Processing and Mechanical Properties of a Tricalcium Phosphate-Dispersed Magnesium-Based Composite

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A magnesium matrix composite comprising Mg-0.5 mass% Ca and 10 vol.% β-tricalcium phosphate (TCP) particles was processed with the aim of developing biodegradable material. The composite was produced by extruding a mixture of two component powders at 538 K. The matrix of the extruded composite comprised fine equiaxed grains (grain size: 1.3 μm). Moreover, isolated β-TCP particles and agglomerated particles (size: 10–15 μm) were observed. Owing to grain refinement, the composite exhibited a high yield strength (>300 MPa) at room temperature and behaved in a superplastic manner at ~548 K. [doi:10.2320/matertrans.M2018304]

(Received September 14, 2018; Accepted October 24, 2018; Published November 23, 2018)

Keywords: magnesium, calcium phosphate, composite, biodegradable, superplasticity

1. Introduction

Magnesium alloys are lightweight materials and hence the use of these alloys as structural materials has increased in recent decades. Magnesium has recently attracted considerable attention for use in orthopedic implants because of its high biocompatibility and biodegradability.1-3 The advantage of biodegradability is that the implant corrodes away after completing the designated function, and is no longer needed in the body. However, in many cases, the degradation rates of magnesium and its alloys outstrip the rate of healing and, hence, the mechanical integrity of the magnesium implants may be lost before complete healing is achieved. Therefore, the degradability of biodegradable magnesium implants must be adjusted so that the implants retain their mechanical properties, thereby allowing a complete healing process.

Hydroxyapatite (HAp) and tricalcium phosphate (TCP) are two major calcium phosphates used as bioceramics.4) HAp is osteoconductive and bone cells can be attached to and propagated on its surface. However, the solubility of TCP in body fluid is higher than that of HAp and, thus, TCP is gradually absorbed into bones and is eventually replaced by natural bone. The two common phases of TCP are α and β, and α-TCP dissolves more readily than β-TCP.5) Combining these calcium phosphates with magnesium yields a magnesium-based composite characterized by a reasonable degradation rate and good biocompatibility.6) Our recent work on electrochemical and immersion tests revealed that the degradation properties of Mg–0.33 mass% Ca (0.2 at% Ca) alloy improved with the addition of α-TCP particles, and the degradation rate decreased with particle refinement.7) Furthermore, the dispersion of β-TCP particles is helpful in enhancing the corrosion resistance of magnesium.8-12)

The widespread use of magnesium/bioceramic composites in orthopedic applications will be limited by the lack of secondary processing procedures, which yield complex product shapes. In general, when the grain size of magnesium is refined to <3 μm, the material exhibits superplasticity at a relatively low temperature of ~523 K and at commercially acceptable production rates.13) However, superplasticity in magnesium/bioceramic composites, which has important implications, has never been reported. Studies focused on realizing superplasticity in these materials are therefore warranted.

This study is aimed at producing a fine-grained magnesium/β-TCP composite and achieving superplasticity at elevated temperatures. A biomedical magnesium alloy of the Mg–Ca system14,15) was chosen as the matrix material. The mechanical properties of the processed composite were determined and compared with those of the alloy without β-TCP.

2. Experimental

2.1 Preparation of materials

The matrix material used in the present study was a Mg–0.5 mass% Ca (0.3 at% Ca) alloy (ASTM designation: X0). A magnesium composite with 10 vol.% β-TCP (hereafter, denoted as X0/β-TCP/10p) was obtained via powder metallurgy. Mg–0.5 mass% Ca powder (particle size: ≤63 μm), produced via atomization, was obtained from Tobata Seisakusho Co., Ltd., Japan. The β-TCP powder (particle diameter: 1–5 μm) was obtained from Taihei Chemical Industrial Co., Ltd., Japan. The morphology of powder particles comprising the magnesium alloy and β-TCP is revealed by the scanning electron microscopy (SEM) image shown in Fig. 1.

The two component powders were mixed together in ethanol using an agate mortar and pestle, and the dried mixtures were then tape-packed into an AZ31 magnesium alloy capsule (outer diameter: 40 mm) in air. Powder densification was achieved by uniaxially pressing the mixed powders at room temperature (pressure: ~0.8 MPa) and then at 448 K (pressure: ~1.5 MPa). For consolidation, the billet (capsule) was extruded into a rod at 538 K with a reduction ratio of 16. For reference, the X0 alloy without β-TCP addition was also produced by extruding the atomized alloy powder.

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2.2 Characterization of the processed materials

The chemical composition of the extruded X0 alloy was determined by means of X-ray fluorescent spectroscopy (XRF) using an empirical calibration method. The extruded rod was halved lengthwise and a wider flat surface was then obtained by compressing the rod at 543 K along the radial direction. Afterward, the compressed rod was ground on a zirconia abrasive paper. The measuring diameter was 20 mm.

The microstructures of the extruded materials were observed using a color laser three-dimensional profi le microscope (in light screen mode) and SEM. In addition, the phases of the extruded X0/β-TCP/10p composite were identified using X-ray diffraction (XRD) with Cu-Kα radiation on the plane parallel to the extrusion direction.

The dynamic Young’s modulus ($E_d$) of rectangular specimens (length: 60 mm, width: 7 mm, and thickness: 1.8 mm) was measured via the free-free transverse vibration method.

The damping capacity was measured at a fundamental resonant frequency (~14 Hz) in flexure using a decay method for the aforementioned rectangular specimens in a cantilever holder. The damping capacity was described by the loss factor $\eta$, which is related to the logarithmic decrement $\delta$ (i.e., $\eta = \delta/\pi$).

The extruded X0/β-TCP/10p composite and extruded X0 alloy were subjected to uniaxial tension and compression tests at room temperature and an initial strain rate of $5 \times 10^{-4}$ s$^{-1}$. The tensile specimens (length and diameter of gage section: 15 mm and 3 mm, respectively) were deformed to fracture. Moreover, the compressive specimens (diameter: 6.5 mm, height: 13 mm) were deformed to a total strain of ~9%. The longitudinal direction of both specimens was parallel to the extrusion direction. The strain was measured by using a clip-on extensometer with a gage length of 10 mm.

The plastic workability of the extruded X0/β-TCP/10p composite and extruded X0 alloy was determined via compression tests performed at elevated temperatures of 523–573 K. Specifically, true stress-strain rate data were collected from strain rate jump tests aimed at measuring the strain rate sensitivity of flow stress $m$ associated with each specimen (diameter: 5 mm, height 7.5 mm). During the tests, the crosshead velocity was increased from 0.15 mm/min to 4.8 mm/min at a fixed temperature. A spray film of boron nitride was used as the lubricant. The deformation mechanism at elevated temperatures of the extruded composite was elucidated via electron backscatter diffraction (EBSD) of the pre- and post-deformation microstructures. The plane perpendicular to the extrusion direction was examined using a field emission scanning electron microscope (FESEM). The specimen was deformed at a temperature and crosshead velocity of 548 K and 0.15 mm/min, respectively, until a true plastic strain of ~0.5 was reached.

Tensile properties at 548 K of the extruded X0/β-TCP/10p composite were characterized by periodically decreasing the strain rate and again returning to the original strain rate. The strain rate difference was ~30% between the base and the jump and the decreased strain rate was maintained for a true strain of 0.07. The specimens had a gage length of 5 mm and a gage diameter of 2.5 mm. The variation in $m$ with strain and elongation after fracture were determined by this test.

3. Results and Discussion

3.1 Microstructures

The XRF-determined chemical composition of the alloy is given in Table 1. Even in small amounts, Ni, Fe, and Cu as impurities in magnesium lead to an increase in the corrosion rate and, hence, the amounts of these elements must be limited to low levels.16) In the extruded X0 alloy, the amount of Fe (0.020 mass%) was close to the tolerance limit (0.017 mass% Fe), and the amounts of Ni and Cu (<0.001 mass%) were lower than the respective limits (0.001 mass% Mg).

<table>
<thead>
<tr>
<th>Ca</th>
<th>Al</th>
<th>Si</th>
<th>Mn</th>
<th>Fe</th>
<th>Ni</th>
<th>Cu</th>
<th>Zn</th>
<th>Mg</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.51</td>
<td>0.084</td>
<td>0.008</td>
<td>&lt;0.001</td>
<td>0.020</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>0.005</td>
<td>Bal.</td>
</tr>
</tbody>
</table>
Ni and 0.13 mass% Cu) in cast pure magnesium. The same chemical compositions were assumed for the matrix of the extruded X0/β-TCP/10p composite and the extruded X0 alloy, as contamination resulting from the mixture of the component powders during the process was prevented.

A typical SEM image of the extruded X0/β-TCP/10p composite is shown in Fig. 2(a). Agglomerated β-TCP particles (sizes: 10–15 µm) were inhomogeneously spread over the cross-section, although several isolated particles were also observed. However, the microstructure was both cavity- and crack-free. This indicates that the extrusion produced a fully dense composite, consistent with the fact that the compressive specimens resisted fracture even after ~9% deformation at room temperature.

An optical micrograph of the extruded X0/β-TCP/10p composite is shown in Fig. 2(b). Many of the dark regions in the figure correspond to agglomerates of the β-TCP particles, as expected from Fig. 2(a). The matrix was composed of fine equiaxed grains, with sizes (grain size: 1.3 µm) comparable to that of the extruded X0 alloy (see Fig. 3 for an optical micrograph of the alloy).

The XRD profile of the extruded X0/β-TCP/10p composite is shown in Fig. 4. The peaks correspond to magnesium and β-TCP, suggesting that neither phase transformation of β-TCP nor chemical reaction occurred during processing.

### 3.2 Mechanical properties

The Young’s modulus ($E_{\text{i}}$) of the extruded X0 alloy and extruded X0/β-TCP/10p composite are listed in Table 2. The agglomeration of ceramic particles leads (in general) to a drop in modulus, to $E < 40$ GPa, in magnesium-based composites. However, the Young’s modulus of the X0/β-TCP/10p composite was comparable to that of the X0 alloy.

Enhanced damping capacity in Mg/HAp composites has been attributed to HAp agglomeration. From this point of view, the damping capacity is considered a good measure for assessing the degree of particle agglomeration in composites. The variation in loss factor (damping capacity) with strain amplitude of the extruded X0/β-TCP/10p composite and extruded X0 alloy is shown in Fig. 5. The results obtained for Mg/HAp composites are also included in the figure. The loss factor of the extruded X0/β-TCP/10p composite was slightly higher than that of the extruded X0 alloy, but the damping capacity of the composite was lower than that of the Mg/HAp composites. Particle agglomeration is weaker (i.e., particles are more uniformly distributed) in the X0/β-TCP/10p composite than in the Mg/HAp composites.

The slight increase in the damping capacity (extruded X0/β-TCP/10p composite vs. extruded X0 alloy) and Young’s
modulus of the composite, which is comparable to that of the alloy, is attributed to this weaker agglomeration.

The tensile and compressive properties of the extruded X0 alloy and extruded X0/β-TCP/10p composite are summarized in Table 2. It is apparent that the addition of β-TCP itself brought about the low tensile ductility in the composite. In addition, the fracture surface of the composite (not shown here) suggested that the presence of agglomerated β-TCP particles further reduced the tensile elongation. The yield strength values ($R_{pt}$ and $R_{pc}$) of the composite exceeded 300 MPa both under tension and under compression. The high yield strength results from the fine grain size (1.3 µm) of the composite. However, the strength of the composite was lower than that of the alloy, indicating that the dispersion of β-TCP had no effect on strengthening. This is attributed to the presence of agglomerated β-TCP particles. The yield strengths, tensile strength ($R_{m}$), and elongation ($A$) of the extruded X0/β-TCP/10p composite were all lower than those of the extruded X0 alloy. Nevertheless, the strength of our composite is higher than that of TCP-containing magnesium composites reported in the literature7,8,11,12,21,22) (Table 3).

Extruded magnesium and its alloys often exhibit an undesirable difference in compressive and tensile yield strength; that is, when an extruded magnesium bar is tested along the extrusion direction, the yield strength in tension is higher than that in compression. This is true for the extruded X0 alloy ($R_{pt}/R_{pc}=1.2$). However, this asymmetry was destroyed, owing to the dispersion of β-TCP and, hence, a $R_{pt}/R_{pc}$ of 1.0 was achieved for the extruded X0/β-TCP/10p composite.

The dependence of the elevated-temperature compressive flow stress on the strain rate applied to the extruded X0/β-TCP/10p composite and extruded X0 alloy is shown in Fig. 6. In the high strain-rate range ($\dot{\varepsilon}>3\times10^{-3}$ s$^{-1}$) the alloy and composite experienced comparable flow stress. The strain rate sensitivity ($m$), which was estimated from the slope of the curve, of the alloy reached a relatively high value of 0.33 at low strain rates. Examination of Fig. 6 revealed that, in the low strain-rate range ($\dot{\varepsilon}<3\times10^{-3}$ s$^{-1}$), the flow stress of the composite is higher than that of the alloy. Consequently, the $m$ of the composite ($m=0.3$) became lower than that of the alloy ($m=0.33$). This suggests that flow was easier in the alloy than in the composite.

The variations of true stress (left axis) and $m$ (right axis) with strain in the extruded X0/β-TCP/10p composite are

### Table 2
Dynamic Young’s modulus ($E_d$), tensile yield strength ($R_{pt}$), tensile strength ($R_{m}$), percentage elongation after fracture ($A$), and compressive yield strength ($R_{pc}$) of the extruded X0 alloy and extruded X0/β-TCP/10p composite at room temperature.

<table>
<thead>
<tr>
<th>Material</th>
<th>$E_d$/GPa</th>
<th>$R_{pt}$/MPa</th>
<th>$R_{m}$/MPa</th>
<th>$A$ (%)</th>
<th>$R_{pc}$/MPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>Extruded X0 alloy</td>
<td>44.6</td>
<td>383</td>
<td>393</td>
<td>6</td>
<td>314</td>
</tr>
<tr>
<td>Extruded X0/β-TCP/10p</td>
<td>43.0</td>
<td>303</td>
<td>328</td>
<td>1</td>
<td>301</td>
</tr>
</tbody>
</table>

### Table 3
Strength of TCP-containing magnesium-based composites.

<table>
<thead>
<tr>
<th>Matrix</th>
<th>Fraction of TCP</th>
<th>$R_{pt}$/MPa</th>
<th>$R_{m}$/MPa</th>
<th>$R_{pc}$/MPa</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg</td>
<td>10 vol.% β-TCP</td>
<td>–</td>
<td>–</td>
<td>70</td>
<td>22</td>
</tr>
<tr>
<td>Mg</td>
<td>20 vol.% β-TCP</td>
<td>–</td>
<td>–</td>
<td>101</td>
<td>22</td>
</tr>
<tr>
<td>Mg</td>
<td>1.5 vol.% β-TCP</td>
<td>–</td>
<td>–</td>
<td>103</td>
<td>12</td>
</tr>
<tr>
<td>Mg–0.5Ca</td>
<td>10 vol.% α-TCP</td>
<td>–</td>
<td>–</td>
<td>227</td>
<td>7</td>
</tr>
<tr>
<td>Mg–0.5Ca</td>
<td>10 vol.% α-TCP (coarse)</td>
<td>–</td>
<td>–</td>
<td>143</td>
<td>7</td>
</tr>
<tr>
<td>Mg–0.5Ca</td>
<td>10 vol.% α-TCP (fine)</td>
<td>–</td>
<td>–</td>
<td>143</td>
<td>7</td>
</tr>
<tr>
<td>Mg–3Zn–0.8Zr</td>
<td>1 mass% β-TCP</td>
<td>–</td>
<td>280</td>
<td>–</td>
<td>8</td>
</tr>
<tr>
<td>Mg–3Zn–1Ca</td>
<td>1 mass% β-TCP</td>
<td>125</td>
<td>150</td>
<td>–</td>
<td>21</td>
</tr>
<tr>
<td>Mg–6Zn</td>
<td>10 mass% β-TCP</td>
<td>–</td>
<td>–</td>
<td>183</td>
<td>11</td>
</tr>
</tbody>
</table>
shown in Fig. 7. The test revealed that a relatively high $m$ of \(~0.3\) is observed not only under compression (Fig. 6) but also under tension up to a true strain of 0.37 (Fig. 7). However, the elongation after fracture was only 71\%. In superplastic metal-matrix composites, elongation values are sometimes very sensitive to the strain rate, and high elongations are, thus, obtained within a narrow strain rate range. For example, fine grained Mg–Zn–Zr–SiC/17p composite shows high superplastic elongation of over 400\% at 10\(^{-1}\) s\(^{-1}\) but the high ductility rapidly drops to less than 50\% at 10\(^{-3}\) s\(^{-1}\).\(^{23}\) It is, therefore, expected that much higher elongations are attained in the extruded X0/\(\beta\)-TCP/10p composite under the optimal deformation conditions.

Magnesium alloys and magnesium-based composites with a relatively high $m$ of \(\geq 0.3\) at elevated temperatures deform either via slip-accommodated grain boundary sliding ($m = 0.5$)\(^{24,25}\) or dislocation glide with solute atmosphere ($m = 0.33$)\(^{26,27}\). Grain boundary sliding (GBS) represents the dominant mechanism of superplastic deformation.\(^{28}\)

For the slip-accommodated GBS mechanism, $m$ values of <0.5 are sometimes observed, owing to the effects of microstructural instability (grain growth hardening) or a threshold stress (minimum stress required for deformation of the material).\(^{29}\) The former has been observed in dilute Mg–Al alloy,\(^{29}\) whereas the latter has often been observed in metal-matrix composites\(^{30}\) and powder metallurgy alloys.\(^{31,32}\) Therefore, identifying the dominant mechanism from $m$-values solely is difficult. To elucidate the deformation mechanism of the extruded composite, pre- and post-deformation microstructures were observed via FESEM-EBSD. The inverse pole figure (IPF) map obtained from EBSD analysis of the undeformed (annealed at 548 K for 0.9 ks) composite is shown in Fig. 8(a). Blue and green grains dominate the map, indicating that the $h\bar{1}0/C\bar{2}2\bar{1}0$ and $h\bar{1}1/C\bar{2}2\bar{2}0$ directions in most grains are distributed parallel to the extrusion axis, as confirmed by the corresponding IPF (see Fig. 8(c)).

For reference, EBSD analysis revealed that the average grain size (diameter) of the annealed alloy (1.3 \(\mu m\)) was almost the same as that of the annealed composite (1.4 \(\mu m\)). In addition, similar textures developed in the alloy and the composite, although the maximum texture intensity of the composite was 1.4 times lower than that of the alloy (the data are not presented here). This implies that the difference in the $m$-value of the composite and the alloy subjected to low strain rates results from the presence of $\beta$-TCP particles.

The IPF map and IPF of the deformed composite are shown in Fig. 8(b) and (d), respectively. The deformation induced two changes. First, gradual grain coarsening occurred, as evident from Fig. 9, where the EBSD-determined grain size distribution is shown. As the figure shows, the post-deformation distribution is shifted (to coarse grain sizes) relative to the pre-deformation distribution.
Furthermore, no new texture components were developed and the texture intensity decreased significantly after deformation. These changes are both attributed to GBS and the accompanying grain rotation.\(^{33}\)

The relatively high \(m\) of 0.3 and texture weakening after deformation suggest that the extruded X0/β-TCP/10p composite deforms via slip-accommodated GBS, and thus behaves in a superplastic manner at temperatures of \(~548\) K. An \(m\) of 0.3, which is smaller than the typical value (i.e., 0.5) for slip-accommodated GBS, results probably from a threshold stress, which has often been observed for metal-matrix composites.\(^{30,34}\)

4. Summary

A magnesium-based composite with a dispersion of bioabsorbable calcium phosphate was produced via powder metallurgy. Specifically, fine β-TCP particles were dispersed in a Mg-Ca alloy. The major results obtained via the microstructural and mechanical-property characterization of the processed composite are summarized as follows:

1) Mg–0.5 mass%Ca alloy with 10 vol.% β-TCP was successfully produced via the extrusion of two component powders. The matrix of the extruded composite consisted of fine equiaxed grains (grain size: 1.3 µm). Furthermore, the XRD profile of the composite revealed that no new phases formed during processing. Although agglomerates of β-TCP particles were observed, the damping capacity and Young’s modulus of the composite implied a relatively uniform dispersion of β-TCP particles.

2) The yield strength of the composite exceeded 300 MPa, owing to the fine grain size. However, the strength of the composite was lower than that of the alloy without β-TCP, suggesting that the dispersion of β-TCP had no effect on strengthening.

3) The plastic workability at elevated temperatures was characterized under compression. From the viewpoint of strain rate sensitivity of the flow stress and texture change during deformation, the composite behaved in a superplastic manner at temperatures of \(~548\) K.

Acknowledgments

This work was supported by JSPS KAKENHI Grant Numbers JP16K06809 and JP17H01327.

REFERENCES

7) N. Ikeo, H. Kawasuki, H. Watanabe and T. Mukai: submitted.