

Review

Al-Mg-Zn(-Cu) Cross-Over Alloys: The New Frontier in High-Strength and Radiation-Resistant Lightweight Materials

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Abstract: Over the past few years, researchers have developed the alloy Al-Mg-Zn(-Cu), a new aluminum alloy based on the technique of ‘crossover alloying’. The main strengthening phase of this novel alloy is T-Mg₃₂(Al, X)₄₉(X is Zn and Cu) after ageing and hardening. This alloy system has exceptional strength and corrosion resistance, making it a promising candidate for applications in fields like automotive, marine, aerospace, and many others. In this work, the research progress of the Al-Mg-Zn(-Cu) alloy based on microstructure control, composition, design, and properties has been reviewed. Future directions for the research of this alloy are highlighted, too. In this work, crossover alloys are presented as a potential novel class of Al alloys implicating a pioneering design approach, with particular emphasis on the aeronautical and aerospace field in which radiation resistance results are one hundred times higher than traditional precipitation hardening alloys.

Keywords: Al-Mg-Zn(-Cu); cross-over alloy; age-hardening; T-Mg₃₂(Al, X)₄₉; microstructure; precipitation strengthening

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1. Introduction

In the context of energy saving, green development and following the goal of minimizing carbon dioxide emissions and reaching carbon neutrality, researchers have focused their attention on the set-up of lightweight materials. Aluminum-based alloys have become a wide-utilization source of applications in fields such as automotive, marine, aerospace, and others thanks to their comprehensive properties such as high specific strength, corrosion resistance, and excellent thermal and electrical conductivity [1]. Especially in transportation industries, the adoption of lightweight materials like aluminum instead of iron-based alloy has been widely used to reduce greenhouse gas emissions. In addition, this strengthening method is not completely effective because the range of properties of commercially available aluminum alloys is often restricted, limiting their usefulness. Traditional Al-Mg alloys, like AA5083 and AA5059, are commonly utilized in ships, vehicles and other industries thanks to their advantageous compromise between strength, weight ratio, and formability [2]. However, such alloys are non-heat-treatable: they are mainly hardened through solution strengthening and work hardening [3,4]. Furthermore, if the Mg content is greater than 2.5 wt%, β -phase precipitation occurs along grain boundaries. There is no positive effect on the strength; nevertheless, this phase shows anodic dissolution and consequent intergranular corrosion due to its lower potential in comparison with that of the Al matrix [5,6]. On the other hand, the precipitation hardening technique is one of the most important strengthening methods used for Aluminum alloys, in particular for 2XXX (AlCu(Mg) with Cu/Mg ratio higher than 1) and 7XXX series (AlZnMg(Cu) with a Zn/Mg ratio higher than 1). In general, the development of a new class of Al alloys requires good compromise between mechanical strength, high-level ductility, corrosion resistance, and, at the same time, forming capability.

If the composition and processing of the alloy are carefully optimized, AlMgZn(Cu) crossover alloys have the potential to offer even greater strength, nearly reaching the levels of commercial high-strength AlZnMg(Cu) alloys. The adoption of a T-phase precipitation reinforcement mechanism allows for this kind of alloy to achieve significant resistance to radiation thanks to the giant unit cell and, at the same time, highly negative enthalpy of formation. Such an approach is ideal for next-generation space materials for designing radiation-resistant alloys.

The primary component of these new alloys is Mg; unlike commercial AlMg alloys, they can be age-hardened, and therefore do not fit into the existing alloy classification system. Therefore, it was suggested to name them “crossover alloys” [7]. The new crossover alloys are the focus of this review, offering a thorough examination and establishing crossover alloying as a groundbreaking design approach in the field of metallurgy. The following overview presents the latest findings on a novel group of materials known as “crossover alloys”, which possess beneficial characteristics typically associated with specific types of commercial aluminum alloys, consolidating crossover alloying as a novel metallurgy design method. It specifically examines the crossover alloys AlMg/AlCuMg (5xxx/2xxx) and AlMg/AlZnMg(Cu) (5xxx/7xxx), highlighting research indicating their potential for high formability and age-hardening capabilities, thereby opening the door to broader industrial application in the near future. Unlike traditional AlMg alloys, these new alloys, which primarily consist of Mg, exhibit age-hardening properties, challenging the existing alloy classification system. Commercial aluminum alloys often exhibit limited formability when processed but possess high strength during use [8] or show good formability but only moderate final strength [9]. The best compromise between formability and attainable strength, which is crucial for future aluminum-based materials in each specific application, can be achieved with alloys or groups of alloys in which composition, thermomechanical treatment, and ageing have been suitable set-up in order to obtain the required microstructure and physical and mechanical properties. If the proper high-temperature treatment (solutioning and quenching) is carried out, the softening can be significantly reduced [10] and, in some cases, prevented altogether with up to 5% [3] or 10% [11] pre-deformation, provided that the alloy composition and heat treatment parameters are adjusted appropriately (Figure 1). A study by Medrano et al. [12] demonstrated that the addition of just 0.12 at% of Cu is enough to induce rapid hardening during the initial stage of ageing at 200 °C. It was observed that strengthening particles (clusters/GPB-zones) showed similar sizes and shapes, but they contain a much lower amount of Cu compared to commercial AlCuMg alloys after 20 min of ageing, consequently explaining the relatively high particle density irrespective of the low bulk Cu content.

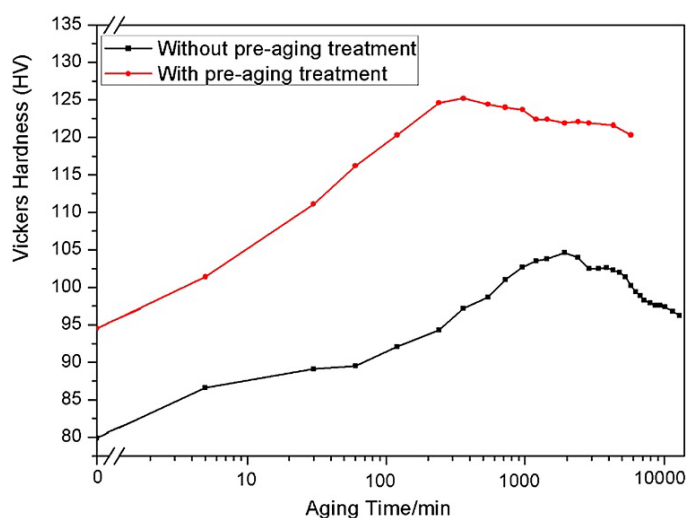


Figure 1. Effect of pre-ageing treatment (modified precipitation microstructure) on the Vickers hardness evolution scale at increasing ageing times in the Al-5.2Mg-0.45Cu-2.0Zn alloy [2].

2. AlMgCu Crossover Alloys

The addition of Cu to AlMg alloys has recently attracted the attention of researchers. The first mention of this alloy type in a publication dates back to the early 1990s [13], and it was noted for its ability to prevent softening during the paint bake process. The hardening was observed when pre-deformed (2%) sheets were heat-treated at 175 °C for 30 min, effectively counteracting recovery processes [14]. Successively, Ratchev et al. carried out initial research on the hardening behaviour observed during ageing at temperatures ranging from 60 °C to 180 °C in various AlMgCu alloys with Cu/Mg ratios ranging from 0.14 to 0.29. When heated at 180 °C, all the studied alloys showed an initial rise in yield strength ($\Delta R_{p0.2} = 20\text{--}40$ MPa), followed by a steady increase until they reached peak hardness ($\Delta R_{p0.2} = 70\text{--}120$ MPa). This strengthening behaviour is similar to that of AlCu(Mg) alloys and was attributed to the precipitation of the S-phase [12,15]. The effectiveness of Cu addition in AlMg alloys and the resulting increase in strength to prevent the softening of pre-deformed sheets relies on the specific recrystallization, solution annealing, and ageing processes used, as well as the deformation amount applied prior to the final ageing treatment.

To achieve effective age hardening, it is necessary to have a supersaturation of vacancies and solutes. This means that the typical recrystallization annealing treatments at moderate temperatures (below 200 °C) are not sufficient when the pre-deformation exceeds 2% [3]. Performing suitable high-temperature solutioning (up to 275 °C) and quenching can significantly reduce the softening during subsequent heat treatments [10] and can even prevent it with pre-deformations of up to 5% [3] or 10% [11] if the alloy composition and heat treatment parameters are appropriately adjusted.

The study by Medrano and colleagues [11] demonstrated that the addition of just 0.12 at% of Cu is enough to induce a rapid hardening response during the initial stage of ageing at 200 °C. They observed that strengthening particles (clusters/GPB-zones) displayed similar size and shape but contained a much lower amount of Cu compared to commercial AlCuMg alloys after 20 min of ageing. This result explains the relatively high particle density despite the low bulk Cu content [12]. Unlike commercial AlMgSi alloys [16–19], negative effects of natural ageing, such as reduced hardenability or limited formability, are not seen in AlMg alloys containing Cu [10,20,21]. Zhang et al. [22,23] explored the use of AlMgCu crossover alloys for equal channel angular pressing (ECAP) processing. They took an AlMg4.3Cu1.2 alloy and subjected it to artificial ageing to achieve under-, peak-, and over-aged conditions before undergoing multiple ECAP passes at 180 °C. During processing, the coarse hardening precipitates (S-phase or its precursors) in the peak-aged condition fractured and dissolved. In the meanwhile, the small precipitates, in the under-aged condition, dissolved but then re-precipitated, leading to a significant increase in yield stress. It was attributed to strengthening contributions from dislocations, grain boundaries, and beneficial interactions of dislocations with solutes and the re-precipitated hardening phase. Post-ECAP ageing did not affect the initial peak-aged samples, but it caused a significant loss of strength in the initially under-aged samples. The inclusion of Cu has demonstrated the ability to prevent the migration of Mg towards grain boundaries and also to inhibit the formation of β -Phase (Al₃Mg₂) in favour of the Cu-bearing hardening phase, resulting in AlMgCu alloys offering improved resistance against intergranular corrosion (IGC) with an appropriate solutioning treatment [3]. When compared to a Cu-free reference alloy, it was observed that the susceptibility to pitting corrosion neither improved nor deteriorated, but the addition of Cu was reported to enhance resistance to filiform corrosion [10].

3. AlMgZn Crossover Alloys

The primary hardening phase in commercial AlZnMg(Cu) alloys, which belong to the 7xxx-series, is η -precipitates [24]. While T-phase hardening is not widely recognized, the existence of this ternary phase has been known since 1936 and was included in Al-Mg-

Zn equilibrium phase diagrams by Koster et al. Although the potential for T-phase hardening was acknowledged in the twentieth century, it received relatively little attention [24,25]. The reason for this might be that alloys deemed commercially interesting, which were expected to consist only of the η -phase and an aluminum matrix under equilibrium conditions, were also observed to harden solely through the η -phase or its precursors. As a result, it was proposed that the T-phase tends to develop from η -particles only at high temperatures ($>200\text{ }^{\circ}\text{C}$) [25,26] rather than forming directly during aging since other T-precursors with a different crystal structure from the equilibrium T are not yet known. However, the exclusive hardening by the T-phase in AlZnMg(Cu) alloys with Zn/Mg ratios lower than 2.2 has recently garnered increased attention [27,28]. Given that the AlMgZn crossover alloys investigated here contain an excess of Mg (Zn/Mg ratio lower than 1), it is similarly anticipated that hardening by the T-phase and its precursors can occur. It is widely acknowledged that the T-phase (referred to as $\text{Mg}_3\text{Zn}_3\text{Al}_2$, $\text{Mg}_{32}(\text{Al},\text{Zn})_{49}$, or $\text{Mg}_{32}\text{Zn}_{31.9}\text{Al}_{17.1}$) exhibits a body-centered cubic unit cell containing 162 atoms under equilibrium conditions. The identification of the T-phase can be based on its specific reflection spots in the aluminum matrix along the $\langle 001 \rangle$ zone axis, revealing characteristic T-phase diffraction spots at the $2/5$ and $3/5$ $\langle 022 \rangle$ Al positions [2]. There is ongoing debate about the precipitation sequence of the T-phase, given that Al and Zn atoms can occupy Al/Zn substitutional lattice sites in the T-phase unit cell at random [29]. Therefore, the precipitation sequence in AlMgZn crossover alloys is significantly influenced by the specific alloy composition. As a result, the Al-Mg-Zn system has seen numerous proposed precipitation sequences (GP $\rightarrow$ intermediate $\rightarrow$ equilibrium).

In an AlMg_{4.9}Zn_{3.2} alloy, Bigot et al. [30] found that the precursor T'- and equilibrium T-phase share similar crystal structures and electron-diffraction signals, as well as comparable orientation relationships with the Al matrix. However, their chemical compositions are distinct and independent of particle size. It is important to note that determining the evolution state of T-phase particles based on chemical composition may be specific to a single alloy composition, as the equilibrium composition of T-phase could be influenced by the overall alloy constitution due to the random occupancy of Al/Zn lattice sites [27].

Hou et al. [4] carried out more recent research on the precipitation sequence in an AlMg_{5.1}Zn_{3.0}(Cu_{0.15}) alloy, focusing on the level of coherency to determine the stage of evolution of precipitates. Early stages of ageing revealed two distinct types of GP zones. The authors identified fully coherent solute clusters with no clear diffraction signals as GPI zones, and slightly larger yet still fully coherent precipitates with distinct diffraction signals were labelled as GPII (T'') zones. Bigot et al. [30] observed that T'- and T-precipitates have similar crystal structures, but they differ in their semi-coherent and incoherent interfaces with the matrix. It should be noted that GPI and GPII zones in AlMgZn crossover alloys are not equivalent to GPI and GPII zones in commercial AlZnMg(Cu) alloys [24,31]. Observing slightly varied precipitation patterns was made possible through the combined use of atom probe tomography (APT), transmission electron microscopy (TEM), and density functional theory (DFT) methods. Their recent hypothesis suggested that temporary η' -surrogates could play a role in the shift from GPI zones to T' in an AlMg_{4.7}Zn_{3.6} alloy [32]. The recent rise in interest in AlMgZn alloys that can cross over can be assigned to their effective hardening potential. At first, small additions of Zn were used to increase the corrosion resistance of AlMg alloys. This positive impact has been linked to the inhibition of the highly anodic β -phase at grain boundaries in favour of the less anodic T-phase after stabilization and sensitization [33–35]. Along with enhanced corrosion resistance, it was also noted that small additions of Zn (smaller than 1 wt%) can increase the yield strength following stabilization treatment (250 $^{\circ}\text{C}/1\text{ h}$). This can be understood as a result of the combined effects of increased solid solution strengthening and hardening precipitates [34,36]. The addition of Zn and the use of solutioning treatment, rather than recrystallization annealing, have been demonstrated to lead to a notable increase in yield strength during both artificial and natural ageing [32,37,38]. Figure 2a,b show the distribution of the precipitates at the grain boundaries through TEM

observations for a modified Al-Mg-Cu alloy Zn (0.6%). The phases are discontinuously precipitated along the grain boundary. The average composition, obtained with EDS (Figure 2c), is 24.2%wt Mg, 13 wt% Zn, and 2.8 wt% Cu in the precipitate, and 5.44 wt% Mg in the matrix. Figure 3 shows the tensile curve for EN-AW 5182 with the addition of Zn and ZnCu [32].

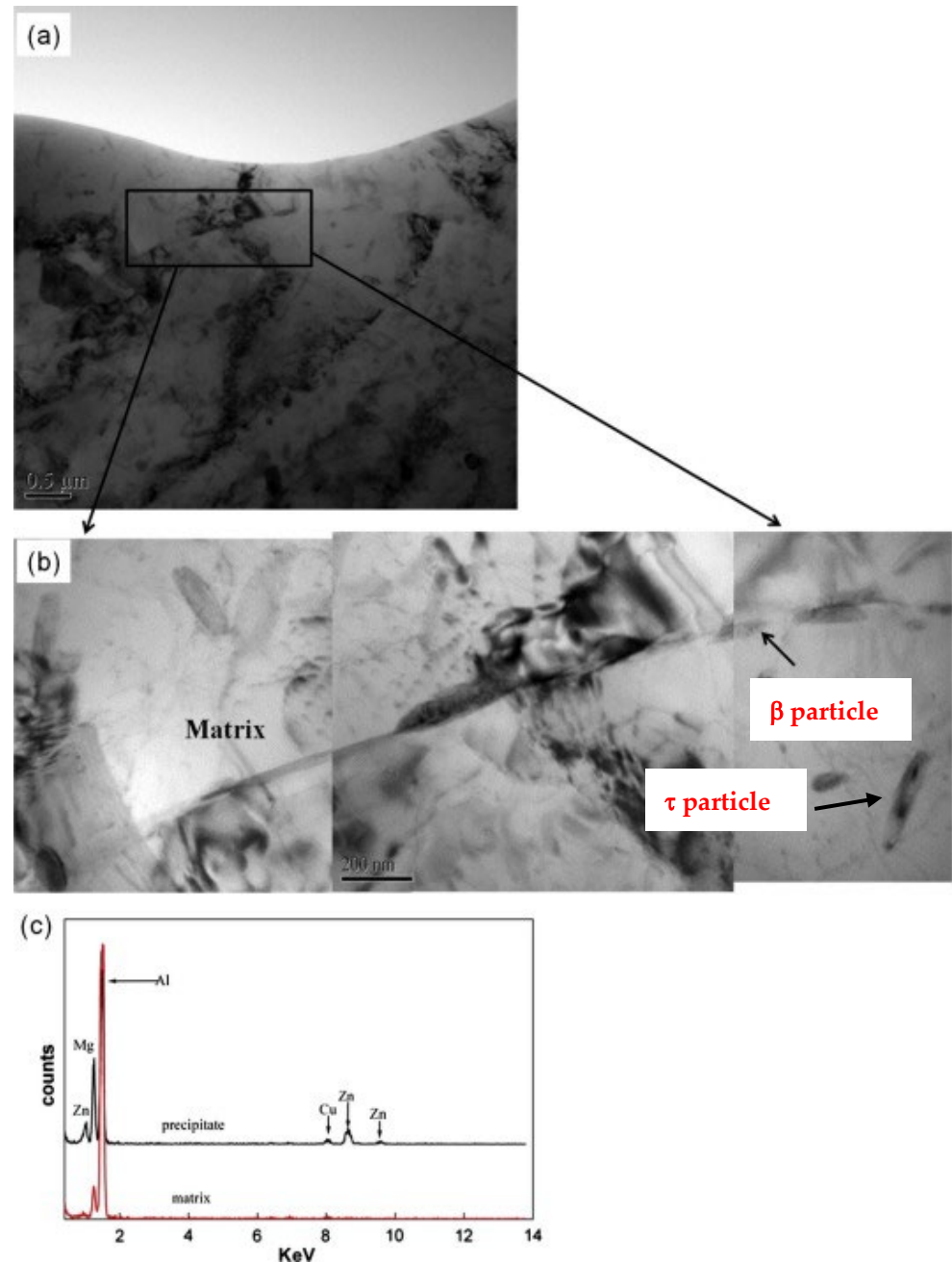


Figure 2. BF TEM observation of grain boundary β -phase of 0.6 wt% Zn alloy after 7 days of ageing (a). Grain boundary details are reported in (b), and EDS analysis for the β (needle-like particles) and τ (rod-like particles) in Zn-rich particles (Al-Mg-Zn) and the matrix are reported in (c) [36].

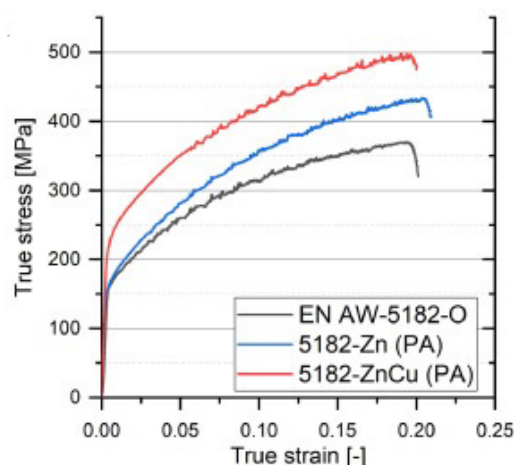


Figure 3. True stress–strain curves of the investigated alloys showing the effect of Zn and Zn-Cu addition on tensile properties [32].

The hardening response during artificial ageing appears to be primarily due to the precipitation of the T-phase and/or its precursors [37,39]. According to Cao et al. [37], the artificial ageing behaviour of an AlMg5.2Zn2.0(Mn0.2) alloy at 180 °C exhibited an incubation period of about 2 h before the hardness increased to its peak level after 24 h of ageing. Yun et al. [39] found that hardening only occurred at Zn levels exceeding 3 wt% in an AlMg5 alloy during ageing at 120 °C. Contrastingly, the hardening incubation period was notably shorter, and the overall level of hardness was considerably greater. These outcomes align with the findings in [40], which examined the ageing behaviour of an AlMg5.0Zn3.8(Mn0.8) alloy within a temperature range of 75–200 °C. The earliest onset of hardening (approximately 1 h) and the most significant increase in hardness was observed at lower temperatures (100 °C), potentially due to a favourable balance between the nucleation and growth of the hardening phase [38]. On the contrary, it was also noted that hardening only started after approximately 16 h at 125 °C in an AlMg4.7Zn3.5(Mn0.4) alloy, resulting in a peak ageing time of 9 days [38]. The previously mentioned studies showed that only T-phase hardening was observed in AlMgZn crossover alloys. However, research by Zhu et al. [41] on Fe-rich (1.5 wt%) AlMg5(Mn0.5) alloys produced by high-pressure die casting (HPDC) found that the addition of Zn (up to 3 wt%) resulted in exclusive η -phase hardening when a low-temperature heat treatment (430 °C/60 min + water quenching + 120 °C/16 h) was employed. These findings suggest that the alloy composition and ageing strategy must be carefully coordinated to achieve an adequate and optimal hardening response. The differences in the hardening behaviour observed in the reported alloys may be due to the presence of additional alloying elements and impurities like Mn, Fe, Si, Cr, Ti, Zr, Sc, etc., which can impact the formation of precipitates, thus either aiding [42] or impairing [43] the hardening process.

In comparison to the hardening behaviour observed in many commercial AlZnMg(Cu) alloys [28], the maximum hardness in T-hardened AlMgZn alloys is obtained with longer ageing times, typically in the range between 24 h [44] and 9 days [38] in the case of one-step ageing. However, this is contingent upon the alloy composition and heat treatment parameters. Given that processing time, particularly the ageing period during the final heat treatment phase is crucial for industrial applications, endeavours should be made to expedite the hardening process. Conducting a pre-ageing treatment at low temperatures (ranging from 3 h to 12 h at 80 °C to 100 °C) before the final high-temperature ageing stage has been proven to expedite the hardening process, resulting in a reduced time to achieve peak hardness. This phenomenon is believed to be due to the creation of stable precursors with a high density, which act as preferred sites for the initiation of the hardening phase [38,45]. It has been observed that subjecting the material to minor

deformation (2%) after pre-ageing also enhances the hardening response, as this is attributed to the improved mobility of solutes aided by dislocations induced by the deformation [32]. Both pre-ageing and natural ageing resulted in both increased yield strength and a shift of the onset of serrated flow to higher strain levels. These changes are ascribed to the strengthening properties and vacancy-trapping nature of low coherent interfaces Mg-Zn clusters/GPI zones [32]. Additionally, despite their potentially higher strength, it has been demonstrated that increased levels of Zn (up to 5 wt%) do not have a detrimental effect on elongation in AlMg alloys with low Mg content (below 5 wt%) both in as-quenched state [40] or pre-aged condition [32]. Geng et al. [46] also noted a partial suppression of Lüders elongation in a pre-aged (485 °C/10 min + water quenching + 80 °C/12 h) AlMg5.1Zn3.0 alloy, which was not observed in AlMg4.6Cu0.15 in a soft-annealed state (450 °C/1 h). A study by Stemper et al. [32] involved a comparison of two pre-aged (PA) crossover alloys—AlMg4.7Zn3.6 and AlMg4.7Zn3.6Cu0.6—with a commercial EN AW-5182 alloy in its specific forming condition. This comparison was based on the plot of the strain hardening rate (SHR) against plastic stress for their respective true stress–strain curves, serving as an indication of stretch-formability. The increased SHR observed across the entire range of plastic stress and the less steep slope of the curves were associated with improved dislocation formation and restricted dislocation annihilation, suggesting better performance in stretch-forming, a common process in automotive sheet manufacturing [47,48]. A comparable conclusion can be drawn from the comparison of results obtained from EN AW-6016 and AA 7075 commercial alloys in similar heat treatment conditions. It is important to observe that these conditions were identified because both alloys require this processing before forming in order to obtain higher strength after the final paint bake treatment (20 min at 185 °C) [47–49]. The findings are published and need further investigation. However, the analysis of the paint bakes response $\Delta R_{p0.2}$ of the alloys also demonstrates a considerable potential for strengthening crossover alloys, which can be customized through minor alloy adjustments. As mentioned earlier, small additions of Zn (<1 wt%) can improve the corrosion resistance of AlMg alloys to IGC with appropriate heat treatment (stabilization). At increasing Zn contents and utilizing artificial ageing treatments to maximize the complete strengthening potential, the susceptibility of AlMgZn alloys to IGC is markedly increased due to the unfavourable galvanic coupling between precipitate-free zones (PFZ) and grain boundary precipitates (GBP) [50]. The Zn/Mg ratio can be increased (below 1) to produce narrower PFZ and discontinuous GBP, allowing the increase in Intergranular Corrosion resistance. Additionally, the addition of Cu or the application of a retrogression and re-ageing (RRA) treatment [51] has been shown to achieve the same effect. The RRA treatment was first introduced by Cina et al. for AlZnMg(Cu) alloys. In overaged AlMgZn crossover alloys, T-phase particles not only have a beneficial strengthening ability but also exhibit significant resistance to heavy ion irradiation (Pb+). The high phase fraction and advanced chemical complexity of the hardening phase are attributed to this resistance, making such alloys potential candidates for utilization in vehicles intended for space exploration.

4. AlMgZnCu Crossover Alloys

The combined addition of Zn and Cu has been found to positively impact the susceptibility to corrosion and the strengthening ability of AlMg alloys. Consequently, the simultaneous addition of these elements was also examined. Although previous studies primarily focused on corrosion, recent research has set out to maximize the strengthening capabilities of AlMgZn(Cu) alloys. Carroll et al. [52,53] explored the influence of various Cu contents (0.075–0.24 wt%) on the behaviour and corrosion resistance of potential secondary phases in Zn-modified (0.6 wt%) 5083 alloys after extensive sensitization (165 °C/175–350 h). At lower Cu additions, only Cu-enriched T-phase ($Mg_{32}(Al, Zn, Cu)_{49}$) was detected at grain boundaries, while alloys with higher Cu levels contained a notable amount of corrosion-vulnerable S-phase within the grain interior. Alloy samples containing Zn and Cu were subjected to tensile tests in an environment that promotes corrosion.

The results showed that adding Cu effectively reduces the susceptibility to stress corrosion cracking (SCC) in AlMgZn alloys as long as the formation of the S-phase is prevented. These alloys exhibited lower ductility compared to commercial 5083 in a non-corrosive environment (dry air) after sensitization, but they performed better in a corrosive (aqueous NaCl) environment [52,53]. Research on the hardening response and microstructural changes in AlMgZn(Cu) alloys began relatively recently in 2016. Cao et al. [37] (Figure 4) studied the effects of combined Zn- and Cu addition by investigating the impact of gradually increasing Zn levels (0.6–1.9 wt%) in an AlMg5.2Cu0.45 alloy during ageing at 180 °C.

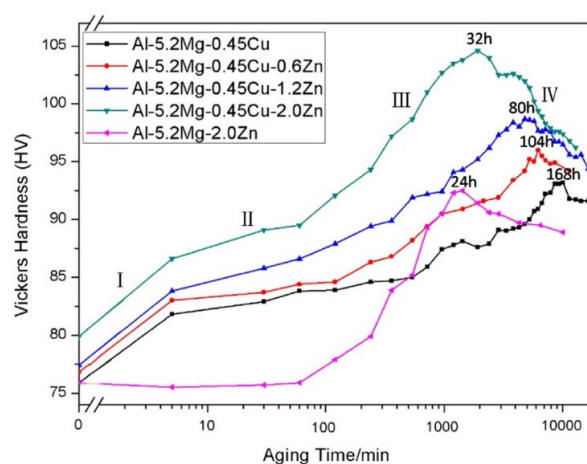


Figure 4. Effect of the Zn content on the hardness in five alloys at increasing Zn content during ageing at 180 °C [37].

During the early stages of ageing, the influence of Zn was not as significant because the rapid hardening process through the creation of Mg-Cu clusters, similar to AlCuMg or AlMgCu alloys, was found to be more dominant than that of Mg-Zn clusters. As the Zn content increased (up to 1.9 wt%), the time required for T-phase precipitation decreased, and the peak hardness shifted to shorter ageing times, significantly improving with the subsequent development of the T-phase. This led to an increase in the Cu/Mg ratio in the matrix and accelerated the formation of the S-phase. The maximum strength was attributed to the combined effects of both T- and S-phases. The hardness only increases moderately due to the low Zn/Mg ratio resulting from the relatively low Zn content under the applied ageing conditions [38,41,45]. However, these results differ from those of Tang et al. [54], who studied the hardening response of a cast alloy AlMg5.0Zn3.0 with a high amount of Cu (1 wt%) during single-step artificial ageing experiments conducted at temperatures ranging from 120 °C to 175 °C. While the peak hardness was nearly unaffected by the ageing temperature and was linked to small globular GPII zones (T'') and large, rod-shaped Cu-enriched T'-particles, the time needed to achieve the highest strength levels was substantially shorter (4 h) at 175 °C than during ageing at 120 °C (125 h). The assumption was made that higher ageing temperatures would encourage the formation of T' over GPII (T'') by promoting the diffusion of solutes (especially Cu). This would result in larger average precipitate sizes, ultimately leading to reduced ductility and decreased impact toughness [38]. For AlMgZn alloys with lower Cu levels (0.15–0.6 wt%), a pre-ageing treatment at low temperatures (3 to 48 h at 80 °C to 100 °C) before subsequent high-temperature final ageing (140–180 °C) was discovered to expedite the hardening response significantly during the second ageing stage. It also caused the peak hardness to occur earlier [2,38,41,55] and resulted in higher hardness levels [2,54] due to significant changes in the microstructure. The high level of hardness was linked to the presence of large, lath-shaped T-phase and needle-like S-phase in a less dense structure when no pre-ageing treatment was used. In contrast, when pre-aged and then subjected to peak ageing, the microstructure contained finely dispersed, equiaxed T-phase particles in a denser

formation. Even though the crystal structures of the T-phase particles were similar in both cases, their chemical compositions were found to be notably different. It is believed that pre-ageing at low temperatures encourages the formation and nucleation of precursors (GP zones) through vacancy-assisted diffusion. These precursors can then develop into Cu-enriched T-phase during subsequent high-temperature ageing through the attachment of Zn and Cu solutes, effectively inhibiting the formation of the S-phase (Figure 5).

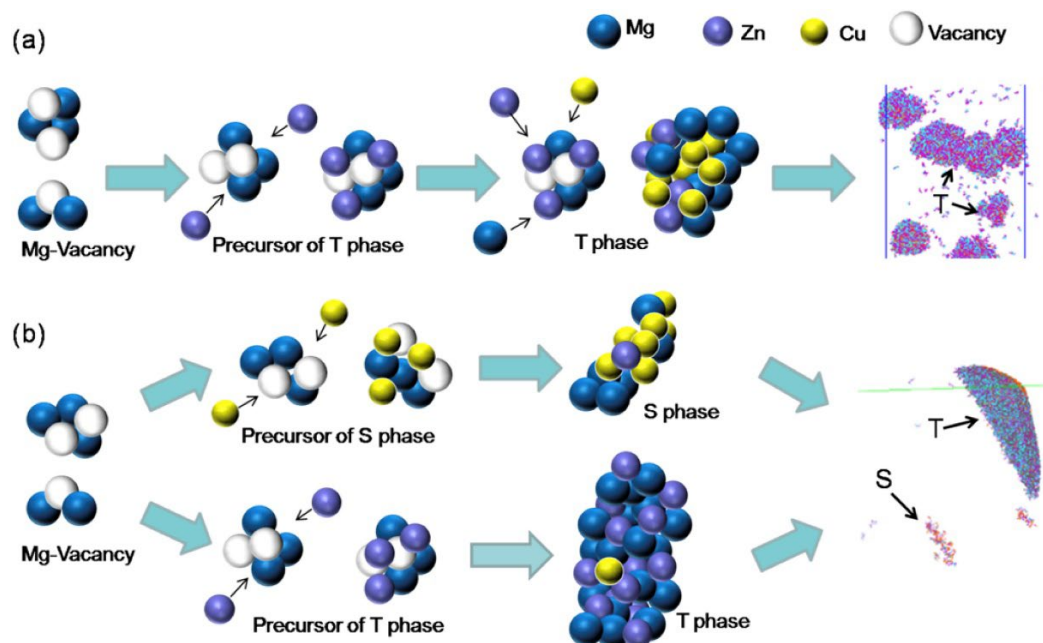


Figure 5. Precipitation evolution scheme in AlMg5.2Zn2.0Cu0.45 after ageing at 180 °C with (a) and without (b) prior pre-ageing treatment (80 °C for 12 h) [2].

The addition of larger quantities of Cu [56] is likely to have a similar effect to the precursors present after pre-ageing in low-Cu AlMgZn alloys [2,38,41] when high-temperature single-step ageing is used, as indicated by previous research. Hou et al. [5] confirmed these findings using a similar approach to Cao et al. [37], where they studied the impact of increasing Zn levels (1–4 wt%) in an AlMg5.1ZnXCu0.15 alloy during two-stage ageing treatments through APT analysis. An improved and accelerated hardening response was found during both natural ageing and successive artificial ageing if Zn content was greater than 3 wt% (Zn/Mg ratio 0.6–0.8). The ability of precursors to undergo further development is significantly influenced by the chemical composition following pre-ageing at 90 °C for 24 h. A crucial factor in optimizing hardening behaviour is the overall alloy composition, as precursors resembling the next evolution stage can more easily undergo transformation due to the gradual evolution of the T-phase. According to research by Hou et al. [4], the sequence of precipitation of Cu-based T-phase in the AlMg5.1Zn3.0Cu0.15 alloy with different ageing conditions is the following: SSSS → GPI zone (completely coherent) → GPII zone (T'', completely coherent) → intermediate T' (semi-coherent) → equilibrium T (incoherent). This was established based on scanning transmission electron microscopy (STEM) investigations. After being pre-aged for 24 h at 90 °C, the increased hardness was due to the presence of two types of small, coherent solute agglomerations. The smaller agglomerations did not show any electron-diffraction signal, while the larger ones had a distinct structure called GPI and GPII (T''). Similar particles were found after natural ageing, but they were smaller and more numerous. Subsequent artificial ageing at higher temperatures led to a significant increase in hardness for pre-aged samples, while the strength of naturally aged samples decreased. This suggests that there is a critical particle size (between 1.5 and 2.5 nm) necessary for the growth and development into T'- and T-precipitates [4]. Similar results were observed in studies

of related alloys (AlMg4.7Zn3.6 with and without 0.6 wt% Cu), which support the findings by Hou et al. The discovery also indicates that precursors need to have a minimum size of approximately 700 atoms and a specific local chemistry ($\text{Mg}/(\text{Zn} + \text{Cu})$ ratio ≥ 0.7) in order to transform into T' -precipitates during the second stage of high-temperature ageing (185 °C) [32]. Due to limited Cu diffusion in the aluminum matrix at lower temperatures [57], precursors formed after pre-ageing contain low levels of Cu and high levels of Zn [2]. Nevertheless, the tiniest clusters (initial nuclei) are found to have a significantly higher Cu/Zn ratio compared to most precursors formed during the pre-ageing process [2]. The absence of Cu results in a lower number density of precursors, leading to a slower and less pronounced hardening response during high-temperature ageing [32,45,54]. It is believed that even small amounts of Cu promote the nucleation of clusters in the initial stages of pre-ageing, similar to observations in Cu-containing AlMg [14] and AlZnMg alloys. DFT calculations [32] showed that the addition of Cu does not affect early-stage cluster formation but significantly reduces the formation energy of η' - and T-phase. APT analysis of the post-pre-ageing precursors in an AlMg4.7Zn3.6Cu0.6 alloy indicated that transient η' may act as a surrogate phase in T-phase development [32]. Cu was discovered to not only enhance the formation trend but also to boost the thermal stability and strengthening capacity of subsequent precursors [32,45]. As a result, precursors containing Cu at high density remain stable during high-temperature ageing, preventing the extensive formation of precipitate-free zones (PFZ) near grain boundaries. This leads to increased strength [40] and enhanced resistance to intergranular corrosion [45]. Pan et al. [57] investigated the impact of an increasing (Zn + Cu)/Mg ratio (0.63, 0.71, 0.85, 0.97, and 1.21) on the double-step hardening response and the IGC resistance of AlMgZn(Cu) alloys. The peak hardness was observed to move to earlier ageing times and higher levels when the (Zn + Cu)/Mg ratio was increased to 0.97. This was due to the reduced size, increased number density, and higher volume fraction of Cu-incorporated T-phase. As the (Zn + Cu)/Mg ratio increased, the lattice spacing of the hardening phase gradually decreased because of the substitution of Al by Zn and Cu, resulting in increased thermal stability and hardenability. At the same time, the IGC resistance improved, linked to smaller differences in galvanic potential between grain boundary precipitates (GBP) and the matrix [57]. The mechanical performance of AlMgZn(Cu) alloys was significantly influenced by variations in Mg content, ranging from 3.5 to 5.6 wt%. Increased levels of Mg were found to elevate the overall strength, ascribed to smaller grain size after solution annealing and higher supersaturation of Mg in the matrix, leading to enhanced grain boundary and solid solution strengthening [58]. As Mg content increased, the resistance to intergranular corrosion (IGC) decreased, especially beyond 4.6 wt% [59]. However, treating the alloy at temperatures near the solvus temperature of the T-phase before artificial ageing could mitigate the decrease in IGC resistance by altering grain boundary occupancy without significantly diminishing the achievable peak strength [60]. The susceptibility to stress corrosion cracking (SCC) showed a similar trend, indicating that lower Mg levels have more beneficial effects due to the inhibition of anodic dissolution of grain boundary precipitates [61]. Studies on exfoliation corrosion in AlMg4.6Zn3.1Cu0.15 alloy under the T6 condition showed a correlation between the alloy's susceptibility to exfoliation corrosion and the microstructure. Although exfoliation corrosion (EXC) appears inevitable in the presence of grain boundary precipitates (GBP), a lower proportion of subgrain stripes (which can be adjusted through proper processing) enhances EXC resistance [62]. In addition to the excellent hardenability of AlMgZn(Cu) alloys, recent research has indicated that adjusting the levels of Zn and Cu can restrict Lüders elongation [46] and serrated flow [63] in the pre-aged state (80 °C/12h). This is believed to be due to a reduced effective Mg content in the matrix available for Mg/dislocation interactions, as it is utilized in precipitate formation during pre-ageing. Furthermore, alloys designed for rapid hardening show the initiation of serrated flow at higher levels of strain compared to non-optimized alloys. This advantage is particularly noticeable at low strain rates ($1.7 \times 10^{-4} \text{ s}^{-1}$), but it diminishes at high strain rates ($3.3 \times 10^{-3} \text{ s}^{-1}$) [64]. Alloys that combine Al, Mg, and Zn(Cu) show

advantageous properties for use in construction materials, making their weldability a crucial factor for broad industrial applications in this field. According to studies conducted by Zhang et al. [64], alloys with low Cu content (0.15 wt%) and a Zn/Mg ratio lower than 1 in peak-aged condition (90 °C/24 h + 140 °C/24 h) exhibit a similarly low tendency for liquation cracking during fusion welding when compared to commercial AlMg alloys. The improved weldability is linked to a smaller difference in solid fraction (precipitates) between the fusion zone (FZ) and partially melted zone (PMZ) during the solidification stage, as compared to Cu-free alloys with Zn/Mg ratios greater than 1. Greater crack healing ability was found due to a higher liquid metal fraction in the PMZ [65]. In a subsequent study, Pan et al. [65] found a comparable pattern in AlMgZn(Cu) alloys with higher Cu content (1 wt%, Cu/Mg ratio lower than 0.25). Resistance to hot cracking was found to increase in comparison with a commercial 7075 alloy (1.6 wt% Cu, Mg/Zn ratio ≥ 2.4 , Cu/Mg ratio ≥ 0.6), also due to a reduced occurrence of micro-cracks in the weld, which is attributed to lower stress concentration during solidification due to a narrower temperature range and an increased liquid metal fraction at the end of welding [65]. AlMgZn(Cu) alloys have proved to be suitable for friction stir welding (FSW) to create strong joints, thanks to their hardenability by T-phase precipitation. When an appropriate post-weld-heat treatment (PWHT) is applied, FSW joints offer significantly greater strength compared to commercial AlMg alloys. The decrease in elongation observed is due to the extensive coarsening of precipitates in the heat-affected zone (HAZ) caused by the higher temperature during FSW. AlMgZn(Cu) alloys, known for their low hot cracking tendency, were also tested for the wire arc additive manufacturing (WAAM) process. Subsequent heat treatment after WAAM revealed improved mechanical performance, confirming their suitability for WAAM processing [66].

5. Next-Generation Radiation Resistant Al-Based Crossover Alloys

The human exploration of the solar system requires the adoption of materials suitably developed to be resistant to extreme environments. Al alloys, especially the age-hardenable, seem to be appealing due to their low weight. However, the radiation resistance to solar energetic particles is too poor in common age-hardening alloys, and consequently, the mechanical strength quickly deteriorates. The methodology of cross-over alloying of 5XXX and 7XXX series Al alloys is a promising solution for the development of future space materials. These alloys, when subjected to extreme heavy ion irradiations within a TEM (up to 1 dpa dose), exhibit a surprising resistance also to extreme irradiation conditions. If the hardening is realized by means of a T-phase ($\text{Mg}_{32}(\text{Zn}, \text{Al})_{49}$), characterized by a giant unit cell and at the same time highly negative enthalpy of formation, this phase exhibits exceptional radiation survivorship and at the same time shows the ability to stabilize an ultrafine-grained structure in response to temperature and radiation. This effectively prevents displacement damage from occurring. No cavities, nucleates, or displacement damage are observed to develop in the form of black spots. According to the results of this research, a high phase-fraction of hardening precipitates represents a crucial parameter in order to achieve adequate radiation tolerance. Such an approach is ideal for the next-generation space materials for designing radiation-resistant alloys [7].

6. Discussion and Conclusions

The metallurgy of lightweight non-ferrous alloys has been a complex and enduring problem due to the need to balance formability and high strengthening potential. Current technological solutions based on aluminum alloys have various limitations, and there is a need for the development of new alloy design strategies and concepts at the cutting edge of current scientific knowledge. This challenge is now associated with the development of materials for a sustainable future, initially focusing on lightweight automotive or other traditional transportation applications that will help lower greenhouse gas emissions. Unexpectedly, it has become clear that the range of applications also includes a new class of space materials.

The combination of advantageous characteristics of current commercial aluminum alloys has established a basis for a fresh aluminum alloy design approach called crossover alloying. The latest advancements and findings in this emerging area of study have been comprehensively examined earlier and can be summarized as follows.

- (1) Crossover alloys containing Al, Mg, and Cu can reduce or offset the decrease in strength that occurs when cold-deformed AlMg alloys are baked with paint. The extent of compensation depends significantly on the degree of deformation and processing used.
- (2) Crossover alloys of AlMgZn with reduced Zn content demonstrate enhanced resistance to corrosion by inhibiting the formation of the β -phase at grain boundaries and instead dispersing T-phase particles uniformly. When Zn levels are raised and proper processing techniques are employed, the degradation of the surface due to the Lüders band is restricted, and the ability to significantly harden through T-phase precipitation is achieved.
- (3) If the composition and processing of the alloy are carefully optimized, AlMgZn(Cu) crossover alloys have the potential to offer even greater strength, nearly reaching the levels of commercial high-strength AlZnMg(Cu) alloys, and improved corrosion resistance compared to Cu-free AlMgZn crossover alloys. Based on the current technology, the crossover alloys discussed here can offer good formability, which seems to be similar to or even better than commercially available alloys. However, it is important to note that there is still limited experimental data in this area and further research is needed.
- (4) The potential of crossover alloys to surpass existing commercial aluminum alloys comes from their superior performance in areas such as mechanical strength and corrosion resistance, which are essential engineering criteria. Additionally, research suggests that it is feasible to create a single alloy system that combines high strengthening ability and good formability, making crossover alloys a viable option for reducing the need for a wide variety of materials used for lightweighting. This, in turn, can contribute to a more sustainable life cycle in the traffic and transportation sectors. Based on the evidence presented in this review, this class of alloys also holds significant promise for further scientific exploration and subsequent technological advancements, which could lead to the emergence of an entirely new commercial aluminum alloy class. Furthermore, it is believed that incorporating controlled amounts of Cu, Zn, or Cu + Zn can greatly enhance the recyclability of the crossover alloys. Evaluating this aspect further is crucial, as it is a key requirement in meeting the current standards of a circular economy. While the current findings show promise, further investigation is necessary to fully capitalize on the potential of aluminum crossover alloys. This exploration should not be restricted to just the crossover between 5xxx/2xxx and 5xxx/7xxx, as discussed here, but should potentially encompass the entire range of aluminum alloy compositions.
- (5) The adoption of a T-phase precipitation reinforcement mechanism allows this kind of alloy to achieve an incredible resistance to radiation, thanks to the giant unit cell and, at the same time, highly negative enthalpy of formation. This effectively prevents displacement damage from occurring and is the ideal solution for the development of next-generation materials for space applications, lightweight and, at the same time, radiation-resistant.

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