Magnesium Composite Materials Prepared by Extrusion of Chemically Treated Powders

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This paper is focused on the preparation of the magnesium composite materials by extrusion of the chemically treated powders. Microstructures with partially preserved borders between particles containing specific elements depending on the preparation method were created by extrusion. Compressive mechanical properties of extruded chemically treated powders were similar to material prepared from atomized powder. The corrosion rate was reduced by three times in the case of chemically treated powder compared to the pure Mg. Ignition temperature of the chemically treated powder increased by up to 200 °C compared to the atomized powder, while ignition temperatures of the extruded samples were only slightly improved.

Keywords: Composite material, corrosion, powder metallurgy, extrusion, ignition temperature.

1 Introduction

Magnesium is a desirable material for an automotive and aviation industry due to its low density and relatively good mechanical properties [1], [2]. Its utilization is limited due to the poor corrosion resistance and loose of mechanical properties at elevated temperatures. Also, the preparation of magnesium is problematic due to the high affinity of magnesium to oxygen [3]. Therefore, it has to be melted under a protective atmosphere of SF_6 for example [4], [5], [6], [7]. The protective layer of MgF_2 is then created on the surface of the melt. Otherwise, the thermal stability of MgF_2 on air is only up to 800 °C, where it starts to convert to MgO [8]. Alloys with improved resistance to oxidation were developed especially due to the cancelation of the ban for magnesium alloys in aircraft cabins by the Federal Aviation Administration (FAA) [1], [9]. Proposed materials have to pass the ignition test, where they can ignite only after a certain temperature. WE43 alloy was approved by the FAA, while AZ91 failed those tests [1], [10], [7]. Therefore, new alloys and methods of preparation were published in order to provide material suitable for this application, as it would reduce the mass of aircraft by up to 30% and subsequently reduce the emission of CO_2 [10], [11].

Another utilization of magnesium is for biodegradable implants due to its good biocompatibility and mechanical properties which are close to the bone tissue and therefore the problem with stress shielding effect is eliminated [12], [13]. Among the greatest disadvantages of the magnesium materials is the high corrosion rate which is associated with hydrogen release. Improving corrosion resistance by alloying is effective, however, the biocompatibility of such implant might be reduced due to the alloying elements. Moreover, magnesium is sensitive to impurities such as Fe, Ni, Cu, and Co and if their concentration exceeds their limits (170 ppm for Fe) there is danger of excessive corrosion rate or localized corrosion [14], [15]. Corrosion rate might be reduced by the creation of composite materials with the low soluble reinforcement. Composite materials are usually also characterised by improved mechanical properties.

Another method for improving the corrosion resistance of magnesium alloys is by using coatings [16], [17], [18]. There are several possible and effective coatings for magnesium biodegradable implants, for example, fluoride conversion coating [18]. This coating is based on the resistance of magnesium in hydrofluoric acid and low solubility of MgF_2. Such coating is very thin (0.1 to 4 μm) and with good adhesive strength (33 to 43 MPa) [19], [20], [21]. According to the cytotoxicity tests, the MgF_2 coating is fully biocompatible and it was even tested on the animals with positive results [20], [21], [22], [23]. MgF_2 coating can reduce the corrosion rate on the tenth of the original value [18]. However, there is danger of disturbing the surface layer and as a consequence, localized corrosion would appear.

The danger of disturbing the surface layer can be reduced by the creation of a continuous network of MgF_2 [24]. Nevertheless, mechanical properties are not high enough after processing by spark plasma sintering. Preparation of such materials is based on the processing of chemically treated powders. Magnesium powder is immersed in hydrofluoric acid and thus a surface layer of MgF_2 is created around each particle. Such a coating is protective against the oxidation of the powder, which might be useful for long-term storage of magnesium powders. However, materials prepared from the treated powder might exert different properties.

Extrusion is a common method for processing of magnesium materials based on thermomechanical processing. Products prepared by extrusion exert good mechanical properties due to the recrystallization process and fine-grained structure [25]. Fine grains can be especially gained by the powder metallurgy route and they also improve corrosion properties [26], [27]. The powder of the material is made by atomization, which is associated with rapid cooling and therefore particles with fine grains and oversaturated solid solutions are created. Nevertheless, magnesium tends to form a texture after deformation and it may result in anisotropy of mechanical properties.

In this work, a preprocessed magnesium powder was extruded at 400 °C in order to obtain a composite material containing MgF_2, which would decrease a corrosion rate, while mechanical properties would be improved. Also, ignition properties of the chemically treated powders and prepared extruded materials were tested.

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. Another powder was just immersed in the HF without pre-boiling it in NaOH.

2.2 Compacting

Magnesium chemically treated powders were then processed cold-pressed at 80kN for 2 minutes. The green compacts were subsequently extruded at 400 °C with extrusion ratio 10 and extrusion rate of 5 mm/min.

2.3 Microstructure

The microstructures of the compact materials were characterized by electron scanning microscopy (SEM - TescanVEGA3) with energy dispersion spectrometry (EDS, AZtec). 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.

2.4 Mechanical properties

Compressive tests were performed on LabTest 5.250SP1-VM at room temperature. The specimens for compressive tests were cylindrical with 5 mm in diameter and 7 mm high. The strain rate of 0.001 s^{-1} was used. Basic mechanical data were evaluated.

2.5 Immersion test

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 weighed. The corrosion rate was calculated from weight changes.

2.6 Ignition test

The surfaces of samples with dimensions 15x15x5 mm were finished by grinding on the paper P1200. Subsequently, samples were put in the Al_2O_3 crucible which was inserted into the resistance furnace. One thermocouple was in direct contact with the sample and the other one was in the middle of the crucible. There was a tube with the airflow on the other side of the crucible. Technical air with airflow of 100 l/h was used to supply the crucible with oxygen. The heat rate of the furnace was set to 35 °C/min. The temperature increased with time until the temperature rose rapidly due to the ignition of the sample. Each sample was measured three times.

3 Results and discussion

3.1 Microstructure

Atomized powder of pure magnesium was characterized with round-shaped particles with a diameter ranging from 10 to 250 μm. The grain size of the powder did not exceed 50 μm. Immersion of powder in HF leads to the creation of homogeneous coating of MgF_2. In order to create thicker coating atomized powder was boiled in NaOH for 2 hours for the creation of $Mg(OH)_2$ coating which was subsequently converted in hydrofluoric acid into MgF_2 thick coating as was presented in the previous work [28].
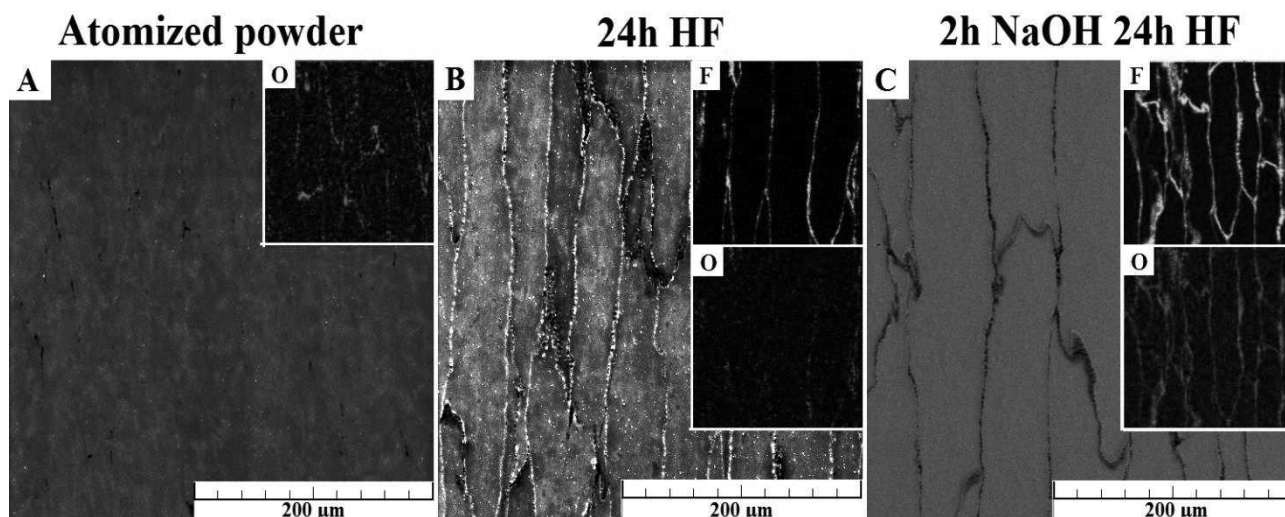

Fig. 1 The microstructure (SEM) and EDS analysis of F and O of extruded A) Mg, B) Mg-HF, C) Mg-NaOH-HF.

Chemically treated powders were cold-pressed and extruded. The final microstructures are shown in Fig.1. Material prepared from the as received atomized magnesium powder were characterized by oxide rich regions around deformed particles of original powder (Fig. 1A). An increased concentration of oxide is due to the presence of the oxide on the surface of the original atomized pow-

der. The total amount of oxygen measured by EDS analysis of the surface of the sample was about 1.5 ± 0.1 wt.%. On the other hand, the bare immersion of magnesium powder in HF leads to the microstructure in Fig.1B which was basically oxide-free (0.2 ± 0.1 wt.%). Instead of the oxide rich regions, there were fluoride-rich regions around each particle deformed in the direction of the extrusion. The low extrusion ratio was probably the reason behind partial preservation of original borders between particles. According to the previous results, better adhesion strength and lower solubility of MgF_2 compared to the MgO can result in better performance of this material [24]. Pre-boiling of the powder in NaOH leads to the very thick borders between deformed particles, which consist of MgF_2 and MgO (Fig.1C). MgO was created during extrusion as the residual $Mg(OH)_2$ decomposed into MgO at elevated temperature. The total amount of oxygen in the structure was therefore increased to 2.7 ± 0.2 wt.%.

3.2 Mechanical properties

The compressive properties of the prepared samples together with other properties are summarized in Tab. 1. One can see that in the case of the pure magnesium compressive properties were not affected by the magnesium fluoride. On the other hand, boiling in NaOH and subsequent immersion in HF caused a slight increase of compressive yield strength, however, also a decrease of ultimate compressive strength and plasticity probably due to the fragile MgO created during extrusion from the residual $Mg(OH)_2$. Nevertheless, the compressive mechanical properties are still much higher than if the material is prepared by spark plasma sintering (SPS) [24], [28].

Tab. 1 Compressive and corrosion properties with ignition temperatures of powders and compact samples.

	CYS [MPa]	UCS [MPa]	D [%]	v_{cor} [mm/y]	T_{ig} [°C]	T_{ig} powder [°C]
Mg	97 ± 4	315 ± 8	12.1 ± 0.9	3.129 ± 0.315	642 ± 6	585 ± 5
Mg HF	99 ± 2	321 ± 6	12.9 ± 1.6	1.031 ± 0.166	675 ± 8	790 ± 6
Mg NaOH HF	109 ± 2	260 ± 10	9.3 ± 2.1	1.239 ± 0.231	673 ± 7	675 ± 6

3.3 Corrosion properties

The corrosion behavior was studied in SBF for 14 days at 37°C and the measured corrosion rates calculated form the weight changes are summarized in Tab. 1. One can see a rapid decrease in corrosion rate of chemically treated extruded samples due to the creation of the barriers of hardly soluble MgF_2 around each deformed particle. These barriers are across the whole sample and, therefore, they effectively reduce the corrosion rate even after breaching the initial barrier as the corrosion front gets through the material it is afterward slowed down on another barrier similarly as it was presented in the previous work for the materials prepared by SPS [24], [28]. The corrosion rate of magnesium with thicker MgF_2 barriers is slightly increased due to the presence of MgO in the structure as it might be dissolved more easily than MgF_2. However, materials prepared by SPS exerted better corrosion resistance than after extrusion as the borders around each particle are better preserved and not partially broken like after extrusion.

3.4 Ignition test

Ignition tests were studied on powders as well as on compact samples in the furnace with the input of technical air. Ignition temperatures are summarized in Tab. 1. Atomized magnesium powder was characterised with very low ignition temperature of 585 °C, which is associated with the increased surface of the powder particles compared to the bulk material. Magnesium powders are therefore extremely dangerous in the means of fire safety. Individual particles have to be immersed in the hydrofluoric acid in order to protect magnesium powder from oxidation as the MgF_2 coating will be created around each particle. MgF_2 coating works similarly as the surface layer of MgF_2 created on the melt during melting under SF_6 atmosphere. Nevertheless, such coating decomposes on air on temperatures above 750 °C [8]. One can see that such a coating leads to the significant improvement of ignition temperature by up to 200 °C. Similar ignition temperature to this material has for example, bulk material of Mg-1.5Nd alloy (780 °C) [3]. However, powders are more prone to burning than bulk materials. Pre-boiling of the powder in NaOH before immersion in HF only increased the ignition temperature almost by 100 °C. Less efficiency of this method is due to the oxide residues which probably deteriorate the effectiveness of MgF_2 coating. The differences of the materials after extrusion are not so significant as in the form of powders. This is due to the uncovered areas of the magnesium, where MgF_2 covers only small portion of the total surface of the sample. Still, extruded materials prepared from chemically treated powders exerted slightly higher ignition temperatures than material prepared from atomized powder.

4 Conclusion

Composite materials with MgF_2 reinforcement were successfully created by extrusion. All materials were characterised by deformed particles in the extrusion direction. Borders between original atomized particles were still distinguishable and they were rich on the specific element depending on the preparation method. Compressive properties of pure magnesium powder were not negatively affected by bare immersion of the powder in HF. Pre-boiling in NaOH leads to the decrease of plasticity. Both preparation methods also decreased corrosion rate three times compared to the pure Mg. Pre-boiling the powder in NaOH lead to the creation of MgO which slightly reduced the corrosion resistance compared to the bare immersion in HF. Chemically treated powders

exerted significantly increased ignition temperatures compared to the atomized powder, while extruded samples were only slightly improved.

Acknowledgment

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