



## Precipitation control of calcium phosphate on pure magnesium by anodization

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### ABSTRACT

Calcium phosphate precipitated on pure magnesium from artificial plasma (modified Hanks' solution) was varied by anodization and autoclaving, aiming the control of corrosion rate of bioabsorbable magnesium. Rough and smooth anodized film was formed depending on anodizing voltage in 1 N NaOH. The amount of calcium phosphate precipitated on the porous film was 2–3 times larger than that on the smooth film. The Ca/P ratio on the porous film was slightly higher than that on the smooth film. The autoclaving did not significantly influence the morphology of anodized film; however, the precipitation of calcium phosphate was restricted. No significant local corrosion occurred after the immersion in modified Hanks' solution. It is demonstrated that the precipitation of calcium phosphate on magnesium can be controlled by anodization and autoclaving.

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### 1. Introduction

Magnesium and its alloys have high potential as bioabsorbable metals because magnesium is one of the essential elements in the human body and it is easily corroded in a physiological solution. In the first attempts of the application of magnesium alloys for implant devices, the too low corrosion resistance of the alloys probably caused the failure like the formation of hydrogen gas cavity around the devices [1–3]. Afterwards, the corrosion resistance of commercial magnesium alloys has been improved [4]. Recently, the application of commercial magnesium alloys (AE21 and WE43) for bioabsorbable stent and orthopaedic implant is attempted [5–9].

In the human body, the bioabsorbable magnesium devices should keep original strength until the affected part of body is healed. Thus, the corrosion of magnesium should be prevented for the required period for healing which depends on the condition of affected part. Additionally, good biocompatibility of the surface of magnesium to the surrounding tissue is desired. Surface modification is useful to improve biocompatibility in addition to control the corrosion resistance of magnesium alloy.

Various types of surface modification were reported on magnesium alloy to improve the corrosion resistance under physiological environment [10–14]. Kuwahara et al. [10] reported that the magnesium-apatite precipitated on the surface of pure magnesium

(3 N) improved the corrosion resistance. In this case, the precipitation of magnesium-apatite in Hanks' solution was accelerated by heat treatment of magnesium in the air. The magnesium carbonate precipitated on the surface of magnesium alloy sometimes improved the corrosion resistance of magnesium alloy in the case of atmospheric corrosion [15]. Al-Abdullat et al. [11] modified the surface of pure magnesium by NaHCO<sub>3</sub> alkali solution to improve the corrosion resistance. Song [12] reported that the anodized coating formed in K<sub>2</sub>SiO<sub>3</sub> + KOH solution retarded the degradation of magnesium in a physiological solution.

Anodization is a common technique to improve the corrosion resistance of magnesium and its alloys for general purpose [16,17]. Ono et al. [18–20] reported that the morphology and composition of surface is varied by anodizing voltage and electrolytes. The porous and smooth anodized film was formed on magnesium and its alloys by anodizing at different voltages in NaOH solution [18].

Based on the above mentioned facts, it should be possible to control the corrosion rate of magnesium and its alloys by varying the amount of calcium phosphate precipitated in the environment. The precipitation of calcium phosphate is expected to depend on the surface morphology and corrosion resistance which can be varied by anodization. Therefore, in this study, the influence of surface morphology of anodized film of pure magnesium on the precipitation of calcium phosphate in artificial plasma was investigated. To clarify the influence of morphology of anodized film, NaOH solution was used for anodization as a simple solution. Steam treatment is commonly applied on anodized metallic materials to improve corrosion resistance by sealing pores, so that autoclaving

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was performed on the anodized film to extend the control range of the precipitation of calcium phosphate. Surface morphology of specimens was observed using scanning electron microscope (SEM). Concentration of precipitated calcium phosphate was analysed using energy dispersive spectroscopy (EDS).

## 2. Experimental

### 2.1. Anodization and autoclaving

Disks with a diameter of 8 mm and a thickness of 2 mm were cut from extruded pure magnesium (99.95%) rod and used as a substrate. Chemical composition of the extruded pure magnesium is shown in Table 1. The average grain size of the extruded pure magnesium was 1  $\mu\text{m}$ . Both sides of the disk with entire surface area of 1  $\text{cm}^2$  were applied for anodization. The surface of disk was polished up to 600 grid SiC paper (Buelher) in ethanol and ultrasonically rinsed in acetone for 60 s. Immediately after polishing and rinsing, a magnesium disk and a carbon counter electrode were immersed in 500 ml of 1N NaOH solution stirred with a magnetic stirrer at room temperature. Anodizing voltages of 2, 7, 20 and 100 V were applied between the two electrodes using a power source (Takasago GPO350-05). The limiting current of the power source was 500 mA. Anodizing time at 2, 7 and 20 V was 600 s and that at 100 V was 180 s. The anodizing voltage was decided based on the result of Ono et al. [18], showing that the morphology of anodized surface varies depending on voltage. The specimens anodized at 7 and 20 V were autoclaved at 393 K for 1800 s. The name of specimens and prepared conditions are summarized in Table 2.

The surface morphology of As-polished Mg and anodized Mg with and without autoclaving was observed using a scanning electron microscope (SEM). The surface composition was analysed using electron dispersive spectroscopy (EDS).

**Table 1**  
Chemical composition (mass%) of extruded pure magnesium

	Al	Si	Mn	Fe	Zn	Cu	Ni	Mg
Pure Mg	0.003	0.003	0.005	0.002	0.004	<0.001	<0.001	99.95

**Table 2**  
The name of specimens and prepared conditions

Name of specimen	Surface treatment condition
As-polished Mg	Mg polished in ethanol
2 V-anodized Mg	Mg anodized at 2 V for 600 s
7 V-anodized Mg	Mg anodized at 7 V for 600 s
20 V-anodized Mg	Mg anodized at 20 V for 600 s
100 V-anodized Mg	Mg anodized at 100 V for 180 s
Autoclaved Mg	Mg autoclaved after polishing
7 V + autoclaved Mg	Mg autoclaved after 7 V anodization
20 V + autoclaved Mg	Mg autoclaved after 20 V anodization

**Table 3**  
Composition ( $10^{-3}$  mol  $\text{L}^{-1}$ ) of modified Hanks' solution and blood plasma

Composition	Modified Hanks' solution	Hanks' solution	Blood plasma
$\text{Na}^+$	99.6	141.9	142
$\text{K}^+$	5.8	5.8	5.0
$\text{Mg}^{2+}$	0.8	0.8	1.5
$\text{Ca}^{2+}$	1.3	1.3	2.5
$\text{Cl}^-$	102.7	136.9	103
$\text{HPO}_4^{2-} + \text{H}_2\text{PO}_4^-$	0.8	0.8	1.0
$\text{HCO}_3^-$	4.2	4	27
$\text{SO}_4^{2-}$	0.8	0.8	0.5

### 2.2. Immersion in artificial plasma

To evaluate the precipitation behaviour of calcium phosphate, artificial plasma was prepared based on the composition of Hanks' solution [21]. Because concentration of chloride ion of blood plasma [22] is lower than that of Hanks' solution and the corrosion of magnesium is very sensitive to the concentration of chloride ion, the concentration of chloride ion of the prepared artificial plasma was adjusted to that of blood plasma. The prepared artificial plasma was named modified Hanks' solution and its composition is shown in Table 3.

The specimens were immersed in 150 ml of aerated modified Hanks' solution warmed at 310 K. Then, the specimen was taken out from the solution every 1 or 2 h to analyse the surface composition using EDS. The fresh solution was always prepared for re-immersion of the specimen. The total integrated immersion time was 40 h.

## 3. Results and discussion

### 3.1. Surface morphology of anodized specimens

The current–time curves of magnesium anodized at 2, 7, 20 and 100 V are shown in Fig. 1. By applying 2 or 20 V, the current abruptly increased to show a peak current and immediately decreased in 30 s to reach a constant current. The constant current at 20 V slightly increased from 300 s, which suggests the growth of anodized film. In the case at 7 and 100 V, the current abruptly increased to 440 and 500  $\text{mA cm}^{-2}$ , respectively, and kept constant. Because the current at 100 V reached the limiting current of the power source, the anodization was stopped after 180 s. The electric charge during anodization was larger in the order of 7 V- >100 V- >>20 V- >2 V-anodized Mg, which indicates that the anodized film on 7 V- and 100 V-anodized Mg is thicker than that on 20 V- and 2 V-anodized Mg.

The optical microscope images of the surface of 7 V- and 20 V-anodized Mg are shown in Fig. 2. The surface images of 100 V- and 2 V-anodized Mg are very similar to those of 7 V- and 20 V-anodized Mg, respectively. The surface of As-polished Mg was similar to that of 20 V-anodized Mg. The 2 V- and 20 V-anodized Mg showed polishing scar and metallic lustre. The lustre on 20 V-anodized Mg was less than that on 2 V-anodized Mg, which indicates that the former anodized film was thicker than that of the latter film. The 7 V- and 100 V-anodized Mg showed greyish white surface without polishing scar. No significant difference was observed between 7 V- and 100 V-anodized Mg.

After autoclaving of As-polished and 20 V-anodized Mg, the polishing scars remained whereas the metallic lustre disappeared, which suggests the growth of air-formed oxide/hydroxide film and anodized film. The 7 V + autoclaved Mg showed similar surface to that of 7 V-anodized Mg.

The SEM images of the surface of 7 V- and 20 V-anodized Mg with and without autoclaving are shown in Fig. 3. The images of 100 V- and 2 V-anodized Mg are very similar to those of 7 V- and 20 V-anodized Mg, respectively. The 2 V- and 20 V-anodized Mg showed polishing scar like that of As-polished Mg and no crack was observed, which suggests that the anodized film is thin and smooth. The 7 V- and 100 V-anodized Mg was covered with relatively thick and porous anodized film with cracks. The relation between anodizing voltage and morphology of anodized film agrees with that reported by Ono et al. [18].

After autoclaving, the cracks on 7 V-anodized Mg slightly decreased. The edge of polishing scars on As-polished and 20 V-anodized Mg became slightly round. These results might indicate the sealing of pores and growth of surface film. However, no significant

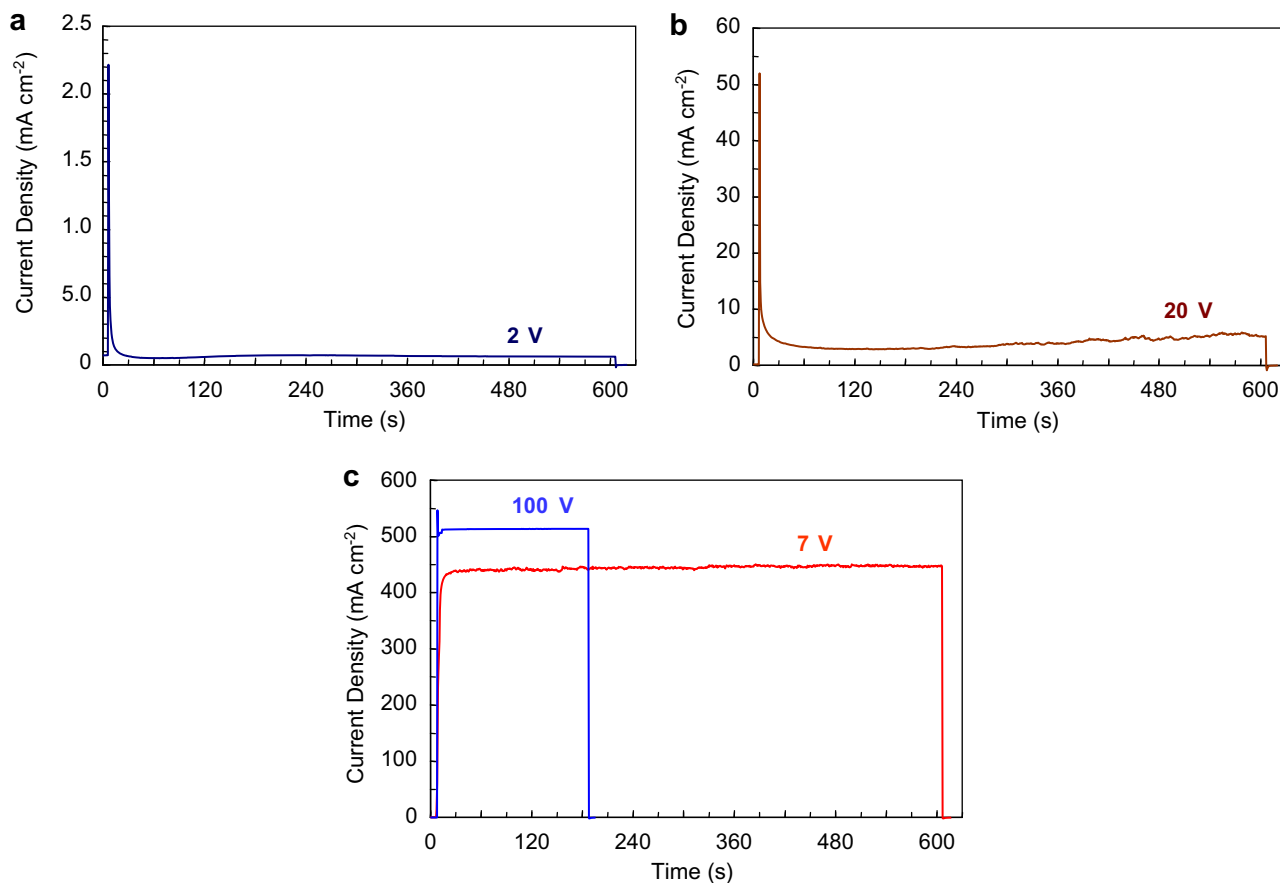


Fig. 1. Current–time curves of pure magnesium anodized in 1 N NaOH at (a) 2 V, (b) 20 V, and (c) 7 V and 100 V.

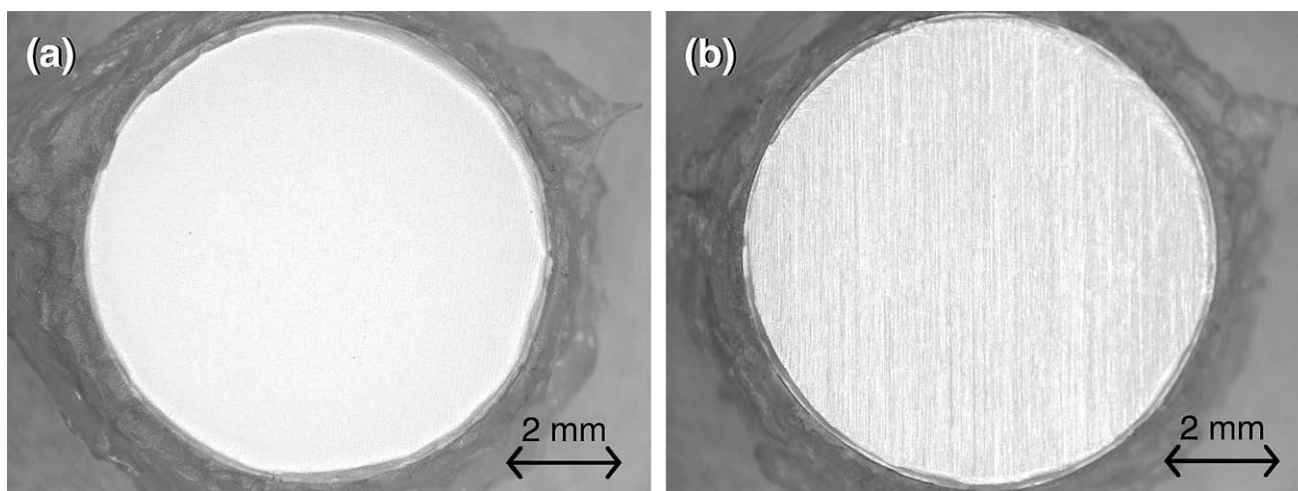


Fig. 2. Optical microscope images of the surface of (a) 7 V-anodized and (b) 20 V-anodized Mg.

influence of autoclaving on the morphology of anodized film was identified by SEM observation.

The surface composition of the specimens analysed using EDS was listed in Table 4. Carbon is suggested to be originated from contamination since carbonate salt of magnesium hardly formed with  $\text{CO}_2$  during the storage of the specimens in a vacuum. The O concentration corresponds to the thickness of anodized film which

increased by anodization and autoclaving, respectively. According to the O concentration, the anodized film of 20 V-anodized Mg was thicker than that of 2 V-anodized Mg, which agrees to the larger electric charge and the less lustre surface of 20 V-anodized Mg than those of 2 V-anodized Mg. The thickness of anodized film of 20 V-anodized Mg became more than double by autoclaving while the less growth of the film of 7 V-anodized Mg was observed. In the

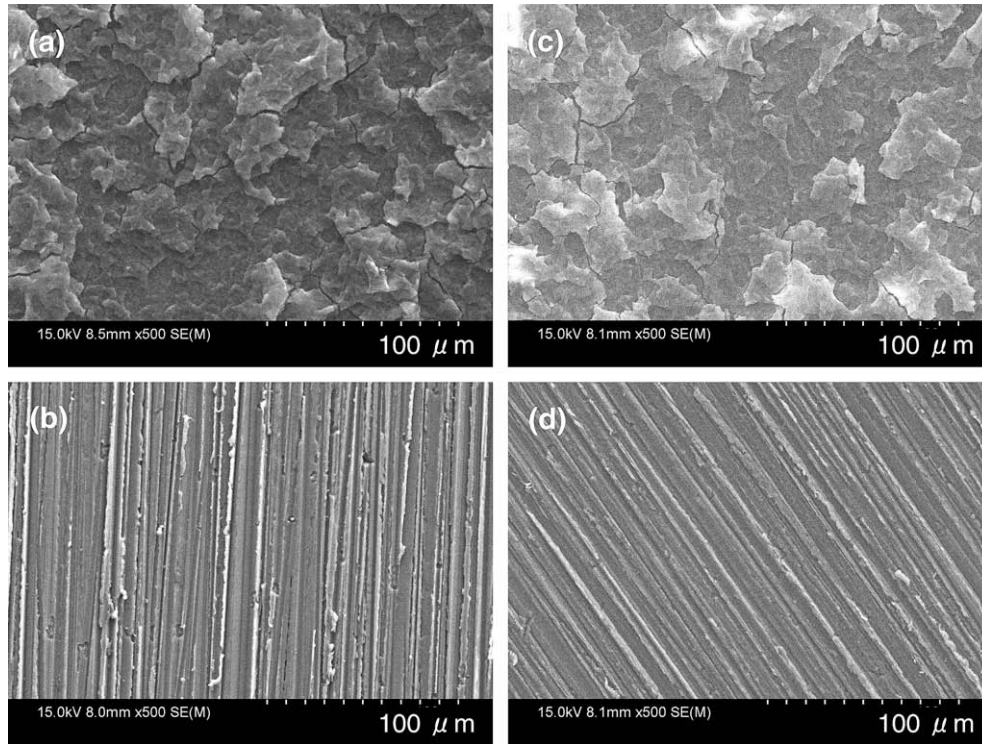


Fig. 3. SEM images of the surface of (a) 7 V-anodized, (b) 20 V-anodized, (c) 7 V + autoclaved and (d) 20 V + autoclaved Mg.

Table 4

Surface composition (at%) of various specimens formed by anodization with and without autoclaving

Specimen	Mg	O	C
As-polished Mg	91.2	3.8	5.0
2 V-anodized Mg	82.7	10.6	6.6
7 V-anodized Mg	43.2	46.8	10.0
20 V-anodized Mg	75.1	17.5	7.4
100 V-anodized Mg	40.1	50.9	9.0
Autoclaved Mg	66.6	28.1	5.3
7 V + autoclaved Mg	35.9	56.6	7.6
20 V + autoclaved Mg	43.9	50.7	5.4

latter case, sealing of pores of anodized film could progress by hydration under the steam of autoclaving like the anodized film of aluminium alloy [23].

3.2. Precipitation of calcium phosphate in modified Hanks' solution

Figs. 4–6 show the concentration of O, Ca and P on the specimens as a function of integrated immersion time in the modified Hanks' solution, respectively. The O concentration of As-polished and anodized Mg increased in the very beginning of immersion while the precipitation of calcium phosphate was very small. This result indicates that the air-formed and anodized film on magnesium grew in the solution. On the other hand, the O concentration of autoclaved specimens did not apparently change during immersion, which indicates that the prolonged oxidation of surface film was prevented by autoclaving. This result also suggests that the corrosion resistance of magnesium in the modified Hanks' solution was improved by autoclaving. In the case of Ca and P, their precipitation behaviour was very similar each other, which indicates that Ca and P precipitate simultaneously and form calcium phosphate.

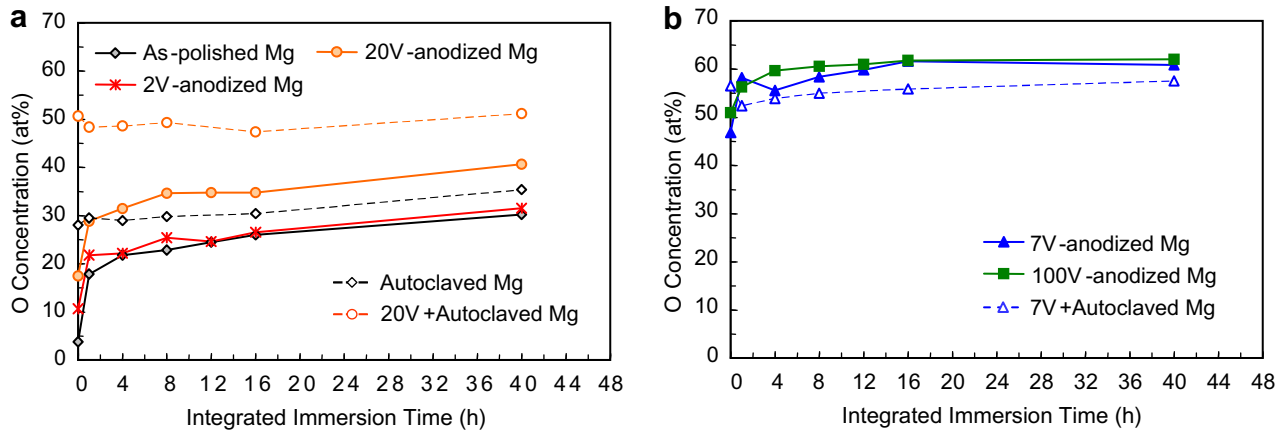
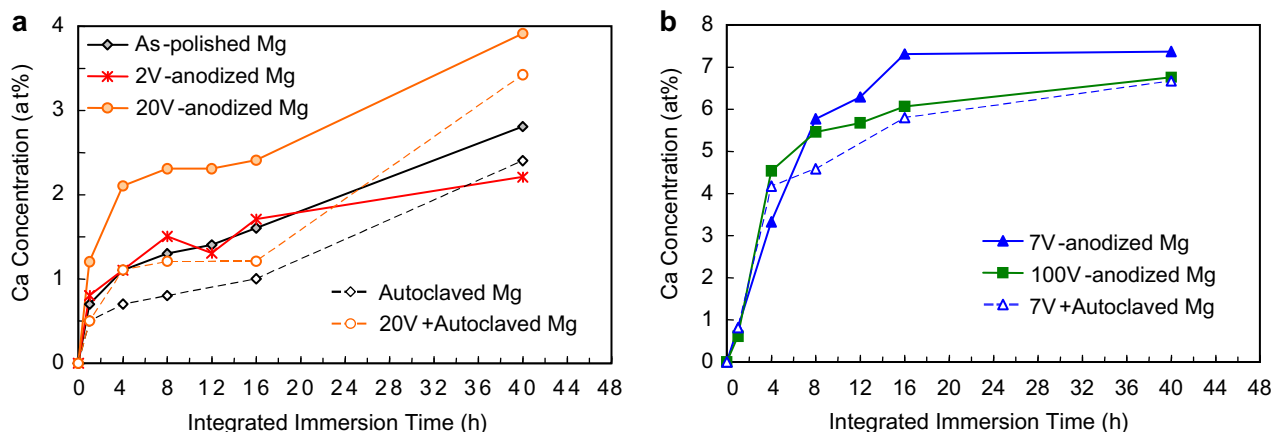
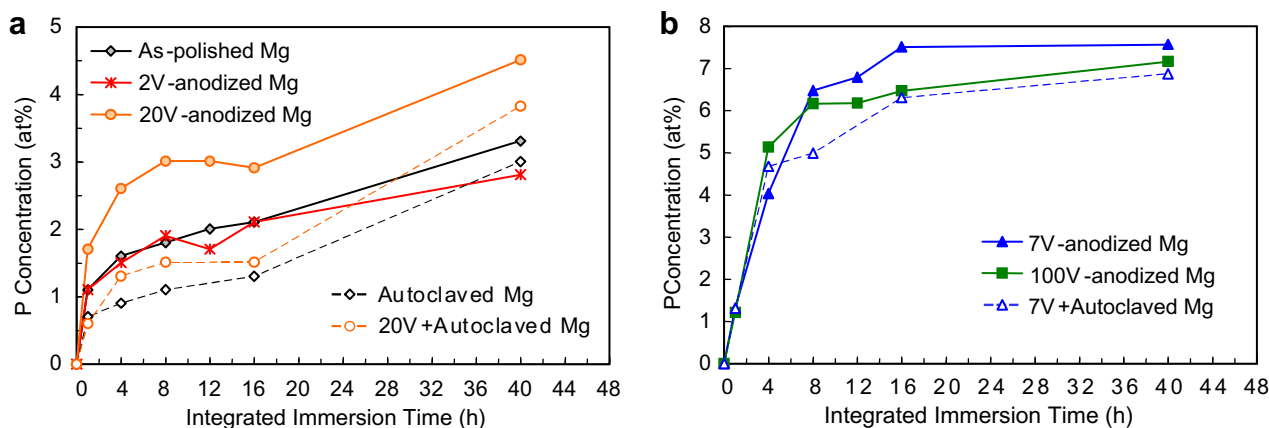


Fig. 4. Concentration of O of the surface of specimens as a function of integrated immersion time in the modified Hanks' solution. Concentration of O on (a) As-polished, 2 V-anodized and 20 V-anodized Mg with and without autoclaving. Concentration of O on (b) 7 V-anodized and 100 V-anodized with and without autoclaving.





**Fig. 5.** Concentration of Ca precipitated on the specimens as a function of integrated immersion time in the modified Hanks' solution. Concentration of Ca on (a) As-polished, 2 V-anodized and 20 V-anodized Mg with and without autoclaving. Concentration of Ca on (b) 7 V-anodized and 100 V-anodized Mg with and without autoclaving.



**Fig. 6.** Concentration of P precipitated on the specimens as a function of integrated immersion time in the modified Hanks' solution. Concentration of P on (a) As-polished, 2 V-anodized and 20 V-anodized Mg with and without autoclaving. Concentration of P on (b) 7 V-anodized and 100 V-anodized with and without autoclaving.

On the smooth film on As-polished and 2 V- and 20 V-anodized Mg with and without autoclaving, the concentration of calcium phosphate showed a steep increase in the initial 4 h followed by a gradual increase. At 40 h of immersion, the concentration of calcium phosphate was higher in the order of 20 V-anodized > 20V + autoclaved  $\approx$  As-polished  $\approx$  Autoclaved  $\approx$  2 V-anodized Mg. Without autoclaving, the thicker anodized film of 20 V-anodized Mg probably caused the larger precipitation of calcium phosphate than the thinner anodized film of 2 V-anodized Mg.

On the porous film on 7 V- and 100 V-anodized Mg with and without autoclaving, the concentration of calcium phosphate showed a steep increase in the initial 4 h followed by a gradual increase until reaching a constant value after 16 h of immersion. In the beginning, there was not a significant difference between specimens. After 40 h of immersion, the concentration of calcium phosphate on 7 V-anodized Mg was slightly higher than those on 100 V-anodized and 7 V + autoclaved Mg. Ono et al. [19] reported that the anodized film formed over dielectric breakdown voltage showed higher corrosion resistance than that formed at lower voltage in the salt spray test. This result suggests that the corrosion resistance of 100 V-anodized Mg is higher than that of 7 V-anodized Mg. The improvement of corrosion resistance of magnesium causes the restriction of pH-increase near the surface, which can retard the precipitation of calcium phosphate from the modified Hanks' solution supersaturated with calcium and phosphate ions at neutral pH.

The concentration of calcium phosphate on anodized Mg, except 2 V-anodized Mg, was higher than those on the As-polished and Autoclaved Mg. This fact demonstrates that the precipitation of calcium phosphate on magnesium is enhanced by anodization. The porous thick anodized film always showed 2–3 times higher concentration of calcium phosphate than the smooth thin anodized film. This is attributed to the increase of surface area and the existence of pores which can be the nucleation site for calcium phosphate.

The concentration of calcium phosphate of the specimens after autoclaving was always lower than that without autoclaving, which demonstrates that the autoclaving restricts the precipitation of calcium phosphate. Generally, the sealing of pores of anodized film in the steam of autoclaving improves the corrosion resistance of magnesium [16,23]. The sealing of pores of anodized film probably leads to the decrease of true surface area and nucleation site for calcium phosphate although significant difference in morphology with and without autoclaving was not identified by SEM observation. These facts suggest that the decrease of calcium phosphate by autoclaving is attributed to the increase of corrosion resistance of anodized film and the decrease of nucleation site.

The Ca/P ratio on the surface of specimens as a function of integrated immersion time in the modified Hanks' solution is shown in Fig. 7. The Ca/P ratio on all the specimens was less than 1.0, which

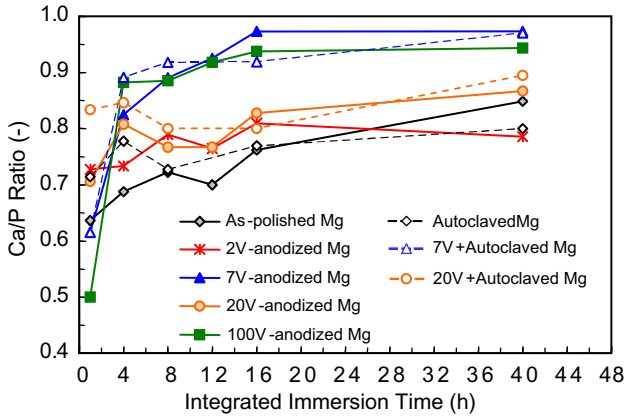


Fig. 7. Ca/P ratio of calcium phosphate precipitated on the surface of the specimens as a function of integrated immersion time in the modified Hanks' solution.

suggests that the precipitated calcium phosphate is amorphous. The Ca/P ratio on the porous anodized film was higher than that

on the smooth anodized film after 8 h of immersion. This result suggests that the morphology of anodized film affects the precipitation mechanism of calcium phosphate.

Eventually, the control of surface morphology by anodization is effective to control the precipitation of calcium phosphate on magnesium. Moreover, the combination of anodization and autoclaving extends the control range of the precipitation of calcium phosphate. The corrosion behaviour and biocompatibility of anodized magnesium in a physiological environment will be reported near future. Additionally, further investigation on the composition as well as morphology of anodized film is necessary to optimize the biocompatibility of bioabsorbable magnesium.

3.3. Surface of magnesium specimens after immersing in modified Hanks' solution

The SEM images of the As-polished, 7 V- and 20 V-anodized Mg with and without autoclaving after the 40-h immersion in the modified Hanks' solution are shown in Fig. 8. The 100 V-anodized Mg showed similar surface to that of 7 V-anodized Mg. On the As-polished and 7 V-, 20 V- and 100 V-anodized Mg, small

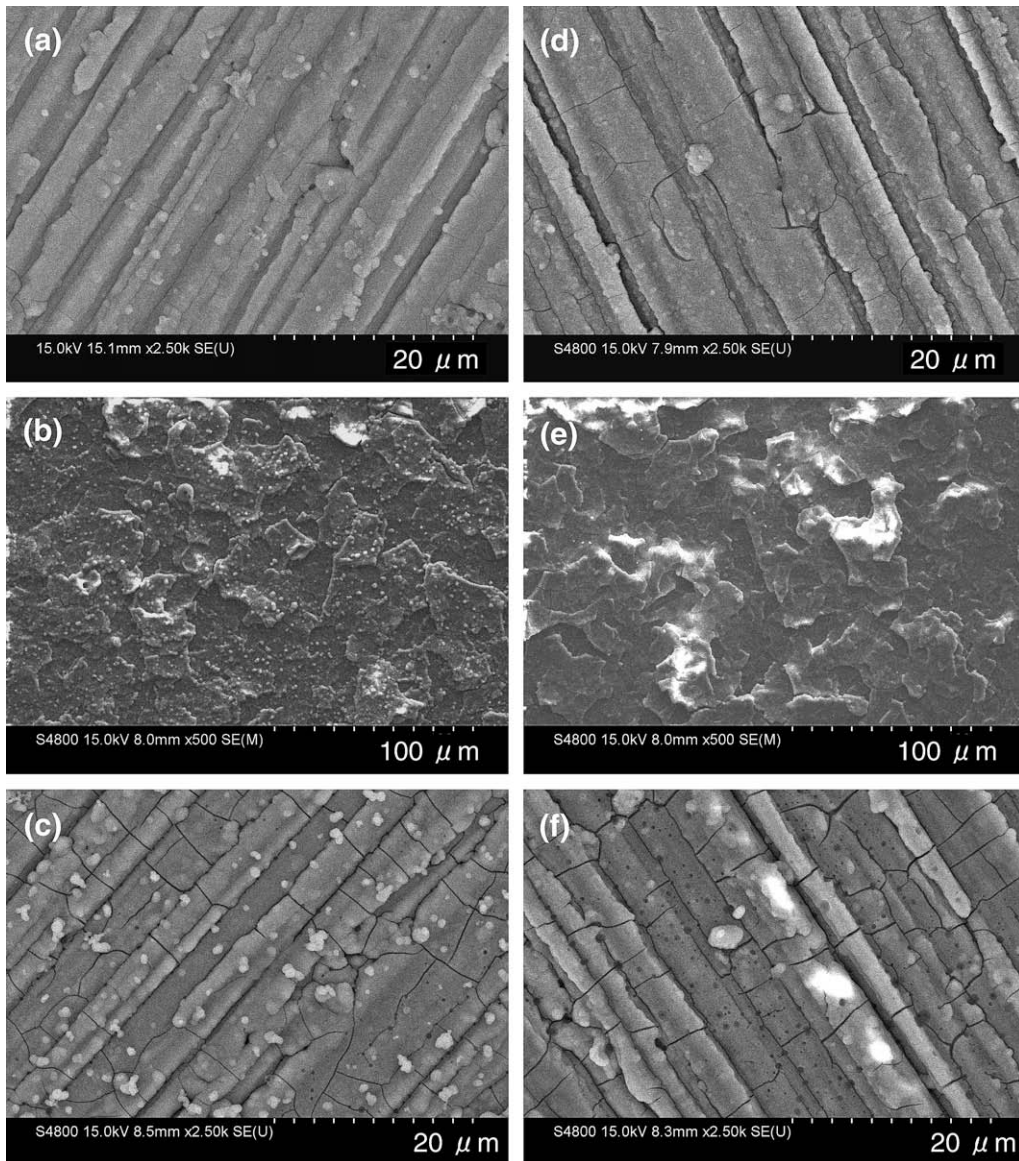
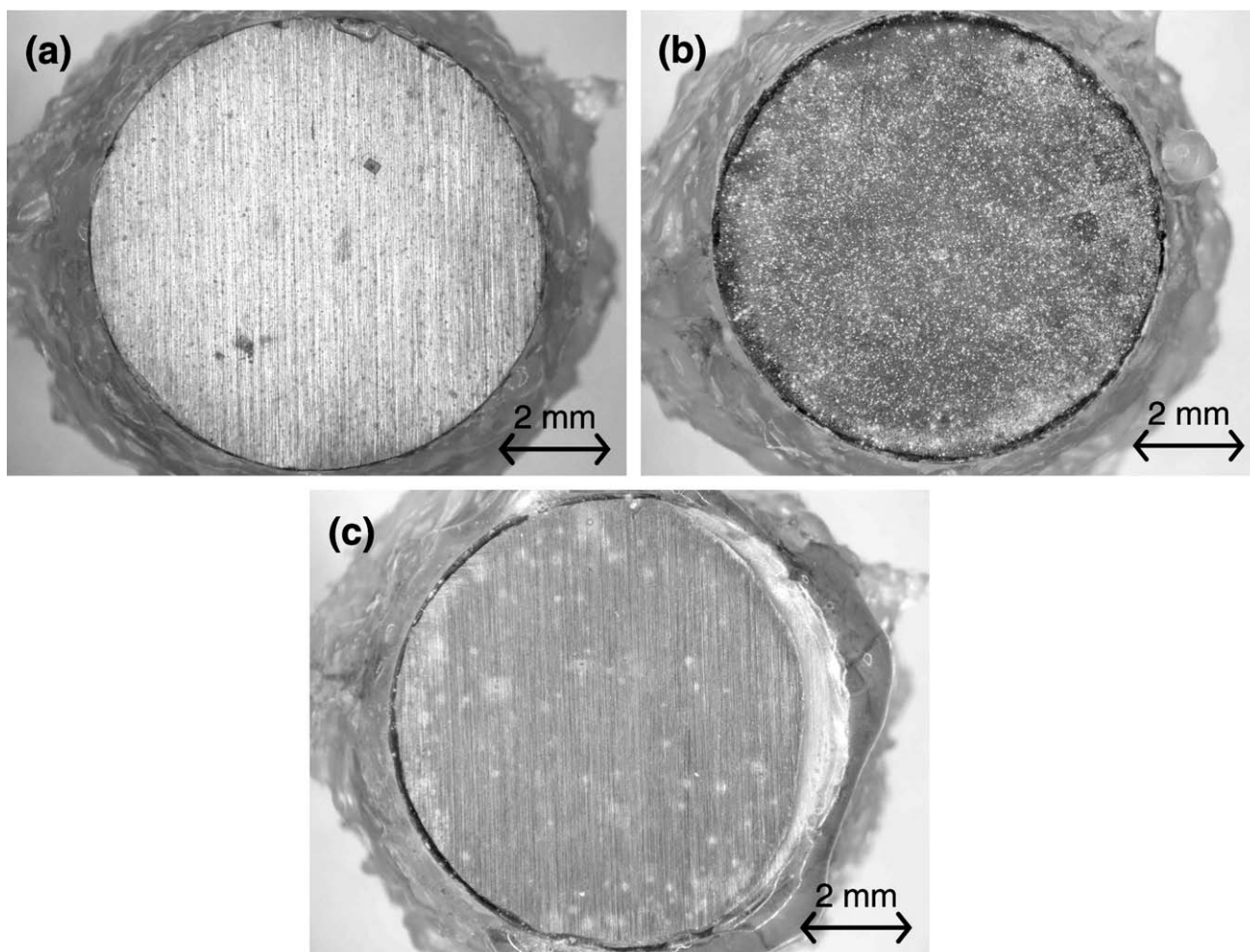


Fig. 8. SEM images of the surface of (a) As-polished, (b) 7 V-anodized, (c) 20 V-anodized Mg, (d) Autoclaved, (e) 7 V + autoclaved and (f) 20 V + autoclaved Mg after immersing in the modified Hanks' solution for 40 h.



**Fig. 9.** Optical microscope images of the surface of (a) As-polished, (b) 7 V-anodized and (c) 20 V-anodized Mg after immersing in the modified Hanks' solution for 40 h.

particles with a diameter of a few  $\mu\text{m}$  were dispersed on the precipitated calcium phosphate layer. The polishing scar and roughness of anodized film did not affect the dispersion of the small particles. The cracks of precipitates layer were formed on 20 V-anodized Mg more than that on As-polished and 2 V-anodized Mg, which indicates that the calcium phosphate layer on the 20 V-anodized Mg was thicker than that on the As-polished and 2 V-anodized Mg.

After autoclaving, the amount of small particles decreased. The concentration of calcium phosphate decreased after autoclaving. These facts suggest that the small particles correspond to the nucleus of calcium phosphate.

Optical microscope images of the As-polished and 7 V- and 20 V-anodized Mg after immersing in the modified Hanks' solution for 40 h are shown in Fig. 9. The surface of 2 V- and 100 V-anodized Mg was similar to those of As-polished Mg and 7 V-anodized Mg, respectively. Interesting thing is that no significant corrosion, especially no local corrosion, was observed on all the specimens. The weight of specimen was measured before and after each immersion, and the weight loss was under the limit of detection ( $<0.5 \text{ mg cm}^{-2}$ ). In this study, the specimen taken out from the solution was exposed to a vacuum for EDS analysis. In a vacuum, the mature of precipitated calcium phosphate layer and magnesium oxide/hydroxide film probably proceeded, leading to the increase of corrosion resistance. Additionally, the breakdown of magnesium oxide/hydroxide film could be prevented with precipitated calcium phosphate.

#### 4. Conclusions

The pure magnesium was anodized in 1 N NaOH solution at various voltages to vary the surface morphology. Autoclaving of the As-polished and anodized Mg was subsequently carried out to grow the surface film and to seal the pores of anodized film. The influence of surface morphology of magnesium on the precipitation behaviour of calcium phosphate was examined in the modified Hanks' solution. The porous anodized film formed at 7 and 100 V showed larger precipitation of calcium phosphate than the smooth anodized film formed at 2 and 20 V, probably owing to the existence of pores providing nucleation site and the larger true surface area. On the other hand, the sealing of anodized film by autoclaving reduced the precipitation of calcium phosphate, owing to the improvement of corrosion resistance and the decrease of nucleation site. The Ca/P ratio of precipitated calcium phosphate layer on the porous anodized film was slightly higher than that on the smooth anodized film. Interestingly, no significant corrosion, especially no local corrosion, occurred on all the magnesium specimens immersed in the modified Hanks' solution for 40 h. It is demonstrated that the precipitation of calcium phosphate on magnesium can be controlled by anodization and autoclaving.

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