the powder particles with oxygen [15], utilizing balls and cups with the same composition of the powders, shortening the milling time, and self-coating of the balls have been suggested as the strategies to overcome the mentioned limitations [9].

Additionally, several other parameters affect the MA process and should be well optimized/controlled to achieve a homogenous, activated, and alloyed powder mixture. The applied kinetic energy through different milling procedures is known as the most effective parameter, and itself depends on variables such as size, shape, and weight of the milling cup, ball-to-powder ratio (BPR), the milling rate, atmosphere, medium, duration, and temperature, powder characteristics, and the type and the fraction of the PCAs [9].

Despite the inspiring research works which have been carried out till now, the mechanical alloying of many of the Mg-based powder mixtures have remained unstudied. This work has been dedicated to the mechanical alloying behavior of a novel Mg-Ca alloy. While the similar cast alloy has shown promising outcomes in mechanical, corrosion, and biocompatibility behavior, the mechanical alloying of the Mg-Ca powder mixture with different low-cost additives has been followed as the first step of the manufacturing process through the powder metallurgy approach. The effects of other MA parameters such as milling time and the fraction of the additives on the phase arrangement, homogeneity, and morphological characteristics of the MAed powder mixtures have been also investigated.

2. Experimental

Commercially pure magnesium (99.9% purity, particle size < 45 μm) powder and machined Mg-7 wt% Ca master alloy (99.9% purity, machined plates < 100 μm) were used as the starting materials to achieve the final composition of Mg-0.7 Ca alloy. The scanning electron micrographs of the starting powder materials are presented in Fig. 1. Different additives, including starch and paraffin, were also used to reduce the adhesion of the particles to the milling media, as well as decrease calcium loss and powder oxidation. Besides the additive-containing samples, a reference sample with no additive was also prepared (known as the pure Mg sample). The powder mixtures were then mechanically milled in a high-energy ball mill (SPEX 8000 M, milling speed of 800 rpm) using stainless steel cup and WC balls at the powder to ball ratio (BPR) of 1/15 under the conditions of normal atmosphere and room temperature (25 $^{\circ}\text{C}$). The milling process was performed at 30, 60, and 90 minutes to evaluate the effect of milling time. 1–2 wt% of stearic acid was also added to the mixture, as the process control agent (PCA) to improve the milling process and reduce

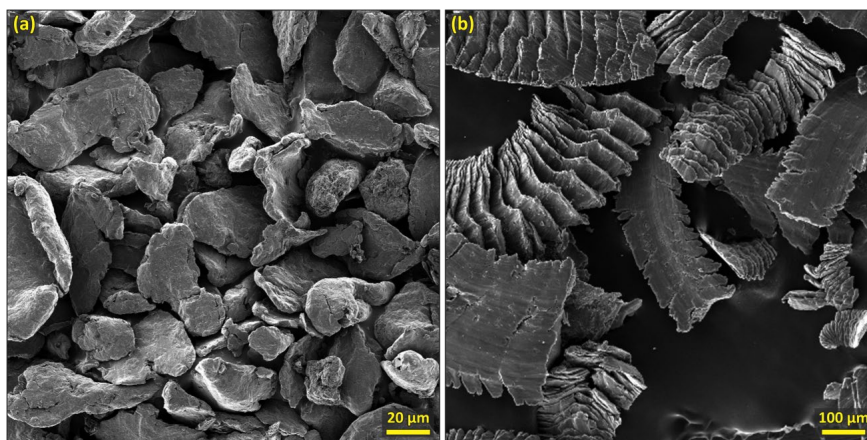


Fig. 1. FESEM micrographs of the starting powders a) pure magnesium and b) machined Mg-7Ca master alloy.

Table 1. Composition, milling conditions, and the coding system of the prepared samples.

Code	Milling time (min)	Additive	Additive fraction (wt%)
30-5St	30	Starch	5
60-5St	60	Starch	5
90-5St	90	Starch	5
Pure Mg	90	Starch	5
60-2.5St	60	Starch	2.5
60-2.5P	60	Paraffin	2.5
60-1St	60	Starch	1

the powder agglomeration. Each sample was obtained through at least three repeated processes to ensure the reliability of the results. The samples were prepared and labeled based on the milling conditions and coding system presented in Table 1, respectively.

The microstructural and morphological investigations of the as-milled alloys were carried out using a field-emission scanning electron microscope (FESEM, MIRA3, TESCAN) equipped with an EDS detector. X-ray diffraction (XRD) spectroscopy using Cu K α ($\lambda = 1.5 \text{ \AA}$) radiation was also used for phase analysis. The crystallite size and lattice strain of the samples were also calculated using the obtained XRD patterns, according to Scherrer and Williamson-Hall methods.

3. Results and discussion

The XRD patterns of the MAed powder mixtures are presented in Fig. 2. As seen, all the samples include the Mg peaks. However, the traces of magnesium oxide (MgO) as well as the amorphous phases can be observed in the patterns of some samples. While the manifestation of the MgO peaks seems to be possible due to the normal atmosphere

of the milling media, the observed amorphous hills in the XRD patterns can be attributed to the presence of carbon originating from the used organic additives. It should be noted that according to the accuracy of the XRD analysis, the peaks of the phases with weight fractions <5% would not necessarily appear in the XRD patterns. Hence, appearing the peaks of MgO and amorphous carbon in some of the samples does not mean that the other samples are free from any oxide and/or remained carbon.

As seen in the magnified part of Fig. 2, increasing the milling time in the samples containing 5 wt% starch as the additive has led to a slight peak shift, which can be attributed to the higher lattice strain of the samples, as well as an increased solid solution. Such observations can be better illustrated according to the crystalline parameters of the processed powders. The findings of the samples' calculated crystallite size and lattice strain using the Scherrer and Williamson-Hall methods are presented in Table 2. The parameters of the pure Mg sample were considered as the starting references for the abovementioned calculations. As seen in Table 2, nevertheless the differences between the calculated parameters of the samples according to the used method, the obtained results of both of the calculation methods follow similar trends. It should be noted that while the Williamson-Hall method can be used in powder and bulk samples, the Scherrer method has been introduced as a relatively accurate calculation method for powder samples. The accuracy of the calculations, however, depends on the resolution of the used XRD instrument, as well as the test parameters (such as the scan rate, step size, etc.). Therefore, in this study, the trends of the obtained results have been qualitatively attended to discuss the MA behavior of the powder mixtures, whereas the obtained numbers may be different in every calculation method [16].

According to Table 2, increasing the milling time from 30 minutes to 60 minutes has led to decreased crystallite size as well as enhanced lattice strain. Such results can be qualitatively confirmed, according to the lower intensities (height) and higher widths (sharpness) of the Mg peaks of the samples milled at longer periods, which addresses higher FWHMs and indicates more randomized crystalline orientations

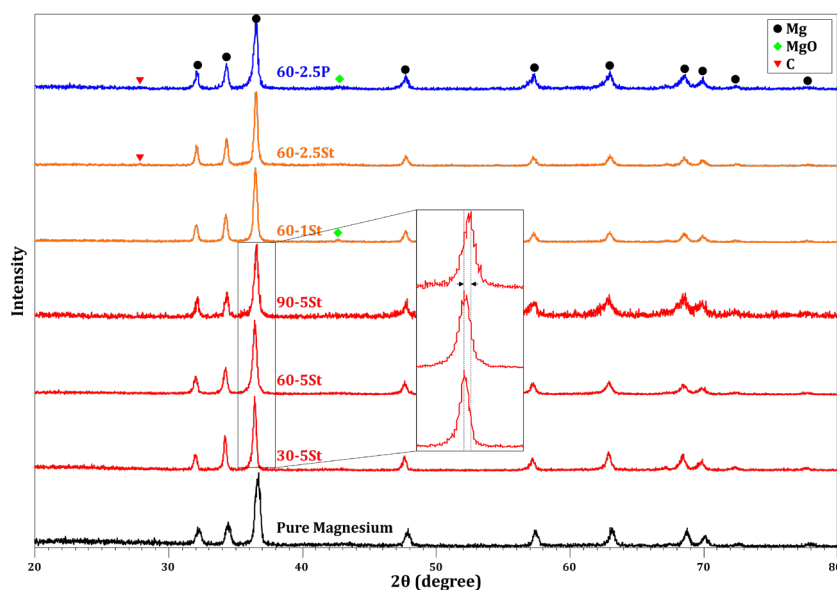
**Fig. 2.** XRD patterns of mechanically milled Mg-Ca alloys.

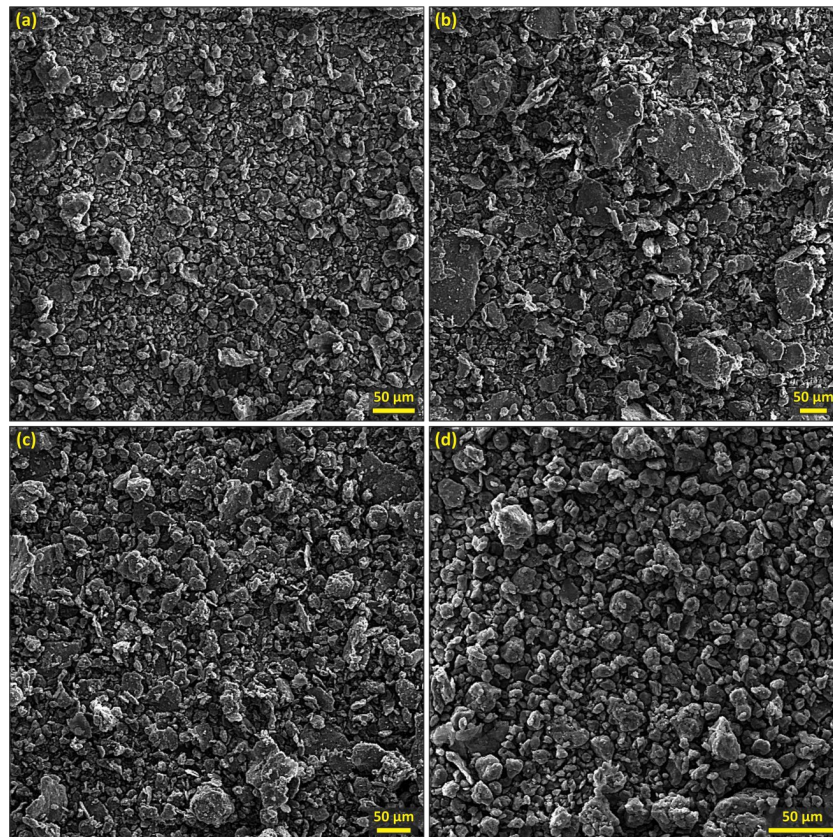
Table 2. Crystallite size and internal strain of Mg-Ca alloys.

Sample code	Scherrer analysis				Williamson-Hall analysis		
	Crystallite size (nm)			Average crystallite size (nm)	Average lattice strain (%)	Crystallite size (nm)	Lattice strain (%)
	$\{10\bar{1}0\}$	$\{0002\}$	$\{10\bar{1}1\}$				
30- 5St	35.0	66.0	38.0	46.3	0.36	62.9	0.05
60- 5St	35.0	31.3	28.8	31.7	0.46	49.9	0.19
90- 5St	42.2	36.8	36.4	38.4	0.39	57.9	0.10
60- 1St	33.6	38.5	33.5	35.2	0.42	65.8	0.08
60- 2.5St	56.6	53.3	49.2	53.0	0.30	45.25	0.11
60- 2.5P	36.6	30.1	32.2	32.9	0.44	60.3	0.14
Milled pure Mg	21.4	22.1	21.5	21.66	0.62	48.27	0.18

(smaller crystallites). Such an improved MA behavior can be attributed to the intensified deformation-work hardening-fracture mechanism in which, the dislocation density is increased and lead to the formation of more low-angle boundaries (crystallite boundaries). While improved MA behavior was observed through increasing the milling time from 30 to 60 minutes, further increase of the milling time to 90 minutes has resulted in enhanced crystallite size, in 5 wt%

starch contained samples. In other words, it seems that the 60-5s sample represents the optimum milling parameters, as well as the lowest detected contaminations (secondary phases such as MgO).

The increased crystallite size of the 90-5St sample can be attributed to the increased temperature of the powder mixture through the relatively long milling process, which causes the dynamic recovery (DRV) of the deformed particles. In other

**Fig. 3.** FESEM micrographs of the MAed powder mixtures a) milled pure Mg, b) 30-5st, c) 60-5st, and d) 60-2.5st.

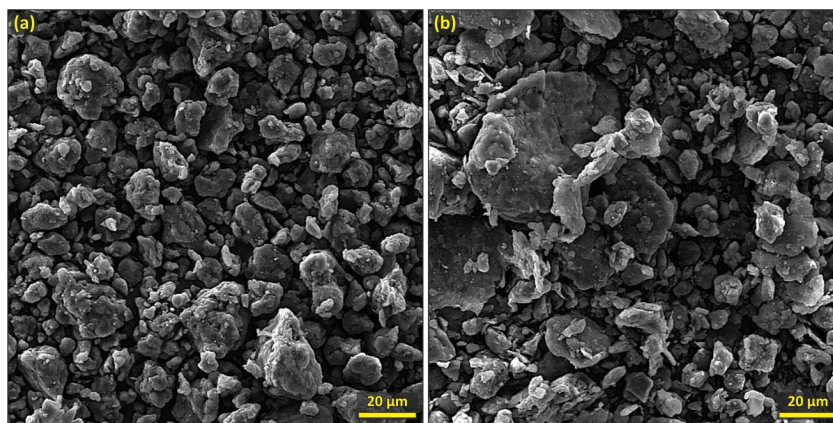


Fig. 4. FESEM micrographs of the MAed powder mixtures with 2.5 wt% a) starch and b) paraffin additives (samples 60-2.5st and 60-2.5P, respectively).

words, while a part of the kinetic energy of the moving balls promotes the plastic deformation of the powder particles and enhances the dislocation density (decreased crystallite size), a considerable part of the mentioned energy results in heating the powder mixture (increasing the temperature) and then, promotes the dislocation rearrangement in the deformed particles. Hence, the consequent immigration and/or removal of the low-angle boundaries which mainly occurred due to the interactions between the positive and negative dislocations manifests as the increased crystallite size of the MAed powder particles. The increased dislocation density, itself provides a higher driving force for the DRV process. Hence, the decreasing trend of the powder's crystallite size may encounter a turning point due to increased temperature accompanied by the enhanced driving force of plastic deformation [17].

It is also worth noting that the progression of the mechanical alloying may also be affected by the degree of the powder agglomeration, which can be intensified through relatively long milling periods [18]. The agglomeration may also be intensified according to the volume fraction and type of the additives, although the stearic acid is used as the PCA to control the degree of the agglomeration. Considering 60-5St as the optimum sample of the 5 wt% starch-containing groups and to decrease the agglomeration and organic contamination of the powder particles, the mechanical alloying process was repeated at the same milling conditions with lower volume fractions of the starch additive.

Besides the additive type and the aims of its application through the mechanical milling, there is always a critical additive volume fraction which is determined based on the optimized MA and later sintering processes. In the case of oxidation protection, while the lower volume fractions can decrease the protection ability of the additive, higher volume fractions may cause powder agglomeration and negatively affect the densification process. According to the data presented in Table 2, the increased crystallite size of the starch-contained samples is seen when the volume fraction of the additive is decreased from 2.5 to 1 wt%, while a slight difference is observed between 2.5 and 5 wt% additive in samples. While the lower volume fraction of the additive seems to promote deformation of the powder particles and lead to decreased crystallite size, such an observation can be attributed to the intensified oxidation of the material which can be confirmed according to the MgO peak appeared in the XRD pattern of the 60-1s sample. It is

also worthy to note that the lower amounts of the starch additive may intensify the adhesion of the powder particles on the balls and cup walls, and result in postponed mechanical alloying and/or powder particle deformation, which can be confirmed according to the calculated crystallite size and lattice strain of 60-1s sample. Hence, if the crystallite size, lattice strain, and the volume fraction of the synthesized oxide are considered as the sintering promotion parameters of the powder mixture, the 60-2.5 sample seems to present the optimum MA conditions. The FESEM micrographs of the MAed powder mixtures are presented in Fig. 3. As seen, compared to the milled pure magnesium powder (Fig. 3a), on one hand, the particle deformation and fracture have been decreased in 1wt% starch-contained sample (60-1st). On the other hand, while the 5 wt% starch-contained sample (Fig. 3c) shows particle agglomeration, a relatively homogenous milled powder mixture can be achieved in 2.5 wt% starch-contained sample (Fig. 3d). Such an observation validates the previously discussed optimum volume fraction of the additive. Hence, the 2.5 wt% starch-contained sample (60-2.5st) is selected as the optimum MAed powder mixture.

To study the effects of additive type on the MA results, while the other MA parameters were kept constant, the starch additive was replaced by the paraffin (60-2.5P sample). As seen in Fig. 2, while the synthesized oxide through the ball-milling cannot be detected via XRD for the 60-2.5st sample, the XRD pattern of the 60-2.5P sample shows the main peak of MgO. Comparatively, such an observation indicates the higher volume fraction of the oxides in the paraffin-contained sample. It is also worthy to note that the calculated crystallite size and lattice strain for the 60-2.5P sample are higher than those of the 60-2.5st sample. It can be attributed to the lubrication effect of paraffin, which liquefies during the milling process due to the increased temperature of the cup, induced by the heat generated from the impacts of the balls. Therefore, while the liquid paraffin can facilitate the interfacial slip of the deformed particles on each other and decrease the energy transfer between the particles through the ball impacts, every particle may experience higher individual impact stress and consequently, intensified lattice strain. Fig. 4 shows the comparative FESEM micrographs of 2.5 wt% starch- and paraffin-contained samples. As seen, whereas the 60-2.5st sample includes 3D deformed particles with relatively homogenous morphology and size, there are several 2D-deformed (crushed) particles in the 60-2.5p sample which confirm the

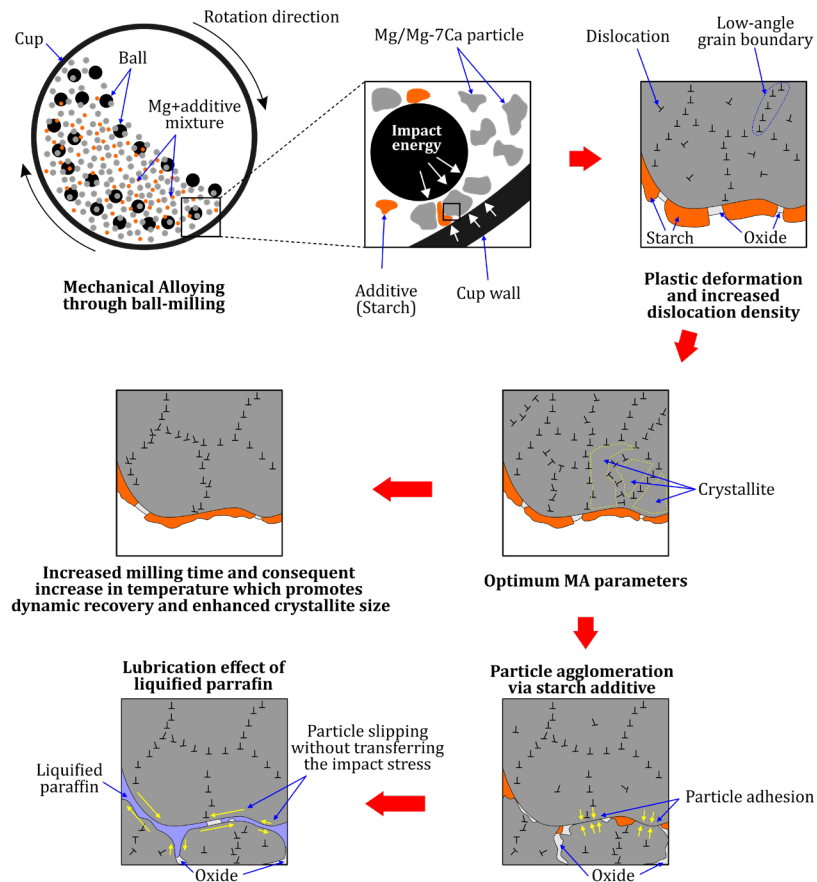


Fig. 5. The graphical illustration of the steps, mechanisms, and phenomena during the mechanical alloying process of this study.

insufficient engagement of the particles through the milling process, due to the lubrication effect of the liquefied paraffin. However, paraffin can still be considered as an effective additive to inhibit oxidation and enhanced the sinterability of the MAed materials, particularly due to its low melting point and high evaporation rate through the sintering which results in a lower volume fraction of impurities in the sintered alloy. The effects of both paraffin and starch on the sinterability of the MAed mixtures will be studied in the 2nd part of this article. Fig. 5 conclusively shows the MA processes and mechanisms of this study.

4. Conclusions

In this study, Mg-0.7 Ca alloys were produced by the mechanical alloying process. Effects of various milling parameters were investigated and the following results have been reached:

- Crystallite size was decreased from the 30 minutes-milled sample to the 60 minutes one, which can be attributed to more fractures and intensified plastic deformation. However, the crystallite size was increased in further milling time (90 min) due to higher temperatures and dislocation rearrangement in the deformed particles.
- Among different additive fractions, the sample with 2.5 wt% of starch displayed an improved milling performance simultaneously according to the crystallite size and the homogenous morphology and size distribution.

- Starch was found as more effective additive through mechanical milling, compared to paraffin. While the lower crystallite size of the starch-contained samples was calculated and approved through XRD analysis, the 3D structure and homogenous distribution of the MAed particles were investigated via FESEM and confirmed the effective role of starch.

Due discussions around the mechanisms and competitive phenome during the mechanical alloying were also included.

CRedit authorship contribution statement

Parisa Golmohammadi: Writing – original draft, Software, Formal Analysis, Validation, Investigation.

Fatemeh Saljooghi: Software, Investigation.

Ahmad Bahmani: Writing – review & editing.

Nader Parvin: Supervision, Funding acquisition, Writing – review & editing, Project administration.

Behzad Nayeji: Writing – original draft, Writing – review & editing, Visualization, Methodology, Conceptualization, Investigation.

Data availability

The data underlying this article will be shared on reasonable request to the corresponding author.

Declaration of competing interest

The authors declare no competing interests.

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