

HARMONIC GRAIN STRUCTURE IN ZINC ALLOY CONTAINING MAGNESIUM AND SILVER

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<https://doi.org/10.37904/metal.2026.5267>

Abstract

This study investigates the microstructural design and mechanical performance of biodegradable Zn-Ag-Mg materials with a pseudo-harmonic architecture fabricated via powder metallurgy. The microstructure consists of a ductile coarse-grained pure Zn core surrounded by a continuous three-dimensional network of a fine-grained Zn-3Ag-1Mg (wt%) alloy skeleton. Powder mixtures were consolidated by spark plasma sintering (SPS) at 300 °C and then hot extruded at 200 °C to disrupt interfacial oxide shells. Hot extrusion promoted dynamic recrystallisation, refining the pure Zn grains to ~23 µm and the alloyed skeleton to ~2.5 µm while fully preserving the bimodal distribution. Characterisation revealed a multi-phase configuration within the skeleton, consisting of stable Mg₂Zn₁₁, MgZn₂, and Ag_{0.12}Zn_{0.88} precipitates. Uniaxial compression testing demonstrated that incorporating just 30% of the fine-grained alloyed skeleton drastically enhances the yield strength by forming a continuous load-bearing framework. The addition of Ag successfully promotes in-situ grain boundary stabilisation and particle strengthening while imparting essential antibacterial activity for temporary biomedical implants.

Keywords: Zinc, harmonic structure, powder metallurgy, microstructure, mechanical strength

1. INTRODUCTION

Biodegradable metallic materials represent a revolutionary shift in the development of medical implants designed for temporary tissue fixation [1]. Unlike traditional permanent metallic materials, these alloys gradually degrade in the organism after fulfilling their mechanical function, thereby eliminating the need for secondary surgical procedures to remove the implant and preventing long-term chronic inflammation. In recent years, pure zinc and its alloys have come to the forefront of research, mainly due to their optimal degradation rates and excellent biocompatibility. Furthermore, their corrosion products are well-tolerated by the human body [2, 3]. Compared with magnesium, which undergoes rapid degradation associated with the undesirable release of hydrogen gas, and iron, whose insoluble corrosion products can induce local toxicity, zinc provides a stable environment for tissue healing [4].

However, the main limitation of pure zinc for orthopaedic applications lies in its insufficient mechanical properties, as it fails to meet the minimum medical requirements for yield strength (at least 230 MPa) and tensile strength (at least 300 MPa) [3]. For this reason, zinc is alloyed with elements such as magnesium, which significantly increases strength by forming intermetallic phases, particularly the cubic Mg₂Zn₁₁ [5]. Nevertheless, conventional metallurgical processes (e.g. casting) often result in a coarse-grained

microstructure with an interconnected network of brittle eutectic phases at grain boundaries, drastically reducing the material's plasticity [6].

As an efficient solution, the concept of heterostructured materials with a so-called harmonic structure has emerged [7]. This model, successfully applied in Zn-Mg systems prepared via powder metallurgy, consists of a ductile coarse-grained core (pure Zn) surrounded by a continuous three-dimensional network of a fine-grained matrix (Zn-Mg) with an ultrafine grain size below 1 μm [7]. The combination of mechanical alloying and rapid compaction via Spark Plasma Sintering (SPS) enables preservation of this synergistic effect. However, the SPS process forms oxide shells on the surfaces of the original powders, which act as barriers to dislocations and reduce toughness. Subsequent thermomechanical processing, such as hot extrusion, can effectively break up these oxide shells into fine dispersoid particles, resulting in a dramatic increase in both strength and plasticity [7].

In this work, we implement this advanced powder metallurgy approach in an innovative Zn-Ag-Mg alloy system. The concept of the harmonic structure is modified by the targeted addition of silver into the fine-grained component of the skeleton. Silver has low solubility in zinc at room temperature, which leads to the precipitation of submicron intermetallic phases (such as the $\epsilon\text{-AgZn}_3$ phase) during processing [8]. These particles should provide additional strengthening and grain-boundary pinning effects beyond the sole magnesium addition. In addition, silver provides an additional value in the form of a demonstrable antibacterial effect of the implant [9]. During the degradation, a controlled release of silver ions acts cytotoxically against a wide range of pathogens, thereby significantly reducing the risk of postoperative infections associated with biomaterials.

2. MATERIALS AND METHODS

Two distinct precursor powders were utilised to synthesise the heterostructured materials in this study: pure zinc with a particle size distributed between 63 and 100 μm , and a mechanically alloyed Zn-3Ag-1Mg (wt%) powder with a particle size below 45 μm . The pre-alloyed powder fraction was synthesised via mechanical milling using a Retsch E-max high-energy ball mill equipped with ZrO_2 milling balls. To prepare the alloy blend, a 30 g mixture containing pure zinc, silver, and magnesium powders in the targeted nominal proportions was introduced into the milling vessel together with 0.04 g of stearic acid. The ball-to-powder weight ratio was strictly maintained at 5:1. The mechanical milling was performed at 800 rpm for 4 hours. For more details, see our previous study [7].

The sequence of powder mixtures with varying ratios (Zn:Zn-3Ag-1Mg = 100:0, 60:40, 50:50, 40:60, 30:70, 0:100) was consolidated via SPS utilising an FCT Systeme HP-D 10 device. Sintering was carried out under a protective argon atmosphere at a temperature of 300 $^{\circ}\text{C}$ for 10 minutes, applying a constant compaction force of 25 kN. To break up the continuous network of brittle oxide shells formed at prior particle interfaces during the SPS processing, and to ensure maximum structural densification, the sintered compacts were subsequently subjected to hot extrusion. The extrusion process was performed at a temperature of 200 $^{\circ}\text{C}$ with a constant ram speed of 0.2 mm.s^{-1} and an extrusion ratio of 10.

The microstructure of the consolidated and extruded specimens was investigated using a Thermo Fisher Scientific Apreo scanning electron microscope (SEM) equipped with an EDAX EDS system and an EDAX EBSD camera. For microstructural observations, the samples were prepared using standard metallographic procedures, involving sequential grinding and polishing steps down to a 1 μm diamond paste. The final preparation step was performed via ion-polishing using a Leica EM RES102 device.

Uniaxial compression tests were performed at room temperature using an Instron 5882 universal testing machine at an initial strain rate of 10^{-3} s^{-1} . Cylindrical specimens with a diameter of 5 mm and a height of 8 mm were machined from the extruded rods with the compression axis oriented parallel to the extrusion direction.

3. RESULTS AND DISCUSSION

The microstructures of the as-sintered specimens were initially evaluated using EBSD to identify grain geometry and size distributions. The sample consolidated from pure zinc exhibits a coarse, fully recrystallised grain structure with an average grain size of $\sim 34\ \mu\text{m}$ (see **Figure 1a**), comparable with previous reports [4]. In sharp contrast, the standalone milled Zn-3Ag-1Mg sample shows a significantly refined grain structure with an average grain size of $\sim 5\ \mu\text{m}$ (see Figure 1c, note the difference in scales). The mixed 50:50 composite material is shown as a representative of pseudo-harmonic samples, see **Figure 1b**. Note that the grain size within the Zn-3Ag-1Mg domains appears marginally smaller than in its standalone counterpart, though this deviation is statistically insignificant. Crucially, the EBSD maps reveal that the fine-grained Zn-3Ag-1Mg powder particles are distributed along the boundaries of the larger, softer pure zinc particles. This spatial configuration confirms the successful engineering of a continuous, three-dimensional pseudo-harmonic network shell encapsulating a ductile core matrix, comparable to our previous research [7].

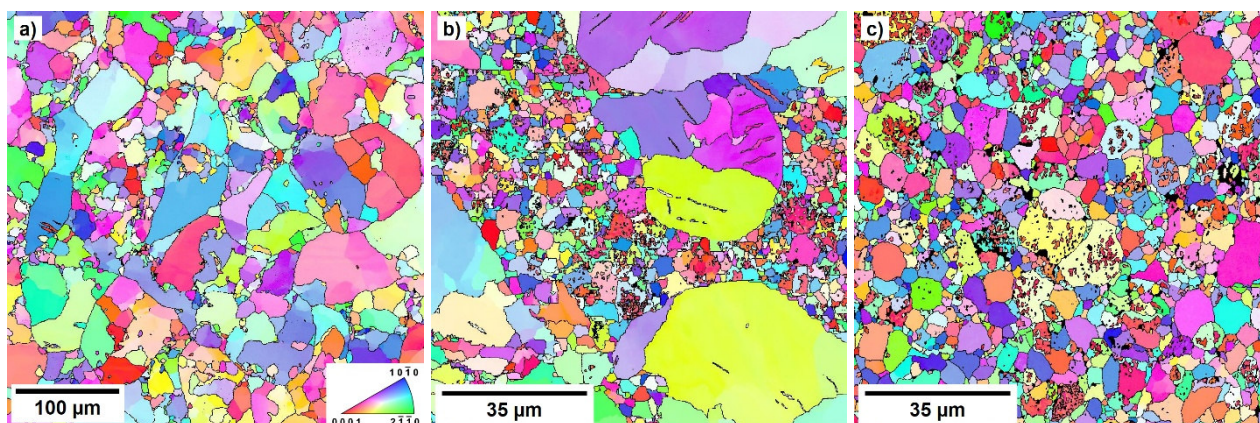


Figure 1 EBSD orientation maps of SPS-prepared a) pure Zn, b) Zn+Zn-3Ag-1Mg (50:50), c) Zn-3Ag-1Mg

To analyse the formation of secondary phases, EDS elemental mapping was employed (**Figure 2**). The resulting maps revealed the distinct formation of three intermetallic phases in the Zn-3Ag-1Mg grains. The moderately dark (in the Z-contrast) particles (denoted by the red arrows) contain a moderate magnesium concentration, matching the stable cubic $\text{Mg}_2\text{Zn}_{11}$ phase typically observed in consolidated Zn-Mg systems [10]. Darker, highly localised particles (denoted by blue arrows) are characterised by an elevated magnesium concentration. According to the previous results, these particles represent the MgZn_2 Laves phase, which is metastably retained due to the high-energy, non-equilibrium conditions of the preceding ball-milling processing followed by a rapid cooling [10]. Highly distinct, bright precipitates (yellow arrows) contain a high concentration of silver. These particles most likely correspond to the $\epsilon\text{-AgZn}_3$ phase (sometimes denoted as $\text{Ag}_{0.12}\text{Zn}_{0.88}$) intermetallic phase, which precipitates during the consolidation thermal cycle due to the limited solid solubility of silver in zinc at lower temperatures [8].

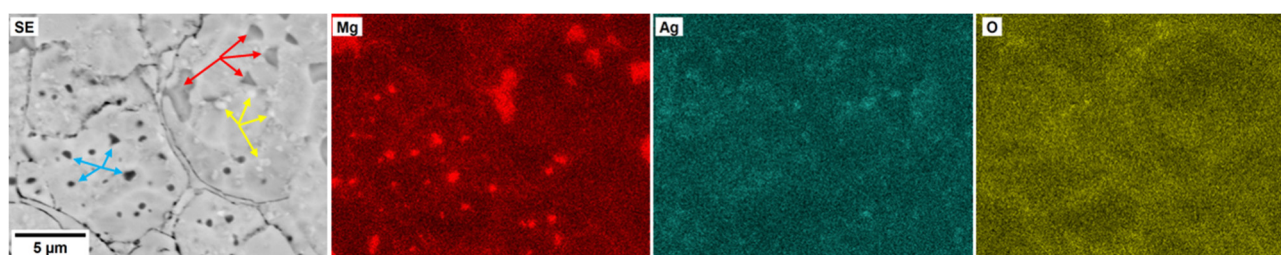


Figure 2 EDS elemental maps of SPS-prepared Zn-3Ag-1Mg

Additionally, the EDS analysis highlighted the presence of thin, dark boundaries delineating the prior particle boundaries of the original powders. Consistent with previous studies of zinc-magnesium systems, these lines indicate the formation of thin oxide shells (predominantly a mixture of zinc and magnesium oxides) generated at elevated temperatures during spark plasma sintering [7]. Because these continuous interfacial oxides can act as crack initiation sites, subsequent hot extrusion is critical to mechanically disrupt this network.

The microstructural changes induced by thermomechanical processing are depicted in the EBSD maps of the extruded (SPS+Ex) specimens in **Figure 3**. The application of high strain during extrusion led to notable refining of the grain structure across all domains. Following extrusion, the pure zinc grains were refined down to an average grain size of $\sim 23 \mu\text{m}$ (see **Figure 3a**), while the alloyed Zn-3Ag-1Mg skeleton dropped to a fine-grain size of $\sim 2.5 \mu\text{m}$ (see **Figure 3c**). Despite this intense directional shear, SEM observation (**Figure 4a**) confirms that the characteristic bimodal arrangement of the harmonic architecture remains fully preserved. The pure zinc grains exhibit clear, morphological elongation parallel to the horizontal (extrusion) direction. The fine-grained Zn-3Ag-1Mg shell maintains a continuous network around the elongated pure zinc cores, preventing localised structural collapse or macro-scale mixing.

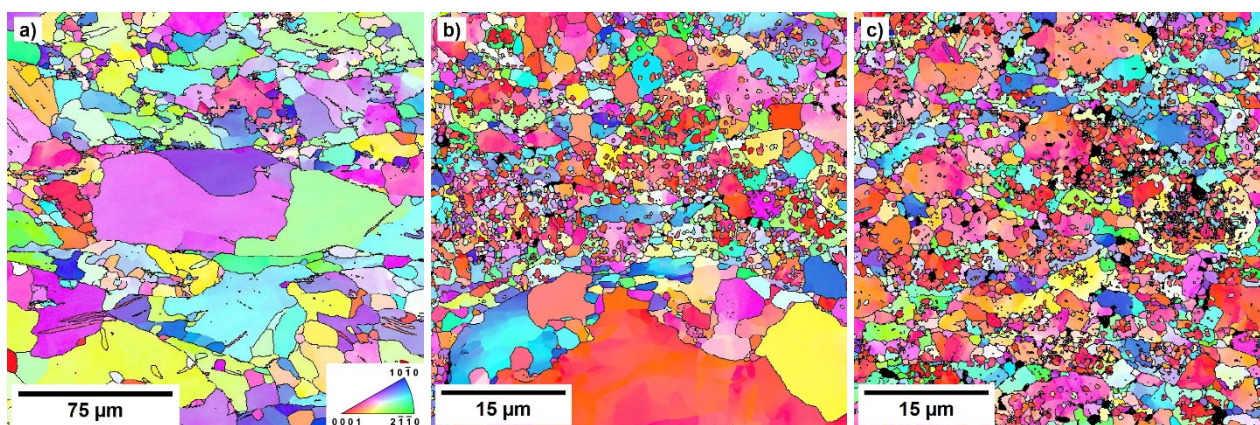


Figure 3 EBSD orientation maps of extruded a) pure Zn, b) Zn+Zn-3Ag-1Mg (50:50), c) Zn-3Ag-1Mg. Extrusion direction is horizontal

The mechanical response of all six sintered and extruded samples was evaluated via uniaxial compression testing, with the corresponding true stress-strain curves plotted in **Figure 4b**. The results demonstrate that incorporating the fine-grained Zn-3Ag-1Mg structural skeleton yields a highly pronounced strengthening effect [11]. Interestingly, introducing just 40% of the fine-grained alloyed skeleton drastically shifts the yield point upward compared to pure zinc.

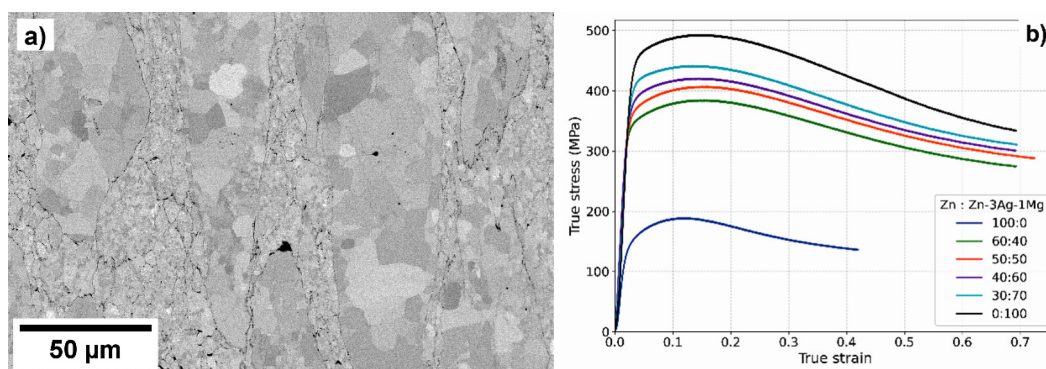


Figure 4 a) Distribution of Zn and Zn-3Ag-1Mg fraction in 50:50 extruded sample (SEM, extrusion direction is horizontal) and b) true strain – true stress compression deformation curves

Increasing the fine-grained fraction beyond 40% results in only a lower increase in the yield strength. This non-linear relationship implies that the initial 40% skeleton fraction is already sufficient to establish a continuous, load-bearing three-dimensional network that effectively shields the softer zinc cores from early plastic deformation [11]. As expected, the compression strength scales monotonically with the total alloy content, reaching its absolute maximum in the 100% Zn-3Ag-1Mg specimen. This behaviour underscores the performance synergy of the engineered system, uniting the high stress-bearing capacity of the fine-grained alloyed shell (governed by grain boundary and particle strengthening) with the core material's stability [12].

4. CONCLUSION

An innovative biodegradable Zn-Ag-Mg alloy system featuring a pseudo-harmonic core-shell architecture was successfully fabricated using mechanical alloying, spark plasma sintering, and hot extrusion. The extrusion effectively disrupted brittle powder particle oxide shells and significantly refined the grains to 23 μm in the pure Zn cores and $\sim 2.5 \mu\text{m}$ within the alloyed skeleton while keeping the bimodal layout intact. The fine-grained skeleton developed a distinct multi-phase structure containing stable $\text{Mg}_2\text{Zn}_{11}$, metastably retained MgZn_2 , and $\epsilon\text{-AgZn}_3$ precipitates. Compression tests revealed a non-linear strengthening effect, in which a threshold fraction of just 30% alloyed skeleton established a continuous load-bearing network that drastically improved the yield point. Ultimately, the integration of silver into the fine-grained skeleton offers a crucial dual benefit: mechanical stability via particle strengthening, alongside the expected antibacterial functionality for temporary implant applications.

ACKNOWLEDGEMENTS

Financial support from the Czech Science Foundation project 25-16144S is gratefully acknowledged. A. Boukalová thanks the specific university research project A2_FCHT_2026_028.

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