

Article

Effect of CaO Addition on Microstructural Evolution Due to the Annealing of AZ31 Alloys Processed by Equal-Channel Angular Pressing (ECAP)

Seong-Hwan Bae ^{1,2} , Young-Chul Shin ³, Ji-Woon Lee ⁴, Ki-Ho Jung ^{3,*} and Soong-Keun Hyun ^{2,*}

¹ Department of Smart Mechanical Design, Korea Polytechnics, Incheon 22121, Republic of Korea; shbae@kopo.ac.kr

² Department of Materials Science and Engineering, Inha University, Incheon 22212, Republic of Korea

³ Korea Institute of Industrial Technology, Incheon 21999, Republic of Korea

⁴ Department of Materials Science and Engineering, Kongju National University, Kongju 32588, Republic of Korea

* Correspondence: markjung@kitech.re.kr (K.-H.J.); skhyun@inha.ac.kr (S.-K.H.)

Abstract: This study demonstrated the application of equal-channel angular processing (ECAP), which was performed via the B_C route, to determine the effect of the addition of CaO on the microstructural evolution of an AZ31 alloy due to annealing. Compression tests were performed to evaluate the mechanical properties of the alloy, and the corresponding microstructures were observed to elucidate the flow behavior. Ca-bearing second-phase particles were fragmented with the increase in the number of ECAP passes. The increase in the yield strength and flow stress with the addition of CaO was attributed to the dispersion of the Ca-bearing second-phase particles. When the CaO-added AZ31 and commercial AZ31 alloys were subjected to annealing, their flow stress decreased owing to the grain growth. However, the extent of the decrease in the flow stress for the CaO-added AZ31 alloy was lower than that for the commercial AZ31 alloy.



Citation: Bae, S.-H.; Shin, Y.-C.; Lee, J.-W.; Jung, K.-H.; Hyun, S.-K. Effect of CaO Addition on Microstructural Evolution Due to the Annealing of AZ31 Alloys Processed by Equal-Channel Angular Pressing (ECAP). *Metals* **2023**, *13*, 1356. <https://doi.org/10.3390/met13081356>

Academic Editor: Manoj Gupta

Received: 28 April 2023

Revised: 17 July 2023

Accepted: 17 July 2023

Published: 28 July 2023



Copyright: © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

Keywords: AZ31; equal-channel angular pressing (ECAP); ultrafine grain; recrystallization; CaO

1. Introduction

Mg alloys are lightweight materials with high specific strength; therefore, they have attracted significant interest as materials that can lower the frame weight of automobiles and other means of transportation [1,2]. AZ31 is a common Mg alloy with medium strength and is utilized in the automobile and aerospace industries. It is generally manufactured by the die casting process that generates products with various casting defects such as shrinkage cavities, excessive inclusions, and pores. These defects limit the utility of AZ31 alloys to applications that do not require high strength such as manufacturing of cases, covers, steering wheel cores, instrument panels, seat frames, and housings [3]. Since metalworking techniques such as extrusion and rolling generate products with negligible internal defects, the mechanical properties of the alloys that are manufactured by metalworking are superior to those that are manufactured by casting. Therefore, the fabrication of wrought Mg alloys by metalworking facilitates the expansion of their applications [4–6]. Recently, the multi-pass continuous screw twist extrusion process by Wu et al. [7], the extrusion-shear process by Shi et al. [8], the simple shear extrusion (SSE) by Sayari et al. [9], and the differential velocity sideways extrusion (DVSE) by Zhou et al. [10] have been developed and extensively studied as methods of severe plastic deformation (SPD) processing.

Equal-channel angular pressing (ECAP) is a severe plastic deformation (SPD) technique that involves the passing of a material according to the angle (Φ) at which the two channels inside the mold meet [11–13]. The application of high shear deformation during ECAP maximizes the grain refinement in the material [14,15]. The Hall–Petch relation

shows that the yield strength of a material increases owing to the generation of well-formed fine grains; therefore, ECAP yields products with excellent mechanical properties [16,17]. However, when the material is severely deformed owing to a high dislocation density, static recrystallization (SRX) occurs at elevated temperatures [18,19]. The grain growth in Mg alloys occurs at temperatures higher than 473 K [20]. Therefore, a commercial AZ31(Mg-3Al-1Zn) alloy is inappropriate for use at high temperatures (>473 K) owing to the weakening of its mechanical properties.

There have been extensive studies to optimize the mechanical properties of Mg alloys at elevated temperatures. The A S series alloys (Mg-Al-Si) exhibit a high creep resistance due to the formation of Mg₂Si precipitates; however, an Si concentration of less than 2 wt.% results in the deterioration of the mechanical properties of the alloy at room temperature [21]. Recently, Kim et al. [22] reported that the addition of a low quantity of CaO to Mg alloys results in the formation of a dense oxide layer (comprising MgO and CaO) in the molten state. This oxide layer minimizes the contact of the surface of the alloy with air, thereby increasing the oxidation and ignition resistance of the alloy. Furthermore, the Ca atoms tend to segregate at the grain boundaries in the form of second-phase particles or solutes [23,24]. This inhibits the grain boundary sliding and the movement of the dislocations, thereby increasing the creep resistance of the alloy [25].

Furthermore, Zhou et al. [26] implemented the differential velocity sideways extrusion (DVSE), a novel severe plastic deformation (SPD) technique, to achieve grain refinement in the AZ31 alloy. Factors such as extrusion temperature and speed ratio influenced the dynamic recrystallization process. As a result, a slight decrease in yield strength was observed, while uniform elongation improved.

It has been proven that the addition of CaO optimizes the mechanical properties of the Mg alloys at elevated temperatures. However, the efficacy of the Ca-bearing second-phase particles has not been examined for the materials that undergo severe plastic deformation at elevated temperatures. Accordingly, this study was conducted to investigate the effect of the addition of CaO on the microstructural evolution in an ECAPed AZ31 alloy due to annealing. ECAP was performed via the B_C route, where the sample was rotated by 90° in the same direction after each pass to obtain the most consistent microstructure [27,28]. The mechanical properties and the corresponding microstructures of the CaO-added AZ31 alloy were compared with those of the commercial AZ31 alloy. A special emphasis is given to demonstrating the suppressed grain growth and reduced strength loss, after annealing, in the ECAP-processed AZ31-CaO alloy compared to the commercially processed AZ31 alloy under the same conditions.

2. Experimental Procedures

The commercial and CaO-added AZ31 alloys were subjected to ECAP in this study. The chemical composition of each alloy was analyzed using inductively coupled plasma mass spectrometry (ICP-MS, Thermo Fisher Scientific, Dover, DE, USA), and the results are listed in Table 1. Billets with a diameter of 100 mm were produced via direct-chill casting and extruded with an extrusion ratio of 8:1. Subsequently, the samples for ECAP (diameter = 10 mm, height = 65 mm) were machined from the extruded rods (Figure 1).

Table 1. Chemical compositions of the experimental alloys (wt.%).

Alloys	Chemical Composition (wt.%)							
	Al	Zn	Mn	Si	Fe	Cu	Ca	Mg
CaO-added AZ31	2.810	0.920	0.220	0.009	0.120	0.008	0.460	Bal.
Commercial AZ31	2.890	0.960	0.310	0.012	0.150	0.011	0.040	Bal.

ECAP was performed using a Shimadzu UH-X 1000 kN universal testing machine (Shimadzu, Kyoto, Japan) at a strain rate of 1 mm·s^{−1}. A separable-type mold with an internal channel was utilized for ECAP. The dimensions of the die used for ECAP were

length of 100 mm $\times$ width of 105 mm $\times$ height of 175 mm. The angle (Φ) of the internal channel was 112.5° , and the corner angle (Ψ) was 30° (Figure 2). The strain (ϵ) was calculated as follows ($\epsilon_1 = 0.75$) [29]:

$$\epsilon_N = \frac{N}{\sqrt{3}} \left[2 \cot \left(\frac{\Phi}{2} + \frac{\Psi}{2} \right) + \csc \left(\frac{\Phi}{2} + \frac{\Psi}{2} \right) \right] \quad (N = 1, 2, 3, \dots, N) \quad (1)$$

where N is the number of passes. A total of four ECAP passes were performed at different temperatures. The first two and last two passes were performed at 523 K and 423 K, respectively, to minimize the grain growth with the increase in the number of ECAP passes. A cumulative strain (ϵ) of 2.85 was applied after four ECAP passes. The error range of the temperature measurement was maintained at ± 1 K for every pass, and the temperature was maintained for 10 min. A lubricant, MoS_2 , was coated on the sample surface prior to each pass to minimize the friction between the sample surface and the wall inside the mold.

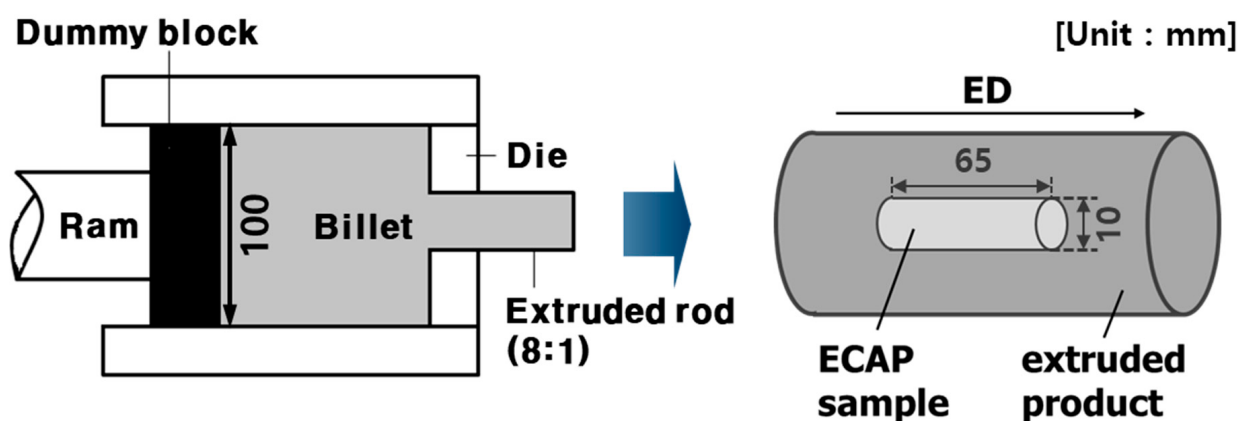


Figure 1. A schematic of the sample preparation procedure for equal-channel angular pressing (ECAP).

Each ECAPed sample was heat-treated at 473 K under an N_2 atmosphere for 24 h and air cooled. Subsequently, the samples were subjected to uniaxial compression tests at room temperature (RT) using an MTS systems MTS 810 universal testing machine (MTS Systems Corporation, Eden Prairie, MN, USA) at a strain rate of $1 \times 10^{-3} \text{ s}^{-1}$. The compressive samples with a diameter and height of 8 mm and 12 mm, respectively, were machined from the linearly extruded samples.

The compressive samples were ground and etched in a solution of 4.2 g picric acid, 10 mL distilled water, and 10 mL acetic acid; subsequently, the deformed microstructures after the compression tests were observed by a Nikon Eclipse MA100 optical microscopy (OM, Nikon, Tokyo, Japan). The average grain size was measured using a Zootos Leopard 2009 TM image analyzer in accordance with ASTM E112-96 (Zootos, Anyang, Republic of Korea). In the Mg alloys studied, the samples for microstructural observation after extrusion are positioned and oriented in a manner where the majority of grains exhibit basal planes parallel to the direction of extrusion [30].

Electron backscattered diffraction (EBSD, JEOL Ltd., Tokyo, Japan) scans were performed over an area of $50 \mu\text{m} \times 50 \mu\text{m}$ (step size = $0.1 \mu\text{m}$); thus, the changes in the microstructure and texture of the samples due to ECAP and heat treatment were observed. The ECAPed samples were mechanically polished and subjected to Ar ion milling to clean and eliminate the deformed surfaces and the oxidized layer that were generated during mechanical polishing. The raw data from the EBSD analysis were obtained using the TSL-OIM software (OIM AnalysisTM, AMETEK, Inc., Berwyn, PA, USA).

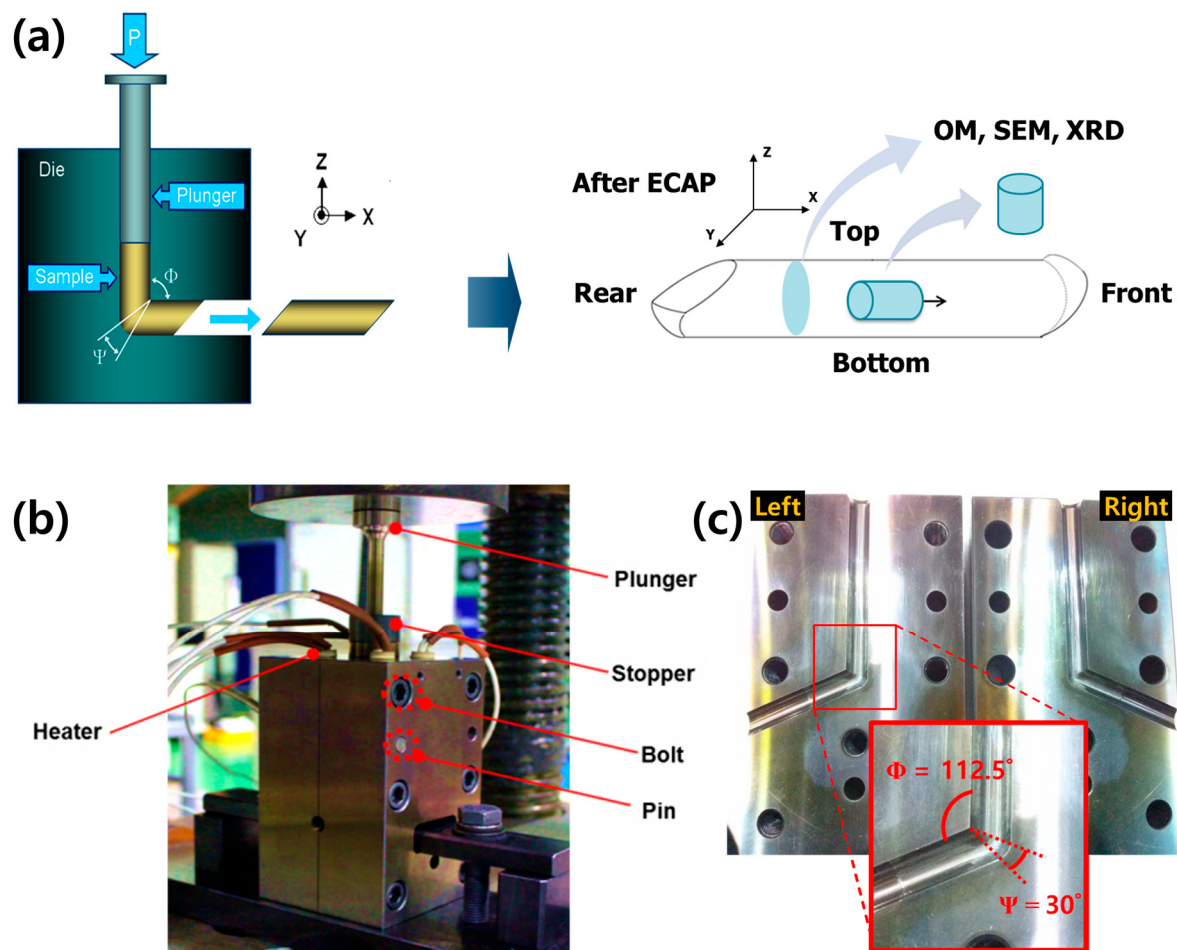


Figure 2. (a) A schematic of the mechanism of ECAP [26]. Photographs of the (b) ECAP mold and (c) the interior channel.

The second-phase particles in the CaO-added AZ31 alloy were analyzed by a Bruker D8 X-ray diffractometer (Bruker Corporation, Billerica, CA, USA). The composition and distribution of the second-phase particles were also analyzed by energy dispersive spectroscopy (EDS, FEI, Hillsboro, OR, USA) in conjunction with an FEI Quanta 200F field-emission scanning electron microscopy (FE-SEM, FEI, Hillsboro, OR, USA) and a Tecnai G² F20 S-Twin transmission electron (FEI, Hillsboro, OR, USA).

3. Results

3.1. Flow Behavior

A uniaxial compression test was conducted at RT to study the effect of the addition of CaO and the annealing on the mechanical properties of the AZ31 alloys. Figure 3 shows the true stress–strain curves, which were obtained from the compression tests, for the ECAPed CaO-added AZ31 and commercial AZ31 alloys. The true stress of both the alloys increased linearly at the initial strain and reached the yield point at a certain strain. The stress decreased slightly beyond the yield point and was maintained until the strain increased to 0.03–0.07, in accordance with the ECAP pass. Subsequently, there was a marked increase in the true stress with an increase in strain until the samples failed. Both the alloys exhibited an increase in stress with the increase in the number of ECAP passes. However, the true stress for the two alloys was similar at high-strain regimes, regardless of the number of ECAP passes. The true stress of the heat-treated (annealed) samples was slightly higher than that of the non-heat-treated samples, except for the commercial AZ31 alloy that was subjected to four ECAP passes.

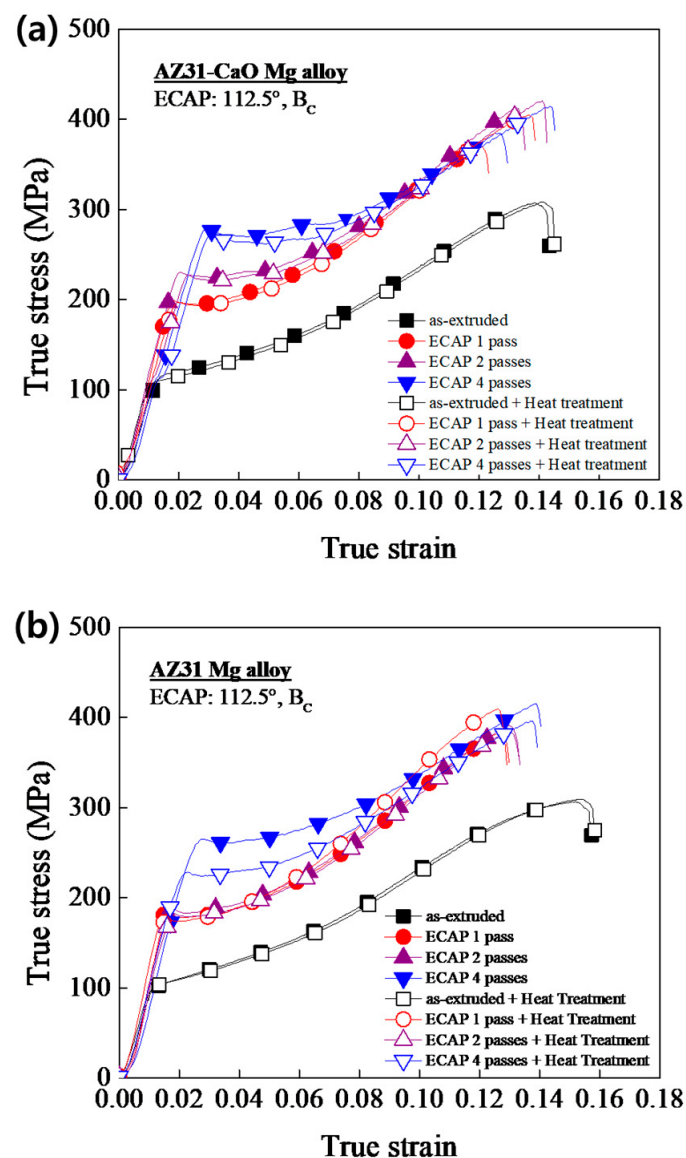


Figure 3. True stress–strain curves of the ECAPed: (a) CaO-added AZ31 and (b) commercial AZ31 alloys with and without heat treatment after the compression tests.

Figure 4 shows a comparison of the yield behavior of the alloys based on the mechanical properties that were obtained from the true stress–strain curves. The yield strength of the CaO-added AZ31 alloy was higher than that of the commercial AZ31 alloy (Figure 4a). The difference in the yield stress of the two alloys after four ECAP passes was approximately 20 MPa. Figure 4b shows the effect of the heat treatment on the mechanical properties of the alloys. After heat treatment, the drop in the yield strength of the commercial AZ31 alloy was definitely higher than that of CaO-added AZ31 alloy; furthermore, the tendency was clearer as the number of ECAP passes increased. The yield stress of both alloys after the first pass of ECAP slightly decreased after the heat treatment. From the second pass, there was a significant decrease in the yield strength of the commercial AZ31 alloy; however, there was no significant decrease in the yield strength of the CaO-added AZ31 alloy. The largest decrease in the yield stress of the commercial AZ31 alloy was 30.2 MPa after the fourth pass. These results indicated that the addition of CaO affected the mechanical properties of the AZ31 alloy. These effects should be discussed in relation to the corresponding deformed microstructures and the formation of second-phase particles.

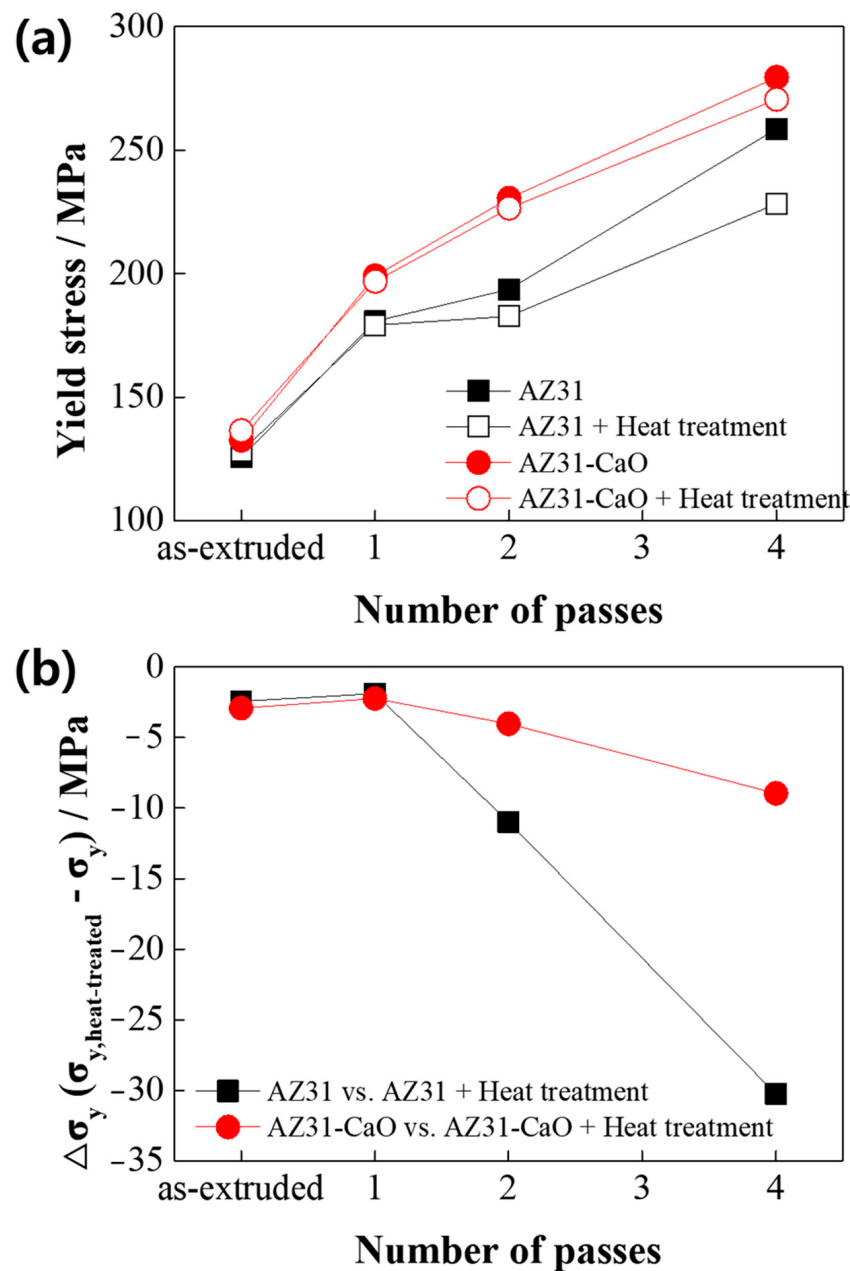


Figure 4. Comparison of the mechanical properties as a function of the number of ECAP passes between the ECAPed CaO-added AZ31 and commercial AZ31 alloys after the compression tests: (a) yield stress and (b) change in the yield stress, $\Delta\sigma_y$, of the AZ31 alloys after heat treatment.

3.2. Deformed Microstructure

Figure 5 shows the microstructures of the as-cast, as-extruded, and ECAPed CaO-added AZ31 and commercial AZ31 alloys with and without heat treatment. Large equiaxed grains ($>100 \mu\text{m}$) were observed in the as-cast samples of both the alloys (Figure 5a). The fine equiaxed grains in the as-extruded samples of the two alloys (Figure 5b) were formed by dynamic recrystallization (DRX) during extrusion. The grain morphologies in the as-cast and as-extruded samples of the two alloys were similar. However, the deformed microstructures of the two alloys (Figure 5c–e) showed differences in the grain structure. The grain size decreased with the increase in the number of ECAP passes for both the alloys; furthermore, the two alloys exhibited different grain structures with the increase in the number of ECAP passes. Both the alloys primarily comprised fine grains; however, some coarse grains were also observed in the commercial AZ31 alloy. When the ECAPed

samples of the two alloys were subjected to heat treatment, the increase in the grain size and the formation of coarse grains indicated the occurrence of grain growth.

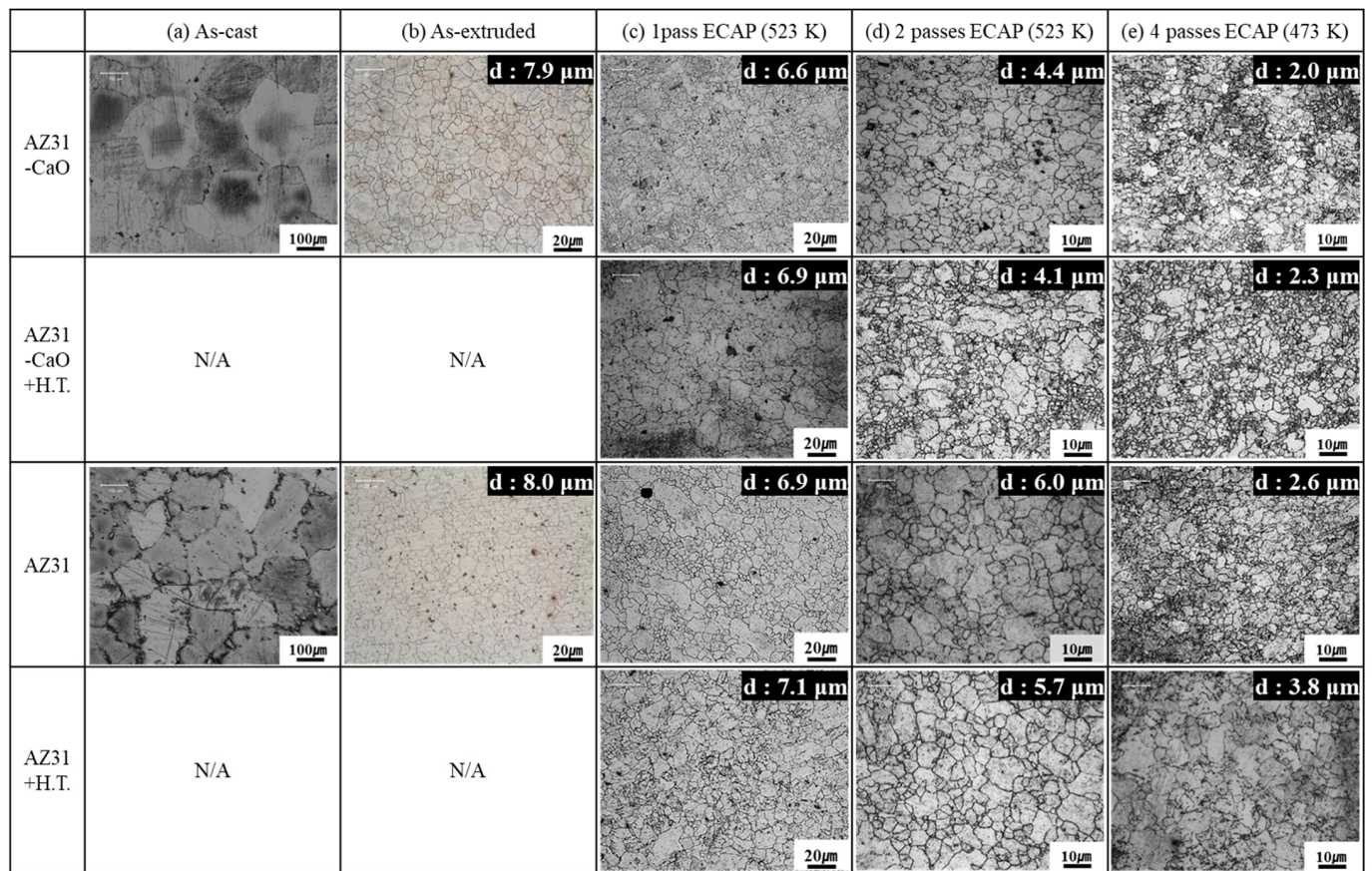


Figure 5. Optical micrographs of the microstructures in the: (a) as-cast sample, (b) as-extruded sample, (c) ECAPed sample (1 pass) at 523 K, (d) ECAPed sample (2 passes) at 523 K, and (e) ECAPed sample (4 passes) at 473 K of the CaO-added AZ31 and commercial AZ31 alloys with and without heat treatment. The average grain size is presented in the top-right corner of each image.

The ECAPed (4 passes) CaO-added AZ31 and commercial AZ31 alloys were subjected to EBSD analysis (Figure 6); thus, the grain structure and grain size distribution in the heat-treated and non-heat-treated alloys were compared. The inverse pole figure (IPF) maps demonstrated the existence of coarse grains in the commercial AZ31 alloy. The histogram of the grain sizes also indicated that the number fraction of the coarse grains in the commercial AZ31 alloy was higher than that in the CaO-added AZ31 alloy. Coarse grains were also observed in the microstructure of the heat-treated samples.

The average grain sizes of the alloys were measured using the OM images (Figure 7) to quantitatively analyze the influence of the added CaO on the grain growth due to heat treatment. The average grain sizes of the as-extruded CaO-added AZ31 alloy and commercial AZ31 alloy were 7.9 and 8.0 µm, respectively. The average grain sizes of the as-extruded CaO-added AZ31 alloy and commercial AZ31 alloy gradually decreased to 2.0 and 2.6 µm, respectively, with an increase in the number of ECAP passes. The average grain sizes of the ECAPed (four passes) CaO-added AZ31 alloy and ECAPed (four passes) commercial AZ31 alloy increased from 2.0 to 2.3 µm and 2.6 to 3.8 µm, respectively, owing to heat treatment. Thus, the increase in the grain size of the commercial AZ31 alloy was four times larger than that of the CaO-added AZ31 alloy.

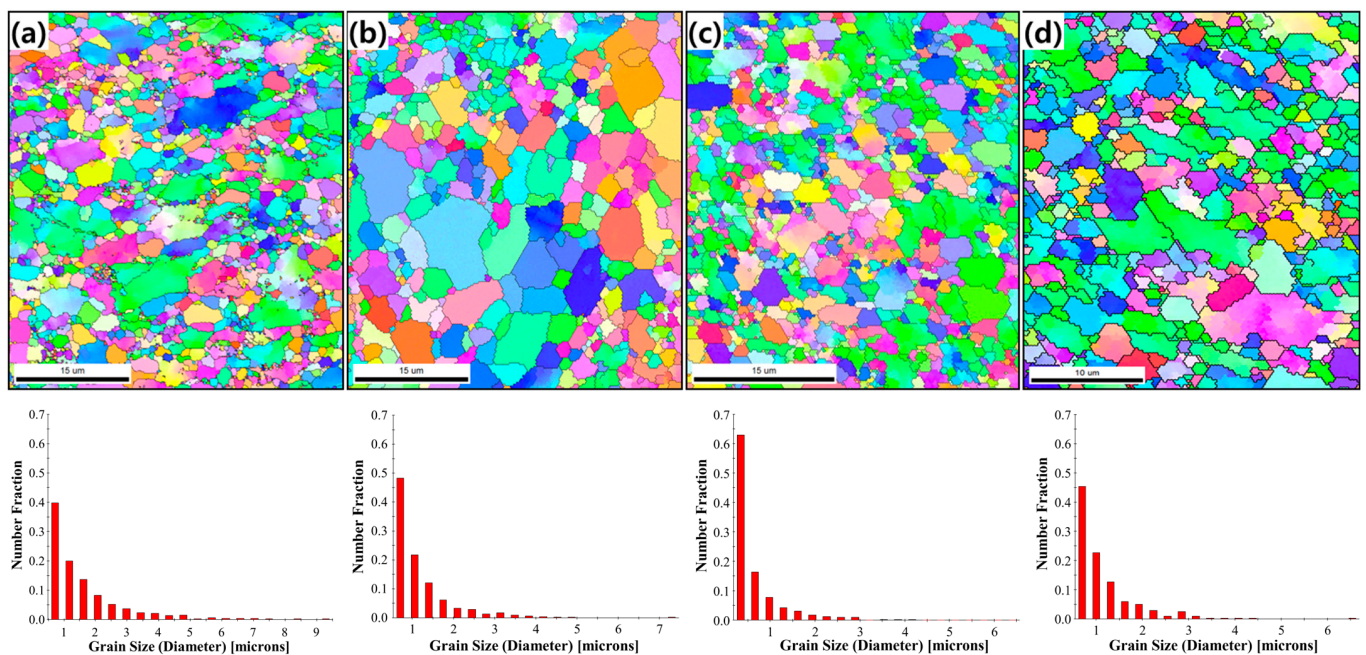


Figure 6. Inverse pole figure (IPF) maps (upper row) and histogram of the grain size (lower row) in the: (a) commercial AZ31, (b) heat-treated commercial AZ31, (c) CaO-added AZ31, and (d) heat-treated CaO-added AZ31 alloys with four ECAP passes.

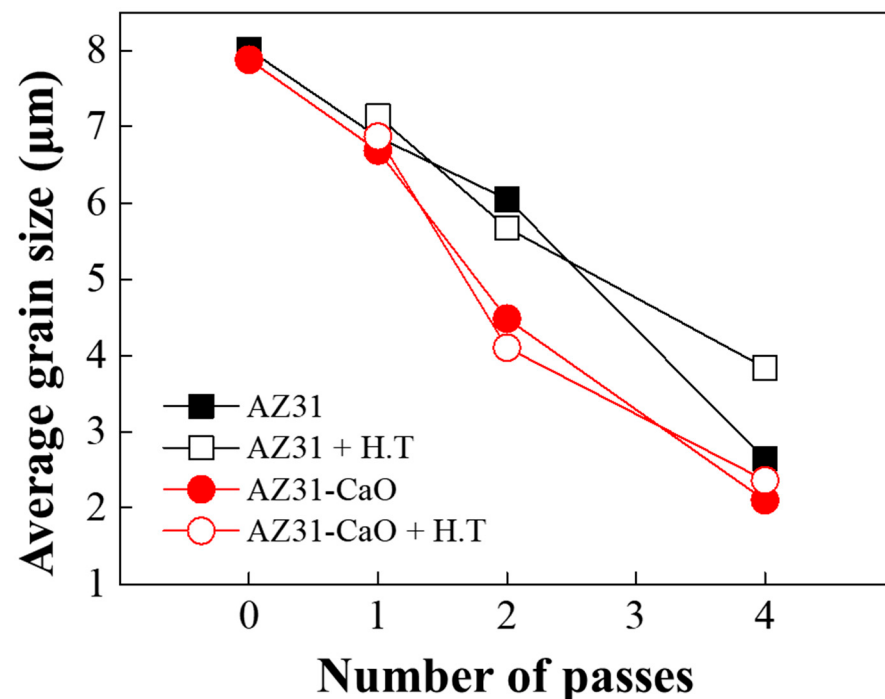


Figure 7. The average grain size of the CaO-added AZ31 and commercial AZ31 alloys as a function of the number of ECAP passes.

Figure 8 shows the bright-field TEM images and selected area diffraction patterns (SADP) of the CaO-added AZ31 and commercial AZ31 alloys. The ring pattern in the SADP is a typical feature of nanostructured materials that are fabricated by severe plastic deformation [31]. The ring pattern of the CaO-added AZ31 alloy was more prominent than that of the commercial AZ31 alloy; furthermore, the number of spots in the ring pattern of the CaO-added AZ31 alloy was higher than that in the ring pattern of the commercial

AZ31 alloy. This indicated the formation of ultrafine grains in the CaO-added AZ31 alloy during four ECAP passes; moreover, the number of grains that were formed in the CaO-added AZ31 alloy was higher than that in the commercial AZ31 alloy during four ECAP passes. This appeared to be consistent with the distribution of the misorientation angle that was determined from the EBSD analysis. The histogram of the distribution of the misorientation angle (Figure 9) showed that the number fraction of the high-angle grain boundaries (misorientation angle $> 15^\circ$) in the CaO-added AZ31 alloy was approximately 11% higher than that in the commercial AZ31 alloy.

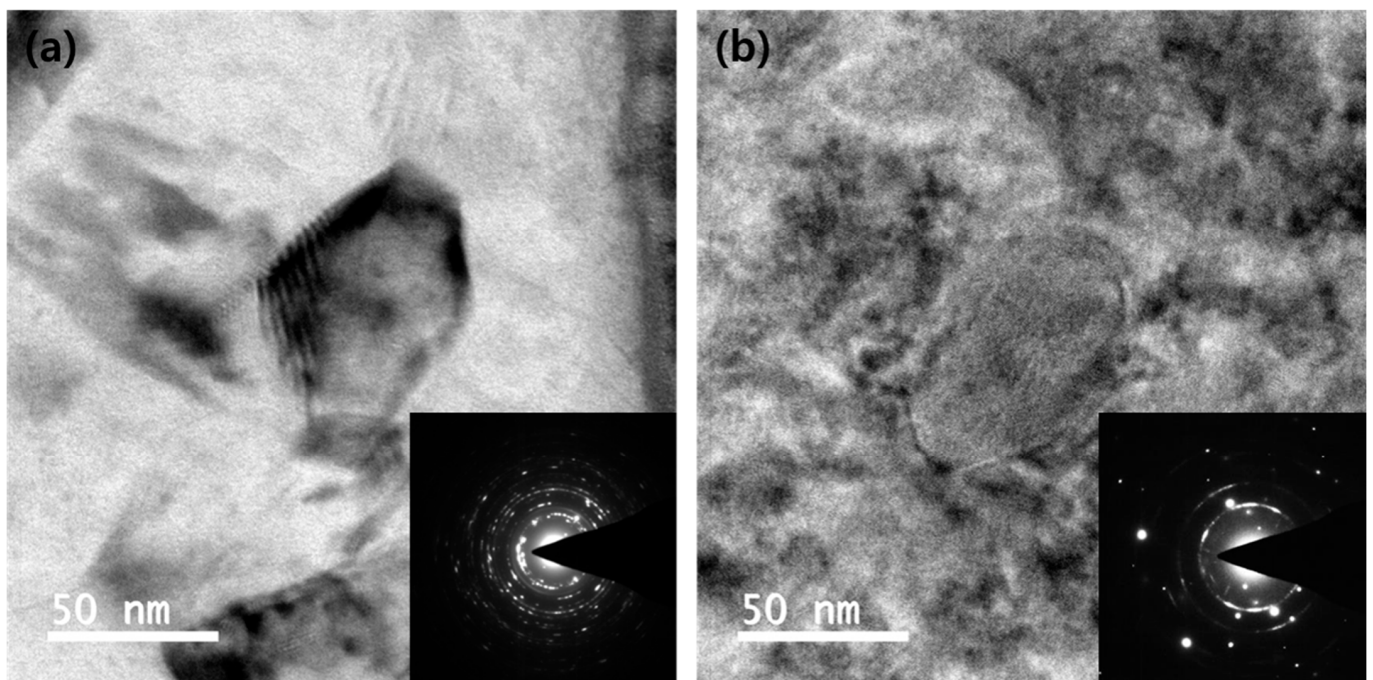


Figure 8. TEM bright-field images and selected area diffraction patterns (bottom-right corner) of the (a) CaO-added AZ31 and (b) commercial AZ31 alloys with four ECAP passes.

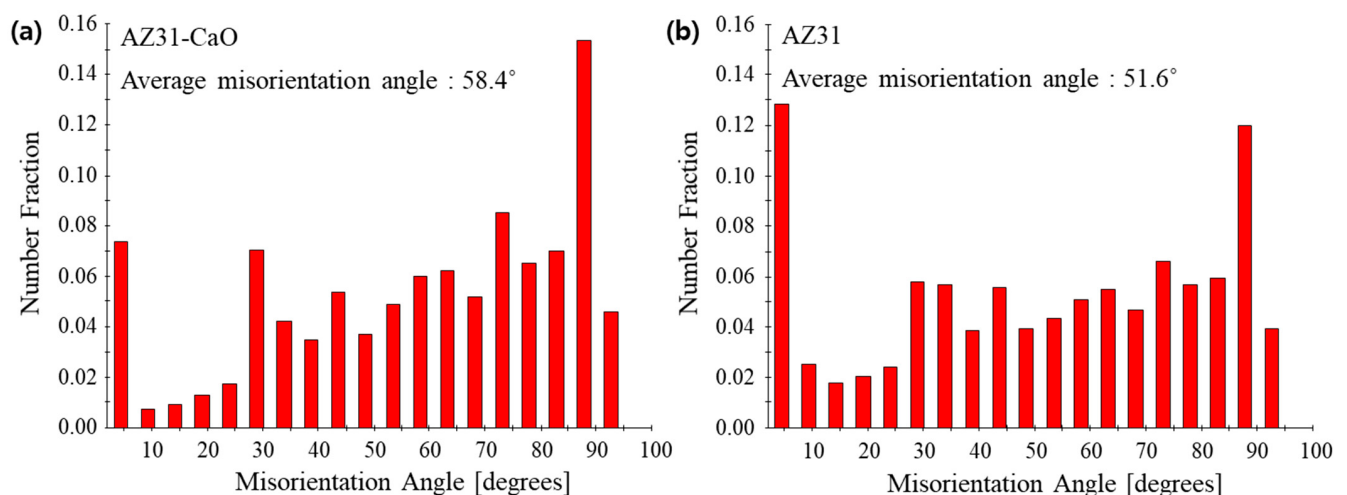


Figure 9. Histogram of the misorientation angle of the (a) CaO-added AZ31 and (b) commercial AZ31 alloys with four ECAP passes.

3.3. Distribution of Second-Phase Particles

The second-phase particles significantly impacted the mechanical properties and the microstructural evolution of the AZ31 alloys. Therefore, the distribution of the second-phase particles in the CaO-added AZ31 and commercial AZ31 alloys was investigated. The

results of the XRD analysis (Figure 10) showed the formation of $Mg_{17}Al_{12}$ and $Al_{11}Mn_4$ in both the alloys; however, Al_2Ca was detected only in the CaO-added AZ31 alloy due to the presence of CaO. Figure 10 shows that the second-phase particles were formed during casting and existed during extrusion and ECAP.

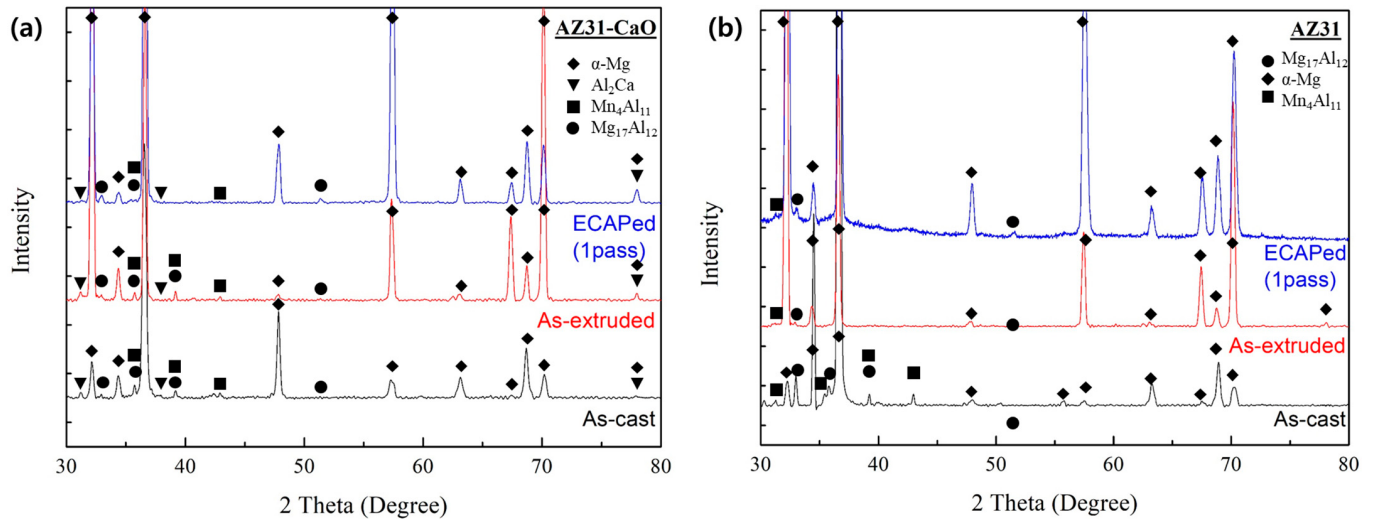


Figure 10. Results of the X-ray diffraction analysis of the (a) CaO-added AZ31 and (b) commercial AZ31 alloys.

Figure 11 shows the shape and distribution of the second-phase particles in the CaO-added AZ31 and commercial AZ31 alloys. The XRD results showed that Al_2Ca was distributed only in the CaO-added AZ31 alloy. Rod-shaped particles of Al_2Ca were formed along the grain boundaries in the cast sample of the CaO-added AZ31 alloy (Figure 11a). The presence of fine, spherical particles of Al_2Ca in the extruded sample of the CaO-added AZ31 alloy indicated the fragmentation of Al_2Ca during extrusion. Rod-shaped and spherical particles of $Al_{11}Mn_4$ were observed in the cast and extruded sample, respectively, of the commercial AZ31 alloy. Furthermore, the higher volume fraction of the second-phase particles in the CaO-added AZ31 alloy as compared to that in the commercial AZ31 alloy was attributed to the addition of CaO.

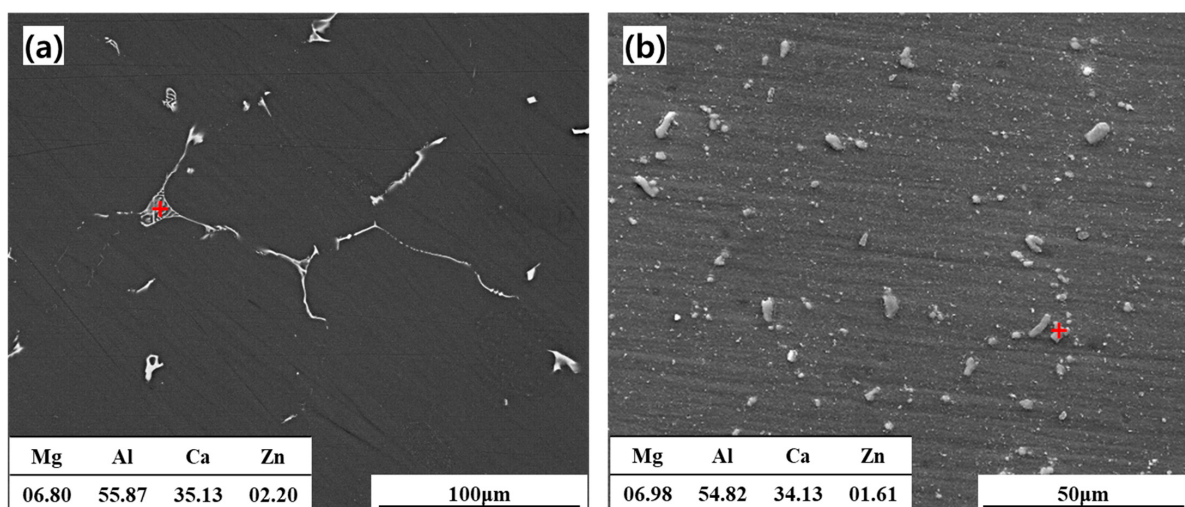


Figure 11. Cont.

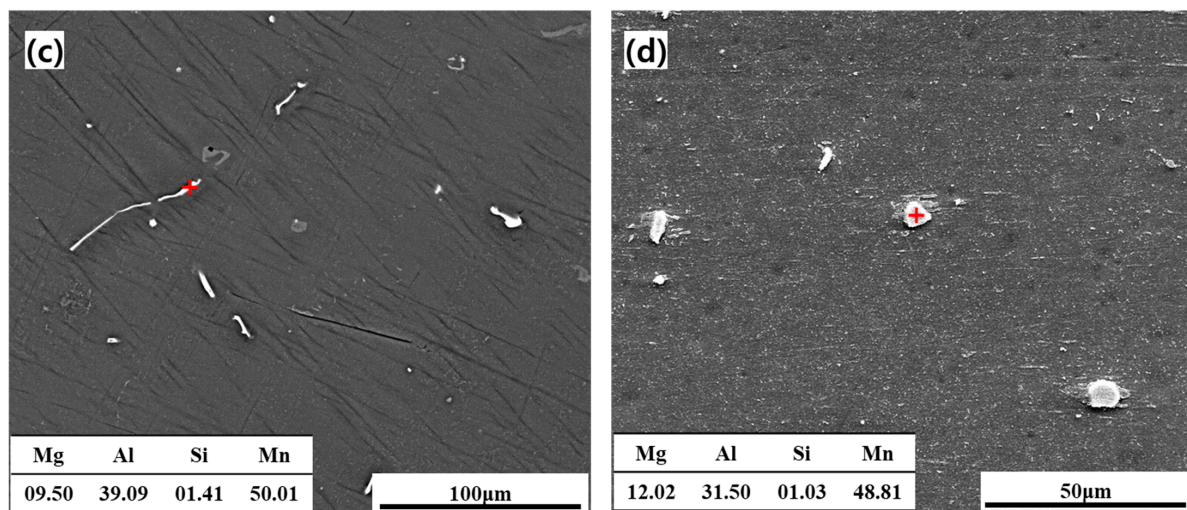


Figure 11. Scanning electron micrographs of the second-phase particles in the: (a) as-cast and (b) as-extruded CaO-added AZ31 alloys, and (c) as-cast and (d) as-extruded commercial AZ31 alloys. The chemical compositions (wt.%) of the marked second-phase particles are listed in the table in the bottom-left inset of each figure.

Figure 12 shows the distribution of the second-phase particles in the ECAPed CaO-added AZ31 and commercial AZ31 alloys. The presence of Al_2Ca and $\text{Al}_{11}\text{Mn}_4$ in the CaO-added AZ31 alloy and $\text{Al}_{11}\text{Mn}_4$ in the commercial AZ31 alloy was consistent with the results of the XRD analysis after ECAP. When the as-extruded alloys underwent ECAP, the second-phase particles were fragmented and the size of the particles decreased with the increase in the number of passes. The AZ31 alloy also exhibited a similar behavior; however, the volume fraction of the second-phase particles in the commercial AZ31 alloy was lower than that in the CaO-added AZ31 alloy.

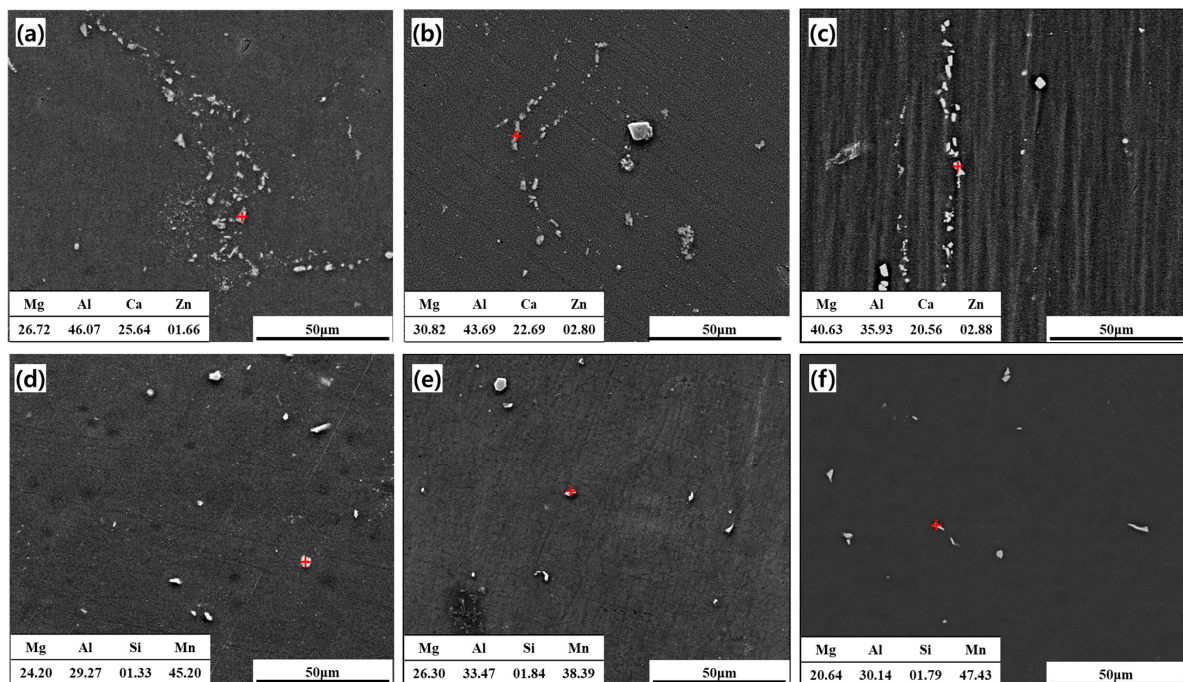


Figure 12. Scanning electron micrographs of the second-phase particles in the: CaO-added AZ31 alloy after (a) one pass, (b) two passes, and (c) four passes of ECAP and commercial AZ31 alloy after (d) one pass, (e) two passes, and (f) four passes of ECAP. The chemical compositions (wt.%) of the marked second-phase particles are listed in the table in the bottom-left inset of each figure.

4. Discussion

The true stress–strain curves showed that the yield strength of the CaO-added AZ31 alloy was higher than that of the commercial AZ31 alloy, with and without heat treatment. This was attributed to not only the differences in the deformed microstructures of the alloys but also the distribution of the second-phase particles, whose formation was induced by the addition of CaO, in the CaO-added AZ31 alloy. Recently, Kim et al. used CaO as an additive to substitute Ca for Mg and Mg alloys [22]. Ca, as an alloying element, increases the creep resistance of Mg alloys [32]. It also forms fine particles of Al_2Ca that contribute to the grain refinement in Mg alloys. However, Ca is expensive and difficult to treat owing to its high affinity for oxygen. Therefore, CaO is utilized as a Ca additive owing to its low cost and ease of use. When CaO is added to Mg, a dense oxide film forms at the surface of the material in the molten state. This oxide film prevents the oxidation and ignition of the molten Mg, thereby alleviating the requirement for SF_6 , a harmful protective gas, during casting. Since CaO-added Mg possesses high oxidation resistance, it is utilized as a novel Mg additive that increases the melt cleanliness and accelerates the DRX of Al alloys during hot deformation [33,34].

The addition of CaO to the AZ31 alloy induced the formation of second-phase particles comprising Al_2Ca that significantly increased the strength of the alloy by dispersion strengthening. Al_2Ca precipitated at the grain boundaries in the CaO-added AZ31 alloy during casting (Figure 11). Subsequently, these precipitates were fragmented and dispersed during extrusion and ECAP. The dispersed precipitates inhibited the movement of the dislocations in the initial stage of the compression tests. Therefore, the yield strength of the CaO-added AZ31 alloy was higher than that of the commercial AZ31 alloy.

The distributed Al_2Ca precipitates also affected the microstructural evolution of the AZ31 alloys during annealing. The grain growth due to annealing in the CaO-added AZ31 alloy was less pronounced than that in the commercial AZ31 alloy (Figures 5 and 7). The dispersion of the Al_2Ca precipitates in the CaO-added AZ31 alloy hindered the movement of the grain boundaries owing to Zener pinning [35], thereby inhibiting the grain growth. This was attributed to the consistently higher flow stress of the heat-treated CaO-added AZ31 alloy as compared to that of the commercial AZ31 alloy, irrespective of the sample preparation mechanism (Figure 3).

The yield behavior of the AZ31 alloys showed the efficacy of the Al_2Ca precipitates to inhibit grain growth. ECAP is known to lower the yield strength of materials [36,37]. Since all the ECAP passes were performed at 523 K in the previous studies, the materials exhibited textural changes and grain growth during ECAP. However, the yield strength and flow stress of the CaO-added AZ31 and commercial AZ31 alloys in the present study increased with the increase in the number of ECAP passes. The increase in the yield strength was attributed to the following possibilities: (1) The decrease in the process temperature from 523 to 473 K for the third and fourth ECAP passes inhibited the grain growth in both the alloys. (2) The Zener pinning effect inhibited the grain growth in the CaO-added AZ31 alloy.

The deformation mechanism of the CaO-added AZ31 alloy due to ECAP is presented in Figure 13 based on the results obtained in this study. Rod- or plate-shaped second-phase particles of Al_2Ca were formed at the grain boundary during casting. The fragmentation of these second-phase particles and DRX occurred simultaneously during extrusion. When the as-extruded sample was subjected to ECAP, grain refinement occurred by the following sequential mechanism: dislocation cell formation, sub-boundary formation, sub-boundary rotation, and high-angle grain boundary formation. The dislocations were pinned, and their movement was inhibited by the second-phase particles (Al_2Ca); therefore, finer grains were formed in the CaO-added AZ31 alloy as compared to those formed in the commercial AZ31 alloy.

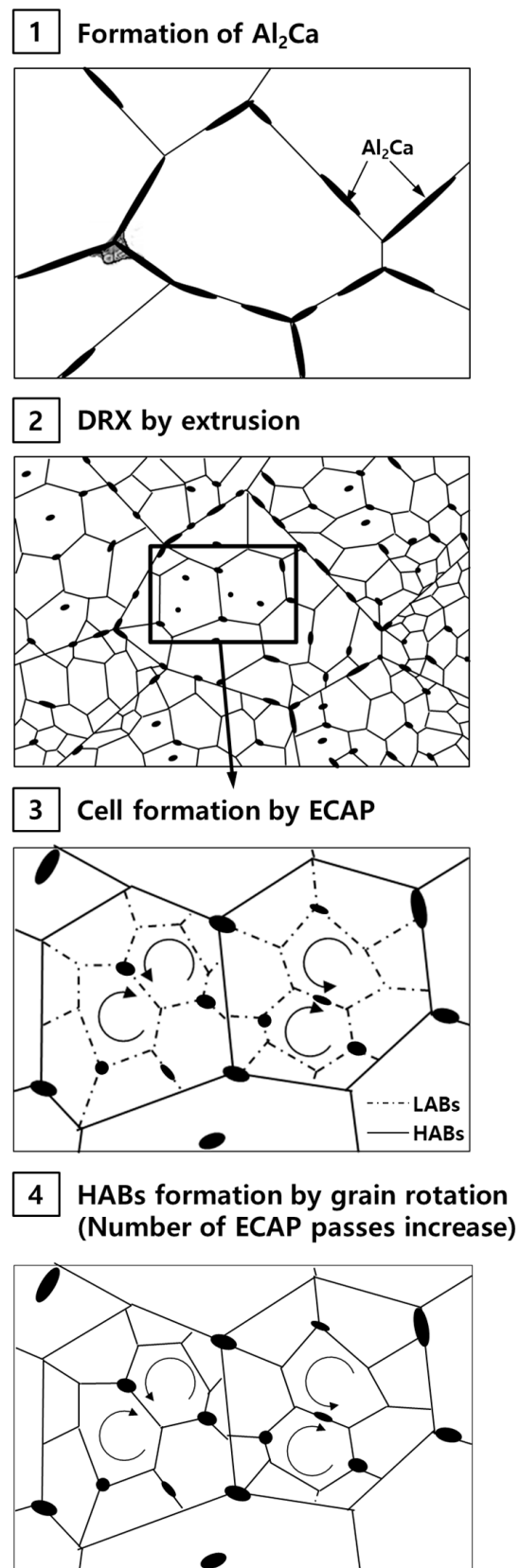


Figure 13. Schematic of the grain refinement mechanism for the ECAPed CaO-added AZ31 alloy. (1) Formation of Al_2Ca , (2) DRX by extrusion, the low-angle boundaries and high-angle boundaries in (3) are abbreviated as LABs and HABs, (4) HABs formation by grain rotation, respectively.

The aforementioned mechanism suggested that the efficiency of severe plastic deformation increases with the introduction of fine and hard second-phase particles in the material. This knowledge is applicable to not only severe plastic deformation but also post-processing techniques such as recrystallization heat treatment.

5. Conclusions

In this study, ECAP was applied to the CaO-added AZ31 alloy to study the effect of the addition of CaO on the grain refinement and microstructural evolution due to annealing. The conclusions of this study are summarized as follows:

- (1) The yield strength of the CaO-added AZ31 alloy was higher than that of the commercial AZ31 alloy, with and without heat treatment.
- (2) The difference in the flow stress between the heat-treated and non-heat-treated CaO-added AZ31 alloys was lower than that between the heat-treated and non-heat-treated commercial AZ31 alloys.
- (3) Ultrafine grains were formed in the alloys owing to ECAP; furthermore, the average grain size of the CaO-added AZ31 alloy was lower than that of the commercial AZ31 alloy owing to the dispersion of the second-phase particles of Al_2Ca in the CaO-added AZ31 alloy.
- (4) The second-phase particles of Al_2Ca were formed at the grain boundaries in the CaO-added AZ31 alloy during casting, and these particles were fragmented and dispersed during extrusion and ECAP.
- (5) The dispersion of the fine second-phase particles (Al_2Ca) optimized the mechanism of grain refinement which was induced by the ECAP of the CaO-added AZ31 alloy.

Author Contributions: Validation, formal analysis, writing-original draft preparation, review, editing, S.-H.B. Conceptualization, methodology, data curation, writing-review, editing, Y.-C.S. and J.-W.L. Conceptualization, writing-review, editing, supervision, funding acquisition, K.-H.J. and S.-K.H. All authors have read and agreed to the published version of the manuscript.

Funding: This work was supported by Inha University Research Grant.

Data Availability Statement: Please note that this project is currently in progress, and the raw/processed data required to reproduce these findings cannot be shared at this time due to relevant legal regulations.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Mordike, B.L.; Ebert, T. Magnesium: Properties—Applications—Potential. *Mater. Sci. Eng. A* **2001**, *302*, 37–45. [\[CrossRef\]](#)
2. Song, J.; She, J.; Chen, D.; Pan, F. Latest research advances on magnesium and magnesium alloys worldwide. *J. Magnes. Alloy.* **2020**, *8*, 1–41. [\[CrossRef\]](#)
3. Kulekci, M.K. Magnesium and its alloys applications in automotive industry. *Int. J. Adv. Manuf. Technol.* **2008**, *39*, 851–865. [\[CrossRef\]](#)
4. Shook, S.O. *Fabricating a Magnesium Part: An Overview*; SAE Technical Paper. #900790; SAE: Warrendale, PA, USA, 1990; p. 49.
5. Dale, B.; Hudspeth, J. *Direct Extrusion of Magnesium Alloy: A Quick Study Method*; SAE Technical Paper. #950426; SAE: Warrendale, PA, USA, 1995; p. 43.
6. Shin, Y.C.; Ha, S.H.; Shah, A.W. Effects of SPD by Biaxial Alternate Forging on the Tensile Properties and Microstructure of AZ31B Magnesium Alloy. *Arch. Metall. Mater.* **2023**, *68*, 97–101.
7. Wu, W.; Wang, L.; Huang, G.; Zhang, H.; Cheng, W.; Wang, H.; Shin, K.S. Effect of multi-pass continuous screw twist extrusion process on microstructure evolution, texture, and mechanical properties of AZ31 magnesium alloy. *Mater. Today Commun.* **2023**, *34*, 105508. [\[CrossRef\]](#)
8. Shi, F.; Piao, N.; Wang, H.; Wang, J.; Zang, Q.; Guo, Y.; Chen, C.; Zhang, L. Investigation of microstructure and mechanical properties of ZK60 magnesium alloy achieved by extrusion-shearing process. *J. Mater. Res. Technol.* **2023**, *25*, 799–811. [\[CrossRef\]](#)
9. Sayari, F.; Roumina, R.; Mahmudi, R.; Hoseini-Athar, M.; Hedström, P. Comparison of the effect of ECAP and SSE on microstructure, texture, and mechanical properties of magnesium. *J. Alloy. Compd.* **2022**, *908*, 164407. [\[CrossRef\]](#)
10. Zhou, W.; Xi, Z. Bending Behaviour Analysis of Aluminium Profiles in Differential Velocity Sideways Extrusion Using a General Flow Field Model. *Metals* **2022**, *12*, 877. [\[CrossRef\]](#)

11. Chen, J.; Jiang, X.; Lyu, L.; Li, Y.; Christian, P.; Sun, H.; Shu, R. Microstructures and mechanical properties of nano-C and in situ Al₂O₃ reinforced aluminium matrix composites processed by equal-channel angular pressing. *J. Alloy. Compd.* **2021**, *876*, 160159. [\[CrossRef\]](#)
12. Valiev, R.Z.; Islamgaliev, R.K.; Alexandrov, I.V. Bulk nanostructured materials from severe plastic deformation. *Prog. Mater. Sci.* **2000**, *45*, 103–189. [\[CrossRef\]](#)
13. Valiev, R.Z.; Langdon, T.G. Principles of equal-channel angular pressing as a processing tool for grain refinement. *Prog. Mater. Sci.* **2006**, *51*, 881–981. [\[CrossRef\]](#)
14. Seikh, A.H.; Baig, M.; Rehman, A.U.; Hashmi, F.H.; Mohammed, J.A. Stress Corrosion Cracking Behavior of Fine-Grained Al5083 Alloys Processed by Equal-Channel Angular Pressing (ECAP). *Molecules* **2021**, *26*, 7608. [\[CrossRef\]](#)
15. Huang, S.J.; Kannaiyan, S.; Sarkar, M.; Mose, M.P. Enhancement of Mechanical Behaviors and Microstructure Evolution of Nano-Nb₂O₅/AZ31 Composite Processed via Equal-Channel Angular Pressing (ECAP). *J. Compos. Sci.* **2023**, *7*, 230. [\[CrossRef\]](#)
16. Mohri, T.; Mabuchi, M.; Nakamura, M.; Asahina, T.; Iwasaki, H.; Aizawa, T.; Higashi, K. Microstructural evolution and superplasticity of rolled Mg-9Al-1Zn. *Mater. Sci. Eng. A* **2000**, *290*, 139–144. [\[CrossRef\]](#)
17. Alsagabi, S.; Charit, I. Fundamental studies on the thermal stability and mechanical characteristics of AZ31 alloy. *Mater. Sci. Eng. A* **2012**, *536*, 64–72. [\[CrossRef\]](#)
18. Jäger, A.; Lukáč, P.; Gärtnerová, V.; Haloda, J.; Dopita, M. Influence of annealing on the microstructure of commercial Mg alloy AZ31 after mechanical forming. *Mater. Sci. Eng. A* **2006**, *432*, 20–25. [\[CrossRef\]](#)
19. Lee, S.E.; Kim, M.S.; Chae, Y.W.; Guim, H.; Singh, J.; Choi, S.H. Effect of intermediate heat treatment during hot rolling on the texture and formability of annealed AZ31 Mg alloy sheets. *J. Alloy. Compd.* **2022**, *897*, 163238. [\[CrossRef\]](#)
20. Kim, W.J.; Lee, B.H. Factors influencing tensile ductility of ultrafine-grained Mg-3Al-1Zn alloy sheet at elevated temperatures. *Mater. Sci. Eng. A* **2010**, *527*, 5984–5989. [\[CrossRef\]](#)
21. Luo, A.; Pekguleryuz, M.O. Cast magnesium alloys for elevated temperature applications. *J. Mater. Sci.* **1994**, *29*, 5259–5271. [\[CrossRef\]](#)
22. Kim, S.K.; Lee, J.-K.; Yoon, Y.-O.; Jo, H.-H. Development of AZ31 Mg alloy wrought process route without protective gas. *J. Mater. Process. Technol.* **2007**, *187–188*, 757–760. [\[CrossRef\]](#)
23. Son, H.W.; Jung, T.K.; Lee, J.W.; Hyun, S.K. Hot deformation characteristics of CaO-added AZ31 based on kinetic models and processing maps. *Mater. Sci. Eng. A* **2017**, *695*, 379–385. [\[CrossRef\]](#)
24. Bugnet, M.; Kula, A.; Niewczas, M.; Botton, G. Segregation and clustering of solutes at grain boundaries in Mg–rare earth solid solutions. *Acta Mater.* **2014**, *79*, 66–73. [\[CrossRef\]](#)
25. Millett, P.C.; Selvam, R.P.; Saxena, A. Improving grain boundary sliding resistance with segregated dopants. *Mater. Sci. Eng. A* **2006**, *431*, 92–99. [\[CrossRef\]](#)
26. Zhou, W.; Lin, J.; Dean, T.A. Microstructure and mechanical properties of curved AZ31 magnesium alloy profiles produced by differential velocity sideways extrusion. *J. Magnes. Alloy.* **2023**, *11*, 493–508. [\[CrossRef\]](#)
27. Iwahashi, Y.; Wang, J.T.; Horita, Z.; Nemoto, M.; Langdon, T.G. Principle of equal-channel angular pressing for the processing of ultra-fine grained materials. *Scr. Mater.* **1996**, *35*, 143–146. [\[CrossRef\]](#)
28. Furukawa, M.; Iwahashi, Y.; Horita, Z.; Nemoto, M.; Langdon, T.G. The shearing characteristics associated with equal-channel angular pressing. *Mater. Sci. Eng. A* **1998**, *257*, 328–332. [\[CrossRef\]](#)
29. Oh-Ishi, K.; Horita, Z.; Furukawa, M.; Nemoto, M.; Langdon, T.G. Optimizing the Rotation Conditions for Grain Refinement in Equal-Channel Angular Pressing. *Metall. Mater. Trans. A* **1998**, *29*, 2011–2013. [\[CrossRef\]](#)
30. Reyes-Ruiz, C.; Figueroa, I.A.; Braham, C.; Cabrera, J.M.; Alfonso, I.; Gonzalez, G. Texture and lattice distortion study of an Al-6061-T6 alloy produced by ECAP. *Mater. Trans.* **2015**, *56*, 1781–1786. [\[CrossRef\]](#)
31. Williams, D.B.; Carter, C.B. Indexing Diffraction Patterns. In *Transmission Electron Microscopy*; Plenum Press: New York, NY, USA; London, UK, 1996; pp. 267–287.
32. Luo, A.A.; Powell, B.R.; Balogh, M.P. Creep and microstructure of magnesium-aluminum-calcium based alloys. *Metall. Mater. Trans. A* **2002**, *33*, 567–574. [\[CrossRef\]](#)
33. Lee, J.W.; Son, K.T.; Jung, T.K.; Yoon, Y.O.; Kim, S.K.; Choi, H.J.; Hyun, S.K. Continuous dynamic recrystallization behavior and kinetics of Al–Mg–Si alloy modified with CaO-added Mg. *Mater. Sci. Eng. A* **2016**, *673*, 648–659. [\[CrossRef\]](#)
34. Lee, J.W.; Son, H.W.; Hyun, S.K. Hot deformation behavior of AA6005 modified with CaO-added Mg at high strains. *J. Alloy. Compd.* **2019**, *774*, 1081–1091. [\[CrossRef\]](#)
35. Humphreys, F.J.; Hatherly, M. *Recrystallization and Related Annealing Phenomena*; Elsevier: Oxford, UK, 2004.
36. Tong, L.; Zheng, M.; Chang, H.; Hu, X.; Wu, K.; Xu, S.; Kamado, S.; Kojima, Y. Microstructure and mechanical properties of Mg–Zn–Ca alloy processed by equal channel angular pressing. *Mater. Sci. Eng. A* **2009**, *523*, 289–294. [\[CrossRef\]](#)
37. Masoudpanah, S.M.; Mahmudi, R. The microstructure, tensile, and shear deformation behavior of an AZ31 magnesium alloy after extrusion and equal channel angular pressing. *Mater. Des.* **2010**, *31*, 3512–3517. [\[CrossRef\]](#)

Disclaimer/Publisher’s Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.