Research Paper

Biodegradable Mg–Zn–Y alloys with long-period stacking ordered structure: Optimization for mechanical properties

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To optimize the mechanical properties for biodegradable orthopedic implant, microstructures and tensile properties of Mg–Zn–Y alloys containing long period stacking ordered (LPSO) phase were investigated. For the as-cast Mg\textsubscript{100–3x}Zn\textsubscript{x}Y\textsubscript{3} alloys, volume fraction of 18R LPSO phase increases with increasing the contents of Zn and Y. Mg\textsubscript{97}Zn\textsubscript{1}Y\textsubscript{2} alloy exhibits the optimal combination of strength and plasticity. Substitution of bioactive element Ca for Y in the Mg\textsubscript{97}Zn\textsubscript{1}Y\textsubscript{2} does not favor the formation of LPSO phase, but involving the formation of Mg\textsubscript{2}Ca phase. By micro-alloying with Zr as grain refinement agent, morphology of α-Mg in the Mg\textsubscript{96.83}Zn\textsubscript{1}Y\textsubscript{2}Zr\textsubscript{0.17} alloy is changed into the equiaxial shape, together with a significant refinement in grain size to 30 μm. It brings about an improvement not only in strength but also in plasticity, in contrast to the Zr-free alloy. In comparison with the as-cast state, warm-extruded alloys manifest significantly improved properties not only in strength but also in plasticity due to the refinement of α-Mg grain by dynamic recrystallization and the alignment of LPSO phase along extrusion direction.

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1. Introduction

Over the past decade, in terms of corrosion features in physiological environment, a considerable attention has been paid to the magnesium alloys as biodegradable material (Hort et al., 2010; Li et al., 2008; Staiger et al., 2006; Witte, 2010; Witte et al., 2008). In comparison with the stainless steels and titanium alloys, biodegradable magnesium alloys are identified as revolutionizing biomaterials (Yun et al. (2009)). Their potential applications are expected at least in several aspects such as vascular stent (Erbel et al., 2007; Mani et al., 2007), orthopedic implants (Li et al., 2008; Willbold et al., 2011; Witte et al., 2005) and tissue engineering scaffold (Geng et al., 2009). It should be noted that, from the perspective of mechanical properties, requirement for the properties of alloy is significantly dependent on the application target. Considering the orthopedic application, in contrast to the stainless steels and Ti alloys, key advantage of magnesium alloys is degradable and absorbable in human body, rather than permanently resident. Then, a second surgery is not necessary, to remove the temporary device after the tissue healed well. Meanwhile, magnesium alloys have low mass density of 1.7–2.0 g/cm\textsuperscript{3} and elastic modulus of about 40 GPa, which are well matched with those of natural bone. It is expected to limit the osteolysis due to the stress shielding effect induced by severe mismatch in modulus (Nagels et al., 2003; Staiger et al., 2006). Compared with biodegradable polymers...
Currently used in clinical practice (Bostman, 1991), magnesium alloys manifest significant advantages including the high strength and ductility, and the reliability for load-bearing implant application. In addition, magnesium alloys are convenient for processing of the machining and sterilization. In the sense of long-term safety, degradation products in physiological environment of magnesium alloys are alkaline rather than acid as the polymer does. As revealed recently (Witte et al., 2005), degraded magnesium ion has a significant effect to stimulate the growth of new bone tissue, to make damaged bone tissue healing more quickly. For orthopedic implants such as screws, pins and plates for fixation, the desirable implants should have a strength as high as possible and an acceptable ductility, together with a controllable degradation rate. As an important issue, alloying elements in the alloy and corrosion products must be non-toxic during degradation in the body. Currently, commercially-available magnesium alloys with high strength, such as AZ31, AZ91 and WE43, contain toxic elements in some extents. For instance, aluminum which plays a role for solid-solution strengthening α-Mg phase is a neurotoxicant, led to a risk for Alzheimers disease (El-Rahman, 2003). Toxicity of rare-earth elements remains in debate. It is believed that accumulation of cerium or praseodymium in the body probably causes severe hepatotoxicity (Nakamura et al., 1997). In addition, fast degradation rate in physiological environment brings about the problems of hydrogen release and loss of mechanical integrity before healing. Therefore, it is of interest to design new magnesium alloys to meet the requirement of each special clinical application.

On the other hand, magnesium alloys with long period stacking ordered (LPSO) phase are reported to have excellent mechanical properties, and the major LPSO structure are 18R and 14H structure (Kawamura and Yamasaki, 2007). The LPSO phase has a similar a-axis with hcp Mg, but its stacking periodicity is lengthened along the c-axis (Luo and Zhang, 2000). Therefore, in the electron diffraction spots of LPSO phase, it presents a series of additional spots besides the spots of hcp Mg. Moreover, the LPSO phase is also a chemically ordered structure, in which the solute atoms are enriched in four atomic layers on the closely packed plane at six-period intervals for 18R structure or seven for 14H structure. So far, LPSO phase has been found to be formed in ternary Mg–Zn–RE (RE¼Y, Gd, Tb, Dy, Ho, Er, Tm) alloy (Kawamura and Yamasaki, 2007). Strengthening mechanism of LPSO phase was explained according to following issues. First of all, the presence of LPSO phase in α-Mg matrix plays a role of increasing the critical resolved shear stress of basal slip and activates non-basal slip (Matsuda et al., 2005a). Next of LPSO phase was explained according to following issues. (Kawamura and Yamasaki, 2007). The LPSO phase on mechanical properties was investigated. Second, substitution of Ca for Y in Mg97Zn1Y2 alloy on the formation of LPSO phase is attributed to large atomic size difference (−0.16 Å), and good biocompatibility. Firstly, by tuning the concentration of Zn and Y in the alloy, the effect of volume fraction of LPSO phase on mechanical properties was investigated. Secondly, substitution of Ca for Y in Mg97Zn1Y2 alloy on the formation of LPSO phase was examined, as well as the influence on mechanical properties. Based on the alloys with optimal mechanical properties, influence of grain refinement by micro-alloying with Zr on mechanical properties was examined. Finally, selecting the typical alloys for warm-extrusion, the microstructure and mechanical properties of the extruded alloys are investigated.

2. Experimental

Commercial pure Mg (99.99%) and Zn (99.999%) with high purity, and intermediate alloys of Mg–30%Y (mass percentage, wt%) and Mg–30%Zr (wt%) were used as starting materials. Alloy ingots with nominal composition in quantities of about 100 g were induction-melted in a graphite crucible under an inert atmosphere. The molten alloys were then cast into the steel mould. In addition, ingots in quantities of 5–6 kg were prepared as well for the warm extrusion. For these large-sized ingots, the pure elements and intermediate alloys were melted in electrical resistance furnace using mild steel crucible protected by mixture gases of N2 and CO2. The alloy melt was held for 30 min at 973 K and then poured into a steel mould with a cavity diameter of 130 mm, which is preheated to 473 K. Warm extrusion of as-cast ingots were performed at 723 K, using an extrusion ratio of 42:1 and extrusion rate of 3 mm/s at atmosphere.
For the observation of optical microscopy (OM) and scanning electron microscopy (SEM), samples cut from the ingots were mechanically polished and then etched with a solution of the picric acid of 5 g, acetic acid of 5 ml, distilled water of 10 ml and ethanol of 100 ml. OM observation was conducted on the Leica optical microscope. SEM characterization was performed on a Quanta 600 (FEI, the Netherlands) microscope. Crystalline phases in the alloys were identified using X-ray diffraction (XRD), at a Rigaku D/max 2400 diffractometer (Tokyo, Japan) with monochromated Cu Kα radiation. Average grain size of the alloys was measured using the linear intercept method. Volume fraction of the LPSO phase in microstructure of the alloys was estimated by image analyzer. Transmission electron microscopy (TEM) was used for characterizing the morphology and phase identification with JEM-2000FXII (Tokyo, Japan). For TEM observation, disks with a thickness of about 300 μm were cut from bulk sample, then ground to a thickness of about 50 μm, and finally thinned into foil with argon ion milling.

Mechanical properties of the alloys were evaluated by standard tensile test at room temperature. Cylindrical tensile bars with a diameter of 3 mm and gauge length of 15 mm were cut from the ingots or extruded bar along the extrusion direction. For the as-extruded specimens, loading axis was taken to be parallel to the extruded direction. Tensile tests were carried out on a Zwick/Roell Z050 Testing System with a strain rate of 1 × 10⁻³ s⁻¹. An extensometer with a gauge length of 15 mm was used to measure the strain response. At least three samples were tested for each state.

3. Results

3.1. Formation of LPSO phase in as-cast alloys

Fig. 1 shows the XRD patterns of as-cast alloys with a nominal composition of Mg₈₀₀₋₃ₓ(Zn₁Y₂)ₓ (x=1, 2, 3). As indicated, all of the alloys are identified as two phases, α-Mg and Mg₁₂YZn phase. With increasing the Zn and Y contents in the alloys as a fixed ratio of 1:2 for Zn:Y, diffraction intensities of Mg₁₂YZn phase gradually increase, indicating the increase of volume fraction of Mg₁₂YZn phase. As the representative, Fig. 2(a) displays a TEM bright field image of the Mg₉₇Zn₁Y₂ alloy. In terms of the contrast, a phase as a bright region marked as A, and a lamellae phase as a dark region marked as B are observed. For the areas of A and B, corresponding selected area electron diffraction (SAED) patterns taken along the ⟨1120⟩ direction are shown in Fig. 2(b) and (c), respectively. From the SAED pattern in Fig. 2(b), region A is identified to be α-Mg with hcp structure. However, as shown in Fig. 2(c), additional reflection spots array at positions n/6 (n is an integer) of the (0 0 0 2) Mg plane, indicating that the Mg₁₂YZn phase (region B) is a typical structure of 18R LPSO (Zhu et al., 2010).

Fig. 3(a)–(d) show backscattered SEM images of as-cast Mg₈₀₀₋₃ₓ(Zn₁Y₂)ₓ (x=1, 2, 3) alloys. In all cases, microstructure in the alloys consists of α-Mg phase with dark contrast, and 18R LPSO phase with bright contrast. At x=1, as seen in Fig. 3(a), fraction of LPSO phase is estimated to be about 25 vol%. Dendritical LPSO phase precipitates in the area between secondary dendrite arm of α-Mg dendrite. Average grain size of α-Mg dendrite is around 150 μm, with secondary dendrite arm spacing of about 25 μm. At x=2, fraction of LPSO phase increases up to ~48 vol%. Grain size of α-Mg remains at about 110 μm, without distinct secondary dendrite as at x=1. LPSO phase grows up into irregular block-like shape. At x=3, fraction of LPSO phase increases up to ~66 vol%. Grain size of α-Mg is reduced to be about 80 μm. LPSO phase becomes the matrix and no secondary dendrite forms.
Based on the Mg$_{97}$Zn$_1$Y$_2$ alloy, element Ca is used to substitute Y in the alloys. Fig. 4 shows XRD patterns of as-cast Mg$_{97}$Zn$_1$Y$_2$-$y$Ca$_y$ ($y=0, 0.5, 1, 1.5$) alloys. With increasing Ca content in the alloys, intensity of diffraction lines for Mg$_{12}$YZn LPSO phase is mitigated. It is accompanied by gradual increase in intensity of diffraction lines for Mg$_2$Ca phase. In the case of the $y=0.5$ and $y=1$, Mg$_2$Ca phase co-exists with LPSO phase. Nevertheless, LPSO phase is no longer detectable at $y=1.5$, whereas Mg$_2$Ca phase exists as the second phase in the alloy only. At $y=0.5$ and $y=1$, microstructures of two alloys are roughly similar. Fig. 5(a) displays a TEM bright-field image of Mg$_{97}$Zn$_1$Y$_1$Ca$_1$ alloy. As observed in Fig. 5(a), three phases present different contrast, marked as A for bright region, B for lamella-structure region and C for spherical-structure region, respectively. Fig. 5(b)–(d) show SAED patterns of these three phases taken along the $\langle 1 1 \overline{2} 0 \rangle$ direction for the areas marked with A, B and C respectively.
atom is large and heat of mixing between Ca and Mg is very negative.

Furthermore, minor amount of Zr is added in the Mg$_{97}$Zn$_1$Y$_2$ alloy as grain refiner. For a comparison Fig. 6(a)–(d) show optical micrographs of as-cast Mg$_{97}$Zn$_1$Y$_2$ and Mg$_{96.83}$Zn$_1$Y$_2$Zr$_{0.17}$ alloys. As indicated, after micro-alloying with Zr, morphology of α-Mg grain changes from dendrite to equiaxed shape, together with the refinement of grain size from 150 μm down to 30 μm. In contrast to the Zr-free alloy, LPSO phase distributes at grain boundary of α-Mg phase Zr-containing alloy. The volume fraction and grain size of LPSO phase remain unchanged. In terms of the XRD pattern (not shown here), Mg$_{96.83}$Zn$_1$Y$_2$Zr$_{0.17}$ alloy also consists of two phases, α-Mg phase and Mg$_{12}$YZn phase, which is the same as the Mg$_{97}$Zn$_1$Y$_2$ alloy, as seen in Fig. 1. In other words, micro-alloying with Zr addition only plays a role of grain refinement for α-Mg matrix.

3.2. Mechanical property of as-cast alloys

As the representative, Fig. 7 displays engineering stress-strain curves of as-cast Mg$_{97}$Zn$_1$Y$_2$ and Mg$_{96.83}$Zn$_1$Y$_2$Zr$_{0.17}$ alloys in tension. In contrast to the Zr-free alloy, Mg$_{96.83}$Zn$_1$Y$_2$Zr$_{0.17}$ alloy exhibits higher yield strength and larger plasticity. As a result, adding Zr as grain refiner has a significant effect to the strength and plasticity.

Fig. 8 shows a plot of the strength and elongation against content of the Zn and Y as well as volume fraction of LPSO phase in Mg$_{100-3x}$Zn$_1$Y$_3$X$_x$ ($x=1$, 2, 3) series as-cast alloys. As indicated, with increasing the Zn and Y contents, tensile yield strength ($\sigma_0$) of the alloy increases from 136 MPa at $x=1$ to 157 MPa at $x=3$, increased by ~15%. Ultimate tensile strength (UTS) of the alloy first increases from 218 MPa at $x=1$ to 236 MPa at $x=2$ with an increase of ~9%, and then decreases to 221 MPa at $x=3$. On the contrary alloy elongation is drastically reduced, from 7% at $x=1$ to 1% at $x=3$. Consequently, the LPSO phase does have a significant effect of strengthening the magnesium alloys, but accompanied by degradation in plasticity.

Fig. 9 shows a plot of the strength and elongation against Ca concentration in Mg$_{97}$Zn$_1$Y$_2$Ca$_y$ ($y=0$, 0.5, 1) series as-cast alloys. As the Ca content increases in the alloys, yield strength increases from 136 MPa for the Ca-free alloy up to 146 MPa at 0.5% Ca with an increase of ~7%, but subsequently decreases to 116 MPa at $y=1$. The UTS is slightly reduced, from 218 MPa at $y=0$ to 205 MPa with a reduction of 5% for
Mg$_{97}$Zn$_1$Ca$_1$ alloy. The elongation decreases from 7% to 5% without remarkable change on further increasing the Ca content. When the Ca content is less than 0.5%, the strength increase, associated with deterioration in the plasticity. When the Ca content is higher than 1%, deterioration in both strength and plasticity is severe.

3.3. Microstructure and mechanical property of as-extruded alloys

To further improve the mechanical properties, microstructure and tension properties of the warm-extruded Mg$_{97}$Zn$_1$Y$_2$ alloys with and without Zr addition were examined. Fig. 10(a)–(b) show optical micrographs of as-extruded Mg$_{97}$Zn$_1$Y$_2$ alloy, taken from the transverse and longitudinal sections along the direction of extrusion, respectively. As seen in Fig. 10(a), subjected to the warm-extrusion, distribution of LPSO phase becomes more uniform, in the form of plate-like or block-like shapes at the transverse section. As shown in Fig. 10(b), the LPSO phase aligns along the direction of extrusion at the longitudinal section. Moreover, the $\alpha$-Mg grains are significantly refined due to dynamic recrystallization, with average grain size of about 17 $\mu$m. In contrast, the grains of LPSO phase distribute in the fiber-like form with a thickness of 5–15 $\mu$m and length of about 100 $\mu$m. Fig. 11 shows the XRD patterns of as-extruded Mg$_{97}$Zn$_1$Y$_2$ alloy, taken from the transverse and longitudinal sections along the direction of extrusion. As seen in the pattern (a), intensities of (1 0 1 -1 0) diffraction plane is stronger at the transverse section, whereas stronger one become (0 0 0 2) basal plane at the longitudinal section in the pattern (b). As a result, it is evident that warm-extrusion processing introduces a basal
Since dynamic recrystallization happens mainly in the α-Mg phase, crystallographic orientation of α-Mg grains is randomly arranged. Thus, formation of the texture is probably caused by the deformation of LPSO phase. In fact, such a texture was also found by Yamasaki et al. (2011), which was explained by that strong texture easily happens in the LPSO phase owing to their crystal rotation during extrusion. Similar microstructure and texture are observed also in the as-extruded Mg_{96.83}Zn_{1}Y_{2}Zr_{0.17} alloy.

Fig. 12 shows a diagram of a comparison of the as-extruded alloys with the as-cast alloys for the tensile strength and elongation. In comparison with the as-cast alloys, extrusion deformation significantly enhances both of the strength and plasticity in two states for the alloys with and without Zr. Subjected to the extrusion, tensile yield strength of Mg_{97}Zn_{1}Y_{2} alloy increases by ~25%, whereas the UTS increases by ~33%, together with an increase by a factor of three in elongation. For the as-extruded alloy, no obvious difference between Mg_{97}Zn_{1}Y_{2} and Mg_{96.83}Zn_{1}Y_{2}Zr_{0.17} alloys is present.

4. Discussion

4.1. Formation of LPSO phase

As well documented, LPSO structure in Mg alloys are present in several forms including 18R, 14H, 10H and 24R (Matsuda et al., 2005b). The 18R type of LPSO structure usually appears in the ingot cooled by conventional rates because it is an equilibrium phase at room temperature, while the 14H type of structure is usually present after solid-solution treatment (Kawamura and Yamasaki, 2007; Zhu et al., 2010). In the current case, we found that the 18R type of LPSO structure is formed in the as-cast Mg_{97}Zn_{1}Y_{2} alloy. Increasing the alloying elements of Zn and Y does not change the solidification path in all Mg_{100-x}(Zn_{1}Y_{2})x alloys, L-α-Mg+LPSO.

From the view of atomic size, Ca (r_{Ca}=0.197 nm) is comparable to Y (r_{Y}=0.182 nm), with an atom radius larger than that of Mg (r_{Mg}=0.16 nm) atom (Takeuchi and Inoue, 2005). Meanwhile, the Ca has negative heat of mixing with the Zn and Mg. However, our results indicate that Ca addition in the alloy does not play a role to enhance the formation of LPSO phase. Complete substitution of Ca for Y in the alloy gives rise to the disappearance of LPSO phase, as shown in Fig. 4. Thus, our findings do not support the suggestion that the formation of LPSO phase is associated with large atom size mismatch with Mg and negative heat of mixing between the components (Amiya et al., 2003). Recently, Kawamura and Yamasaki (2007) proposed that adding the elements with large solid solubility in the Mg probably favors to the formation of LPSO phase in Mg-Zn-RE alloys. It is noteworthy that lower solid solubility of Ca in Mg is consistent with this suggestion. Consequently, the LPSO phase formed in Mg_{97}Zn_{1}Y_{2}Ca_{0.5} and Mg_{97}Zn_{1}Y_{2}Ca_{1} alloys is mainly due to the presence of Y. In these Ca-containing alloys, solidification path is the same as in the Ca-free alloy besides the formation of Mg_{2}Ca intermetallics. In the microstructure, the LPSO phase and Mg_{2}Ca phase alternatively arrange in the lamellar form.

During solidification of the melt, dendrite grains of α-Mg with low solute concentration precipitate as primary phase, and then the remaining melts with a high concentration of solutes solidify as the LPSO phase into the gap of dendrite arms. α-Mg grains grow into large dendrite with secondary dendrite arm in the alloy only in the case of lower fraction of LPSO phase. With increasing the concentration of alloying elements, melt composition shifts towards the eutectic point. It suppresses the formation of secondary dendrite, and the precipitation of LPSO phase is in large-sized block as the matrix.

4.2. Strengthening effect via grain refinement

As well known, grain refinement is conventional approach to strengthen the alloys without sacrificing the ductility. Relationship between strength and grain size is empirically described as Hall–Petch relation \( \sigma_y = \sigma_0 + k d^{-1/2} \). In this equation, the value of \( k \) represents the extent of enhancement in yield strength with the reduction of grain size. In the magnesium alloys, strengthening effect is more sensitive to the grain size, because the \( k \) value of magnesium is high (\( k=2–15 \text{ MPa/mm}^{1/2} \)) (Barnett et al., 2004). For as-cast alloys, alloying with minor addition Zr has significant effect to refine the grain size. Refinement validity of a given element can be evaluated by growth restriction factor (GFR) (Lee et al., 2000).

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**Fig. 12** – Strength and elongation of Mg_{97}Zn_{1}Y_{2} and Mg_{96.83}Zn_{1}Y_{2}Zr_{0.17} alloys in as-cast and as-extruded state.
Zr element of GFR=38 has been recognized to be the most effective grain refiner for the Mg alloys.

In the as-cast Mg_{96.83}Zn_{1}Y_{2}Zr_{0.17} alloy, micro-alloying with Zr element leads to a transition of α-Mg dendrites into equiaxed crystals in the microstructure. Because Zr atoms in the melt provide abundant nucleation sites for α-Mg grain, it made α-Mg easier to form as equiaxed crystals. In contrast to the primary dendrite in the Mg_{97}Zn_{1}Y_{2} alloy, grain size of α-Mg in Mg_{96.83}Zn_{1}Y_{2}Zr_{0.17} alloy is refined from 150 μm to 30 μm. It is such microstructure that yields a combination of strength and plasticity in Mg_{96.83}Zn_{1}Y_{2}Zr_{0.17} alloy, superior to the Zr-free Mg_{97}Zn_{1}Y_{2} alloy.

As shown in Fig. 12, both the strength and plasticity are significantly improved after warm-extrusion. During the extrusion, plastic deformation at the interface between the Mg matrix grain and LPSO phase is incompatible, since the LPSO phase exhibits strong plastic anisotropy (Hagihara et al., 2010b). It yields a large stress concentration at the interface. Then, dynamically recrystallization only occurs within the “soft” α-Mg grains as the deformation zones. Subject to the recrystallization in as-extruded Mg_{97}Zn_{1}Y_{2} alloy, α-Mg grains manifest equiaxed shape and small grain size of about 30 μm. It brings about the improvement of the mechanical properties after extrusion deformation. Our results indicate that warm-extrusion is more crucial to improve the plasticity, as indicated by an elongation of 30% for the extruded alloy.

4.3 Effect of LPSO phase on the strength and plasticity of alloys

In the Ca-containing alloys, although Mg_{2}Ca phase precipitates as additional secondary phase besides LPSO phase, volume fraction of α-Mg is almost equal to the case of Mg_{97}Zn_{1}Y_{2} alloy. No obvious difference in grain size of α-Mg dendrite is observed between the alloys with and without Ca. As indicated in Section 3.2, the mechanical properties of Ca-containing alloys are inferior to those of Mg_{97}Zn_{1}Y_{2} alloy. In other words, it indicates that the effect of strengthening and toughening from Mg_{2}Ca phase are incompetent to LPSO phase, which mainly result from the good deformability of LPSO phase. Plastic deformation in the LPSO phase operates via two routes, (0 0 0 1) basal slip and kinking deformation (Hagihara et al., 2010b). In as-cast alloys, crystal orientation of LPSO grains is random. Then, it is certain that some LPSO grains with a large Schmid factor for the (0 0 0 1) <1 1 2 0> basal slip exist. Consequently, these basal slips of LPSO phase are responsible for its large plasticity.

As noticed, effects of strengthening and toughening of LPSO phase depend on the fraction of LPSO phase in the alloy, as shown in Fig. 7. As shown by Hagihara et al. (2010a) grain size effect of LPSO phase on the strength in Mg alloys also follows to the classical Hall–Petch relation. It means that the morphology and grain size of LPSO phase are key factors on the mechanical properties. In the Mg_{97}Zn_{1}Y_{2} alloy, LPSO phase precipitates in the form of thin plate-like phase dispersed in the secondary dendrite. For the Mg_{97}Zn_{1}Y_{2} alloy, however, LPSO phase assemblies to thick block-like shape as the matrix, together with large length and thickness. Consequently, global properties of the alloys are controlled by a combination of the grain size and fraction of LPSO phase. With increasing the fraction of LPSO phase, yield strength of the alloys increases slightly, while the plasticity dramatically decreases.

Since the LPSO phase has a large ratio of critical resolved shear stress (CRSS) of basal slip to non-basal slip (Yamasaki et al., 2011), twin deformation and dynamic recrystallization is difficult under extrusion deformation. As a result, LPSO phase has a strong propensity to create the basal texture, in which the c axis of LPSO grains is perpendicular to the direction of extrusion. Such unique texture plays an important role responsible for the deformation of LPSO phase. Under the tension loading condition, loading axis of the specimen is parallel to the extrusion direction of ingot. Then, the loading axis is parallel to the (0 0 0 1) basal plane of LPSO phase. It results in that the Schmid factor for the (0 0 0 1) <1 1 2 0> basal slip is negligible, and that the operation of basal slip is suppressed in the as-extrusion specimen, and kinking deformation occurs. Hagihara et al. (2010b) investigated the deformation mode of LPSO phase in the alloys prepared by directional solidification during compression test, and proposed the kinking-deformation mechanism of LPSO phase. Elastic buckling in LPSO phase, which occurred in the region with high stress, induces the creation of basal dislocation pairs with an opposite Burgers vector, and their motion in opposite directions leads to the formation of deformation kink bands. In addition, Yamasaki et al. (2011) suggested that kinking deformation contributes to the major deformation in tensile loading. Under the kinking deformation, crystal orientation of LPSO grain changed. In this way, the basal slipping can be operated after large plastic deformation, which is responsible for the large plasticity of the alloy.

4.4 Comparison with other biodegradable magnesium alloys

Fig. 13(a) and (b) display diagrams to summarize the yield strength and elongation of some typical magnesium alloys for biomedical applications in the as-cast and extruded state, respectively. As indicated, in all cases, strength and elongation of the as-extruded alloys are higher than those as-cast alloys, except for as-extruded Mg–1Ca binary alloy. As indicated in Fig. 13(a), elongation of as-cast alloys is less than 15%, and T6 treated WE43 alloy manifests the highest yield strength at 185 MPa together with elongation of ~7% (Avedesian, 1999). Our Mg_{96.83}Zn_{1}Y_{2}Zr_{0.17} alloy exhibits good comprehensive mechanical properties, comparable to the as-extruded Mg–1Ca binary alloy. For the group of as-extruded alloys, as seen in Fig. 13(b), ZYbK520 alloy (Gunde et al., 2011) has the highest yield strength of 350 MPa. Nevertheless, the current Mg_{97}Zn_{1}Y_{2} alloy has the largest elongation of 30%, which can rival to ZW21 alloy (Hanzi et al., 2009). In addition, the alloy has high uniform elongation of 21%.

As shown in Section 3.2, in the alloys with Ca substitution, there is only a modest reduction of strength and a rather more significant reduction in elongation. Considering the advantages in biocompatibility, such a change in mechanical properties is acceptable. Finally, besides the mechanical properties, degradation performances under simulated physiological condition for the Mg–Zn–Y alloys with LPSO microstructure are investigated as well in the additional work, to be presented elsewhere.
5. Conclusions

In as-cast Mg_{100-3x}(Zn_{x}Y_{2}) alloys, volume fraction of 18R LPSO phase increases with increasing the contents of Zn and Y, which has a strong effect on plasticity and little effect on yield strength. Substitution of bioactive element Ca for Y in the Mg_{97}Zn_{2}Y_{2} does not favor the formation of LPSO phase, but involving the formation of Mg_{2}Ca phase. It indicates that large atom-size mismatch and negative heat of mixing between alloying elements and Mg are not necessary issues as previously claimed. By micro-alloying with Zr as grain refinement agent, morphology of α-Mg in the Mg_{96.83}Zn_{1}Y_{2}Zr_{0.17} alloy is changed into the equiaxial shape, together with a significant refinement in grain size to 30 μm. It brings about an improvement not only in strength but also in plasticity, in contrast to the alloy without Zr. In comparison with the as-cast state, warm-extruded alloys manifest significantly improved properties not only in strength but also in plasticity due to the refinement of α-Mg grain by dynamic recrystallization and alignment of LPSO phase along the extrusion direction. The yield strength and elongation of warm-extruded Mg_{97}Zn_{2}Y_{2} alloy is 170 MPa and 30%, respectively, which is a promising candidate as degradable orthopedic implants.

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