Research on Preparation and Extrusion Process of Magnesium Calcium Alloy

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Abstract. Magnesium calcium alloy has attracted more and more attention in the medical metal field as it has the similar mechanical properties with human bone and biodegradable property. In this paper, the preparation and modification of the alloy were studied. It was found that, extrusion parameters had an important impact on the quality of product in extrusion process, like extrusion ratio, extrusion temperature and extrusion speed. Vickers hardness, and tensile mechanical properties test and bending mechanical properties were carried on as-cast and extruded alloy to obtain mechanical parameters, the mechanical property of MgCa0.8 alloy greatly improved after extrusion, and the extrusion process can be applied to other calcium content alloys.

1. Introduction
Magnesium (Mg) alloy attracts the attention of scholars because of its good mechanical and biodegradable properties [1]. Medical magnesium alloy applied to the field of bone fracture plate which replaces the original non degradable metal materials will effectively avoid the secondary damage caused by removing the plate after recovery [2].

Calcium (Ca) is one of a small number of alloying elements that can be included in implants. Binary magnesium calcium alloy has better corrosion resistance as the accession of calcium element, causing grain refinement. As the result of this similarity, it stimulates bone cells to attack the implant surface and make proper bonding [3, 4].

As a substitute of biomedical devices, magnesium calcium alloy is bound to be one of the main development directions of biomedical implants. According to the mechanical properties of magnesium calcium alloys and corrosion resistance, scholars carried out a series of studies [5-7]. These findings suggest that, we can improve the densification microstructure of alloy materials to control the content of Ca, thus improving the mechanical properties of magnesium alloy and corrosion resistance. It is found that MgCa0.8 will be the most suitable magnesium calcium alloy in the field of orthopedics implantation [8-10].

2. The preparation of magnesium calcium alloy
Magnesium ingot and MgCa15 master alloy were used for smelting in the experiment within the resistance furnace. The target alloys prepared of smelting were MgCa0.8. Follows were the steps:

(1) Calculated and prepared the raw materials for smelting.

(2) Raised the temperature of the furnace to 730°C and stopped for half an hour as the temperature reached to 400°C and then protection gas was access into the furnace. The crucible with magnesium ingot was put into the furnace as the temperature reached to 500°C.
(3) MgCa15 master alloy was added after the magnesium ingot melted.
(4) Adjusted the temperature to 720℃ and stirred the crucible well after MgCa15 master alloy melt.
(5) Skimming was operated in the atmosphere of protection gas and the melted metal was poured into preheated graphite mold. The parts were taken out after the mold had colt in room temperature.

Since the chemical character of magnesium is very active and it was prone to oxidation and burning, which made the melting process must be under the environment of protection gas mixed with CO₂ and SF₆.

Inductively Coupled Plasma Emission Spectrometer (Optima 2100 DV) generated by Perkin Elmer was used to detect the composition of casting alloy. The protection gas mixed with CO₂ and SF₆ could stop the oxidation in the process of melting, but it could not stop evaporation of melted magnesium and calcium. So some difference appeared between tested value and calculated value. The right ratio of raw materials was continued to explore and then casted the alloys. Tested composition of Ca was 0.78 wt. %

3. Orthogonal Extrusion Experiment of magnesium calcium alloy

Extrusion parameters have an important impact on the quality of product in extrusion process, extrusion ratio, temperature and extrusion speed which had large influence on extrusion effect were chosen for orthogonal experiment.

The extrusion ratio was 8.1, 15.9, 29.5, extrusion temperature was 250℃, 300℃, 350℃, and extrusion speed was 10mm/s, 30mm/s. The level of 10mm/s was considered as a quasi-level in the orthogonal experiment which used L₉ (3³) orthogonal table. Table 1 shows the experiment plan, and the casting parts were treated at 370℃ for 6 hours for homogenization and turning to remove the oxide layer before experiment.

**Table 1. Orthogonal experiment plan**

| No. | Ratio | Temperature /℃ | Speed /mm • s⁻¹ | No. of product bar |
|-----|-------|-----------------|-----------------|-------------------|
| 1   | 8.1   | 250             | 10              | A1                |
| 2   | 8.1   | 300             | 10              | A2                |
| 3   | 8.1   | 350             | 30              | A3                |
| 4   | 15.9  | 250             | 10              | B1                |
| 5   | 15.9  | 300             | 30              | B2                |
| 6   | 15.9  | 350             | 10              | B3                |
| 7   | 29.5  | 250             | 30              | C1                |
| 8   | 29.5  | 300             | 10              | C2                |
| 9   | 29.5  | 350             | 10              | C3                |

Phase analysis, mechanical property test and corrosion resistance test were carried on for a suitable extrusion process.

3.1. X-ray Diffraction Analysis

XRD analysis of the sample was used D8-ADVANCE type X-ray diffract meter generated by Brooks. Follows were its working parameters: copper target, operating voltage40kV, operating current 100mA, scanning speed of 4 °/min, scanning range 30°~ 90°.
3.2. Mechanical Properties Tests
In order to study the effect of different extrusion process on the mechanical properties of the alloy, Vickers hardness, and tensile mechanical properties test and bending mechanical properties were carried on as-cast and extruded alloy to obtain mechanical parameters.

3.2.1. Vickers Hardness Test. Samples taken from different alloys respectively, were tested on digital micro hardness tester with applied pressure of 50N after mosaic, grinded and polished. The hardness would be the average of 5 points which tested on the same condition. Figure 2 shows the digital micro hardness tester.

Figure 3 shows the influence of different extrusion process on the Vickers hardness of MgCa0.8. It was found that the hardness decreased and then increased with the increase of extrusion temperature, and a sharp decrease of 7.2% with the temperature reached 300°C from 250°C according Figure 3(a). It was the same trend with the increase of extrusion ratio in the basis of Figure 3(b). The hardness reached the maximum of 67.4 HV as the extrusion ratio was 8.1, extrusion temperature was 250°C, and extrusion speed was 10mm /s, which was 21% higher than that of cast alloy.

Figure 2. Digital micro hardness tester
3.2.2. Tensile and Bending Test. The tensile and bend test were carried out on WDW-100A type electronic universal testing machine. Figure 4 illustrated the dimension of tensile and bending samples, which were produced by wire cutting machine.

It was observed that the stress of casting alloy reached the yield point and fracture occurred abruptly, which showed a large brittleness. On the contrary the extruded alloy was broken after reaching yield point and then subjected to a certain length of elongation, which indicated the alloy obtained a certain degree of toughness during extrusion process. Table 2 listed the tensile parameters of as-cast and extruded alloys, from which it was found that the tensile strength of extruded alloy was significantly higher than that of the as-cast alloy. The maximum tensile strength was 245.42MPa and the maximum elongation was 12.32%, which was 477% and 254% higher than that of casting alloy respectively, resulted from the recrystallization and gain refinement and secondary phase refinement and distribution.

![Figure 3](image3.png)  
**Figure 3.** Influence of different extrusion process on Vickers hardness of MgCa0.8

![Figure 4](image4.png)  
**Figure 4.** Samples of mechanical properties test
Table 2. Tensile mechanical parameters of MgCa0.8 alloys

| Samples | Tensile strength $\sigma_b$/MPa | Elongation $\delta$/% | Elastic modulus $E$/GPa |
|---------|-------------------------------|----------------------|------------------------|
| casting | 42.50                         | 3.48                 | 31.58                  |
| A1      | 212.71                        | 8.54                 | 45.22                  |
| A2      | 215.63                        | 12.32                | 46.51                  |
| A3      | 182.78                        | 10.38                | 42.76                  |
| B1      | 245.42                        | 8.08                 | 51.18                  |
| B2      | 198.13                        | 11.60                | 41.35                  |
| B3      | 220.42                        | 8.91                 | 46.02                  |
| C1      | 185.00                        | 10.44                | 42.54                  |
| C2      | 232.71                        | 8.34                 | 48.13                  |
| C3      | 234.17                        | 7.44                 | 35.77                  |

Figure 5 shows the SEM pictures of casting MgCa0.8 alloy tensile fracture surface. As could be seen from figure 5(a), the surface was relatively rough as some short and curved tearing edge on. The gains were pulled up entirely in local area and crack expanded along gain boundary, with the characteristic of intergranular fracture. The comparison of matrix and precipitation phase of as-cast alloy could be clearly seen in figure 5(b). Precipitation phase Mg$_2$Ca was distributed along grain boundary and scattered within grain, as the white lines and sporadic white points in the photo were Mg$_2$Ca. The crack expanded along with the grain boundary revealing the brittleness of casting MgCa0.8 alloy.

Figure 6 shows the SEM pictures of extruded MgCa0.8, from which it was unable to intuitively distinguish the difference of matrix and precipitation phase, different from pictures of as-cast alloy, indicating that the precipitation phase experienced a greater degree of refinement along with the recrystallization. The pictures also showed the deformation of the grain after extrusion. Precipitation phases scattered were pulled off the matrix entirely in the process and displayed as micro-spherical morphology.

(a)  
(b)  

Figure 5. SEM pictures of casting Mg-Ca alloy tensile fracture surface  
((a) Electronic scanning pictures (b) Back scattered pictures)
Figure 6. SEM pictures of extruded MgCa0.8 alloy tensile fracture surface

Table 3 listed the bending parameters of as-cast and extruded alloys, from which it was found that the bending strength of extruded alloy was significantly higher than that of the as-cast alloy. The maximum bending strength was 379.2MPa, which was 405.6% higher than that of casting alloy, resulted from the recrystallization and gain refinement and secondary phase refinement and distribution. There was some difference between bending parameters of different extruded alloys because of the different degree of matrix and phase refinement due to dissimilar extrusion process.

Table 3. Bending mechanical parameters of MgCa0.8 alloys

| Samples | Bending strength $\sigma_{bz}$/MPa | Maximum bending force /KN |
|---------|----------------------------------|---------------------------|
| Casting | 67.50                            | 0.13                      |
| A1      | 379.20                           | 0.79                      |
| A2      | 360.02                           | 0.75                      |
| A3      | 292.80                           | 0.61                      |
| B1      | 384.04                           | 0.80                      |
| B2      | 314.40                           | 0.66                      |
| B3      | 362.44                           | 0.76                      |
| C1      | 285.62                           | 0.60                      |
| C2      | 348.04                           | 0.73                      |
| C3      | 364.80                           | 0.76                      |
4. Conclusions

In this paper, alloys of MgCa0.8 were prepared, extruded and tested for mechanical properties and corrosion resistance. Conclusions can be summered as follows:

(1) It was found that mechanical properties of extruded alloy increased greatly in the research of extrusion process of MgCa0.8 alloy. The maximum tensile strength reached to 245.42MPa, maximum elongation to 12.32%, maximum bending strength to 379.20MPa, and different extrusion parameters had significant influence on mechanical properties of alloys.

(2) Compared with traditional medical metal materials, the mechanical properties of extruded alloy MgCa0.8 were similar to human bone. From the viewpoint of mechanical properties, MgCa0.8 was suitable for implant material within the quantity range of element Ca mentioned this paper.

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