Improving Strength and Ductility of a Mg-3.7Al-1.8Ca-0.4Mn Alloy with Refined and Dispersed Al$_2$Ca Particles by Industrial-Scale ECAP Processing

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Abstract: Tailoring the morphology and distribution of the Al$_2$Ca second phase is important for improving mechanical properties of Al$_2$Ca-containing Mg-Al-Ca based alloys. This work employed the industrial-scale multi-pass rotary-die equal channel angular pressing (RD-ECAP) on an as-cast Mg-3.7Al-1.8Ca-0.4Mn (wt %) alloy and investigated its microstructure evolution and mechanical properties under three different processing parameters. The obtained results showed that RD-ECAP was effective for refining the microstructure and breaking the network-shaped Al$_2$Ca phase. With the increase of the ECAP number and decrease of the processing temperature, the average sizes of Al$_2$Ca particles decreased obviously, and the dispersion of the Al$_2$Ca phase became more uniform. In addition, more ECAP passes and lower processing temperature resulted in finer α-Mg grains. Tensile test results indicated that the 573 K-12p alloy with the finest and most dispersed Al$_2$Ca particles exhibited superior mechanical properties with tensile yield strength of 304 MPa, ultimate tensile strength of 354 MPa and elongation of 10.3%. The improved comprehensive mechanical performance could be attributed to refined DRX grains, nano-sized Mg$_{17}$Al$_{12}$ precipitates and dispersed Al$_2$Ca particles, where the refined and dispersed Al$_2$Ca particles played a more dominant role in strengthening the alloys.

Keywords: Mg-3.7Al-1.8Ca-0.4Mn alloy; Al$_2$Ca phase; equal channel angular pressing; refinement; mechanical properties

1. Introduction

Developing strong and ductile magnesium alloys has been one of the main research areas in the last twenty years, as they exhibit great potential in aerospace, military, new energy automobile, medical instrument and electronic applications [1–5]. High strength magnesium alloys with ultimate tensile strength higher than 400 MPa have already been successfully prepared with the addition of abundant rare-earth (RE) elements, owing to the intense second phase (precipitate) strengthening effect [6–8]. However, the RE addition impairs the lightweight advantage of magnesium alloys, and increased their cost as well, making them difficult to use for cost-sensitive industry applications [9–11]. Therefore, design and preparation of reinforced RE-free magnesium alloys have recently regained people's attention.

Mg-Al based (AZ series) alloys are one of the most commonly used commercial magnesium alloy series, whose strengthening precipitate is mainly Mg$_{17}$Al$_{12}$ phase [12–14]. Mg$_{17}$Al$_{12}$ possesses a
relatively low melting point (730 K) and tends to be softened above 473 K, thereby exhibiting a weak
strengthening effect, especially at high temperatures [15,16]. In the last few years, the Mg-Al-Ca (-Mn)
adloys, which were employed as typical heat-resistant casting magnesium alloys formerly, have been
researched for high strength wrought Mg alloys. Ultrahigh strength characteristics involving tensile
yield strength exceeding 400 MPa have already been obtained for high-Ca-content Mg-Al-Ca-Mn
alloys [17–21]. However, excessive Ca addition intrinsically deteriorated the ductility of Mg alloys,
whose elongations were always lower than 5%, even after remarkable grain refinement [17–20]. To
balance the strength and ductility, Ca content should be decreased in these alloys.

With the increase of Ca content in Mg-Al-Ca alloys, Mg₁₇Al₁₂ phase turns into three laves phases
in sequence, namely, Al₂Ca (C15), (Mg,Al)₂Ca (C36) and Mg₂Ca (C14) phases, respectively [17].
Among these intermetallic compounds, Al₂Ca phase possesses the highest melting point, approximately 1352
K [22]. Studies of the first-principles calculation also proved that Al₂Ca phase exhibits the best thermal
stability for the three laves phases [23]. Moreover, Al₂Ca phase could form with low or moderate
Ca addition, which might facilitate a maximum combination of strength and ductility. So far, most
Al₂Ca-containing magnesium alloys were prepared by hot extrusion, and they usually exhibited
remarkably improved strength [24–26]. Although Al₂Ca network phases were crushed after extrusion,
large particles remained and the broken particles were not uniformly distributed within a α-Mg matrix.
As a consequence, local stress concentration was easy to generate at the junctions of brittle second phase
particles and α-Mg matrix during a tensile test, resulting in nucleation and propagation of microcracks
at an early time [19]. Therefore, it is essential to develop an effective method to refine Al₂Ca phases
and increase their dispersibility, in order to improve the ductility of these high strength alloys.

Our previous studies have already shown that the multi-pass equal channel angler pressing
(ECAP) is effective to refine large Al-Si particles, and network-shaped second phases in magnesium
alloys [27–33]. As for Al₂Ca containing alloys, no attempt of ECAP processing has been reported.
Therefore, in the present work, we prepared an Al₂Ca-dominated Mg-3.7Al-1.8Ca-0.4Mn (wt %) alloy
first, and then systematically investigated its microstructural evolution and mechanical properties
under an industrial-scale ECAP processing at three different processing parameters. By refining and
dispersing Al₂Ca second phase particles, we successfully prepared a high strength and high ductility
Al₂Ca-containing magnesium alloy block.

2. Materials and Methods

The raw materials for preparation of studied Mg-3.7Al-1.8Ca-0.4Mn (wt %) alloy were pure Mg,
pure Al, Mg-30 wt % Ca and Mg-10 wt % Mn master alloys. The designed alloy was prepared by
semi-continuous casting method, with an ingot diameter of 90 mm. Then large cuboid samples with
dimension of 50 mm × 50 mm × 100 mm were cut from the center of the ingot for further industrial-scale
ECAP. To explore the influence of processing parameters on refinement of Al₂Ca-containing alloys,
three ECAP routes were proposed, i.e., 4 passes at 623 K, 12 passes at 623 K, and 12 passes at 573 K.
The ECAP die employed was a self-design rotary-die (RD) with die angle of 90° and outer arc angle of
0°, which was described detailedly in our previous work [33]. Before ECAP, the sample was inserted
in the die and both were heated and kept at a set temperature for 20 min within an induction heating
furnace. Then multi-pass RD-ECAP were performed successively by an automatic control system
without intermediate heating. This ECAP process is time-saving, and the total processing time for 12
passes was less than 15 min.

Metallographic specimens were then cut from the cast and ECAP specimens, mechanically grinded
by #80, #400, #1000 and #2000 SiC abrasive papers, polished and etched with a 4 mL nitric acid and
96 mL ethanol mixed solution. Then, microstructure characterizations of the alloys were carried out
by the X-ray diffractometer (XRD, Cu-Kα, Bruker D8, DISCOVER, Bruker Corporation, Karlsruhe,
Germany), optical microscope (OM, Olympus BX51M, Olympus, Tokyo, Japan), and a scanning electron
microscope (SEM, Sirion 200, FEI Company, Hillsboro, OR, USA) equipped with an X-ray energy
dispersed spectrometer (EDS, Genesis 60S, FEI Company, Hillsboro, OR, USA). To further identify
various phases, observation of the transmission electron microscope (TEM, Tecnai G2, FEI Company, Hillsboro, OR, USA) was conducted. The TEM samples were prepared by mechanical grinding and ion thinning. To reveal the grain size distributions of ECAP alloys, the electron back-scattered diffraction (EBSD) analyses were conducted (SEM, Hitachi S-3400N, Hitachi, Tokyo, Japan). Moreover, the average particle sizes were measured by counting at least 100 particles in three SEM images through the Image-J software (Image 1.48, National Institutes of Health, Bethesda, MD, USA). To evaluate the mechanical properties, tensile tests were performed via a CMT5105 electronic universal testing machine (MTS, Shenzhen, China) with a ram speed of 0.5 mm/min at room temperature. The dumbbell shaped specimens with gauge dimension of 7.5 mm × 2 mm × 2 mm were cut from the center section of ECAP samples with the loading direction parallel to the extrusion direction. For each processing situations, three tensile specimens were employed.

3. Results and Discussions

3.1. Microstructure of As-Cast Alloy

Figure 1 shows the XRD patterns of as-cast alloy and three ECAP alloys. Two phases, α-Mg and Al₂Ca phases, are indexed from the diffraction peaks for all alloys, which suggests no obvious phase transformation occurs during hot deformation. Since the Ca/Al ratio of this alloy is lower than 0.8, Al₂Ca phase becomes the main second phase [24]. Figure 2a,b show the optical and SEM micrographs of as-cast Mg-3.7Al-1.8Ca-0.4Mn alloy. Dendritic α-Mg grains and continuous-network interdendritic second phases (marked by A in Figure 2b) could be observed. Seen from the enlargement of the network phase shown in Figure 2c, it exhibits a lamellar shape, consistent with the morphology of a typical eutectic structure. The corresponding EDS result (Figure 2e) reveals high contents of Al and Ca elements, indicating they could have a Al₂Ca + α-Mg eutectic structure. Figure 3 shows the TEM image of the eutectic structure. Black and white stripes are arranged alternately. The index of the corresponding selected area electron diffraction (SAED) pattern of the black stripes (inset of Figure 3) further demonstrates the existence of Al₂Ca phase.

Figure 1. X-ray diffractometer (XRD) patterns of as-cast and ECAP-ed alloys.
Figure 2. Microstructure of the as-cast alloy. (a) Optical image; (b,c,d) scanning electron microscope (SEM) images and enlargements of (c) the eutectic structure and (d) cubic particle; The corresponding EDS results of (e) the eutectic and (f) the particle.

Moreover, some cubic particles (marked by B in Figure 2b) are observed near the eutectic network. EDS analysis on one particle (Figure 2d) was performed and the result (Figure 2f) suggested that it
contains much higher Mn and Al elements, which should be Al₈Mn₃ phase [19]. However, Al-Mn particles were not detected from the XRD patterns due to the fact that the content is extremely low.

3.2. Microstructure of ECAP Alloys

Figure 4 shows the SEM images of three Mg-3.7Al-1.8Ca-0.4Mn ECAP alloys processed at different temperatures and passes. Seen from the low-magnification images of Figure 4a,c,e, the continuous network eutectic structure became distorted after ECAP, and more ECAP numbers and a lower processing temperature resulted in a finer microstructure and narrower dendrite spacing. Moreover, as can be seen from the enlarged SEM images of Figure 4b,d,f, the distorted Al₂Ca dendritic phases were broken into ultrafine particles (with particle size lower than 1 µm). However, the average sizes of broken Al₂Ca particles are different in three ECAP alloys. High ECAP numbers refined the Al₂Ca particles from 0.6 µm to 0.5 µm for 623K-4p and 623K-12p alloys, while lower ECAP temperature was more effective to refine these particles, and the average size of Al₂Ca particles was approximately 0.3 µm in 573 K-12p alloy.

![Figure 4. SEM images of ECAP alloys processed at (a,b) 623 K-4P, (c,d) 623 K-12P and (e,f) 573 K-12P with (a,c,e) low and (b,d,f) high magnifications.](image-url)
ECAP alloys along the extrusion direction. The 623 K-4p alloy showed an uneven grain size distribution. Both coarse and fine grains were identified, suggesting an incomplete dynamic recrystallized (DRX) microstructure. After 12p ECAP at either 623 K or 573 K, homogeneous grain size distribution was observed (Figure 5c,d), indicating a high degree of DRX. Furthermore, Figure 6 shows the area fraction of DRX grains and un-DRX grains in three ECAP alloys. It is apparent that the fraction of DRX grains in two 12p alloys were much higher than the 4p alloy.

**Figure 5.** Electron back-scattered diffraction (EBSD) maps and its corresponding grains distributions of ECAP alloys processed from (a,b) 623 K-4P, (c,d) 623 K-12P and (e,f) 573 K-12P.

**Figure 6.** Area fraction of the recrystallized and un-recrystallized grains in three ECAP alloys.
Owing to the high DRX ratios, the average grain sizes of two 12p alloys were smaller than 4p alloy. The average grain sizes were estimated to be 9.2 µm, 4.3 µm and 3.7 µm for 623 K-4p, 623 K-12p and 573 K-12p alloys, respectively. It can be seen that higher ECAP numbers and lower processing temperature contributed to refinement and uniformity of α-Mg grains. Two factors resulted in finer grains for 573 K-12p alloy. For one thing, lower processing temperature could restrain the migrations of grain boundaries. For another, fine and dispersedly distributed Al2Ca particles are more effective to hinder the growth of DRX grains. Figure 7 shows the TEM images of DRX regions in three ECAP alloys. High density of dislocations and sub-structures were observed in 623 K-4p alloy (Figure 7a). When the ECAP number increased to 12, the density of dislocations declined obviously, and the boundaries of DRX grains became distinct, either in 623 K and 573 K processed alloys. Overall, the grain sizes of DRX grains in these alloys are in good agreement with EBSD results.

![Figure 7](image)

**Figure 7.** Dynamic recrystallized (DRX) grains and sub-structured in (a) 623 K-4P, (b) 623 K-12P, (c) 573 K-12P alloys.

As can be seen from the Kernel Average Misorientation (KAM) maps shown in Figure 8, the distribution of dislocation density varied for three ECAP alloys (shown in green and yellow colors). It is shown in Figure 8a that fine DRX grains and coarse deformation grains were mixed in 623 K-4p alloy. Plenty of dislocations existed within coarse deformed grains, while fine DRX grains had little dislocations within, because the operation of DRX consumed dislocations. After increasing ECAP number to 12, more DRX fine grains and less deformation grains suggested a lower density of dislocations (Figure 8b). Moreover, compared with Figure 8b,c, it can be concluded that lower temperature processing led to stronger strain accumulation for ECAP alloys at the same pass (shown in green color).
Figure 8. Kernel Average Misorientation (KAM) maps of alloys processed by (a) 623 K-4P, (b) 623 K-12P and (c) 573 K-12P.

Figure 9 shows the inverse pole figures of three ECAP alloys. A typical fiber texture (i.e., c-axes perpendicular to the extrusion direction) was formed for 623 K-4P alloy, and its maximum texture intensity was 2.40 (Figure 9a). Increasing processing number to 623 K, the orientations (c-axes) of grains exhibited a tendency to be parallel to extrusion direction, and the maximum intensity was 4.89 (Figure 9b). With the decrease of processing temperature to 573 K, the maximum texture intensity declined to 2.80. Similar texture evolutions have also been found in other recrystallized Mg-RE and AZ series magnesium alloys [34,35].

Figure 9. Inverse pole figures of ECAP alloys processed from (a) 623 K-4P, (b) 623 K-12P and (c) 573 K-12P.
Figure 10 exhibits the TEM observation of Al$_2$Ca second phase in three deformed alloys. In early ECAP passes at 623 K, lamellar Al$_2$Ca eutectic phase was partially broken into fine particles, as can be seen from the Al$_2$Ca laths and particles shown in Figure 10a,b, respectively. Since Al$_2$Ca is a brittle phase, its refining mechanism is more like a mechanical crushing process. Therefore, the crush of Al$_2$Ca eutectic phase was incomplete and uneven owing to the low deformation strains at low ECAP pass. When the ECAP number was increased to 12, the Al$_2$Ca phase broke thoroughly into submicron particles (Figure 10b,c), though they were still aggregated.

Figure 10. TEM images of Al$_2$Ca phase particles in (a,b) 623 K-4P, (c) 623 K-12P and (d) 573 K-12P alloys.

Furthermore, TEM observations demonstrated that abundant nano-sized precipitates were observed within un-DRX $\alpha$-Mg grains (including sub-grains) of all ECAP alloys (Figure 11), while the density of precipitates was relatively low in DRX grains. These precipitates were dynamically precipitated during hot deformation, which was commonly observed in Mg-Al-Ca based alloys. Most of the precipitates had a spherical shape (marked by yellow arrows), and a few exhibited rod shapes (red arrows). Seen from Figure 11a, the diameters of these spherical precipitates were around 5–15 nm in 623 K-4p alloy. With increased ECAP numbers, the density of precipitates increased for 623 K-12p alloy, and both rod-like and spherical precipitates were observed. The rod-like precipitates are usually larger than spherical particles, exhibiting a diameter of 20–30 nm and a length of 30–60 nm. After 12 passes of ECAP at 573 K, precipitates with diameter of 10–20 nm were also detected (Figure 11c), and the precipitation density was the highest for three deformed alloys. Furthermore, Figure 11d shows the corresponding SAED patterns of the precipitates. The diffraction patterns exhibit near-ring characteristic, and index of the diffraction rings demonstrates that the precipitates are Mg$_{17}$Al$_{12}$ phases. The Mg$_{17}$Al$_{12}$ precipitates are usually reported in AZ91 alloys [36]. As for Mg-Al-Ca alloys, Al$_2$Ca phase served as the main precipitates during hot deformation or aging in most cases [24], and precipitation of Mg$_{17}$Al$_{12}$ particles was barely reported. Taking into account the alloy composition and microstructure of this studied alloy, most Ca elements were concentrated within the eutectic phases,
and Al elements were more inclined to be enriched in some grains, which caused the precipitation of Mg₁₇Al₁₂ phases under the interaction of heat and strain during multi-pass ECAP.

Figure 11. TEM micrographs of the precipitates in (a) 623 K-4P, (b) 623 K-12P, and (c) 573 K-12P alloys, as well as (d) the corresponding SAED patterns of the precipitates.

3.3. Microstructure of ECAP Alloys

Figure 12 shows the tensile mechanical properties of as-cast and ECAP alloys. The as-cast alloy possessed low mechanical properties with tensile yield strength (TYS) of 70 MPa, ultimate tensile strength (UTS) of 161 MPa and poor ductility (elongation of 5.1%). After the ECAP process, all samples exhibited a remarkable improvement in both strength and ductility. Generally, an increase in the ECAP numbers improved the strength and ductility simultaneously, while decreases in ECAP temperatures further enhanced the alloy, but impaired the ductility slightly. The 573 K-12p alloy showed the highest strength, with TYS of 304 MPa and UTS of 354 MPa, together with a moderate ductility. In addition, by comparing with other commercial Mg alloys and Mg-RE based alloys prepared by ECAP (Figure 12c) [27–32,37–39], this 573 K-12p alloy exhibits a relatively high specific yield strength, which is comparable to those Mg-RE ECAP alloys with high RE contents. Overall, this non-RE low-alloying ECAP alloy with refined and dispersed Al₂Ca particles exhibits great potential as high performance magnesium alloys.

Figure 13 shows the SEM fractograph of as-cast and ECAP alloys after tensile tests. Seen from Figure 13a, many laminated cleavage steps appear on the fracture surface of the as-cast alloy, suggesting a brittle fracture. Owing to the large eutectic structures at grain boundaries, microcracks tend to be formed around the eutectic, which leads to early break and poor ductility of the as-cast alloy. After ECAP, a few dimples and laminated cleavage steps are observed on fracture surface of 623 K-4p alloy (Figure 13b), indicating a mixed fracture mechanism. As for two 12p alloys (Figure 13c,d), although the fracture surfaces become fine and flat, some cleavage steps still exist.
Figure 12. Mechanical properties of Mg-Al-Ca-Mn alloys. (a) Typical tensile curves of as-cast and ECAP alloys; (b) The summary of yield strength (YS), ultimate tensile strength (UTS) and elongation of various alloys; (c) Comparison of specific yield strength and elongation between this work and other high performance ECAP Mg alloys [27–32,37–39].

Figure 13. SEM images of fracture surfaces of (a) As-cast, (b) 623 K-4P, (c) 623 K-12P and (d) 573 K-12P alloys. Insets of the images are the corresponding enlarged micrographs.

3.4. Influence of Al$_2$Ca Size and Distribution on Mechanical Properties

Based on above tensile results, it can be confirmed that multi-pass ECAP is beneficial for improving the mechanical properties of an Al$_2$Ca-containing alloy. Considering the microstructural evolutions,
the improved strength of ECAP alloys could be mainly ascribed to three factors, i.e., refined DRX grains, dynamically precipitated $\text{Mg}_{17}\text{Al}_{12}$ precipitates, and dispersed $\text{Al}_2\text{Ca}$ particles. To quantitatively describe the contributions of various strengthening factors, Table 1 lists the characteristic parameters of DRX grains and second phase particles.

| Microstructural Characteristics | 623 K-4P | 623 K-12P | 573 K-12P |
|--------------------------------|----------|----------|-----------|
| Grain ($\mu$m)                 | 9.2 ± 1.9| 4.3 ± 1.5| 3.7 ± 1.2 |
| $\text{Al}_2\text{Ca}$ ($\mu$m)| 0.6 ± 0.2| 0.5 ± 0.2| 0.3 ± 0.1 |
| Ribbonlike $\text{Al}_2\text{Ca}$ arm spacing ($\mu$m)| 17 ± 4 | 11 ± 2 | 8 ± 2 |
| $\text{Mg}_{17}\text{Al}_{12}$ (nm) | 12 ± 4 | 22 ± 7 | 14 ± 6 |
| $\text{Mg}_{17}\text{Al}_{12}$ volume fraction (%) | 2.5% | 6.7% | 6.1% |

The contribution of fine grain strengthening could be estimated from the Hall-Petch equation:

$$\sigma_y = \sigma_0 + kd^{-0.5},$$

where $\sigma_y$ is yield strength, $\sigma_0$ is material constants, $k$ is Hall-Petch slope and $d$ is grain size. The value of $k$ was employed as 170 MPa$\cdot$μm$^{0.5}$ on the basis of average grains in this work [40]. Accordingly, the contribution of grain refinement strengthening on tensile yield strength could be estimated to be 55 MPa, 97 MPa and 105 MPa for 623 K-4p, 623 K-12p, and 573 K-12p alloys, respectively.

In case of $\text{Mg}_{17}\text{Al}_{12}$ nano-particles precipitated at grain internal, they could pin dislocation movement and strengthen the alloy by Orowan strengthening mechanism [41]. The increment of YS associated with $\text{Mg}_{17}\text{Al}_{12}$ particles have already been given in an early report [41], and the equation is shown in Equation (2).

$$\Delta\sigma_{\text{Orowan}} = \beta \frac{0.4\mu_mb}{\pi(d^2/4f_v - 1)} \ln(d/b) \sqrt{1 - \nu_m},$$

where $\beta$ is constant (1.25), $\mu_m$ is shear modulus (16.5 GPa), $b$ is Burgers vector (0.32 nm), $d$ is the average size of $\text{Mg}_{17}\text{Al}_{12}$, $f_v$ is the volume fraction of $\text{Mg}_{17}\text{Al}_{12}$, and $\nu_m$ is Poisson ratio (0.35). Moreover, is should be noticed from above TEM observations that the nano-sized $\text{Mg}_{17}\text{Al}_{12}$ particles were most dynamically precipitated in the un-DRX grains, and they were seldom seen in DRX grains, which has also been reported in other Mg-Al-Ca-Mn alloys [19]. Therefore, we assumed that the Orowan strengthening mechanism caused by $\text{Mg}_{17}\text{Al}_{12}$ precipitates is only activated in un-DRX grains, and it could be calculated by the following equation:

$$\Delta\sigma_{\text{Mg}_{17}\text{Al}_{12}} = (1 - f_{\text{DRX}})\Delta\sigma_{\text{Orowan}},$$

where $f_{\text{DRX}}$ is the volume fraction of DRX grains showed in Figure 6.

As long as the strengthening caused by grain refinement and $\text{Mg}_{17}\text{Al}_{12}$ precipitates was estimated, the rest of strengthening effect should be caused by the $\text{Al}_2\text{Ca}$ second phase strengthening, and it is calculated by Equation (4),

$$\Delta\sigma_{\text{Al}_2\text{Ca}} = \sigma_{\text{YS}} - \sigma_{\text{Cast}} - \sigma_{\text{Hall-Petch}} - \sigma_{\text{Mg}_{17}\text{Al}_{12}},$$

where $\sigma_{\text{YS}}$ is the tested tensile yield strength of ECAP alloys, and $\sigma_{\text{Cast}}$ is the tested tensile yield strength of cast alloy.

Figure 14a displays the quantitative contributions of grain refinement, dynamic precipitated $\text{Mg}_{17}\text{Al}_{12}$ precipitates and dispersed $\text{Al}_2\text{Ca}$ second phase particles, to TYS values of three ECAP alloys. It is apparent that for 623 K-4p and 12p alloys, fine grain strengthening plays a more important role than other two strengthening factors. With the dispersion of $\text{Al}_2\text{Ca}$ phase in 573 K-12p alloy, the strengthening contribution of the $\text{Al}_2\text{Ca}$ phase exceeds the other two factors. To intuitively describe
the strengthening effect of a dispersed $\text{Al}_2\text{Ca}$ second phase, Figure 14b shows the relationship between $\Delta \sigma_{\text{Al}_2\text{Ca}}$ and the distance of ribbonlike $\text{Al}_2\text{Ca}$ arm spacing [42]. It is obvious that with the decrease of $\text{Al}_2\text{Ca}$ arm spacing, the contribution of the $\text{Al}_2\text{Ca}$ phase increases remarkably. Therefore, to further improve the mechanical properties of $\text{Al}_2\text{Ca}$ containing Mg-Al-Ca-Mn alloys, additional effort should be focused on the refining and dispersion of $\text{Al}_2\text{Ca}$ second phase particles.

**Figure 14.** (a) The contributions of various strengthening factors to tensile yield strength of ECAP alloys. (b) The relationship between the ribbonlike $\text{Al}_2\text{Ca}$ arm spacing and the contribution of $\text{Al}_2\text{Ca}$ particles to tensile yield strength of ECAP alloys.

### 4. Conclusions

The microstructure evolutions and mechanical properties of a Mg-3.5Al-1.7Ca-0.4Mn (wt %) alloy during ECAP at different processing numbers and temperatures were systematically investigated. The main conclusions can be drawn as follows:

1. The microstructure of as-cast Mg-3.5Al-1.7Ca-0.4Mn (wt %) alloy was composed of interdendritic $\alpha$-Mg grains, network $\text{Al}_2\text{Ca}$ phase and a few $\text{Al}_8\text{Mn}_5$ particles. During multi-pass ECAP, the $\text{Al}_2\text{Ca}$ network phase was gradually broken into ultrafine particles. More ECAP passes and lower processing temperature resulted in finer sizes and a more dispersed distribution of $\text{Al}_2\text{Ca}$ particles, as well as finer $\alpha$-Mg grains.

2. Multi-pass ECAP simultaneously enhanced the tensile strength and ductility of Mg-3.5Al-1.8Ca-0.4Mn alloy. The 573 K-12p processed alloy exhibited superior mechanical properties with a tensile yield strength of 304 MPa, ultimate tensile strength of 354 MPa and elongation of 10.3%. The improved comprehensive mechanical performance could be attributed to refined DRX grains, nano-sized Mg$_{17}$Al$_{12}$ precipitates and dispersed $\text{Al}_2\text{Ca}$ particles. Moreover, quantitative contribution analysis suggested that the refined and dispersedly distributed $\text{Al}_2\text{Ca}$ particles played a dominant role in strengthening the $\text{Al}_2\text{Ca}$ containing alloys.

**Author Contributions:** A.M., H.L. and J.J. designed the project and guided the research; C.W., J.S. and H.L. prepared the manuscript; C.W., H.H. and Z.Y. performed the experiment and analyzed the data; X.Z., H.H. and C.W. prepared the figures; A.M., H.L. and J.J. reviewed the manuscript.

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**Data Availability:** The raw/processed data required to reproduce these findings cannot be shared at this time as the data also forms part of an ongoing study.

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