Study on Preparation and Properties of Corrosion Resistant 3D Printing Magnesium Alloy Materials

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Abstract. In this paper, the medical magnesium alloy melt containing Mg, Zn, Ca, Nd elements was prepared by liquid forming technology. Through atomization, the medical magnesium alloy powder material for 3D printing was obtained. The microstructure of the alloy was observed by SEM and XRD. The corrosion resistance of the alloy was tested by electrochemistry. The final results show that the 3D printing material of medical magnesium alloy has good structure uniformity and corrosion resistance can be effectively improved by adding Nd element.

1. Introduction
3D printing technology, as a kind of rapid prototyping with special new materials, modeling with computers, copying and combining the process of traditional manufacturing process, realizes additive manufacturing. It is quite different from the traditional processing technology, and no longer needs the traditional tools such as cutting tools or molds that have been created for a long time. 3D printing technology uses computers to design three-dimensional solid models, through 3D Printing equipment can print all kinds of special materials according to the model to meet people's needs. 3D printing technology has become very important and widely used in medicine, such as the application of 3D printing in surgical aids and implants. The operation assistant tool is an assistant operation tool to assist doctors to determine the best point of inserting needle and dropping knife before operation. At present, in the field of medicine, the application of spine pedicle navigation board, children's congenital bone transplantation navigation board, bone joint navigation board and mouth tooth auxiliary orthopedic equipment is relatively mature, and many operations based on 3D printing spine navigation have been successfully implemented at home and abroad. The Japanese successfully printed out the tubular vessels by 3D printing technology, the Russians printed the thyroid gland, the American Organovo company printed the liver, the American Northwest University successfully printed the mouse ovary, and the Australian Wollongong printed the human induced pluripotent stem cells [1].

Biomaterials play an important role in the development of 3D printing, so the extent of its development also determines the breadth and depth of the application of 3D printing technology in the medical field. Medical 3D printing materials should meet the requirements of bionics, and have corrosion resistance, wear resistance and good compatibility.

At present, the main medical metal materials used in clinic are stainless steel, titanium alloy and cobalt chromium alloy. These materials have excellent mechanical properties and corrosion resistance. However, the elastic modulus of these materials is quite different from that of natural bone, which may cause stress shielding effect in the process of use, which is not conducive to the healing of bone. What's more, most of these metal materials are permanent implant materials. After fracture healing,
patients need to be taken out after two operations, which increases patients’ pain and economic burden [2-3].

In view of the limitations of the existing medical implant materials, the development of new medical metal materials with good biocompatibility, excellent mechanical properties, and automatic degradation of human absorption has become a research hotspot in the field of biomedical metal implant materials. Magnesium and magnesium alloy as medical metal materials have the following advantages: (1) the modulus of elasticity of magnesium alloy is about 45gpa, which is closer to the modulus of elasticity of human bone and can effectively reduce the stress shielding effect; (2) it has good biocompatibility, non-toxic and can be degraded in vivo to avoid secondary surgery; (3) it has high specific strength and specific stiffness, which can meet the requirements of medical implants Material requirements. However, the degradation rate of biomagnesium alloy in human body environment is too fast, which leads to the decrease of mechanical properties, which can not meet the requirements of mechanical properties of medical metal implant materials; at the same time, the increase of gas and pH produced by degradation may cause inflammation. Therefore, improving the corrosion resistance of biomedical magnesium alloy is an urgent problem [4-8].

In this paper, the medical magnesium alloy melt containing Mg, Zn, Ca, nd elements was prepared by liquid forming technology. Through atomization, the medical magnesium alloy powder material for 3D printing was obtained. The 3D printing material of medical magnesium alloy has good structure uniformity, and the corrosion resistance of the material can be effectively improved by adding nd element. The medical magnesium alloy powder material can print the artificial bone scaffold in 3D at low temperature, which greatly improves the degree of anastomosis between the artificial bone scaffold and the original human bone, is conducive to the healing of the bone, and improves the efficiency of precise treatment. The results of this study will promote the development of precision 3D printing artificial bone scaffolds, reduce the cost of artificial bone scaffolds, and create certain economic benefits for the society.

2. Material Preparation Process

Raw materials: 4wt% for Zn, 1wt% ~ 3wt% for Nd, 0.5wt% for Ca, and Mg as margin.

The specific preparation process is as follows:
(1) Surface cleaning: clean the surface of high-purity magnesium, magnesium zinc and magnesium calcium intermediate alloy;
(2) Mold preheating: use sandpaper to polish the mold, remove the rust and other impurities on the surface, and then put the steel mold into the preheating furnace for preheating;
(3) Smelting: clean up the impurities in the iron crucible, put the cut magnesium ingot into the crucible, and then put the crucible into the protective atmosphere resistance furnace for heating to 350-450 °C, and then put in the protective gas. When the temperature rises to the complete melting of the magnesium ingot, add the weighed intermediate alloy, and at the same time fully stir the refined alloy to mix evenly;
(4) Cooling: after the alloy is evenly mixed, the temperature of the protective atmosphere resistance furnace is reduced to 650-700 °C, and then it is standing, the alloy is slagged, and the oxygen inclusions on the surface are removed;
(5) Atomization: under the protective atmosphere, the alloy solution after refining and slagging is poured into the preheated mold for smelting to obtain medical magnesium alloy molten solution. The medical magnesium alloy melt is overheated, and then placed in an atomizing device for atomization to obtain medical magnesium alloy powder. The medical magnesium alloy powder is collected, screened and packaged to obtain the medical magnesium alloy material for 3D printing.

3. Test and Analysis of Material Properties

The 3D printed medical magnesium alloy material prepared by the process has good biocompatibility, and the added neodymium, zinc and calcium are all essential elements for human body function, and the alloy material designed by the concept of miniaturization is adopted. The magnesium alloy material has good absorbability and biocompatibility. In orthopedic implant, it has the density and elastic modulus close to bone. Its degradation products have no toxic effect on human body and can be
absorbed by human body. The density and elastic modulus of the magnesium alloy are close to that of human bone, which can effectively reduce the stress shielding effect.

Figure 1 shows the XRD pattern of the casting state of magnesium alloy in this process; Figure 2 shows the SEM pattern of magnesium alloy matrix with different content of Nd in this process; Figure 3 shows the polarization curve of magnesium alloy material with different content of Nd in this process.

Figure 1 the XRD results show that: no phase of magnesium and other added alloy elements is detected. According to the phase diagram of magnesium and zinc, the solubility of zinc in magnesium is 6.2% at 325 °C, and the cooling rate during pouring is faster than that measured by phase diagram, so more zinc is solid soluble in magnesium, and some zinc may desolve to form zinc compounds, but it is difficult because of the low content It can be found that the existence of zinc oxide may be caused by the oxidation of zinc in the alloy by oxygen in the air.

The SEM appearance of Fig. 2 shows that the alloy matrix is mainly composed of gray phase, and irregular white particles are distributed on the matrix, the shape and distribution of particles are related to the type of alloy elements; compared with MG-4% zn-0.5% Ca, when 1% nd is added, the white particles coarsen into vermicular shape, and the distribution is more uniform; according to the energy spectrum, the matrix is mainly magnesium rich phase, and the nd content at the particles is more uniform The amount is 24 times of the average composition and the Zn is 9 times of the average composition, so the white particles are rich in Nd and Zn; when 2% and 3% nd are added, the second phase coarsens with the increase of Nd content, the worm structure is more complete and the distribution uniformity is improved. The results show that the proper amount of Nd element can refine the structure of the alloy effectively and make the phase separation of the magnesium alloy material finer. Excessive nd will consume more Zn and lead to the coarsening of mg Zn phase, which will decrease the mechanical properties of magnesium alloy.

**Figure 1.** XRD pattern of as cast magnesium alloy
**Figure 2.** SEM of magnesium alloy matrix with different content of Nd

**Figure 3.** Polarization curve of magnesium alloy with different content of Nd
In order to explore the effect of Nd content on the corrosion resistance of magnesium alloy materials, electrochemical detection was carried out on the electrochemical workstation of chi660d (Shanghai Huake). The solution used was SBF solution at room temperature. In the traditional three electrode system, the auxiliary electrode is platinum plate, the reference electrode is saturated calomel electrode, and the working electrode is the test sample. The test methods are: open circuit potential time curve measurement, Tafel polarization curve measurement. The test area is 1cm², the test range is open circuit potential ± 0.5V, and the scanning speed is 1mV / s. The results show that with the increase of Nd content, the corrosion potential of the matrix increases, and the corrosion resistance increases obviously. The corrosion resistance is the best when the Nd content is 3%.

4. Conclusion
(1) The medical magnesium alloy melt containing Mg, Zn, Ca and Nd elements was prepared by liquid forming technology, and the medical magnesium alloy powder material for 3D printing was obtained by atomization. The preparation process was successful.

(2) Neodymium, zinc and calcium added to the 3D printing medical magnesium alloy material prepared by the process are all essential elements for human body function, so that the material has better absorbability and biocompatibility. The magnesium alloy material has the density and elastic modulus close to the bone in orthopedic implant, effectively reduces the stress shielding effect, and its degradation products have no toxic effect on human body and can be absorbed by human body.

(3) The proper amount of Nd can refine the structure of the alloy effectively, and make the phase separation of magnesium alloy thin. The excessive rare earth Nd will consume more Zn element in the alloy and lead to the coarsening of Mg Zn phase, which will reduce the mechanical properties of magnesium alloy.

(4) With the increase of Nd content, the corrosion potential of the matrix increases, and the corrosion resistance increases obviously. The corrosion resistance is the best when the Nd content is 3%.

5. Acknowledgments
This work was financially supported by the Special Scientific and Technological Innovation Projects of Universities in Guangdong Province (2017KTSCX177).

6. References
[1] Wang Bo. On the development and application of 3D printing technology [J]. Electromechanical Technology, 2014, (05):160.
[2] Gross-Kosche P, Low SP, Guo R. Deposition of nonfouling plasma polymers to a thermoplastic silicone elastomer for microfluidic and biomedical applications [J]. Journal of Applied Polymer Science, 2014, 131(14SI).
[3] Lu Y, Tekinalp HL, Eberle CC. Nanocellulose in polymer composites and biomedical applications [J]. Tappi Journal, 2014, 13(6):47-54.
[4] Albertius-Henning P, Adolfsson E, Grins J, Fitch A. Triclinic oxy-hydroxyapatite [J]. Journal of materials science, 2001, 36(3): 663-668.
[5] Meidanis H, Baciu, DE, Papavassiliou, G. Electrospun ceramic and ceramic-polymer composite nanofibers for bone tissue engineering applications [J]. Journal of Optoelectronics and Advanced Materials, 2014, 16(3-4):414-421.
[6] Huang YY, Lin WS, Chen, K. Thermoresponsive fluorescence of a graphene-polymer composite based on a local surface plasmon resonance effect [J]. Physical Chemistry Chemical Physics, 2014, 16(23): 11584-11589.
[7] Troitskii V, Tsitrin D. The resorbing metallic alloy ‘Osteosinthezit’as material for fastening broken bone [J]. Khirurgiia, 1994, 8(1): 41-44.
[8] Cheng ZQ, Li JF, Yan, JT. Synthesis and properties of a novel superabsorbent polymer composite from microwave irradiated waste material cultured Auricularia auricula and poly (acrylic acid-co-acrylamide) [J]. Journal of Applied Polymer Science, 2013, 130(5): 3674-3681.