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DEGRADATION CHARACTERIZATION AND MECHANISMS OF WARM ROLLED Mg-1.6Gd WITH 95% REDUCTION RATIO FOR BIODEGRADABLE IMPLANT APPLICATIONS

Mg-1.6Gd binary alloy was subjected to uniaxial warm rolling at a unidirectional and cross-sectional with a reduction ratio of 95% in order to observe the relationship between its microstructural changes to the degradation behavior. The warm rolling was performed at a temperature range of its recrystallization temperature, which were 400°C and 560°C, and a feed rate of 10 mm/min. Degradation behaviors of Mg-1.6Gd binary alloy was evaluated by means of potentiodynamic polarization and hydrogen evolution test in modified Kokubo's SBF solution at temperature of 37 ± 1ºC. The lowest corrosion rate of 0.126 mm/year derived from potentiodynamic polarization test was showed by unidirectional-rolled specimen at temperature of 560 °C. Hydrogen evolution test results showed the lowest hydrogen gas formed during 24 hours of immersion was found on unidirectional-rolled specimen at temperature of 560°C with a rate of 0.268 cc/cm^2/hours. While cross rolled specimens showed a high corrosion and hydrogen evolution rate of 20 mm/year and 0.28 cc/cm^2/hours.

Keywords: Biodegradable Implants, Mg-1.6Gd, Warm Rolling, Mg-RE, EIS

1. Introduction

Magnesium (Mg) based alloys have been extensively studied as biodegradable and bio-absorbable metallic implant due to its low density, biocompatibility and the similarity of its elastic modulus to natural bone [1-3]. Mg alloys containing rare earth metals, such as Gd and Y, showed high strength, high ductility at a relatively low density [4]. The addition of rare earth metals known to have "scavenger effects" in magnesium alloys in which it will reacts with impurities and settle at the bottom of the alloy during melting process [5]. Furthermore, the high solubility of Gd in Mg found to be beneficial as it could improve the mechanical and corrosion properties significantly. However, large amounts of Gd found to be detrimental for both biocompatibility as well as its mechanical and corrosion properties [6].

Thermomechanical treatment such as rolling known to improve corrosion resistance of Mg-based alloys by refining its grain size and distributing the metallic precipitate uniformly [7].

This study aims to evaluate the effect of warm unidirectional and cross-rolling to its degradation behavior of Mg-1.6Gd in modified Kokubo' SBF solution.

2. Experimental

TABLE 1

Specimens coding of warm rolled Mg-1.6Gd

Specimens Code	Rolling Direction	Rolling Temperature
A	Unidirectional	400°C ±5°C
B		560°C ±5°C
C	Cross	400°C ±5°C
D		560°C ±5°C

Mg-1.6Gd alloy was subjected to unidirectional and cross-directional rolling at temperature of 400°C ±5°C and 560°C ±5°C, the name coding was presented in Table 1. 12 mm in diameter and 5 mm in thickness specimens were cut from the alloy ingots followed by sequentially ground using 320-2000 grit of silicon carbide (SiC) papers. The microstructural features of specimens were observed using optical microscope and a scanning electron microscope (FEI-420) equipped with energy dispersive X-ray spectroscopy (EDS) instrumentation.

The electrochemical test was conducted in a flat cell containing 300 ml modified Kokubo's simulated body fluid

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(m-Kokubo's-SBF [8]) solution at pH 7.41 and a temperature of 37±1°C using a PGSTAT302N. A three-electrode cell was used for potentiodynamic polarization tests, where the reference electrode was a silver-silver chloride electrode (SSC) in saturated KCL solution, the counter electrode was made of platinum plate, and the specimen was the working electrode. All experiments were carried out at a constant scan rate of 0.25 mV/s, initiated at −250 mV below the open-circuit potential.

3. Results and discussion

Fig. 1 displays the optical microscopy images of warm rolled Mg-1.6Gd compared to as-cast specimen. The as-cast specimen showed a rather large and long grain with non-uniform distribution of grain size and shape. Following the rolling process at temperature of 400°C, both unidirectional and cross-rolling supposedly introducing new refined grain size due to its dynamic recrystallization. Furthermore, high temperature rolling found to be redistributing intermetallic precipitate at grain boundaries uniformly.

There was a distinct microstructural feature observed in unidirectional rolled specimens (A and B). At a high rolling temperature of 560°C, the grain size seemed to be fine and uniform in size. While in 400°C, the grain size seemingly to be large in size and shows large amount of twinning. Twinning at 400°C of unidirectional rolling formed due to plastic deformation and accumulation of dislocation inside the grain and act as an initial site for recrystallization [9]. While at 560°C of unidirectional rolling, the higher temperature during rolling resulting in the less formation of twinning inside the grain.

A significantly different behavior observed in cross-rolled specimens C and D, the grains were homogenous and equiaxed. This particular behavior resulted by the cross orientation of rolling process which developed from transformations of sub-grain on twin-twin intersections [10].

Fig. 2 shows SEM images of warm rolled Mg-1.6Gd at a different temperature. It appears that there were large amounts of intermetallic precipitate could be observed in as-cast specimen. This intermetallic precipitate shows similarity in Mg-Gd ratio to Mg_5Gd where the nominal Gd fraction required was 48.2±6.3 wt% [11]. However, the fraction of Gd observed us-

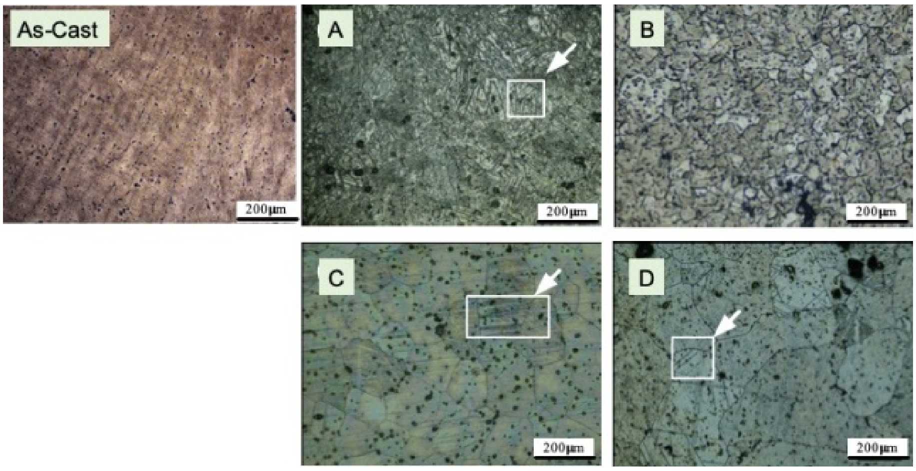
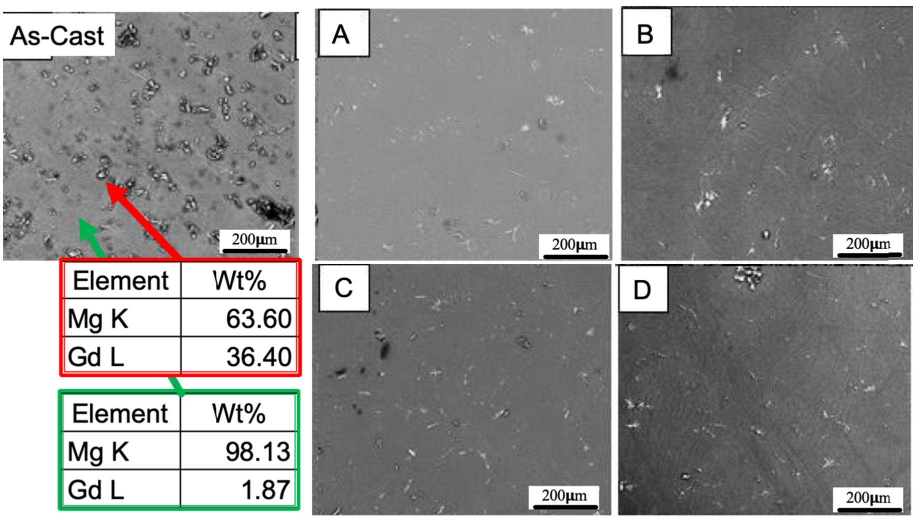


Fig. 1. OM images of warm-rolled Mg-1.6Gd



Element	Wt%
Mg K	63.60
Gd L	36.40

Element	Wt%
Mg K	98.13
Gd L	1.87

Fig. 2. SEM images of warm rolled Mg-1.6Gd

ing EDS was only 36.4 wt%, this could be caused by the small particle size of the precipitate that it limits the reading of EDS instrumentation. While in the warm rolled specimens, there was no clear evidence of intermetallic precipitate with comparable size to as-cast specimen. This could mean that the precipitate was redistributed in a smaller size along the grain boundary.

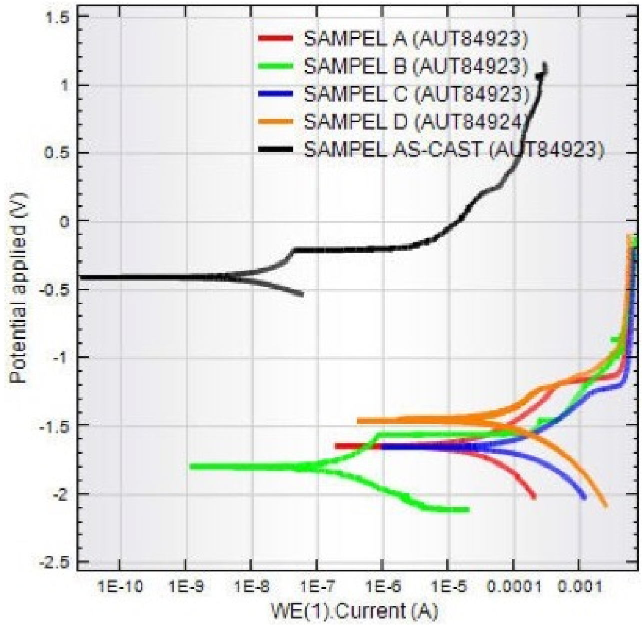


Fig. 3. Polarization curves of warm rolled Mg-1.6Gd

The potentiodynamic polarization curve of warm rolled Mg-1.6Gd was displayed in Fig. 3. While the corrosion parameters derived from the curve were presented in Table 2. It appears that the as-cast specimen showed relatively high corrosion potential and low corrosion current density compared to the warm rolled specimens. This behavior agrees to the corrosion behavior of pure Mg in a similar SBF solution where the as-cast specimen showed a higher corrosion rate compared to hot-rolled specimen [12]. It was also worth noting that the slight passivation behavior observed from the curve of specimen A and C where the rolling temperature was 400°C for both unidirectional and cross-direction. Lower rolling temperature resulting in a larger amount of residual stress received by the specimens, thus accelerating the initial reactions occurred on the surface of specimens. The formation of the corrosion product accumulated on the surface of specimens reduces further reaction. Even though

TABLE 2

Corrosion parameters of warm-rolled Mg-1.6Gd

Specimen	Ecorr (V)	icorr (μA/cm^2)	rate (mm/year)
As-Cast	–0.40	46.81x10-3	0.015
A	–1.65	34.4910	11.268
B	–1.82	0.387	0.126
C	–1.65	210.920	68.908
D	–1.46	61.8160	20.196

the corrosion potential of specimen B seems to be the lowest, the overall corrosion resistance appeared to be the highest amongst the rolled specimens. This behavior corresponds to the evidence where specimen B showed the finest grain size among the rolled specimens [13].

Fig. 4. demonstrates hydrogen gas evolved of immersed warm-rolled Mg-1.6Gd in modified Kokubo's SBF solution at temperature of 37 ± 1ºC. Following the immersion, it appears that the volume of hydrogen gas evolved of warm rolled specimens was significantly higher compared to as-cast one. Similar behavior to the results calculated using potentiodynamic polarization parameters where the initial rate for warm rolled specimens were high. However, prolonged to immersion time, the hydrogen evolution rate was significantly decreased for warm rolled specimen until 6 hour of immersion and gradually increasing afterwards. However, for as-cast specimen, the hydrogen evolution rate was slowly increasing since the initial immersion time. This behavior agrees with the idea of corrosion product formation that slows down the overall corrosion rate even though the nature of its corrosion products was porous [12].

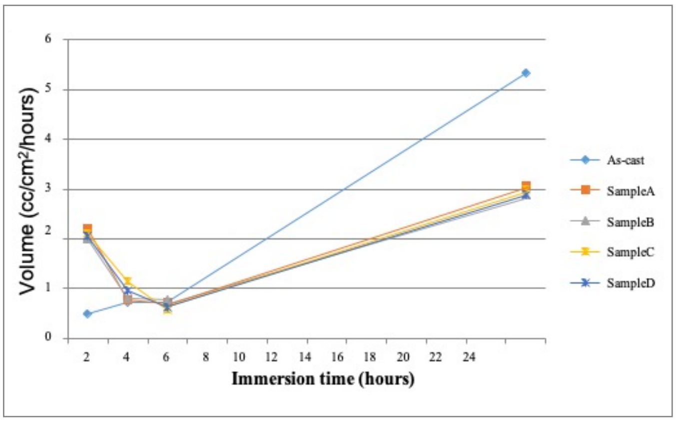


Fig. 4. Hydrogen gas evolved as a function of immersion time

The average changes in pH level of Mg-1.6Gd as a function of immersion times was displayed in Fig. 5. During the immersion, the pH level on the surroundings of specimens would likely to increase based on the amount of hydrogen gas evolved during the immersion [14]. In Fig. 5, it appears that the pH changes

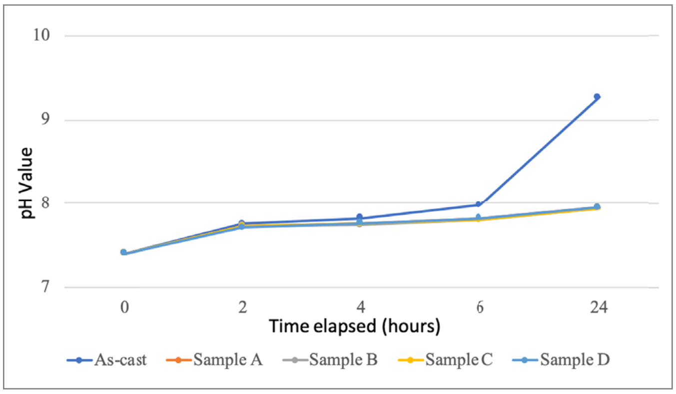


Fig. 5. pH level change as a function of immersion time

of immersed specimens equal to the amount of hydrogen gas evolved where the as-cast specimen possesses the highest pH level changes compared to the warm rolled specimens. The high level of local pH would be detrimental to the surrounding tissue as it could affect its performance and slows down the healing process. While the low changes in pH level of warm rolled specimens could be beneficial during the implantation.

4. Conclusions

Warm cross-rolling of Mg-1.6Gd resulting in a rather homogenous and equiaxed grain compared to unidirectional-rolling due to the orientation change during rolling. Unidirectional-rolled specimen at 560°C showed the lowest corrosion rate of 0.126 mm/year during the immersion test compared to the other warm rolled specimens. Furthermore, the pH changes of warm rolled specimen showed less value compared to as-cast one.

Acknowledgments

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