Mechanical properties of replicated cellular Zn and Zn1.5Mg in uniaxial compression

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Abstract

We present here a study of the mechanical behavior of cellular Zn and Zn1.5Mg with densities between 11.9 and 24.5%, produced by replication processing using NaCl as a spaceholder. Cellular Zn and Zn1.5Mg deform homogeneously during quasi-static compression. The plateau stress scales with the relative density according to a power-law of exponent of 2.8 for both materials; recorded values are 6.0 ± 0.6 MPa for cellular Zn of relative density 24% and 10.0 ± 0.5 MPa for cellular Zn1.5Mg of relative density 23%. In ambient-temperature creep tests with loads up to 50% of the plateau stress, after more than 70 hours deformation remains negligible (in the range of experimental error). This observation, coupled with other measured mechanical properties, indicate that replicated cellular Zn and Zn1.5Mg are viable materials in the context of their application as a low load-bearing implant material.

Keywords: Cellular, replication, biodegradable, zinc, implant

1. Introduction

Some implants, currently made of highly corrosion-resistant materials such as Ti6Al4V, CoCr F75 or stainless steel, have a temporary function since they are no longer needed once the body has healed. Some of the issues related to the long-term presence of implants in the human body are inflammation, thrombus formation and long-term implant migration [1]. Surgical removal of the implant is undesirable in many cases due to the possibility of infection, anesthesia-related complications, or surgical error. Moreover, when the tissue has grown into or has fully encapsulated the implant, surgical removal of the implant might be impossible. It would therefore be preferable to make implants from a biodegradable material and let the body absorb and remove the implant after it has performed its temporary function.

Biodegradable polymer implants are in clinical use today but have low strength; furthermore, their degradation products can lead to delayed foreign body reactions [2]. Higher strengths are achievable with metal implants and some biodegradable Mg alloy implants are in clinical use today [3]–[5]. The long-term effect of some of the alloying elements used in Mg alloy implants to improve the mechanical properties and/or control the degradation rate has been questioned, however [6]–[8]. It is therefore relevant to explore alternative biodegradable implant alloy systems; zinc and its alloys is one such alternative.

For orthopedic implants aimed at bone regeneration, it is recommended to incorporate porosity in the design of the implant [9]. Open porosity enables growth of bone into the implant, such that bone can gradually substitute the dissolving implant within the region to be repaired. In addition, porosity allows to tune the mechanical properties of the implant material so as to make them closer to the properties of bone. Replication processing (RP) is one approach towards the production of highly porous metals. It is based on the production of a composite of the metal and bonded particles that can be later leached. In one variant of the process, the metal is pressure infiltrated into open pores of a NaCl preform [10], [11]; this approach has notably been used to produce cellular pure Zn with relative

density of up to 29% [12],[13]. The present publication aims to complete those studies with mechanical property measurements that are of critical importance to the application of those materials in implants: (i) we explore the relationship between porosity and strength and (ii) we explore whether the fact that Zn is known to creep at room temperature might prevent the implants from being mechanically stable over a period of at least a few months [1],[14]. Additionally, we explore the influence of a biocompatible alloying element, namely magnesium: it is known that the addition of e.g. 0.8 wt% Mg can increase the yield strength of non-cellular Zn fivefold [15],[16].

2. Materials and methods

2.1. Production

Particulate NaCl was purchased from Sigma Aldrich (product nr 71382) and sieved with a 315 μm or 500 μm Retsch test sieve, Figure 1a. Special High Grade Zn and Commercial Purity Mg ingots were purchased from Affilips NV (Tienen, Belgium). Zn1.5Mg ingots were produced by melting the two metals in appropriate proportions in an Al_2O_3 crucible using an Indutherm TF4000 furnace under Ar. The furnace was heated to 823 K for 15 minutes before casting the alloy in cylindrical graphite molds. Subsequently, both pure Zn and Zn1.5Mg ingots were machined to shape prior to use.

Replication processing started with cold isostatic pressing (CIP) of the NaCl powder. The CIP pressure determines the density of the NaCl preform and thus the porosity of the resulting cellular metal. The following pressures were used: 7.7, 12.8, 28.1 and 40.8 MPa. This resulted in NaCl preforms of relative density between 75 and 88%, as calculated from the final mass and volume of the preforms. The preform and the metal were then placed, the latter over the former, in an alumina crucible in a cylindrical steel container and evacuated below $2 \cdot 10^{-2}$ mbar. The setup was heated to 753 K for 45 minutes under vacuum. Once the metal was molten, argon gas was injected into the chamber until a gas pressure of 0.6 MPa was reached, Figure 1b, so as to force the liquid metal against adverse capillary forces into open pores of the preform [17]. The steel container was then removed from the furnace and suspended in the ambient environment to cool down. Samples for mechanical testing were machined from the resulting salt-zinc composite into cylinders of diameter 10 mm and height 15 mm using a hollow drill on a lathe.

The salt preform was removed from the Zn/NaCl composite by submersion in 200 ml demineralized water per sample, with application of ultrasonic agitation, for 1 hour at 328 K. The demineralized water was changed every 10 minutes in order to avoid a high Cl^- concentration and possible Zn corrosion. Samples were dried in a hot air furnace at 333 K. After drying, the sample relative density was calculated based on its mass and volume. For these calculations, a density of 7.14 g/cm^3 was used for Zn and 6.82 g/cm^3 for Zn1.5Mg. The latter value is an estimation, calculated as the volume-weighted average of the density of Zn and Mg atoms in pure form.

Figure 1: a) Scanning electron microscopy image of NaCl spaceholders. b) Schematic of the infiltration process.

2.2. Characterization

A GE Nanotom with W target was used for micro-CT imaging at a voltage of 85 kV, a current of 300 mA and using a 0.1 mm Cu filter during scanning. Scans were performed in the fast scanning mode with 30 minutes scan time per sample and a voxel size of 8 μm . Phoenix datos|x software was used for reconstruction and CTAn software for further analysis. Automatic global thresholding was performed using the Otsu method [18].

Selected porous metal samples for metallographic examination were embedded in slow-setting resin (KEM90, ATM GmbH), ground with 320-1200 grit SiC paper and polished with diamond paste (1 - 0.25 μm). Zn1.5Mg samples were etched with a 5% nital solution before observation. A Nikon Eclipse MA100 was used to study the sample microstructure under polarized light.

A Scanning Electron Microscope (SEM, FEI XL40 and XL30) was used for powder, sample pore architecture, and strut deformation analysis. The local chemical composition of replicated polished Zn and Zn1.5Mg samples was measured with a JXA-733 JEOL Electron Microprobe. Measurements were performed in the qualitative mode and were used to detect possible impurities in the material (20 kV acceleration voltage, probe diameter 100 μm , 3 locations per sample). A Bruker D8 Advance X-Ray Diffraction (XRD) system was used to determine the phases in replicated Zn1.5Mg. Measurements were done on a polished non-cellular sample of the same metal, which had solidified as excess material on top of the NaCl preform. The diffractometer used Cu $K\alpha$ radiation and was operated at 40 kV and 40 mA in the Bragg-Brentano geometry. 2θ step intervals of 0.02° were applied from 15° to 90° with a counting time of 1 s per step.

Compression testing was performed on an Instron 5985 universal mechanical testing apparatus based on the ISO 13314 standard [19]. The crosshead speed was 0.9 mm/min corresponding to a nominal strain rate of 10^{-3} s^{-1} . A 0.05 mm Teflon sheet was placed between the ends of the sample and the compression platens to minimize friction and ensuing barreling. The plateau stress was computed as the average stress between 20 and 30% total strain. The strain was computed from the cross-head displacement after subtraction of the load train contribution, determined by compressing a material of known stiffness and high yield stress, namely Arne steel (Uddeholm, elastic modulus 190 GPa). The force required to compress the samples studied in this work was mostly below 500 N, which leads to a load train deformation of around 0.1 mm, while cross-head displacements related to sample deformation during compression testing were above 9 mm, making the machine compliance correction relatively inconsequential in computing stress-strain curves. On the other hand, since the sample elastic deformation generated displacements of the same order of magnitude as those due to load train deformation, the sample elastic properties could not be measured accurately. For each material-process combination, one sample was compressed to only 5% strain to study the local strut microfracture mechanism by subsequent observation in the SEM.

Creep tests were performed by loading cylindrical cellular samples of diameter 10 mm and height 15 mm under a dead weight and measuring the displacement in time with a Linear Variable Differential Transformer (LVDT) of accuracy $\pm 1.5 \mu\text{m}$ (DS805SR5, Magnescale, Japan). As in monotonic compression testing, a 0.05 mm Teflon sheet was placed between each end of the sample and the compression plates to minimize friction and ensuing barreling. Replicated Zn samples of relative density between 12 and 16% was tested at 293 K at a stress of 0.75 MPa. Replicated Zn1.5Mg samples of relative density between 15 and 21% was tested at 293 and 323 K at stress values between 0.71 and 1.20 MPa. For every condition, three replicates were tested simultaneously for a minimum of 90 h.

3. Results and discussion

The relative density of the replicated samples varied between 11.9 and 23.7% for Zn samples and between 12.3 and 24.5% for Zn1.5Mg. In both systems the density could be controlled by adjusting the NaCl preform CIP pressure, with the lower achievable density being limited by the fragility of the resulting porous metal.

SEM images and CT analysis showed that (i) the porosity is open, (ii) the shape of the salt grains is replicated accurately and (iii) NaCl grains have been removed, see Figure 2a-c. In total, four Zn and four Zn1.5Mg samples were analyzed by CT and their relative density was compared to the mass-and-volume (m&v) based values. The relative density obtained by CT was always somewhat higher than the m&v relative density, with minimum, average and maximum deviations of 0.24, 0.43 and 1.92 percentage points, respectively. As the CT analysis showed complete removal of NaCl particles, the systematic difference between results produced by the two methods is probably linked to the partial volume effect, which is well-known in CT analysis of bone, and is also applicable to the thinner and thicker structures produced by RP shown in Figure 2b [20]. and the partial volume effect probably influenced the results. Given the small difference between m&v and CT results, no further steps were taken to correct for this effect.

Figure 2: Scanning electron micrograph of replicated Zn at a) low and b) high magnification. c) Computed tomography slice of replicated Zn after binarization.

Electron microprobe analysis showed that no sign of contamination during the different production steps: only Zn and Mg were detected. The measured Mg content in the cellular Zn1.5Mg varied between 1.45 and 1.88 wt%. The grain size of the replicated Zn is difficult to measure within the cellular material. It could however be estimated from a micrograph of the non-cellular material solidified next to the NaCl preform, as shown in Figure 3a: the grain size is in the mm range, without grain refinement visible in the metal along the outer pore layer (former NaCl/Zn interface). The latter observation implies that, as for aluminum and magnesium, NaCl does not act as a grain nucleation catalyst, leading in turn to expect that the grain size within the cellular material does not fall below that in the salt-free ingot over the metal/NaCl composite. Hence the metal grain size far exceeds the pore size, as is the case for replicated cellular Al, Mg and alloys thereof [10].

The Zn1.5Mg microstructure consists of α -Zn and a two-phase eutectic, illustrated in Figure 3b. Figure 3b and c show that the primary α -Zn phase grows mainly in the middle of the strut, away from the former Zn/NaCl interface. This is a common feature of the solidification of primary metal phases when growing in the presence of a stationary inert dense second phase that does not serve as a nucleation catalyst for the solid primary phase [21],[22]. As a result, the eutectic phase, consisting of α -Zn and MgZn_2 , as confirmed by XRD (Figure 3d), lines most of the strut surfaces. In equilibrium conditions, only pure Zn and $\text{Mg}_2\text{Zn}_{11}$ are expected [23]. In reality, the phases that are formed depend on the growth rate of the solid phase; a Zn-Mg Zn_2 mixture is formed at a growth rate of 0.01-0.1 mm/s [24], a low growth rate that is not unrealistic here, as the infiltration cylinder was suspended in air during cooling. Figure 3c shows that a spiral-shaped eutectic had formed in some locations. This is not unusual for Zn-Mg alloys and is caused by a particular anisotropy in growth rate in the two eutectic phases [24],[25].

During compression testing, replicated Zn and Zn1.5Mg deformed uniformly, as illustrated by the smooth stress-strain curve in Figure 4. For replicated Zn, no maximum stress was reached before a smooth plateau-like region of low strain hardening rate. This behavior is typical for cellular elastic-plastic materials and has been reported for replicated Zn as well as replicated Al and Mg alloys [26]-[30]. With replicated Zn1.5Mg, there is a (small) decrease in stress after a first maximum, Figure 4; thereafter, the material shows a smooth plateau-like region similar to that of replicated Zn.

Figure 3: a) Grains of non-cellular Zn solidified next to the NaCl preform of replicated cellular material showing grains in the mm size range and an absence of enhanced metal nucleation along the former NaCl/Zn interface. b) Microstructure of a Zn1.5Mg scaffold. c) Spiral eutectic in the microstructure of a Zn1.5Mg scaffold. d) XRD pattern of Zn1.5Mg.

The measured plateau stress, σ_{pl} , scales with relative density according to a power-law of exponent 2.8 for both Zn and Zn1.5Mg, Figure 5. This is well above the theoretical exponent linking the flow stress to the relative density for a perfect elastic-plastic strut non work-hardening plastic material in a bending-dominated structure, which is 1.5 [29]-[32]; however, in practice exponent values higher than 1.5 have been reported for the yield or plateau stress of several different cellular metals [33]. This includes replicated cellular aluminum [30] and powder-metallurgically produced replicated Zn (also with pore architecture similar to the present material) [26], both of which have flow stress values that scale with relative density with a power-law exponent of 2.5, a value close to that measured here. For replicated materials, an exponent higher than 1.5 can be explained by a change of strut shape and coordination with the relative density [34].

The plateau stress σ_{pl} for the replicated Zn in this study is higher than the 2.8 MPa σ_{pl} that was reported for a relative density of 29% in [13]. The difference can be attributed to the more equiaxed shape of the NaCl particles used in this study, which leads to a higher modulus and higher strength [35]. These flow stress values are in the same range as for Mg alloys AZ63, AZ91 and ZWM200 with the same relative density [27],[36]. Note that the compressive strength of cortical bone is much higher than those values [37].

Figure 4: Example of compressive stress-strain curve for a replicated Zn sample with relative density 22% and replicated Zn1.5Mg sample with relative density 23%.

Figure 5: The plateau stress of replicated cellular Zn1.5Mg and Zn as a function of relative density: a) linear scale and b) logarithmic scale.

As the material deforms, it accumulates internal damage. Zn struts fracture individually by transgranular cleavage, as shown in Figure 6a-b, and the frequent observation of such parallel cleavage fracture surfaces across entire struts supports the hypothesis that the replicated Zn grain size is well above the pore size. The out-of-flatness features visible on Fig. 6a-b could be twist hackles, caused by a twist in the axis of principal tension during deformation [38]. Fractographic images of replicated Zn1.5Mg show that both the α -Zn phase and the eutectic fracture locally by cleavage during compression of the cellular material, see Figure 6c-d. Those observations are consistent with the behavior of the dense metal: cleavage fracture of (dense) Zn1.5Mg in tensile testing has been reported earlier [39]. The fracture mechanism is not different from replicated Zn but the eutectic between the α -Zn phase dendrites limits the free path for cleavage fracture in Zn1.5Mg, likely reducing damage accumulation and contributing to the measured increase in strength over pure Zn.

Figure 6a-d show a crystal-like deposit on the surface of the struts. This could be formed during removal of NaCl from the metal/NaCl composite and should be ZnO [40]. Given that it is not a continuous dense film, the influence of the deposit on the mechanical properties of the cellular metal is expected to be small.

Figure 6: a,b) Zn struts fractured by transgranular cleavage. c) α -Zn and d) eutectic cleavage fracture in broken Zn1.5Mg struts.

Figure 7 shows a plot of true strain versus time for one of the creep tests. After an initial increase of strain, likely due to Teflon sheet deformation, elastic deformation of the sample and settling of sample and compression plates, a steady-state regime is reached. The average strain rate in this regime can be estimated by dividing the difference in strain between 20 h and 90 h of test time by the time difference, i.e. 70 h. Results are given in Table 1. Replicated Zn with a relative density of 12% deforms to more than 5% strain under a stress of 0.75 MPa. Given a σ_{pl} of around 0.8 MPa for this material, that extensive creep be observed after testing close to the yield stress is not surprising. For replicated Zn with a relative density of 16% under an applied stress near 0.75 MPa, displacements measured with the LVDT are below 10 μ m, such that corresponding strains are below 10^{-3} (Table 1). Given the 1.5 μ m accuracy of the LVDTs and the presence of other sources of uncertainty in the measurement of the displacement (e.g., differential thermal expansion also liable to give errors on the displacement on the order of a few μ m), the results for Zn in Table 1 are within experimental error, with corresponding total creep strains below 10^{-3} , even though the applied stress is still relatively close to the yield strength of the samples (0.75 MPa is around 50% of σ_{pl} at a relative density of 16%).

A plausible explanation for the low creep rates found here is the fact that the metal grain size far exceeds the strut size in the replicated pure Zn samples in this work. Indeed, it has been documented that grain boundaries are essential contributors to the ambient temperature creep of pure Zn, and a linear decrease in ambient temperature creep rate with increasing metal grain size has been measured for hexagonally close packed metals including pure Zn [14]. Here, most struts are single crystals [10], as confirmed here by observation of grains in the metal adjacent to the cellular material (see Figure 3a). Quantitatively, the steady-state creep rate of cellular materials can be estimated as [31]:

$$\dot{\epsilon} = (F_E)^{-\frac{1-n}{2}} \cdot \left(\frac{\rho_c}{\rho_s}\right)^{-\frac{n+1}{2}} \cdot K \cdot \sigma^n \quad (1)$$

with $\dot{\epsilon}$ the creep rate, n the steady-state creep rate stress exponent, K a material-and temperature-dependent factor, σ the stress on the cellular metal, and F_E the ratio of the elastic modulus of the cellular metal to that of the strut material: $F_E = A \cdot (\rho_c/\rho_s)^\alpha$. According to [14], n is equal to 3.4 for Zn at ambient temperatures and one can derive from the plotted data that K should be equal to $1.34 \cdot 10^{-32}$ for Zn with a 100 μ m grain size, decreasing to $1.34 \cdot 10^{-33}$ for Zn with a 1 mm grain size, with K in

units that lead to strain rates in $1/s$ if the stress is given in MPa. If one assumes that the stiffness scales for replicated cellular zinc as it does for aluminum, then $A = 2.39$ and $\alpha = 2.37$. Equation (1) then predicts a creep rate of $2.4 \cdot 10^{-9} s^{-1}$, causing a corresponding deformation of $9 \mu m$ in a sample $15 mm$ long, corresponding to a strain $\approx 5 \cdot 10^{-4}$, which is consistent with the experimental data.

Figure 7: True compressive strain as a function of time during creep testing of a Zn1.5Mg sample with a relative density of 15% at 323 K for a stress of 0.74 MPa.

Table 1: Deformation was very small for the applied creep test conditions. Replicated Zn with a relative density of 12% was loaded to a stress above its yield stress, which resulted in considerable deformation. Positive deformation values indicate compressive strain.

Material	Relative density %	Stress MPa	Temperature K	Strain after 70 h
Zn	11.9	0.75	293	19%
	11.7	0.74	293	15%
	11.8	0.74	293	19%
	16.1	0.75	293	$< 10^{-3}$
	16.0	0.75	293	$< 10^{-3}$
	15.8	0.74	293	$< 10^{-3}$
Zn1.5Mg	15.1	0.72	293	$< 10^{-3}$
	14.8	0.74	293	$< 10^{-3}$
	15.2	0.74	293	$< 10^{-3}$
	19.1	0.71	293	$< 10^{-3}$
	19.1	0.71	293	$< 10^{-3}$
	19.2	0.71	293	$< 10^{-3}$
	16.5	1.18	293	$< 10^{-3}$
	16.5	1.16	293	$< 10^{-3}$
	16.3	1.17	293	$< 10^{-3}$
	20.5	1.15	293	$< 10^{-3}$
	20.8	1.17	293	$< 10^{-3}$
	20.9	1.17	293	$< 10^{-3}$
	15.9	1.20	323	$< 10^{-3}$
	15.8	1.17	323	$< 10^{-3}$
	15.9	1.20	323	$< 10^{-3}$

With alloyed samples, displacements measured with the LVDT were again always smaller than 10 μm , regardless of sample relative density, stress or temperature, such that corresponding strains were all below 10^{-3} (see Table 1). In addition, there was considerable variability in the data and some of the expected trends, such as an increase in deformation rate with an increase in temperature, were not confirmed, indicating that data values were too small to be distinguished from experimental error. Given that cellular pure Zn does not show significant creep near its plastic flow stress and the fact that the activation energy for creep of the eutectic second phase, MgZn_2 , is 9 times higher than that for pure Zn, it is not surprising that there be negligible creep in the cellular alloy in the parameter space explored here [14],[41]. Knowing that the exponent α (contained in F_E) exceeds 2 and $n = 3.4$, equation (1) reveals that the dependence of the creep rate on the relative density is steep. Hence creep rates might be higher for relative densities below the range explored here.

Trabecular bone is known to deform by compressive creep, with creep failure after 28 h for 8 MPa [42]. With 8 MPa being the lowest stress tested so far, it is unknown whether a creep threshold stress exists and hence whether trabecular bone would creep at the stress levels explored here.

4. Conclusion

- Replicated cellular Zn reaches a plateau stress of 6.0 ± 0.6 MPa for a relative density of 24%, whereas replicated cellular Zn1.5Mg has a plateau stress of 10.0 ± 0.5 MPa for a relative density of 23%. This is in the same range as Mg alloys AZ63, AZ91 and ZWM200 with the same relative density, but much lower than cortical bone (200 MPa).
- The flow (plateau) stress of the replicated Zn and Zn1.5Mg depends strongly on the relative density, showing a scaling exponent between flow stress and relative density around 2.8, which is slightly higher than observed for replicated aluminum (2.5) of similar pore architecture.
- The grain size of the cast metal around the cellular Zn is high (> 1 mm) and fracture surfaces of individual struts show characteristics of single-plane cleavage fracture. These observations indicate that the individual struts in the two microcellular metals are likely monocrystalline.
- The absence of grain boundaries within the individual struts of replicated pure Zn provides an explanation for the observation that room-temperature creep rates in this material are below 10^{-8} s^{-1} in the range of parameters explored, comprising testing at applied stresses near one-half of the flow stress of the material.
- The microstructure of the replicated Zn1.5Mg consists of a Zn-MgZn₂ mixture, with the eutectic lining most of the strut surfaces. Both the α -Zn phase and the eutectic fracture by cleavage in a compression tests suggesting that the Zn grain size is again well above the strut size. Similar to cellular Zn, the room-temperature creep rates for cellular Zn1.5Mg are negligibly small for the conditions explored. This is attributed to the absence of grain boundaries in the struts and to the presence of MgZn₂.

Summing up, mechanical properties reported here suggest that replicated cellular Zn and Zn1.5Mg are viable materials in the context of their application as a low load-bearing implant materials.

Acknowledgements

The authors gratefully acknowledge the financial support for this project from the VLAIO (Flanders Agency for Innovation and Entrepreneurship, IWT140257), and from the internal base budget of the Laboratory of Mechanical Metallurgy at EPFL.

Author contributions

The research was conceived and supervised by K.L., J.V., A.M. and L.W.. XRD measurements were performed by T.L., other experiments and data analysis were performed by K.L.. The creep testing setup was designed and manufactured by J.V.D.. The results were discussed by all authors. The manuscript was written by K.L. then reviewed and modified by all authors.

Additional information

Competing financial interests: The authors declare no competing financial interests.

Data availability

The processed data required to reproduce these findings are available to download from <https://3dsystems.sharefile.com/d-s03cc24dba9d4a269>.

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