



# **A Review of Progress in the Study of Al-Mg-Zn(-Cu)** Wrought Alloys

Guwei Shen <sup>1,2</sup>, Xiaolin Chen <sup>1,2,\*</sup>, Jie Yan <sup>1,2</sup>, Longyi Fan <sup>1,2</sup>, Zhou Yang <sup>1,2</sup>, Jin Zhang <sup>1,2</sup> and Renguo Guan <sup>1,2,\*</sup>

- Key Laboratory of Near-Net Forming of Light Metals of Liaoning Province, Dalian Jiaotong University, Dalian 116028, China
- <sup>2</sup> Engineering Research Center of Continuous Extrusion, Ministry of Education, Dalian Jiaotong University, Dalian 116028, China
- \* Correspondence: cxiaolin@djtu.edu.cn (X.C.); guanrenguo@sina.cn (R.G.)

**Abstract:** Modern industrial development has put forward higher demands on the performance of metallic structural materials, especially in terms of light weight, high strength and corrosion resistance. All of these characteristics are of particular importance in transportation fields. As one of the most representative structural materials, aluminum and alloys have exhibited significant advantages in light weight. Most of the alloys are prominently featured in one specific aspect. The overall performance still needs to be improved. In recent years, researchers have developed Al-Mg-Zn(-Cu) alloy, a new wrought aluminum alloy, whose design strategy is known as "crossover alloying". This novel alloy is an age-hardened Al-Mg alloy with a T-Mg<sub>32</sub>(Al, X)<sub>49</sub> (X is Zn, Cu) phase as the main strengthening phase. This system of alloys exhibits excellent properties in terms of strength and corrosion resistance, which makes it promising for applications in automotive, marine, aerospace and other fields. This paper summarizes the research progress of Al-Mg-Zn(-Cu) alloy, and analyzes the basic methods of microstructural control in terms of composition design and property research. Finally, the future directions of this alloy are proposed.

Keywords: Al-Mg-Zn(-Cu); age-hardening; T-Mg<sub>32</sub>(Al, X)<sub>49</sub>; comprehensive properties



Citation: Shen, G.; Chen, X.; Yan, J.; Fan, L.; Yang, Z.; Zhang, J.; Guan, R. A Review of Progress in the Study of Al-Mg-Zn(-Cu) Wrought Alloys. *Metals* **2023**, *13*, 345. https:// doi.org/10.3390/met13020345

Academic Editor: Marcello Cabibbo

Received: 25 December 2022 Revised: 23 January 2023 Accepted: 6 February 2023 Published: 9 February 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/).

# 1. Introduction

Under the background of energy saving and green development, and guided by the target of peaking carbon dioxide emissions and achieving carbon neutrality, the development of lightweight materials has attracted the attention of scientific researchers. Aluminum alloys have been widely used in automotive, marine, aerospace and other fields owing to their excellent comprehensive properties, such as high specific strength, corrosion resistance and very excellent thermal and electrical conductivity [1–3].

Traditional Al-Mg alloys, such as AA5083 and AA5059 are widely used in ships, vehicles and other fields because of the advantageous balance between the strength to weight ratio and good formability [4–6]. However, they are non-heat treatable alloys with medium strength, which can be strengthened mainly by solution strengthening and work hardening [7–9]. Moreover, when the Mg content is higher than 3.5 wt%,  $\beta$ -phase (Al<sub>3</sub>Mg<sub>2</sub>) precipitation is formed continuously along the grain boundary. This phase has no apparent positive effect on the strength of Al-Mg alloys, and more importantly, the  $\beta$ -phase tends to suffer from anodic dissolution, as it has lower potential (–1.15 V) compared with that of Al matrix (–0.82 V). This dissolution process proceeds along the grain boundaries, thus referring as intergranular corrosion (IGC) [10,11]. Both of these shortcomings greatly restrict its further application.

Precipitation strengthening is one of the most effective strengthening methods to improve the mechanical properties of aluminum alloy, especially for 2xxx series and 7xxx series alloys. They are high-strength aluminum alloys, which can be age-strengthened. The main strengthening elements in 2xxx series alloys are Cu and Mg, with an optimum

Cu/Mg ratio of greater than 1, and the strengthening phases are  $\theta$ -Al<sub>2</sub>Cu phase and S-Al<sub>2</sub>CuMg phase. While for the 7xxx series alloys, the main strengthening elements are Zn and Cu, with an optimum Zn/Mg ratio of greater than 2, and the strengthening phase is  $\eta$ -MgZn<sub>2</sub> phase. To improve the strength and achieve the age-hardening of traditional Al-Mg alloys, researchers combined 2xxx (Al-Cu), 5xxx (Al-Mg) and 7xxx (Al-Zn) alloys, obtaining beneficial properties of these materials, such as high strength and good formability. The new mixture can be subjected to age hardening to form a complex crystal structure of  $Mg_{32}(Al, X)_{49}$  (X stands for Zn, Cu) named T-phase. The novel Al-Mg-Zn(-Cu) wrought alloys (with a Zn/Mg ratio of no more than 1 and a Cu/Mg of no more than 0.5) can be strengthened by T-phase. This "crossover alloy" [12–16] exhibits Mg as a major constituent, but on the contrary to commercial Al-Mg alloy, is indeed heattreatable. Moreover, formation of the T-phase with a higher potential at the grain boundary will reduce the potential difference between the grain boundary precipitation and Al matrix, greatly improving the corrosion resistance. Current studies on Al-Mg-Zn(-Cu) wrought alloys describe them as alloys fabricated in the state of sheets. The preparation processes include melting and casting, homogenization, scalping, hot rolling, cold rolling, solid solution and artificially aging. In this review, the research progress, as well as the future perspectives regarding these novel Al-Mg-Zn(-Cu) alloys is reviewed.

## 2. Alloy Design

#### 2.1. Design Principles

To improve the strength of traditional Al-Mg alloys, scholars have efficiently screened the element selection of age-hardened Al-Mg alloys by means of first-principle calculation and phase diagram calculation, providing theoretical support for the design of Al-Mg alloys.

Shoichi Hirosawa et al. [17] predicted the interaction energy between atoms and between atoms and vacancies by first-principle calculation (Figure 1). According to the results, microalloying elements can be divided into two categories: inhibiting precipitation and promoting precipitation. A negative interaction energy indicates a stronger mutual attraction, while a positive interaction energy indicates a stronger mutual repulsion. Figure 1a,b demonstrate the interaction energy diagrams of the neighboring atoms of the same element and between element and vacancy in the Al matrix. Elements with positive and large absolute values of  $E^{II}_{X-X}$  will suppress precipitation by vacancy annihilation, and elements with negative and large absolute values of  $\tilde{E}^{II}_{Vacancy-X}$  will suppress precipitation by vacancy capture. It can be seen that the absolute values of  $E^{II}_{X-X}$  and  $E^{II}_{Vacancy-X}$  of Zn and Cu are very small, indicating that Zn and Cu will not inhibit precipitation, because they will neither form intermediate compounds that reduce the quenched vacancy concentration in the form of vacancy annihilation, nor easily capture the quenched vacancy. In Al-Mg-Cu alloys, the interaction energies of Mg-X ( $E^{II}_{Mg-X}$ ) and Cu-X ( $E^{II}_{Cu-X}$ ) [18] are shown in Figure 2. It can be seen that  $E^{II}_{Mg-Zn}$  and  $E^{II}_{Cu-Zn}$  are negative, indicating that Zn and Cu play a role in promoting precipitation in Al-Mg alloys, which provides theoretical support for the formation of precipitates in Al-Mg-Zn(-Cu) alloys.

Based on the aforementioned first-principle calculation results, Pan et al. [19] used FactSage software to calculate the phase diagram of Al-Mg-Zn(-Cu) alloys. As shown in Figure 3, it can be seen that the main precipitated phase at a lower temperature is the T-Mg<sub>32</sub>(Al, Zn, Cu)<sub>49</sub> phase. These results not only theoretically prove the possibility of precipitation of the T-phase instead of the β-phase, but also provide an elemental selection reference for the novel Al-Mg-Zn(-Cu) alloys as well as a theoretical basis for the formulation of the aging progress.



**Figure 1.** Two-body interaction energies between nearest-neighbor X atoms,  $E^{II}_{X-X}$  (**a**), and between nearest-neighbor X atom and vacancy,  $E^{II}_{Vacancy-X}$  (**b**) for various microalloying elements X in Al [17].



**Figure 2.** Two-body interaction energies between Mg-X atoms ( $E^{II}_{Mg-X}$ ) and between Cu-X atoms ( $E^{II}_{Cu-X}$ ) in Al-Mg-Cu alloys [18].



**Figure 3.** Phase diagram of Al-Mg-Zn-Cu alloys calculated by FactSage software: (**a**) Al-5.3Mg-3.3Zn-xCu, (**b**) Al-5.3Mg-0.5Cu-xZn [19].

With respect to the T-phase in the phase diagram calculation results, Zhang et al. [20] applied the integrated computational materials engineering (ICME) framework (Figure 4) to the design and optimization of novel heat-treatable Zn modified Al-Mg alloys. The effect of the Zn content and two-step aging treatment on the precipitation behavior of the T-phase, mechanical properties and their intrinsic relationship are investigated. On one hand, the integrated modeling framework can be used to illustrate the influence of alloying elements and heat treatment processes on the microstructure evolution and mechanical property. On the other hand, this framework can be further applied to design and develop material with the coupled CALPHAD database. This design strategy provides the advantages of shortening the development cycle, compensating for the shortcomings of the long design duration and high-cost of the traditional "trail-and-error" and empirical methods, and inspiring the design and optimization of novel aluminum alloys.



Figure 4. Flowchart of integrated microstructural and strength modeling framework methodology [20].

#### 2.2. Role of Main Alloying Elements: Mg, Zn, Cu and Ag

(1) Mg

Mg is the main alloying element in conventional Al-Mg alloys and plays the role of solid solution strengthening in the Al matrix. Within the range of solid solubility, the strength of alloys increases with the increase of the Mg content [9,11]. In Al-Mg-Zn(-Cu) alloys, in addition to solid solution strengthening, Mg is also involved in the formation of age-strengthened T-Mg<sub>32</sub>(Al, Zn)<sub>49</sub> phase. The precipitation of the T-phase decreases the soluble Mg content and reduces the precipitation possibility of the  $\beta$  phase, thus improving the IGC resistance. However, with the reduction of the Mg content, the proportion of the low angle grain boundaries (LAGBs) increases, and the grain boundary precipitates (GBPs) along the LAGBs present a more discontinuous distribution, leading to enhanced IGC resistance [21].

(2) Zn

The addition of a small amount of Zn (even 0.68–0.70 wt%) to Al-Mg alloys can preclude the formation of the  $\beta$ -Al<sub>3</sub>Mg<sub>2</sub> phase and form the T-phase at the grain boundaries [22]. This also indicates that the T-phase can form extensively in Zn-lean alloys, unlike in 7xxx series alloys where relatively high levels of Zn are required to form the T-phase. Furthermore, the T-phase is with a higher corrosion potential, which reduces the potential difference compared to the Al matrix, significantly improving the corrosion resistance [22–25]. At the same time, the Zn addition promotes the precipitation of the T-phase, while suppressing the formation of S-Al<sub>2</sub>CuMg and  $\beta$ -Al<sub>3</sub>Mg<sub>2</sub> phases. As the T-phase has a huge potential for age hardening response [16,26,27], Zn content will significantly enhance the age-hardening effect [28], greatly improving the strength.

(3) Cu

Cao [29] and Geng et al. [30] found that Cu promotes the formation of the precursor GP zones of the T-Mg<sub>32</sub>(Al, Zn)<sub>49</sub> phase during the pre-aging process, improving the agehardening response. Furthermore, Cu also improves the thermal stability of the T-phase. In addition, Cu participates in the grain and along the grain boundary of the T-Mg<sub>32</sub>(Al, Zn, Cu)<sub>49</sub> phase [31]. The addition of Cu will dramatically narrow the width of precipitation free zones (PFZs) and decrease the corrosion current density [29]. The reduced corrosion potential difference between the grain and the PFZ will lead to the enhanced IGC resistance.

# (4) Ag

Guo et al. [32] have shown the schematic illustration of atomic aggregation, as shown in Figure 5, from which the effect of Ag on the precipitation of Al-Mg-Zn based alloys can be clarified. Ag-vacancy complexes are trapped to Mg atoms, resulting in the formation of numerous Mg-Ag co-clusters. Subsequently, Zn atoms will diffuse into Mg-Ag clusters and act as the nucleation sites for the Ag-containing T-Mg<sub>32</sub>(Al, Zn, Ag)<sub>49</sub> phase. Meanwhile, the formation of Mg-Ag co-clusters increases the ratio of Zn/Mg in the supersaturated solid solution. The redundant Mg and Zn atoms therefore tend to bond together and transform to the  $\eta'$ -MgZn<sub>2</sub> phase.



Figure 5. Schematic illustration showing the atomic aggregation [32].

According to the investigation of Zhang et al. [33], the addition of Ag greatly increases the nucleation density of precipitations in Al-4.5Mg-0.6Zn-0.5 Cu alloys, resulting in a higher aging hardening response. However, the peak hardness did not move to a shorter aging time, indicating that the addition of Ag appears to have no significant effect on the precipitation kinetics. This conclusion is similar to the results obtained by Lukas Stemper et al. [26].

## 3. Properties

## 3.1. Mechanical Properties

The main strengthening mechanism of Al-Mg-Zn(-Cu) alloys is precipitation strengthening, which substantially improves the strength compared with that of the conventional Al-Mg alloys. Cao [8,34] and Hou et al. [9] investigated the precipitation behavior of Al-Mg-Zn-Cu alloys during different aging treatments (see Figure 6). The precipitation sequence of the Cu-containing T-phase [9] is illustrated, which is SSSS (supersaturated solid solution)  $\rightarrow$  GPI zone (fully coherent)  $\rightarrow$  GPII zone (intermediate phase T", fully coherent)  $\rightarrow$  intermediate phase T' (semi-coherent)  $\rightarrow$  equilibrium phase T (incoherent). During single-step artificial aging treatment, Cu and Zn participate in the S-phase and T-phase, respectively (see Figure 6b), and there is a certain competition between the precipitation of the S-phase and T-phase. Without pre-aging treatment, the precipitation in peak aged condition consists of a coarse lath-like T-phase and needle-like S-phase, and the peak hardness is derived from the synergetic effect of the coarsening of the T-phase and hardening of the S-phase. During two-step artificial aging treatment, pre-aging promotes the formation/nucleation of precursors (GP zones) by vacancy-assisted diffusion; they are able to grow and evolve into the Cu-enriched T-phase upon subsequent second-stage aging by solute attachment, then suppressing the S-phase formation (see Figure 6a). The microstructure in the peak aged condition with pre-aging treatment only consists of the high density of finer and the equiaxed T-phase with the S-phase disappearing, and the peak hardness results from the homogeneously distributed T-phase. As shown in Figure 7, applying a pre-aging treatment was found to significantly accelerate and improve the hardening response, and shift the peak hardness to an earlier time and generate higher hardness levels [8,26,35].

Pan et al. [19] investigated the changes of mechanical properties with different (Zn + Cu)/Mg ratios, and the schematic diagram is shown in Figure 8. When the (Zn + Cu)/Mg ratio is below 1.0, the size of precipitates in the grain decreases and the number density increases rapidly as the (Zn + Cu)/Mg ratio increases, which leads to the increase of the mechanical properties. Upon further increasing the (Zn + Cu)/Mg ratio, the formation of GP zones is promoted, and the high-density GP zones formed in the pre-aging stage are partially dissolved during subsequent high-temperature aging. The T-phase will nucleate and grow elsewhere as adjacent GP zones dissolve, resulting in abnormal precipitate growth in grains and the formation of inhomogeneous precipitates. In general, the mechanical properties of alloys with lower (Zn + Cu)/Mg ratios are determined by the average grain size and number density of the T-phase, while alloys with higher (Zn + Cu)/Mg ratios are strengthened by the multi-scale intragranular T-phase.



**Figure 6.** Schematic illustration showing the precipitation behaviors in Al-5.2Mg-2Zn-0.45Cu with (**a**) and without (**b**) pre-aging [8].



**Figure 7.** Age-hardening response of Al-5.2Mg-2.0Zn-0.45Cu during aging at 180 °C with or without pre-aging treatment [8].



**Figure 8.** Schematic diagram of the mechanical properties and the IGC resistance of Al-Mg-Zn(-Cu) alloys: (a) (Zn + Cu)/Mg = 0.63, (b)  $(Zn + Cu)/Mg = 0.71 \sim 0.85$ , (c) (Zn + Cu)/Mg = 0.97, (d) (Zn + Cu)/Mg = 1.21 [19].

Pan [36] studied the effect of alloy components on the mechanical properties of Al-Mg-Zn(-Cu) under a T6 peak-aging state, which are listed in Table 1. The addition of Cu into the system will result in the increase of the tensile strength and yield strength and the decrease of elongation (sample 1# and 2#). Increasing the Zn content will also increase strength and decrease elongation (sample 2#, 3# and 4#). When the Zn content remains unchanged, the mechanical properties are similar regardless of the Mg and Cu content (comparison between sample 2# and 5#, or between sample 4# and 6#). In addition, the tensile strength and yield strength of Al-Mg-Zn-Cu alloys are comparable to AA7075 alloy (570 MPa, 500 MPa) under the same process, but with a slightly higher elongation. Compared with commercial aluminum alloys of the 5xxx series and 7xxx series reported in literature [37–40], Al-Mg-Zn-Cu alloys show significant advantages in mechanical properties.

	Alloy Component	Tensile Strength (MPa)	Yield Strength (MPa)	Elongation (%)	Zn/Mg	Cu/Mg	Reference
	(1#)Al-5.3Mg-3.3Zn	496	405	17.9	0.62	0	
	(2#)Al-5.3Mg-3.3Zn-0.5Cu	525	440	15.7	0.62	0.10	
Al-Mg-	(3#)Al-5.3Mg-4.0Zn-0.5Cu	550	478	14.6	0.75	0.10	
Zn(-Cu)	(4#)Al-5.3Mg-4.6Zn-0.5Cu	573	508	13.0	0.88	0.10	[36]
	(5#)Al-4.6Mg-3.3Zn-1.0Cu	513	423	16.6	0.72	0.22	
	(6#)Al-4.6Mg-4.6Zn-1.0Cu	571	503	12.9	1.00	0.22	
7075	Al-6.0Zn-2.5Mg-1.6Cu	568	505	12.0	2.40	0.64	
7085	Al-7.4Zn-1.5Mg-1.8Cu-0.1Zr	542	489	13.0	4.93	1.20	[37]
7050	Al-6.4Zn-2.0Mg-2.3Cu-0.1Zr	465	408	9.6	3.20	1.15	[38]
5182	Al-4.6Mg-0.4Mn	275	140	21.0	-	-	[39]
5052	Al-2.3Mg-0.2Cr-0.1Mn	271	227	6.9	-	-	[40]

**Table 1.** Mechanical properties of the different alloy states at room temperature [36–40].

Liu et al. [41] investigated the effect of Ag on the microstructure and tensile strength of Al-Mg-Zn alloys. It is found that Ag improves the age-hardening response of Al-5Mg-3Zn alloys owing to the stimulation of matrix precipitation. Moreover, the size and density of matrix precipitates (MPTs) were refined and improved by Ag. Whereas Ag atoms reduce the coherent distortion at the interface between MPTs and matrix, resulting in the weakened ability of MPTs to obstruct the dislocation motion. So the addition of Ag does not significantly improve the strength of Al-Mg-Zn alloys.

Application of the final thermo-mechanical treatment (FTMT) further improves the strength of alloys by enhancing the deformation strengthening effect and increasing the number density of precipitates. The tensile strength of Al-5.3Mg-4.6Zn-0.5Cu is up to 691 MPa when cold rolling deformation is introduced prior to the second aging treatment. When introducing warm rolling at 100~110 °C prior to the second aging treatment, the tensile strength and yield strength can reach 746MPa and 696MPa, respectively, exceeding the strength of most 7xxx series alloys [36].

Ding [42,43] found that the contribution of precipitation strengthening to the overall strength in age-hardening Al-Mg-Zn alloys can be more than 80%. The effect of grain boundary strengthening is weak and does not change significantly with the grain size. Furthermore, the increase of Mg content in a certain range will increase the effect of solid solution strengthening, but also increases the difficulty of rolling.

Regarding the study of the fracture toughness of Al-Mg-Zn-Cu alloys, the effect of aging precipitates and the structure of grains is mainly considered because there are almost no intermetallic compounds and dispersed particles in these alloys. It was found that the fracture toughness decreases with the increase of the Zn/Mg ratio. When the Mg content is high, the addition of a small amount of Cu is unfavorable to the toughness. Compared with that of Cu, Zn has a greater influence on the fracture toughness, which decreases rapidly along with increasing the Zn content. When the content of other elements is certain, the higher the Mg content, the lower the toughness. In addition, compared with the morphology obtained from the T6 treatment, when the alloys are treated using the FTMT process, a large number of deformed structures are fabricated, in which the low angle grain boundary accounts for a large proportion, and the fully recrystallized structure accounts for a small proportion. Grain deformation leads to the rapid increase in the yield stress gap between the intragranular and grain boundary, improving the fracture toughness to some extent [36].

According to the results (Figure 9) of Liu et al. [41], the addition of 0.2 wt% Ag improved the fracture toughness of Al-5Mg-3Zn alloys because of the weak dislocation pile-up around MPTs and the low fraction of deformed grains. The addition of 0.4 wt% and 0.6 wt% Ag decreases the fracture toughness, even lower than that of the Ag-free alloys, because an array of coarse constituents promotes the micro void nucleation, growth and crack propagation.





#### 3.2. Corrosion Behavior

The IGC mechanism of Al-Mg-Zn-Cu alloys is the anodic dissolution of the T-phase along the grain boundaries, and the relevant schematic diagram is shown in Figure 8. The IGC resistance of alloys increases with the increase of the (Zn + Cu)/Mg ratio. For alloys with lower (Zn + Cu)/Mg ratios (Figure 8a,b), the main factor affecting the IGC resistance is the potential difference between GBPs and the Al matrix. At higher (Zn + Cu)/Mg ratios (Figure 8c,d), the IGC resistance mainly depends on the continuity of GBPs [19,36].

Meng et al. [23] investigated the effect of the Zn content on the IGC behavior of Al-5.8Mg alloys. The addition of Zn transforms GBPs from  $\beta$ -Al<sub>3</sub>Mg<sub>2</sub> to T-Mg<sub>32</sub>(Al, Zn)<sub>49</sub>, significantly improving its IGC resistance. Moreover, Zn increases the number of the low angle grain boundary, which is beneficial to the improvement of IGC.

Zhang et al. [33] studied the influence of Cu, Ag and T6 heat treatment on the IGC performance of Al-Mg-Zn-Cu-Ag. The weight loss of alloys after nitric acid mass loss test (NAMLT) are shown in Figure 10. It can be seen that the IGC performance of alloys is related to different aging states: the alloy at a solid solution state has the best IGC resistance; the under-aging and over-aging states come second; and the peak aging state has the worst IGC resistance. The difference in IGC resistance is mainly related to the continuity of GBPs and it can be explained in Figure 11. At the solid solution state, there is no phase precipitation at the grain boundaries and within the grains, and the electrical potential in the microstructure is equal everywhere, showing excellent corrosion resistance. In the subsequent aging process to peak aging, the T-phase gradually precipitates at the grain boundary and tends to become larger and distribute continuously. The continuous precipitation phase acts as a channel for corrosion, leading to the occurrence of IGC. When the alloy reaches the over-aging state, the coarser grain boundary precipitation phase distributes discontinuously, resulting to the improvement of the IGC resistance. From Figure 10b, with the addition of the Ag element, the weight loss of alloys shows a trend of increasing and then decreasing, which is mainly related to the width of PFZs and the potential difference between GBPs and the matrix.

Hou et al. [44] introduced high temperature pre-treatment (HTPT) which is kind of heat treatment process after the solution, but before the aging treatment. The effect of HTPT at different temperatures on the mechanical properties and IGC of Al-5.16Mg-3.12Zn-0.15Cu alloys has been investigated. The relationships between mechanical properties, IGC resistance and microstructure evolution during HTPT and the subsequent aging process have

been established, as shown in Figure 12. It can be seen that the IGC resistance is enhanced with the decreasing pre-aging temperature, resulting from the discontinuity degree of GBPs, as well as the Mg and Zn element concentration difference between GBPs and PFZs. Compared with the T6 treatment, 410HTPT + T6 treatment can improve the IGC resistance of alloys without significant strength loss. This is related to the preferentially segregated Mg and Zn atoms along the grain boundaries, and the solid solution state in grains with uniform dispersion distribution and high number density.

Ma et al. [45] studied the effect of retrogression and re-aging (RRA) treatment on the IGC behavior of Al-5Mg-3Zn alloys. When retrogressed at 405 °C or 420 °C, the alloys own discontinuously distributed GBPs and small Mg and Zn content difference, result in a small potential difference between GBPs and PFZ. Therefore, RRA treatment allows alloys to exhibit a better IGC resistance compared with the T6 treatment.



**Figure 10.** Mass loss after NAMLT (**a**)the alloy 5 after aging at 180 °C for different aging times, (**b**) all of the tested five alloys during peak aging at 180 °C (alloy 1: Al-4.5Mg-0.6Zn-0.2Cu; alloy 2: Al-4.5Mg-0.6Zn-0.5Cu; alloy 3: Al-4.5Mg-0.6Zn-0.5Cu-0.2Ag; alloy 4: Al-4.5Mg-0.6Zn-0.5Cu-0.4Ag; alloy 5: Al-4.5Mg-0.6Zn-0.5Cu-0.7Ag) [33].



**Figure 11.** Schematic diagram of the microstructure evolution of alloys during aging at 180 °C (T-1, T-36, T-72 indicate aging for 1 h, 36 h and 72 h, respectively) (the four pictures represent the solid solution state, under-aging state, peak aging state and over-aging state, respectively) [33].



**Figure 12.** Mechanical properties, corrosion depth, and microstructure evolution of Al-5.16Mg-3.12Zn-0.15Cu alloys after various treatments [44].

## 4. Summary and Outlook

The novel age-hardening Al-Mg-Zn(-Cu) wrought alloys are strengthened by the T-Mg<sub>32</sub>(Al, X)<sub>49</sub> phase, which can synergically improve the mechanical properties and corrosion resistance of Al-Mg alloys. This kind of crossover alloy also provides an idea for the fabrication of 500 MPa high-strength hot stamping aluminum alloy materials [46]. Excellent comprehensive properties (strength, toughness, corrosion resistance, etc.) make it promising for applications in automotive [47–52], marine [53], aerospace [36], armor materials [54] and so on.

However, the complex service environment and rapid economic growth have raised expectations for the performance of alloys. As a result, further research is needed in many aspects of this system of alloys. In light of current state of scientific research and industrial application requirements, future research directions of Al-Mg-Zn(-Cu) alloys can be summarized as follows.

(1) The thermodynamics and kinetics of the T-phase precipitation in Al-Mg-Zn(-Cu) alloys require in-depth research, especially the effect of trace elements Mn, Cr and Fe on the precipitation behavior of the T-phase. Alloy design can be further explained and optimized by the phase diagram in the form of isothermal sections. At the same time, it is necessary to accelerate the age-hardening response rate by means of composition design and process optimization. A relatively short heat treatment process of Al-Mg-Zn(-Cu) alloys can reduce the cost of industrialization practice;

(2) With the help of thermodynamic calculation and phase diagram simulation, trace alloying elements, such as Sc and Zr can be added based on the composition of Al-Mg-Zn(-Cu) alloys. The synergistic strengthening of biphasic or even multiphasic precipitation of the T-phase and Al<sub>3</sub>(Sc, Zr) phase can improve the strength and fracture toughness simultaneously;

(3) Attempts can be made to fine-tune the precipitation of the T-phase by adding micro-alloying elements and optimizing the heat treatment process. The discontinuously distributed T-phase at the grain boundaries during peak aging state can greatly improve the IGC resistance;

(4) Current research on Al-Mg-Zn(-Cu) alloys focuses on the mechanical properties and corrosion performance. However, many other important issues also need be studied in depth, such as fatigue properties, susceptibility to plastic shaping and joining technologies, as well as susceptibility to machining, all of which play a critical role in industrial applications. Take fatigue properties as an example, fatigue properties of wrought Al alloys can be improved by enhancing the tensile strength, improving the microstructure homogeneity and reducing defect size or density. Are these methods suitable for improving fatigue properties of Al-Mg-Zn(-Cu) alloys? The effect of element content and heat treatment process on fatigue properties of Al-Mg-Zn(-Cu) alloys can be a future research direction, so as to enhance the overall performance of alloys and achieve industrial applications;

(5) The commercialization and practical applications of new materials are often hindered by the following two critical factors: scalability of the technology for industrial production and the cost. A lot of problems may be encountered for commercializing this alloy, such as consistent production at a large scale, purchasing and installing a production facility as well as the cost of producing the product itself. These factors need to be well-considered to achieve industrial application of Al-Mg-Zn(-Cu) alloys.

**Author Contributions:** Literature search, data collection, data analysis and writing–original draft, G.S.; writing–review and editing, X.C.; literature search and data collection, J.Y., L.F. and Z.Y.; writing–review and editing, J.Z.; supervision and funding acquisition, R.G. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by Dalian High-level Talents Innovation Support Program (2021RD06).

Data Availability Statement: Not applicable.

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

#### References

- 1. Williams, J.C.; Starke, E.A. Progress in structural materials for aerospace systems. *Acta Mater.* 2003, *51*, 5775–5799.
- 2. Toros, S.; Ozturk, F.; Kacar, I. Review of warm forming of aluminum–magnesium alloys. J. Mater. Process. Technol. 2008, 207, 1–12.
- 3. Dursun, T.; Soutis, C. Recent developments in advanced aircraft aluminium alloys. *Mater. Des.* (1980–2015) **2014**, 56, 862–871.
- Liu, M.P.; Roven, H.J.; Murashkin, M.Y.; Valiev, R.Z.; Kilmametov, A.; Zhang, Z.; Yu, Y. Structure and mechanical properties of nanostructured Al–Mg alloys processed by severe plastic deformation. *J. Mater. Sci.* 2013, 48, 4681–4688.
- Feistauer, E.E.; Bergmann, L.A.; Barreto, L.S.; dos Santos, J.F. Mechanical behaviour of dissimilar friction stir welded tailor welded blanks in Al–Mg alloys for Marine applications. *Mater. Des.* 2014, 59, 323–332. [CrossRef]
- Krishna, K.S.V.B.R.; Chandra Sekhar, K.; Tejas, R.; Naga Krishna, N.; Sivaprasad, K.; Narayanasamy, R.; Venkateswarlu, K. Effect of cryorolling on the mechanical properties of AA5083 alloy and the Portevin–Le Chatelier phenomenon. *Mater. Des.* 2015, 67, 107–117.
- Alil, A.; Popović, M.; Radetić, T.; Zrilić, M.; Romhanji, E. Influence of annealing temperature on the baking response and corrosion properties of an Al–4.6 wt% Mg alloy with 0.54 wt% Cu. J. Alloys Compd. 2015, 625, 76–84. [CrossRef]
- 8. Cao, C.; Zhang, D.; Zhuang, L.; Zhang, J. Improved age-hardening response and altered precipitation behavior of Al-5.2Mg-0.45Cu-2.0Zn (wt%) alloy with pre-aging treatment. *J. Alloys Compd.* **2017**, *691*, 40–43. [CrossRef]
- Hou, S.; Liu, P.; Zhang, D.; Zhang, J.; Zhuang, L. Precipitation hardening behavior and microstructure evolution of Al–5.1 Mg– 0.15Cu alloy with 3.0Zn (wt%) addition. J. Mater. Sci. 2018, 53, 3846–3861.
- 10. Zhang, D.; Zhang, Z.; Pan, Y.; Jiang, Y.; Zhuang, L.; Zhang, J.; Zhang, X. Current-driving intergranular corrosion performance regeneration below the precipitates solvus temperature in Al–Mg alloy. *J. Mater. Sci. Technol.* **2020**, *53*, 132–139.
- Guo, C.; Zhang, H.; Li, S.; Chen, R.; Nan, Y.; Li, L.; Wang, P.; Li, B.; Cui, J.; Nagaumi, H. Evolution of microstructure, mechanical properties and corrosion behavior of Al-4Mg-2Zn-0.3Ag (wt.%) alloy processed by T6 or thermomechanical treatment. *Corros. Sci.* 2021, *188*, 109551.
- 12. Raabe, D.; Tasan, C.C.; Olivetti, E.A. Strategies for improving the sustainability of structural metals. *Nature* **2019**, *575*, 64–74. [CrossRef]
- 13. Tunes, M.A.; Stemper, L.; Greaves, G.; Uggowitzer, P.J.; Pogatscher, S. Prototypic lightweight alloy design for stellar-radiation environments. *Adv. Sci.* 2020, *7*, 2002397. [CrossRef]
- Tunes, M.A.; Quick, C.R.; Stemper, L.; Coradini, D.S.R.; Grasserbauer, J.; Dumitraschkewitz, P.; Kremmer, T.M.; Pogatscher, S. A fast and implantation-free sample production method for large scale electron-transparent metallic samples destined for MEMS-based in situ S/TEM experiments. *Materials* 2021, 14, 1085.
- 15. Stemper, L.; Tunes, M.A.; Tosone, R.; Uggowitzer, P.J.; Pogatscher, S. On the potential of aluminum crossover alloys. *Prog. Mater. Sci.* **2022**, *124*, 100873.
- 16. Raabe, D.; Ponge, D.; Uggowitzer, P.J.; Roscher, M.; Paolantonio, M.; Liu, C.; Antrekowitsch, H.; Kozeschnik, E.; Seidmann, D.; Gault, B.; et al. Making sustainable aluminum by recycling scrap: The science of "dirty" alloys. *Prog. Mater. Sci.* 2022, 128, 100947.
- Shoichi, H.; Nakamura, F.; Sato, T. First-principles calculation of interaction energies between solutes and/or vacancies for predicting atomistic behaviors of microalloying elements in aluminum alloys. *Mater. Sci. Forum* 2007, 561–565, 283–286.

- Shoichi, H.; Omura, T.; Suzuki, Y.; Sato, T. Improvement of bake-hardening response of Al-Mg-Cu alloys by means of nanocluster assist processing (NCAP) technique. *Mater. Sci. Forum* 2006, 519–521, 215–220.
- 19. Pan, Y.; Zhang, D.; Liu, H.; Zhuang, L.; Zhang, J. Precipitation hardening and intergranular corrosion behavior of novel Al–Mg–Zn(-Cu) alloys. *J. Alloys Compd.* **2021**, *853*, 157199. [CrossRef]
- Zhang, Z.; Li, Y.; Li, H.; Zhang, D.; Zhao, Z.; Du, Q.; Zhang, J. ICME guided design of heat-treatable Zn-modified Al–Mg alloys. *Calphad* 2021, 74, 102298. [CrossRef]
- 21. Ding, Q.; Zhang, D.; Zuo, J.; Hou, S.; Zhuang, L.; Zhang, J. The effect of grain boundary character evolution on the intergranular corrosion behavior of advanced Al-Mg-3 wt%Zn alloy with Mg variation. *Mater. Charact.* **2018**, *146*, 47–54.
- 22. Carroll, M.C.; Gouma, P.I.; Mills, M.J.; Daehn, G.S.; Dunbar, B.R. Effects of Zn additions on the grain boundary precipitation and corrosion of Al-5083. *Scr. Mater.* 2000, *42*, 335–340.
- Meng, C.; Zhang, D.; Cui, H.; Zhuang, L.; Zhang, J. Mechanical properties, intergranular corrosion behavior and microstructure of Zn modified Al–Mg alloys. J. Alloys Compd. 2014, 617, 925–932.
- Meng, C.; Zhang, D.; Zhuang, L.; Zhang, J. Correlations between stress corrosion cracking, grain boundary precipitates and Zn content of Al–Mg–Zn alloys. J. Alloys Compd. 2016, 655, 178–187.
- Zhao, J.; Luo, B.; He, K.; Bai, Z.; Li, B.; Chen, W. Effects of minor Zn content on microstructure and corrosion properties of Al–Mg alloy. J. Cent. South Univ. 2016, 23, 3051–3059. [CrossRef]
- Hou, S.; Zhang, D.; Ding, Q.; Zhang, J.; Zhuang, L. Solute clustering and precipitation of Al-5.1Mg-0.15Cu-xZn alloy. *Mater. Sci. Eng. A* 2019, 759, 465–478. [CrossRef]
- 27. Stemper, L.; Tunes, M.A.; Oberhauser, P.; Uggowitzer, P.J.; Pogatscher, S. Age-hardening response of AlMgZn alloys with Cu and Ag additions. *Acta Mater.* **2020**, *195*, 541–554. [CrossRef]
- 28. Stemper, L.; Tunes, M.A.; Dumitraschkewitz, P.; Mendez-Martin, F.; Tosone, R.; Marchand, D.; Curtin, W.A.; Uggowitzer, P.J.; Pogatscher, S. Giant hardening response in AlMgZn(Cu) alloys. *Acta Mater.* **2021**, *206*, 116617. [CrossRef]
- 29. Cao, C.; Zhang, D.; Wang, X.; Ma, Q.; Zhuang, L.; Zhang, J. Effects of Cu addition on the precipitation hardening response and intergranular corrosion of Al-5.2Mg-2.0Zn (wt.%) alloy. *Mater. Charact.* **2016**, *122*, 177–182. [CrossRef]
- 30. Geng, Y.; Song, Q.; Zhang, Z.; Pan, Y.; Li, H.; Wu, Y.; Zhu, H.; Zhang, D.; Zhang, J.; Zhuang, L. Quantifying early-stage precipitation strengthening of Al–Mg–Zn(-Cu) alloy by using particle size distribution. *Mater. Sci. Eng. A* 2022, *839*, 142851.
- Carroll, M.C.; Gouma, P.I.; Daehn, G.S.; Mills, M.J. Effects of minor Cu additions on a Zn-modified Al-5083 alloy. *Mater. Sci. Eng.* A 2001, 319–321, 425–428.
- 32. Guo, C.; Zhang, H.; Li, J. Influence of Zn and/or Ag additions on microstructure and properties of Al-Mg based alloys. *J. Alloys Compd.* **2022**, *904*, 163998.
- 33. Zhang, H.; Nan, Y.; Guo, C.; Cui, J. Age hardening and intergranular corrosion behavior of new type Al-4.5Mg-0.6Zn-0.5Cu-XAg (wt%) alloy. *J. Alloys Compd.* **2022**, *910*, 164767. [CrossRef]
- Cao, C.; Zhang, D.; He, Z.; Zhuang, L.; Zhang, J. Enhanced and accelerated age hardening response of Al-5.2Mg-0.45Cu (wt%) alloy with Zn addition. *Mater. Sci. Eng. A* 2016, 666, 34–42. [CrossRef]
- Cao, C.; Zhang, D.; Zhuang, L.Z.; Zhang, J.S.; Liu, J.b. Effect of pre-aging treatment on room temperature stability of Al-5.2Mg-0.45Cu-2.0Zn alloy sheet. *Rare Met. Mater. Eng.* 2020, 49, 1166–1170.
- Pan, Y. Study on Compositional Design, Microstructure and Properties of Novel High Strength-Toughness Al-Mg-Zn-Cu Aluminum Alloy with Good Weldability and Corrosion Resistance. Ph.D. Thesis, University of Science and Technology Beijing, Beijing, China, 2021.
- 37. Zou, Y.; Cao, L.; Wu, X.; Wang, Y.; Sun, X.; Song, H.; Couper, M.J. Effect of ageing temperature on microstructure, mechanical property and corrosion behavior of aluminum alloy 7085. *J. Alloys Compd.* **2020**, *823*, 153792. [CrossRef]
- Liu, T.; Jiang, H.; Sun, H.; Wang, Y.; Dong, Q.; Zeng, J.; Bian, F.; Zhang, J.; Chen, F.; Sun, B. Effects of rolling deformation on precipitation behavior and mechanical properties of Al-Zn-Mg-Cu alloy. *Mater. Sci. Eng. A* 2022, 847, 143342.
- 39. Ebenberger, P.; Uggowitzer, P.J.; Gerold, B.; Pogatscher, S. Effect of compositional and processing variations in new 5182-type AlMgMn alloys on mechanical properties and deformation surface quality. *Materials* **2019**, *12*, 1645. [CrossRef]
- 40. Wang, S.; Xiao, A.; Lin, Y.; Cui, X.; Sun, X. Effect of induced pulse current on mechanical properties and microstructure of rolled 5052 aluminum alloy. *Mater. Charact.* **2022**, *185*, 111757. [CrossRef]
- 41. Liu, H.; Zhang, Z.; Zhang, D.; Zhang, J. The effect of Ag on the tensile strength and fracture toughness of novel Al-Mg-Zn alloys. *J. Alloys Compd.* **2022**, *908*, 164640.
- 42. Ding, Q.; Zhang, D.; Pan, Y.; Hou, S.; Zhuang, L.; Zhang, J. Strengthening mechanism of age-hardenable Al–xMg–3Zn alloys. *Mater. Sci. Technol.* **2019**, *35*, 1071–1080. [CrossRef]
- 43. Ding, Q. Microstructure and Properties of Age-Hardenable Al-Mg-Zn Aluminum Alloy and the Process Optimization. Ph.D. Thesis, University of Science and Technology Beijing, Beijing, China, 2020.
- 44. Hou, S.; Zhang, D.; Pan, Y.; Ding, Q.; Long, W.; Zhang, J.; Zhuang, L. Dependence of microstructure, mechanical properties, and inter-granular corrosion behavior of Al-5.1Mg-3.0Zn-0.15Cu alloys with high temperature pre-treatment. *Mater. Charact.* 2020, *168*, 110512. [CrossRef]
- 45. Ma, Q.; Zhang, D.; Zhuang, L.; Zhang, J. Intergranular corrosion resistance of Zn modified 5××× series Al alloy during retrogression and re-aging treatment. *Mater. Charact.* **2018**, 144, 264–273. [CrossRef]

- Guan, R.; Lou, H.; Huang, H.; Liang, X.; Xiao, X.; Li, H.; Li, F.; Wang, J.; Yun, X.; Zeng, L. Development of Aluminum Alloy Materials: Current Status, Trend, and Prospects. *Strateg. Study CAE* 2020, 22, 68–75. [CrossRef]
- 47. Matsumoto, K.; Aruga, Y.; Tsuneishi, H.; Iwai, H.; Mizuno, M.; Araki, H. Effects of Zn addition and aging condition on serrated flow in Al-Mg alloys. *Mater. Sci. Forum* **2014**, *794–796*, 483–488. [CrossRef]
- Ma, P.; Zhang, D.; Zhuang, L.; Zhang, J. Effect of alloying elements and processing parameters on the Portevin-Le Chatelier effect of Al-Mg alloys. *Int. J. Miner. Metall. Mater.* 2015, 22, 175–183.
- 49. Ma, P. Effect of Microstructure and Texture on the Formability and Serrated Deformation Behavior of 5xxx Series Aluminum Alloy. Ph.D. Thesis, University of Science and Technology Beijing, Beijing, China, 2015.
- 50. Matsumoto, K.; Aruga, Y.; Tsuneishi, H.; Iwai, H.; Mizuno, M.; Araki, H. Effects of precipitation state on serrated flow in Al-Mg(-Zn) alloys. *Mater. Trans.* **2016**, *57*, 1101–1108.
- 51. Geng, Y.; Zhang, D.; Zhang, J.; Zhuang, L. On the suppression of Lüders elongation in high-strength Cu/Zn modified 5xxx series aluminum alloy. *J. Alloys Compd.* 2020, *834*, 155138. [CrossRef]
- 52. Geng, Y.; Zhang, D.; Zhang, J.; Zhuang, L. Zn/Cu regulated critical strain and serrated flow behavior in Al–Mg alloys. *Mater. Sci. Eng. A* **2020**, 795, 139991. [CrossRef]
- 53. Meng, C. Corrosion Mechanism and Development of the Zn-Containing 5xxx Series Al Alloy for Shipbuilding Industry. Ph.D. Thesis, University of Science and Technology Beijing, Beijing, China, 2016.
- Liu, H.; Zhao, Z.; Zhang, D.; Zhang, J. Mechanical property and microstructure evolution of novel Al–Mg–Zn(–Cu) alloys under dynamic impact. *Mater. Sci. Technol.* 2021, 37, 852–862.

**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.