Corrosion Resistant Magnesium-Based Composite Material with MgF_2 Continuous Network Prepared by Powder Metallurgy

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This paper enhances an innovative way of preparation of the composite materials by powder metallurgy. Magnesium-fluoride composite material prepared by spark plasma sintering exerted improved corrosion resistance. Magnesium powder was coated by boiling of Mg powder in concentrated NaOH and subsequent immersion in HF. Treated powder was successfully compacted via spark plasma sintering. The composite material with a continuous network of MgF_2 is prepared and it exerts improved mechanical and highly enhanced corrosion resistance compared with the pure magnesium.

Keywords: Biomaterials, composite material, corrosion, powder metallurgy, sintering.

1 Introduction

Magnesium and its alloys find utilization in medicine for its good biocompatibility and mechanical properties close to bone tissue [1]. This similarity is advantageous because it eliminates the problems with stress shielding effect observed for permanent implants with extremely high mechanical properties [2]. However, the disadvantage of pure magnesium is in its high corrosion rate. Corrosion resistance of magnesium may be improved by alloying, coatings and processing methods. Alloying is associated with the addition of another element which can affect the final biocompatibility of alloy. Magnesium alloys containing aluminum are for example questioned due to the influence of Al on the Alzheimer's decease [3]. According to some research pure magnesium can be more corrosion resistant than the alloys if the magnesium is very pure and without dangerous metals as Fe, Ni, Cu and Co [4]. The maximum allowance of Fe in magnesium is 170 ppm [5]. The mechanical properties of magnesium can be increased by thermomechanical processing. For example, extrusion is associated with the recrystallization process, so as a result the fine-grained structure is obtained [6]. The finer structure is known to decrease corrosion rate [7]. The fine structure may be achieved also by the progressive method of powder metallurgy [8]. Powder metallurgy is based on the preparation of compact samples out of powders. The powder is usually prepared by atomization of the melted metal. Such powder is characterized by the round shaped particles with fine grains due to the rapid cooling. There are several methods of compacting of the powder in order to obtain compact material. Each method has its advantages and disadvantages. An innovative way of the compacting is the spark plasma sintering [9]. Spark plasma sintering is based on the pressing of the powder and subsequent fast sintering by the high current which goes through the sample. This technology allows the material to be compacted within just a few minutes. Short time on high temperature reduces the grain growth. So the final material should exert good mechanical properties [10].

The corrosion rate may be further reduced by the application of corrosion resistant coatings [11], [12], [13]. Such coatings are usually based on the insoluble salts or components such as hydroxyapatite. Such coating may increase biocompatibility and reduce the corrosion rate. The problem with coatings may lay in the bonding strength to the surface of the material and with the thickness and porosity of such coating. The promising coating on the magnesium is the MgF_2 layer [13]. This layer is usually thin (0.1 to 4 μm) [14], [15], [16]with good adhesion strength of 33 to 43 MPa [14], [15]. Also, the cytotoxicity tests revealed no negative effects of the MgF_2 on the cells [17], [18]. Fluoride coating also exerted antibacterial properties [17]. Magnesium fluoride coatings on various magnesium alloys were successfully tested on animals with positive results [15], [16].

Present work tries to improve the new approach of preparation of composite materials with a continuous network of MgF_2 introduced in the previous research [19].

2 Materials and methods

2.1 Powder treatment

Magnesium commercial atomized powder with impurities measured by ICP-MS (Elan DRC-e) (90 ppm Fe, 10 ppm Cu, 20 ppm Ni) was boiled in 200 g/l NaOH for 2 hours. The powder was then rinsed with distilled water and ethanol and desiccated at 50 °C. The powder was afterward immersed in 40 % HF and stirred for 24 hours. After immersion, the powder was again rinsed with distilled water and ethanol and desiccated at 50 °C.

2.2 Compacting

Magnesium and chemically treated powders were then processed by spark plasma sintering at 500 °C with a heating rate of 100 °C/min and 7 kN pressure level and with operation time 10 minutes. The SPS machine HP D 10 FCT system GmbH was used. The final cylindrical rods had a diameter of 20 mm and height of approximately 10 mm.

2.3 Microstructure

The microstructures of the compact materials were characterized by electron scanning microscope (SEM - TescanVEGA3) with energy dispersion spectrometry

(EDS, AZtec). Porosity was evaluated by image analysis (ImageJ) of 10 cuts. Samples were ground on SiC grinding papers (P80-P2500) and polished on diamond paste D3, D2, and D0.7. The final polishing was done on Etosil E.

Compressive tests were performed on LabTest 5.250SP1-VM at room temperature. The specimens for compressive tests were rectangular (5 × 5 × 7 mm). The strain rate of 0.001 s^{-1} was used. Basic mechanical data were evaluated.

Immersion tests were performed in simulated body fluid (SBF) at 37 °C for 14 days. The ratio of solution volume to the surface area was 100 $ml \cdot cm^{-2}$. After 14 days, 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 $g \cdot l^{-1}$ CrO_3, 10 $g \cdot l^{-1}$ $AgNO_3$, 20 $g \cdot l^{-1}$ $Ba(NO_3)_2$ at room temperature. Samples were then dried and weighted. The corrosion rate was calculated from weight changes and released magnesium ions.

3 Results and discussion

3.1 Microstructure

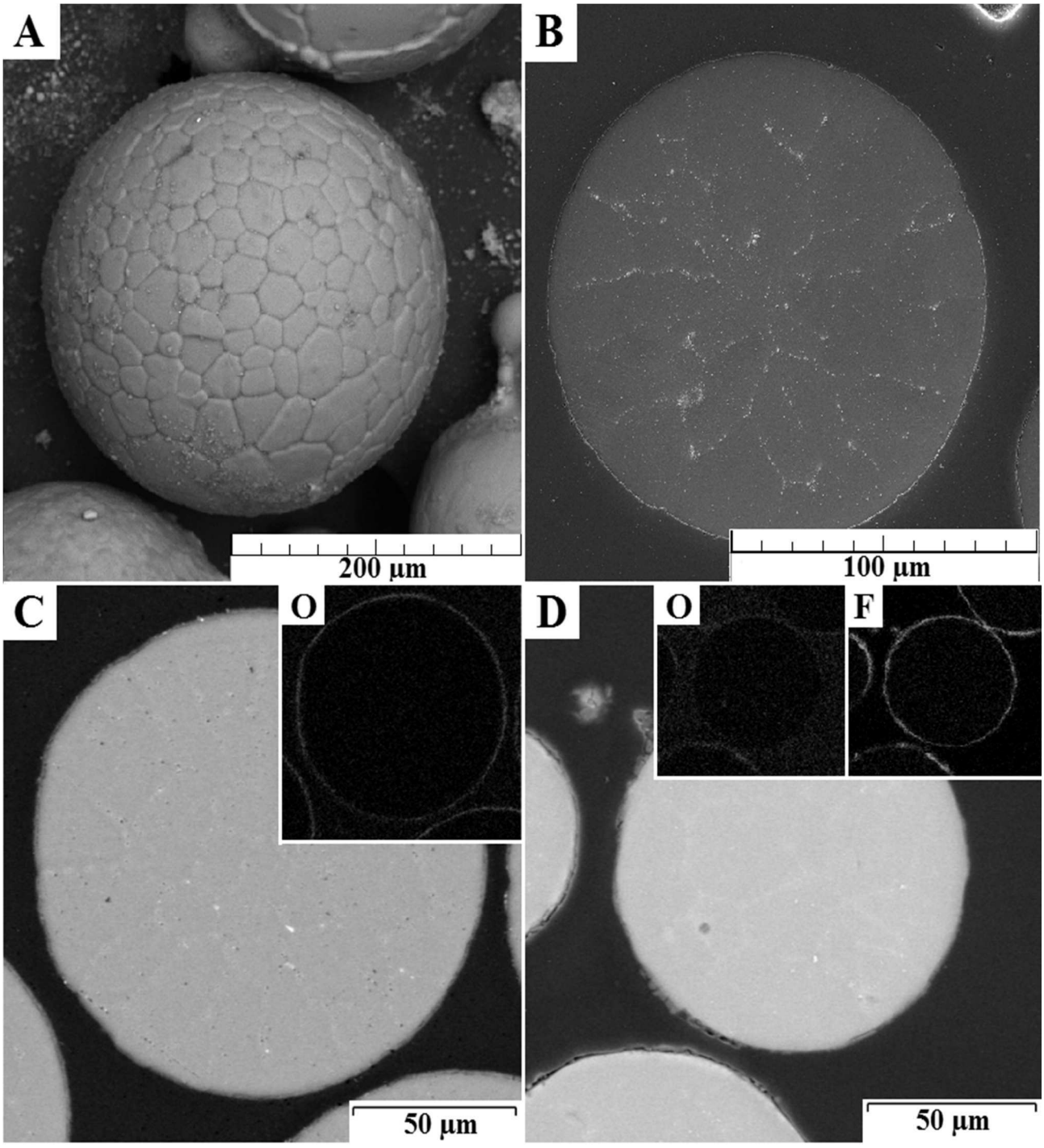

Fig. 1 *The microstructure (SEM) of A) Mg powder, B) Mg powder-cut, C) Mg powder after boiling in NaOH with EDS analysis of O, D) Mg powder after boiling in NaOH and immersion in HF (with EDS analysis of O and F)*

As received magnesium powder was characterized with round shaped particles (Fig. 1a) with most particle size ranging between 50 and 200 µm. Each particle was filled with relatively fine grains not exceeding 50 µm (Fig. 1b). Magnesium powder after boiling in NaOH was surrounded by magnesium hydroxide according to the XRD analysis, which is represented by EDS analysis of O in Fig. 1c. Subsequent treatment in HF provides a thick homogeneous layer of MgF_2 on the surface, however, there were residues of magnesium hydroxide beneath this layer as can be seen in Fig. 1d, even though no magnesium hydroxide was detected by XRD analysis of the powder. The boiling in the NaOH increased the thickness of MgF_2 layer compared with bare immersion in HF, which was studied in a previous study [19]. The coating is in this work predominantly created by the conversion of $Mg(OH)_2$ into MgF_2. Boiling in NaOH allows the creation of a thick layer of $Mg(OH)_2$ which could be subsequently converted into MgF_2. Longer immersion in HF might lead to the total conversion of $Mg(OH)_2$.

Structures of the sintered samples are pictured in Fig.2. The porosity of all samples was below 0.3%. Sintered samples were characterized by the distinguishable particles of the powder. After sintering of as received of atomized powder, there were just residues of oxides between particles (Fig. 2a). The total amount of oxide detected by the EDS analysis was 1.5 ± 0.1 wt.%. On the other hand after sintering of the powder boiled in NaOH, there were thick borders between particles (Fig. 2b). Borders consist of magnesium oxide which was created from magnesium hydroxide, as this reaction occurs at 332 °C. EDS analysis detected 4.5 ± 0.3 wt.% of O in the sample. Sintering of the boiled and immersed powder resulted in the structure in Fig. 2c. Such structure is also characterized by the thick borders which in this case consist of MgF_2 with residues of MgO. The thickness of the layer and the residual MgO are the main differences between this material and material prepared by sintering of powder immersed just in HF [19]. The total amount of O and F detected by EDS was 1.6 wt.% and 2.6 wt.% respectively. The thickness of the MgF_2 coating was identified by the line scan analysis and it ranged between 4 and 6 µm, which is slightly thicker than in the previous work [19].

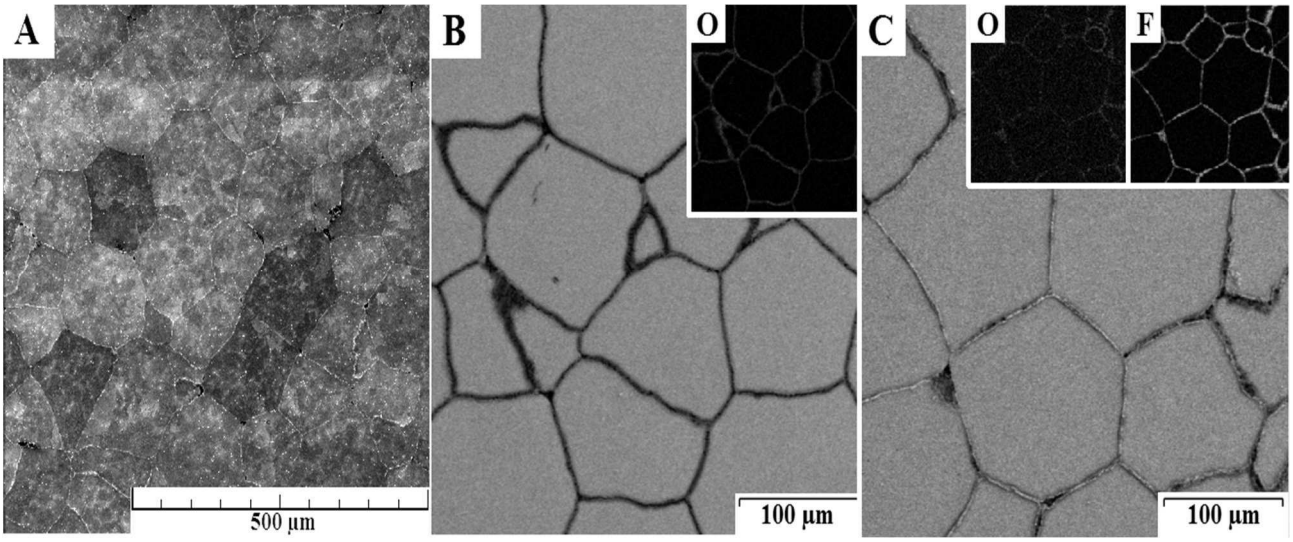

Fig. 2 *The microstructure (SEM) of sintered A) Mg, B) Mg-NaOH with EDS analysis of O, C) Mg-NaOH-HF with EDS analysis of O and F.*

3.2 Mechanical properties

The compressive properties of the prepared samples are summarized in Fig. 3. The worst mechanical properties were obtained by the sample prepared from the boiled powder in NaOH. The oxide interface was very brittle and it has probably bad adhesion between particles. Contrary, fluoride interface improved mechanical properties. The compressive yield strength is about 30 MPa higher than in the case of bare Mg. The average bonding strength of the Mg/MgF_2 is 33 to 44 MPa, which probably contributed to the increased mechanical properties. MgF_2 network works as a reinforcement of the material in the compression. Nevertheless, the compressive properties of fluoride composite are the same as in the previous study [19].

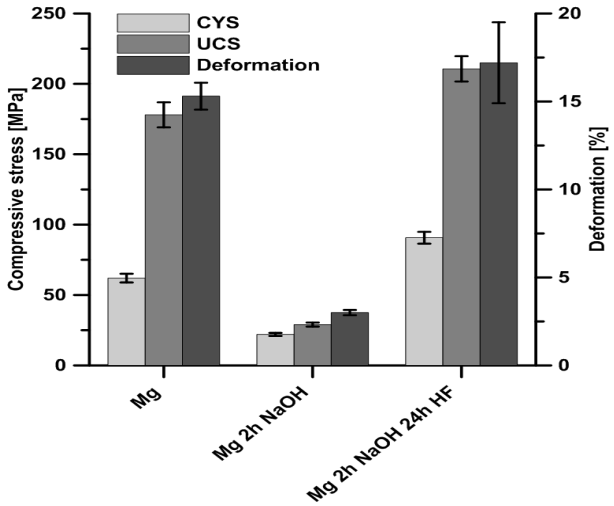

Fig. 3 *Compressive properties of prepared samples.*

3.3 Corrosion properties

The corrosion rate of sintered Mg immersed in SBF for 14 days was 2.2 ± 0.2 mm/y. The corrosion rate of oxide composite could not be measured as all the samples crumbled during the exposition. The increased degradation of the sample was probably associated with the bad mechanical properties as the corrosion progress through the sample the individual particles might be pulled off by the corrosion products with higher volume. Contrary, the MgF_2 network worked as a barrier and successfully slowed down the corrosion on the value of 1.1 ± 0.1 mm/y. The corrosion front is slowed down on each particle interface, which is displayed in Fig. 4a. The effectiveness of this barrier is evident from the surface of the sample after removing the corrosion products (Fig. 4b). The surface is occupied with residues of the MgF_2 shells, which were not removed with the corrosion products. The total amount of F on the surface according to EDS is about 24 wt.%, which represents the barrier effect. This increase in the amount of F is however twice higher than in the previous study, where the amount of F raised from 2 to 12 wt.%. Nevertheless, the total reduction of degradation was lesser than in the previous study [19]. This might be connected with the occurrence of residual oxides which were not observed in the previous work or with the larger thickness of the layer. Generally, thinner layers are usually considered as better in means of mechanical and corrosion properties.

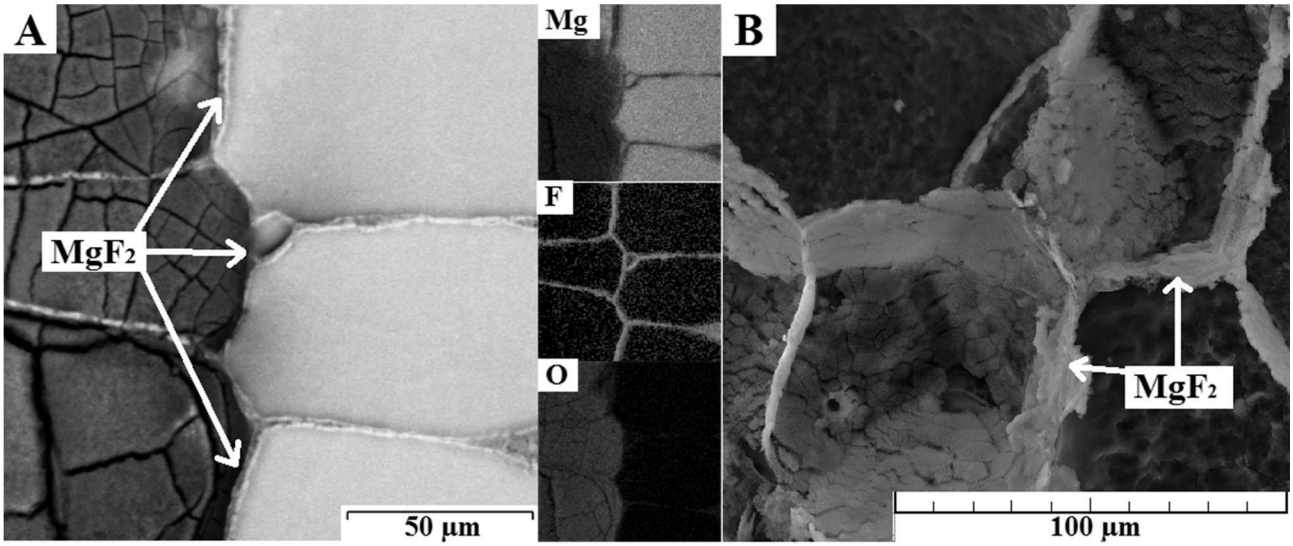

Fig. 4 *The microstructure (SEM) of the composite after corrosion A) Cut with EDS map of Mg, F, and O, B) Surface after removing the corrosion products.*

4 Conclusion

A thick layer of $Mg(OH)_2$ was created on the surface of the magnesium atomized powder by boiling it in NaOH. This layer was successfully converted into a thick coating of MgF_2. Powders were sintered via SPS and the composites of Mg-MgO and Mg-MgF_2 were created. Mg-MgO composite was characterized with poor mechanical and corrosion properties due to the brittle MgO phase. Mg-MgF_2 composite material exerted improved mechanical properties. Especially corrosion rate was reduced on the half value of the pure Mg. Therefore such preparation method has a potential to be used for the material processing.

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