Improved corrosion resistance of WE43 magnesium alloy with continuous network of MgF$_2$ prepared by powder metallurgy

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Abstract. This paper deals with the preparation of the composite materials with a continuous network of MgF$_2$ in magnesium matrix. Powder of the WE43 magnesium alloy was boiled in NaOH to obtain a thick layer of Mg(OH)$_2$ and it was subsequently immersed in HF. Mg(OH)$_2$ was converted into a thick layer of MgF$_2$. The chemically treated powders were processed by spark plasma sintering. As a result, composite materials with a continuous network of MgO and MgF$_2$ respectively were formed. The corrosion resistance of the sample containing the network of MgF$_2$ was superior compared to the products from untreated powder.

Keywords: Composites; Corrosion; Sintering; Powder metallurgy.

1 Introduction

Magnesium alloys are considered as suitable biodegradable materials as they have similar mechanical properties as a bone tissue [1]. The main disadvantage of magnesium lies in the high corrosion rate which is associated with hydrogen release. The corrosion rate may be reduced by alloying, preparation method or by coatings. Alloying is associated with including another element which may result in lowered biocompatibility, but it can significantly improve corrosion resistance. WE43 alloy (2.4-4.4 wt.% of Nd, 3.7-4.3 wt.% of Y, >0.4 wt.% of Zr, >0.5 wt.% of Gd and Dy) is an example of magnesium alloy with improved corrosion resistance due to the positive effect of neodymium and yttrium dissolved in the matrix [1], [2], [3].

The preparation method is associated with the structure of the material. Finer and more homogeneous structures are usually characterized by higher corrosion resistance [4]. The preparation method has also influence on the formation of intermetallic phases. Intermetallic phases should be small and homogeneously dispersed in the matrix and have potential close to the magnesium matrix. Powder metallurgy method resulted in many cases in the improved mechanical and corrosion properties [4], [5]. The atomized powder is the input material used for the sample preparation. It is characterized by a very fine structure which can be preserved if the compacting method is fast enough. Spark plasma sintering (SPS) is a progressive method of sintering by high current [6]. The advantage of SPS is a short time of exposure to the high temperature (several minutes) and therefore the material preserves its fine structure after atomization. The compact sample is usually characterized by low porosity.
Coatings may further reduce the corrosion rate of substrate materials. Magnesium fluoride conversion coating was reported to have a very positive effect on the corrosion resistance even in low thicknesses of the coating [7], [8], [9], [10], [11]. The fluoride coating can be easily prepared by immersion in hydrofluoric acid for several hours. As a result, a very thin film (0.1 to 4 μm) of MgF₂ is created on the surface of the material [7], [9], [10], [11]. The thickness of the coating can be adjusted by immersion time and by the concentration of HF as well as by temperature. Another advantage of fluoride coating is in the good adhesive properties (33 to 43 MPa) [7], [12], [8], [9]. The corrosion rate is reduced by the barrier effect of the hardly soluble MgF₂ layer. The positive effect of fluoride coating was reported for the majority of magnesium alloys [7], [8], [9]. On the other hand, Trinidad et al. [13] and Höhlinger et al. [14] showed some difficulties with the coating of the WE43 alloy. Both authors observed inhomogeneous coating. The fluorine was concentrated around intermetallic phases. Nevertheless, the coating was effective even though it was inhomogeneous. The good biocompatibility of MgF₂ coatings was proven by cytotoxicity tests as well as by animal tests [10], [12].

The disadvantage of every coating is its localized disruption by possible mechanical loading. The disturbed coating no longer protects the coated material and the corrosion is localized on the one spot with increased intensity. Uneven corrosion may lead to premature implant failure due to the reduced loading area. The solution to this danger can be a composite material. We have introduced the innovative way of preparation of the composite material with the continuous network of MgF₂ via powder metallurgy [15]. It was proven that this structure has a strong impact on the corrosion resistance and mechanical properties. This paper applies this method to the WE43 alloy. To prevent the inhomogeneity of the coating, the powder was first boiled in the NaOH as was proposed by Weber et al. [16] for MgNd2 alloy. The pretreatment converted the surface into Mg(OH)₂ which could be easily converted into MgF₂.

2 Materials and methods

2.1 Fluoride treatment of the powder

Gas atomized powder of WE43 alloy (4.0 wt.% of Y, 2.2 wt.% of Nd, 0.4 wt.% of Gd, 0.4 wt.% of Dy, 0.5 wt.% of Zr) was characterized by laser diffraction to determine the particle size, which ranged between 10 and 200 μm. Fifty grams of powder was boiled in NaOH solution with a concentration of 200 g/l for 2 hours. The boiled powder was then rinsed with distilled water and ethanol. The powder was dried at 50 °C in air. Part of the boiled powder was immersed and stirred in the 300 ml of 40% HF for 24 h. The HF was then poured out and the powder was rinsed with distilled water multiple times, filtered through filter paper and rinsed with ethanol multiple times. The powder was then dried at 50°C in air. In the following text, the uncoated material is referred as WE, the boiled powder as WE-BT and boiled with fluoride treatment as WE-BT+FT.

2.2 Compacting of samples

Both coated and uncoated WE43 powders were processed by the SPS method at 500 °C with a heating rate of 100 °C/min and 7 kN pressure level and with the operation time of 10 minutes. The SPS machine HP D 10 FCT system GmbH was used. The final cylindrical samples had a diameter of 20 mm and a height of 10 mm.

2.3 Microstructure characterization

The input powders and microstructure of the compact materials were characterized by scanning electron microscope SEM TescanVEGA3 LMU with energy dispersion spectrometry (EDS, AZtec). Samples were mounted in an epoxy resin. Subsequently, they were ground on SiC grinding papers (P80-P2500) and polished on diamond paste D3, D2, D0.7. The final polishing was performed on Etosil F. Porosity was determined by image analysis of 10 sections of each sample. Phase analyses were performed using X-ray diffraction (XRD, X’Pert Philips, 30 mA, 40 kV, CuKα X-ray radiation).
2.4 Mechanical properties
Compressive tests were measured using LabTest 5.250SP1-VM at room temperature on rectangular samples with dimensions of 5×5×7 mm. Constant deformation speed of 0.001 s⁻¹ was used. Compressive yield strength (CYS), ultimate compressive strength (UCS) and total deformation to fracture were determined.

2.5 Immersion test
Immersion tests were performed in simulated body fluid at 37 °C for 14 days. The ratio of solution volume to the surface area was 100 ml/cm². Samples were removed from the immersion solution and were rinsed in distilled water and dried. The corrosion products were removed by the solution of 200 g/l CrO₃, 10 g/l AgNO₃, 20 g/l Ba(NO₃)₂ according to ASTM-G31-72. Samples were then dried and weighted. The corrosion rate was calculated from weight changes after immersion and removing of corrosion products.

3 Results and discussion

3.1 Microstructure characterization
The atomized powder was characterized by round shape particles (Figure 1A). The very fine dendritic microstructure was presented in each particle. XRD analysis revealed the presence of α-Mg solid solution and metastable β'-phase, with a composition close to β-phase (Mg₁₄Nd₂Y). Boiling in NaOH resulted in a thick layer of Mg(OH)₂ which was detected by XRD and is also displayed in Figure 1B. Subsequent immersion in HF led to the conversion of Mg(OH)₂ into the thick and homogeneous coating of MgF₂. There were residues of Mg(OH)₂ which were not detected by XRD analysis. However, they were noticeable by EDS analysis especially around small particles (Figure 1C).

Figure 1. The microstructure of the powder particles in cross-sections: A) WE, B) WE-BT with EDS distribution map of O, C) WE-BT+FT with EDS distribution map of O and F.

All powders were processed by spark plasma sintering in order to obtain compact samples. The final structures are displayed in Figure 2. Individual particles are distinguishable in all samples. The WE sample is characterized by a small porosity of 0.1 % and by shells rich on Y and partially O around each particle (Figure 2A). This behavior is typical for Mg-Y alloys as a higher content of Y improves resistance to oxidation at higher temperatures by the formation of Y₂O₃ on the surface [17]. However, as the Y in the solid solution is consumed for the formation of this layer, the area beneath it (about 4 µm) is depleted on Y. Nevertheless, the Y₂O₃ layer should have a positive effect on the corrosion resistance [17]. On the other hand, the network of depleted areas has a negative effect on the corrosion behavior, because the micro-galvanic corrosion is promoted by the inhomogeneous concentrations of Y. The insides of the particles are the same for all samples and they consist of the α-Mg solid solution and very fine intermetallic phases. These phases were identified as Mg₂₄Y₅ and β-phase (Mg₁₄Nd₂Y).
Material prepared by compacting of the powder boiled in NaOH (WE-BT) resulted in structure displayed in Figure 2B. The porosity of this sample was about 4.6 %. This can be explained by the decomposition of Mg(OH)$_2$ into MgO and H$_2$O at an elevated temperature during sintering, which disturbed the sintering process. Nevertheless, the structure with a continuous network of thick MgO and without any yttrium rich shells is created. The total amount of oxygen in the surface layer of the sample was measured by the EDS analysis and it was determined to be about 14.0 ± 2.3 %. However, part of it comes from the partially oxidized surface after polishing.

WE-BT+FT sample was characterized by a porosity of 2.8 % due to the presence of residues of Mg(OH)$_2$, which is decomposed. Otherwise, the continuous network of thick MgF$_2$ was successfully formed without any yttrium enrichment of the shells (Figure 2C). The enrichment of the shells was prevented by the thick layer of magnesium oxide and magnesium fluoride respectively. The thickness of the MgF$_2$ interface was measured by line scan analysis by EDS and it was determined to be 4-6 µm. The total amount of oxygen and fluorine in the compacted WE-BT+FT sample, measured by EDS analysis, was about 3.2 ± 0.3 wt.% and 5.8 ± 0.5 wt.% respectively. The amount of F is almost by 3 wt.% higher value than that measured for the Mg-MgF$_2$ composite material prepared by the simple immersion of the powder in HF and processing by SPS [15]. The increased value of F can be attributed to the pretreatment by boiling of the powder.

3.2 Mechanical properties
Compressive properties are summarized in Tab.1. Properties of human bone are displayed for comparison. The properties of prepared fluoride composite meet the properties of bone tissue and may be therefore used in medicine as materials for biodegradable implants. The mechanical properties of oxide composite are very low due to the high porosity and worse adhesive properties of the oxide layer. The compressive yield strength of the WE-BT+FT composite material is comparable with the uncoated sample. However, the ultimate compressive strength and plasticity are severely reduced. This reduction may be associated primarily with porosity and the residues of MgO in the interfaces as well as with the adhesion strength of the fluoride coating. Also there might be slower diffusion between magnesium fluoride layers due to its higher melting point. Contrary, improvement of mechanical properties after application of fluoride network was observed in previous study with pure Mg [15].
Table 1. Mechanical properties of the prepared materials compared with the bone [18], [19].

| Material    | CYS [MPa] | UCS [MPa] | D [%]   |
|-------------|-----------|-----------|---------|
| WE          | 225 ± 5   | 421 ± 10  | 16.0 ± 0.9 |
| WE-BT       | -         | 125 ± 23  | 1.2 ± 0.6 |
| WE-BT+FT    | 210 ± 8   | 297 ± 18  | 7.2 ± 1.4 |
| Bone [18], [19] | 130 - 180 | -         | -       |

3.3 Corrosion properties

The corrosion tests were performed in simulated body fluid at 37°C for 14 days. The corrosion rate of bare WE was 3.15 ± 0.27 mm/y. This is a relatively high corrosion rate as was expected due to the existence of depleted areas on Y. Nevertheless, the assumption that the Y$_2$O$_3$ layer improves corrosion resistance was confirmed in Figure 3A, as the corrosion front is slowed down on the yttrium rich interface. This interface works as a hardly soluble barrier, however, after disturbing the barrier the corrosion quickly progresses through Y depleted areas as they are prone to corrosion.

The corrosion rate of WE-BT composite was 6.5 ± 0.44 mm/y, which is twice higher than the bare WE material. This may be due to the high porosity. The corrosion progresses through the material then the corrosion products may peel the whole layer of uncorroded material. Otherwise, the corrosion front is also slowed down on the MgO interface (Figure 3B).

The WE-BT+FT composite material was characterized by the lowest corrosion rate of 1.69 ± 0.05 mm/y. The reduced corrosion rate is associated with the fluoride interfaces which effectively slowed down the corrosion (Figure 3C). The effectiveness can be demonstrated by the amount of fluorine on the surface after removing of the corrosion products. The amount of F raised from 5.8 to 19.5 wt.%. The corrosion of the material is expected to be generally more uniform as the corrosion is slowed down on each barrier. Such material should not suffer from the deep localized attacks caused by impurities like Fe or Ni [20], as the effect of these impurities should be localized to just one particle. The corrosion rate was reduced on the half-value compared with the bare WE. In the previous study with Mg, the corrosion rate was reduced on one third [15]. This might be connected with the porosity of the material which promotes corrosion.
4 Conclusion

Powder of the WE43 alloy was boiled in NaOH and subsequently chemically treated in hydrofluoric acid. As a consequence, the coating of MgF$_2$ was formed on the surface. Treated powders were compacted by spark plasma sintering. Specimen prepared from non-treated atomized powder was characterized by the oxide shells rich in yttrium and areas depleted in alloying elements beneath them, which degrade corrosion properties of the material. Materials prepared from powders processed by boiling in NaOH were characterized by increased porosity due to the decomposition of Mg(OH)$_2$ which highly deteriorate mechanical properties. However, materials containing MgF$_2$ (WE-BT+FT) showed best corrosion resistance as the fluoride barriers successfully slowed down the corrosion progress and promising CYS slightly exceeding the corresponding value for human bone.

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