Magnesium Technology 2011
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TMS (The Minerals, Metals & Materials Society), 2011

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Addendum

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CONTROLLING THE BIODEGRADATION RATE OF MAGNESIUM-BASED IMPLANTS THROUGH SURFACE NANOCRYSTALLIZATION INDUCED BY CRYOGENIC MACHINING

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Keywords: biodegradable implants, nanocrystallized grain, cryogenic machining, magnesium alloys

Abstract

Magnesium alloys are emerging as a new class of biodegradable implant materials for internal bone fixation. They provide good temporary fixation and do not need to be removed after healing occurs, providing the relief to the patients and reducing the healthcare costs. However, premature failure of these implants often occurs due to the high biodegradation rate caused by low corrosion resistance of magnesium alloys in physiological environments. To control biodegradation/corrosion of magnesium alloys, grain refinement on the surface was achieved through machining-induced severe plastic deformation. Liquid nitrogen was used during machining to suppress grain growth. White layers, which consist of nanocrystallized grain structures, are reported herein for the first time in magnesium alloys. By controlling the machining conditions, white layers with various thicknesses were fabricated. *In vitro* corrosion tests proved that different machining conditions can significantly change the biodegradation rate of magnesium alloys.

Introduction

In the U.S. alone, physician visits for orthopedic surgery reached 48,066,000 in 2006 [1]. Nine out of the twenty five most common orthopedic surgeries involve repair of bone fractures [2]. Internal bone fixation implants, such as bone plates and screws, are widely used to provide temporary fixation for fractured bones. Stainless steels and titanium alloys are two major biomaterials currently used for these implants. However, their excessively stronger mechanical properties compared to bones may lead to stress shielding. The corrosion and fatigue of these materials will inevitably generate metallic ions and particles that may activate adverse tissue reactions. To avoid further reactions after bone healing, these implants need to be removed during a second surgery, which adds additional morbidity (pain, refracture, etc.) to the patients and increases healthcare costs.

While various approaches are being investigated to increase the bio-inertness of traditional implant materials, magnesium alloys are emerging as a novel biodegradable material in which the relatively fast corrosion phenomenon is used as a unique advantage for temporary fixation implants. The potential of magnesium alloys as a biodegradable implant material was explored by several researchers in the first half of the twentieth century. The results of these research investigations were summarized by Staiger et al. [3]. No systematic reaction occurred and little inflammation was observed in these human trials. A marked stimulatory effect for bone healing was also reported. However, the premature failure of magnesium-based implants due to the poor corrosion resistance in physiological environments and gas bubbles generated due to the high corrosion rate impeded further investigation until recently.

In 2005, Witte et al. found results similar to the early researchers through *in vivo* study of magnesium alloys. A stimulatory effect for bone growth was also reported [4]. The formation of a biomimetic layer comprised of magnesium and calcium phosphate at the implant/bone interface was found to be the cause for accelerated bone formation [5, 6].

Despite their attractive features, little progress has been achieved in controlling the biodegradation rate of magnesium alloys. Alloying and coating are two approaches widely studied [7, 8]. However, alloying may introduce elements which may lead to adverse biological reactions. Stability of the coating under cyclic loading in physiological conditions is a great challenge while the complexity of coating techniques may significantly increase the cost of implant.

Mechanical processing of magnesium alloys provides an alternative approach to control the biodegradation rate. Hot rolled magnesium AZ 31 samples were reported to have a marked reduction in biodegradation rate compared with squeeze cast samples [9]. The reduction was attributed to grain refinement from 450 μm to 20 μm. However, further grain refinement by equal channel angular pressing (ECAP) to 2.5 μm did not decrease the biodegradation rate. With the same material, Alvarez-Lopez et al. [10] found that samples with 4.5 μm grain size processed by ECAP and followed by rolling had better corrosion resistance than the initial samples with 25.7 μm grain size. Deep rolled magnesium MgCa3.0 samples were reported to have a pronounced reduction in biodegradation rate [11]. Machining with different cutting speeds also leads to different corrosion rates [11].

Surface and subsurface integrity in machined products is emerging as the new focus in machining research. The performance of the components can be significantly modified by machining through changes in surface integrity factors, such as microstructure, hardness and residual stresses [12]. Significant grain refinement occurs at the machined surface/sub-surface through severe plastic deformation. Nanocrystallized grains of about 5 - 20 nm in size were reported in the white layer of AISI 52100 steel after machining [13]. Ultrafine grains about 175 nm were formed on the machined surface of copper [14]. Due to grain growth caused by the large amount of heat generated during machining, the nanocrystallized grains can be found only at the top surface of the machined component and the cutting speed is limited to very low range. A novel technique based on machining was developed to fabricate thick nanocrystallized layers with the help of the liquid nitrogen cooling [15]. The results proved that

severe plastic deformation under cryogenic conditions can successfully introduce nanocrystallized grain structures to the surface and sub-surface layers.

However, only a few studies on controlling the grain refinement through advanced process control have been reported. Also, the relationship between grain refinement, especially in the nanocrystalline range, and biodegradation rates in magnesium alloys is still unknown. Therefore, the aim of the present work was to investigate the microstructural changes under different machining conditions and their influence on biodegradation rate of magnesium alloys incubated in simulated body fluid (SBF).

Experimental Work

Work Material

The work material studied was the commercial AZ31 B-H24 magnesium alloy. *In vivo* tests showed the potential of magnesium AZ31 alloy as a bone implant was significant [16, 17]. The work material was received in the form of 3 mm thick sheet. Disc specimens were made from the sheet and subsequently subjected to orthogonal machining.

Machining Experiments

The machining experiments were conducted on a Mazak Quick Turn-10 Turning Center equipped with an Air Products liquid nitrogen delivery system. The experimental setup is shown in Figure 1.

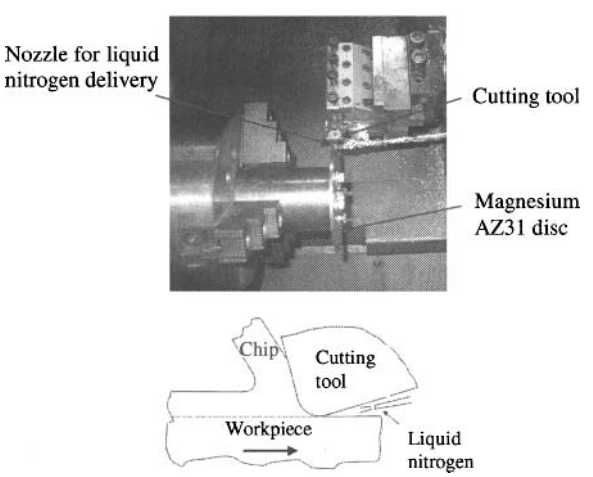


Figure 1. Machining setup with an Air Products liquid nitrogen delivery system

The machining conditions controlled during the experiments were cooling methods and the edge radius of the cutting tool. For dry machining, no coolant was used. For cryogenic machining, liquid nitrogen was applied to the machined surface from the clearance side of the cutting tool. The cutting tools used were uncoated carbide C5/C6 inserts from Kennametal. These cutting tools were ground to three different edge radii. The actual edge radius before machining was measured using a ZYGO New View 5300 measurement system which was based on white light interferometry. A sample measurement is shown in Figure 2.

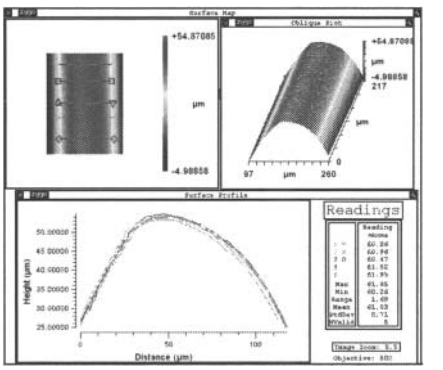


Figure 2. Edge radius measurement of the cutting tool using ZYGO New View 5300

The matrix for the machining experiments is shown in Table I. For each machining experiment, a KISTLER 3-Component Tool Dynamometer was used to measure the cutting forces.

Table I. Matrix for the machining experiments

No.	Cooling Method	Edge Radius (μm)	Cutting Speed (m/min)	Feed Rate (mm/rev)
1	Dry	30	100	0.1
2	Cryogenic	30	100	0.1
3	Cryogenic	68	100	0.1
4	Cryogenic	74	100	0.1

In vitro Corrosion Test

To mimic the human body environment, a simulated body fluid (SBF) was prepared: 8.0 g/l NaCl, 0.4 g/l KCl, 0.14 g/l $CaCl_2$, 0.35 g/l $NaHCO_3$, 1.0 g/l $C_6H_{12}O_6$ (D-glucose), 0.2 g/l $MgSO_4 \cdot 7H_2O$, 0.1 g/l $KH_2PO_4 \cdot H_2O$ and 0.06 g/l $Na_2HPO_4 \cdot 7H_2O$. The pH of the SBF was adjusted to 7.4. The solution was kept in an incubator to maintain the temperature at 37 ± 1 °C. To evaluate the biodegradation rates, hydrogen evolution method [18] was used to continually monitor the corrosion process for 7 days. To reduce the effects of pH increase and accumulation of corrosion products on corrosion rate, large solution volume/surface area (SV/SA) ratio (SV/SA=433) was used [19].

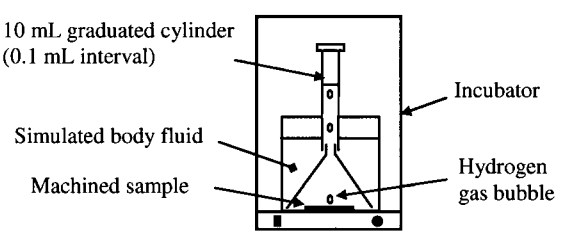


Figure 3. *In vitro* corrosion test setup

Characterization Method

Metallurgical samples were cut from the machined discs. After cold mounting, grinding and polishing, acetic picric solution was used as the etchant to reveal the grain structure. Optical and scanning electron microscopes were used to observe the

microstructure of the magnesium alloys. An atomic force microscope (AFM) was used to explore the possible structure of the top layer of the machined samples. For AFM characterization, the samples were observed after grinding and polishing but without etching. The chemical composition of the top layer was determined by energy dispersive spectroscopy (EDS).

Results and Discussion

Microstructure

The initial microstructure before machining experiment is shown in Figure 4. The grain boundaries are clearly visible throughout the sample.

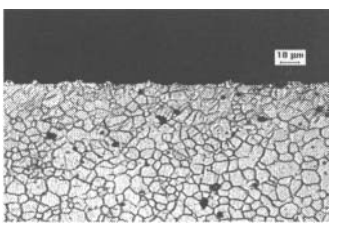


Figure 4. Initial microstructure before machining experiment

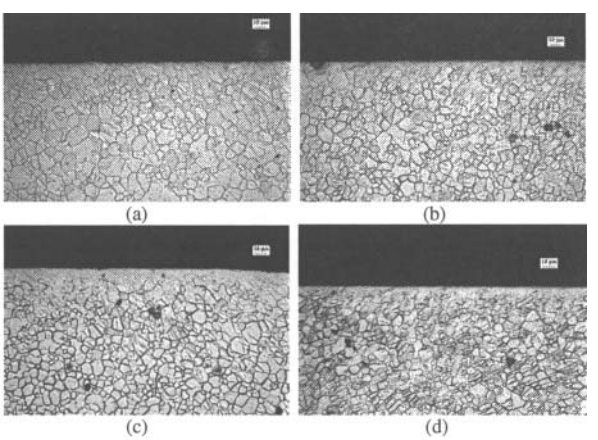


Figure 5. Microstructure of magnesium alloy discs after machining: (a) dry machining, edge radius = 30 μm, (b) cryogenic machining, edge radius = 30 μm, (c) cryogenic machining, edge radius = 68 μm, (d) cryogenic machining, edge radius = 74 μm.

The microstructures of the samples machined under different conditions are presented in Figure 5. Although the grain structures of the bulk material were similar under all machining conditions, significant differences were apparent in the surface layers of different machined samples. For dry machined samples (Figure 5(a)), grain boundaries are clearly visible on the surface. For cryogenic machined samples (Figure 5(b), (c) and (d)), surface layers of different thicknesses, where grain boundaries are not discernable, were formed. This layer of indiscernible grain structure was also reported in other materials after machining, especially in steels, where the term "white layer" was frequently used [13]. While significant research has been done in white layer formation in steels, white layer in magnesium alloys is reported here for the first time.

The influence of machining conditions on white layer formation is clearly seen in Figure 6. Dry machining of magnesium alloys using a tool with 30 μm edge radius did not lead to white layer formation. However, using the same edge radius, a white layer of about 7 μm thickness was formed under cryogenic machining conditions. Under the same cooling condition, the edge radius of the tool played a remarkable role in white layer formation. The thickness of the white layer was increased to about 15 μm when the edge radius was increased to 68 μm. However, further increase in edge radius to 74 μm reduced the white layer thickness.

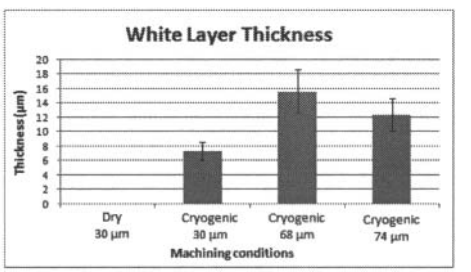


Figure 6. White layer thickness under different machining conditions

Force Analysis

Cutting force and radial force data during machining were analyzed to explore the influencing factors in white layer formation. Both the cutting force and radial force were stable during the 30 second cutting time, indicating little tool-wear and tool/chip adhesion. The cutting forces for all the four experiments remained at about 180 N. However, a significant influence of tool edge radius and cooling method on radial force was present. Figure 7 shows the radial force recorded for the machining experiments. In the cryogenic group, the radial force became larger with increasing edge radius of the tool. A large increase was observed when the edge radius was increased from 30 μm to 68 μm, which corresponds to the large increase in white layer thickness. The radial force was further increased using the tool with 74 μm edge radius. Higher stresses introduced by the large edge radius lead to more deformation twinning within the grains compared with 30 μm and 68 μm. However, the white layer thickness decreased. This may indicate that white layer formation was dependent on both mechanical and thermal effects, which agrees with the research in white layer formation in steels [20].

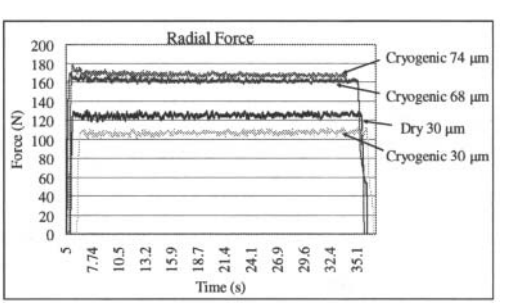


Figure 7. Radial force measurement under different machining conditions

EDS Analysis

To explore the chemical composition of the white layer, energy dispersive spectroscopy (EDS) was used. Figure 8 shows the results of the EDS analysis. Only a little chemical difference between the bulk material and the white layer was found.

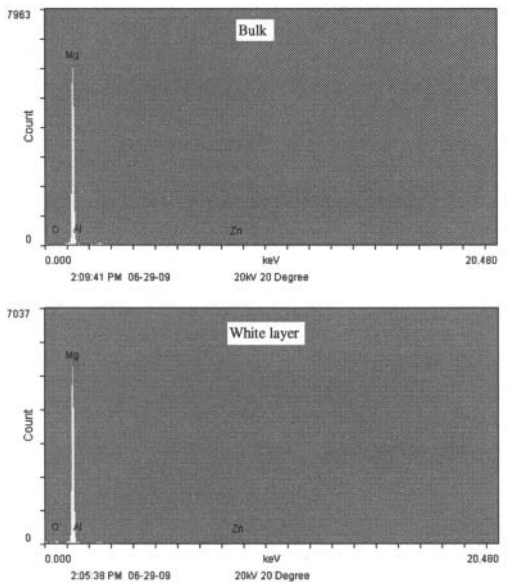
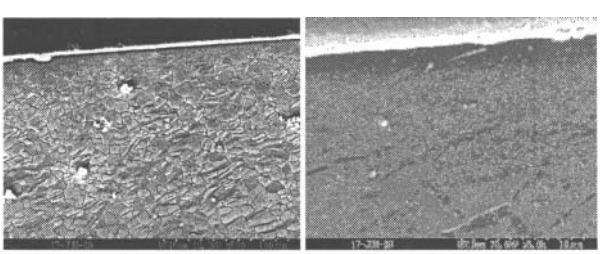


Figure 8. EDS analysis of the bulk material and the white layer

SEM Characterization

Nanocrystallized grain structures were found in white layers in steels [13]. A thick nanocrystallized layer was also found on copper processed by a surface mechanical grinding treatment (SMGT) under liquid nitrogen cooling [15]. Due to the similarity that both cryogenic SMGT and cryogenic machining in producing severe plastic deformation, it is expected that the white layer formed on cryogenically machined magnesium AZ31 samples consisted of nanocrystallized grain structures. To explore this assumption, scanning electron microscope (SEM) and atomic force microscope (AFM) were used to observe the white layer formed on Sample No. 3 (Table I).

Figure 9(a) shows that grain boundaries are clear except the top layer of the sample, and twinning was present more than 100 μm away from the machined surface. Figure 9b shows that grain boundaries in the white layer were not visible even under ×5000 magnification.



(a) (b)

Figure 9. SEM pictures of Sample No. 3: (a) ×500 (b) ×5000.

AFM Characterization

The ability of atomic force microscope (AFM) to measure grain size was studied by several researchers [21, 22]. Phase imaging tapping-mode AFM was reported to successfully provide grain boundary details and the accuracy of the grain size measurements was comparable to TEM measurement with ±10% depending on AFM calibration accuracy. After grinding and polishing, the top portion of the white layer on Sample No. 3 was observed using tapping-mode AFM. The phase image is shown in Figure 10. While no structures were discernable in optical microscope or SEM pictures, some grain-like features were present in the AFM phase image. The mean size of the features was about 45 nm and all the features were smaller than 100 nm. Based on the AFM picture and the literature review on nanocrystallized grains in white layers of steels and copper, a preliminary conclusion can be made that the white layer on the machined surface of magnesium alloys consisted of nanocrystallized grain structures. Further investigation using transmission electron microscope (TEM) will be conducted to verify this conclusion.

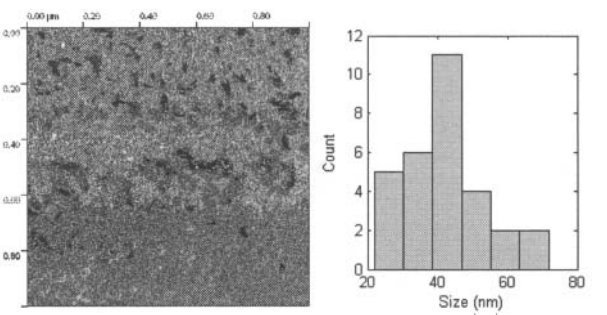


Figure 10. AFM tapping mode phase image of the white layer

In vitro Corrosion Test

The influence of different machining conditions on the biodegradation rate of magnesium alloys was investigated by the *in vitro* corrosion tests. Figure 11 shows accumulative hydrogen evolution per unit area from magnesium AZ31 discs machined under different conditions. The machined samples were left in air for two weeks before the *in vitro* corrosion test, which simulated the passivation stage of implant preparation; a passivated layer was formed on the machined surface due to the oxidation of magnesium in air. This passivated layer was attributed to the different shape of the biodegradation curves compared with other studies, where a very high biodegradation rate occurred at the beginning of the corrosion test.

Preliminary corrosion test results clearly demonstrated the influence of machining conditions on corrosion resistance of magnesium alloys in physiological environment. The slowest corrosion rate occurred on the machined sample with the thickest white layer. However, the sequence of corrosion rates did not agree with the sequence of white layer thickness. Other factors, like deformation twins, may also contribute to the variation in corrosion rate. Other corrosion analyses, such as weight loss and electrochemical methods, will be conducted to verify the results from this preliminary experiment.

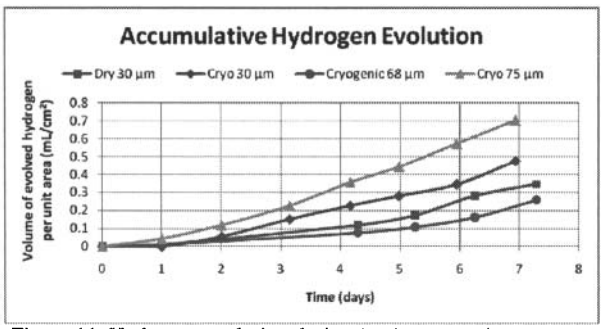


Figure 11. Hydrogen evolution during *in vitro* corrosion test

An interesting phenomenon during the corrosion test was found between the cryogenic machined sample using tool with 68 µm edge radius and the dry machined sample using tool with 30 µm edge radius. The former had the thickest white layer (about 15 µm), while the latter did not have white layer. During the corrosion process, relatively large black spots caused by pitting were formed on the sample without white layer. However, for the sample with the thickest white layer, the whole surface gradually turned dark over time without formation of large black spots. This difference suggested that the sample machined under cryogenic condition underwent more homogeneous corrosion than the one under dry condition. This homogeneity is expected to be beneficial in orthopedic implant applications. The most attractive benefit is the formation of a uniform implant/tissue reaction layer, which may lead to better osseointegration. Also, stress concentration may be avoided due to the homogeneity of the pitting.

Conclusion

The present study shows that the biodegradation rate of the magnesium alloys can be effectively altered by controlling the machining conditions. White layer in magnesium alloys is reported for the first time. The slowest corrosion rate occurred on the cryogenically machined sample with the thickest white layer. Also, corrosion on this sample was found to be more homogeneous compared with the dry machined sample that did not have a white layer.

The AFM phase image suggests that the white layer consisted of nanocrystallized grain structures. The remarkable grain refinement was the combined result of dynamic recrystallization through machining-induced severe plastic deformation and effective suppression of grain growth by liquid nitrogen cooling.

The edge radius of the cutting tool has an important influence on the thickness of the white layer. A combined thermal-mechanical effect for white layer formation was detected.

The preliminary results from the present study reveal a great opportunity to control biodegradation rate of magnesium alloys through advanced process control techniques. Existing knowledge on surface integrity of machined products and various predictive modeling techniques can significantly facilitate the development of a machining-based process to control the biodegradation rate of magnesium alloys. *In vitro* corrosion tests can correlate the surface integrity factors with the corresponding biodegradation rate. In the end, magnesium-based implants with specific biodegradation rate customized to individual medical demands can be manufactured.

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