EFFECT OF CITRIC ACID AS A CHELATING AGENT ON THE MICROSTRUCTURE AND COMPOSITION OF HYDROTHERMALLY-PREPARED CAP COATINGS ON AZ31 MAGNESIUM ALLOY

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Abstract

In this study, the effect of citric acid as a chelating agent on the microstructure, chemical, and phase composition of hydrothermally prepared CaP coatings on AZ31 magnesium alloy was observed. The coatings were deposited in a reaction mixture at pH 5, 7, and 9, where the concentration of the chelating agent was set at 5, 50, and 500 mM, respectively. The microstructure and chemical composition of all deposited coatings were characterized by scanning electron microscopy with an energy dispersive spectrometer (SEM-EDS). The measured data were compared with thermodynamic calculations using Hydra-Medusa chemical equilibrium software.

Keywords: AZ31 magnesium alloy, CaP coatings, citric acid, chelating agent, hydrothermal synthesis

1. INTRODUCTION

Magnesium-based materials and magnesium alloys have gained much attention as biodegradable metals due to their similar mechanical properties to human bone, biocompatibility, and biodegradability [1,2]. Calcium phosphate (CaP)-based biomaterials are currently very promising materials. In addition, their properties can be positively influenced by the use of chelating agents such as ethylenediaminetetracetic acid (EDTA), nitrilotriacetic acid (NTA), citric acid, gluconic acid, etc [3]. These agents prevent the precipitation of divalent and trivalent metal cations in alkaline media and form a stable complex with Ca ions (**Figure 1**) in which the metal ions are bound tightly enough to prevent them from reacting further [3-5]. Furthermore, these reagents prevent the complex from further reactions that may occur during processing. The structure of CaP coatings and the size of the crystals are further influenced by the reaction temperature, reaction time, and pH value [4,6]. The aim of this study is to assess the effect of citric acid as a chelating agent on the structure of CaP coatings prepared at various pH values.

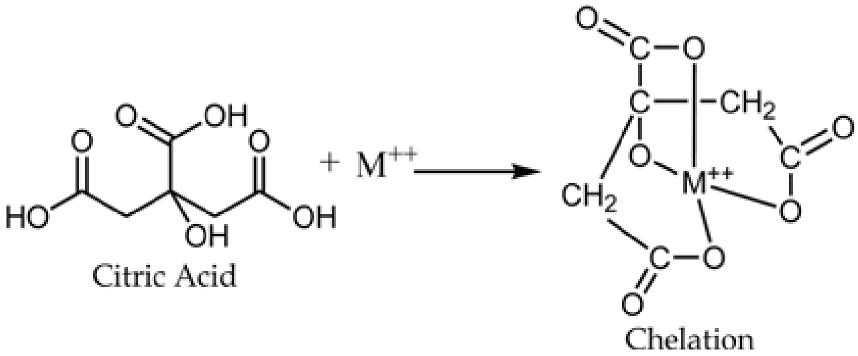

Figure 1 Coordination of metal ions with citric acid [3]

2. EXPERIMENTAL

The samples of AZ31 magnesium alloy were cut from origin sheets to samples with dimensions of 20×20×5 mm. The elemental composition of AZ31 magnesium alloy was the same as in our previous studies [6-7]. The surface of magnesium samples was ground using #1200 SiC paper. Then, the samples were rinsed in distilled water and ethanol and air-dried.

To unify the surface, and to prevent the excessive dissolution of the Mg substrates during the hydrothermal synthesis, a stable and compatible $Mg(OH)_2$ layer was deposited on the surface of ground samples. $Mg(OH)_2$ layer was prepared under hydrothermal conditions in 2 mol/l NaOH solution at 120 °C for 12 hours. After this, the samples were rinsed in distilled water and ethanol and air-dried [8].

The preparation of the reaction mixture was carried out at laboratory temperature. The reaction mixture was prepared by mixing 175 ml of solution A containing 0.15 mol/l $Ca(NO_3)_2 \cdot 4H_2O$ and citric acid with different concentrations (0, 5, 50, or 500 mM). Then, 125 ml of solution B containing 0.14 mol/l of $NH_4H_2PO_4$ was dropwise added into vigorously stirred solution A. The pH value was then adjusted to the pH values 5, 7, or 9 using 1 mol/l NaOH solution.

Magnesium samples were hung on a special holder covered with Teflon and were transferred into a 250 ml Teflon-lined stainless steel pressure vessel containing 150 ml of the prepared reaction mixture. The pressure vessel was placed into the Memmert UF55 (Memmert GmbH + Co.KG, Büchenbach, Germany) electric oven heated up to 120 °C for 150 minutes. After the deposition, coated magnesium samples were rinsed with distilled water, and alcohol, and air-dried.

The surface morphology and chemical composition of the prepared coatings were analyzed using Zeiss EVO LS-10 scanning electron microscope (SEM) (Carl Zeiss Ltd., Cambridge, UK) with energy dispersive spectrometer (EDS) Oxford Instruments Xmax 80 mm^2 (Oxford Instruments plc, Abingdon, UK). AZtec software (version 2.4, Oxford Instruments, High Wycombe, UK) was used to analyze the obtained EDS data.

3. RESULTS AND DISCUSSION

Figure 2 shows the SEM morphology of deposited CaP coatings upon the addition of the various concentrations of a chelating agent (citric acid) for selected pH values (5, 7, and 9). By comparing the individual structures, we can see a significant effect of the concentration of citric acid and pH value on the morphology of CaP coatings.

In the first series, a CaP coating was prepared without the addition of a chelating agent. The coating was prepared only from potassium dihydrogen phosphate and calcium nitrate precursors. As can be seen from **Figure 2**, at pH 5, 7, and 9, a finely structured coating consisting of lamellar crystals was formed. By comparing the individual coatings, it is clear that the coating deposited at pH 5 is slightly different from the coating prepared at pH 7 and 9. The coating deposited at pH 5 is relatively homogeneous from a macroscopic point of view, with no structural defects (such as cracks, flakings, etc.). On a close inspection, a lamellar substructure consisting of fine ribbon-like CaP particles is evident. At pH 7 and 9 (**Figures 2b-c**), the coatings were similar, and no noticeable difference was observed. From detail, it is clear that the coatings at pH 7 and 9 are slightly denser than the coating deposited at pH 5 and the individual CaP lamellae are coarser. In addition, at pH 9 (**Figure 2c**), the presence of 10-15 um fine globular formations could be observed on the surface of the coating. These are likely to be adherent precipitates of CaP particles from the coating mixture. These formations are composed of very fine needles. The EDS analysis of all deposited coatings without citric acid is summarized in **Table 1.** Based on the available literature and the EDS analysis performed, it was found that the coating deposited at pH 5 would most closely correspond in composition to the tricalcium phosphate (TCP) phase or to mixtures of TCP and dicalcium phosphate dihydrate (DCPD). In the case of the coating deposited at pH 7 and 9, the atomic composition is between HAp and OCP (**Table 1**) [9,10].

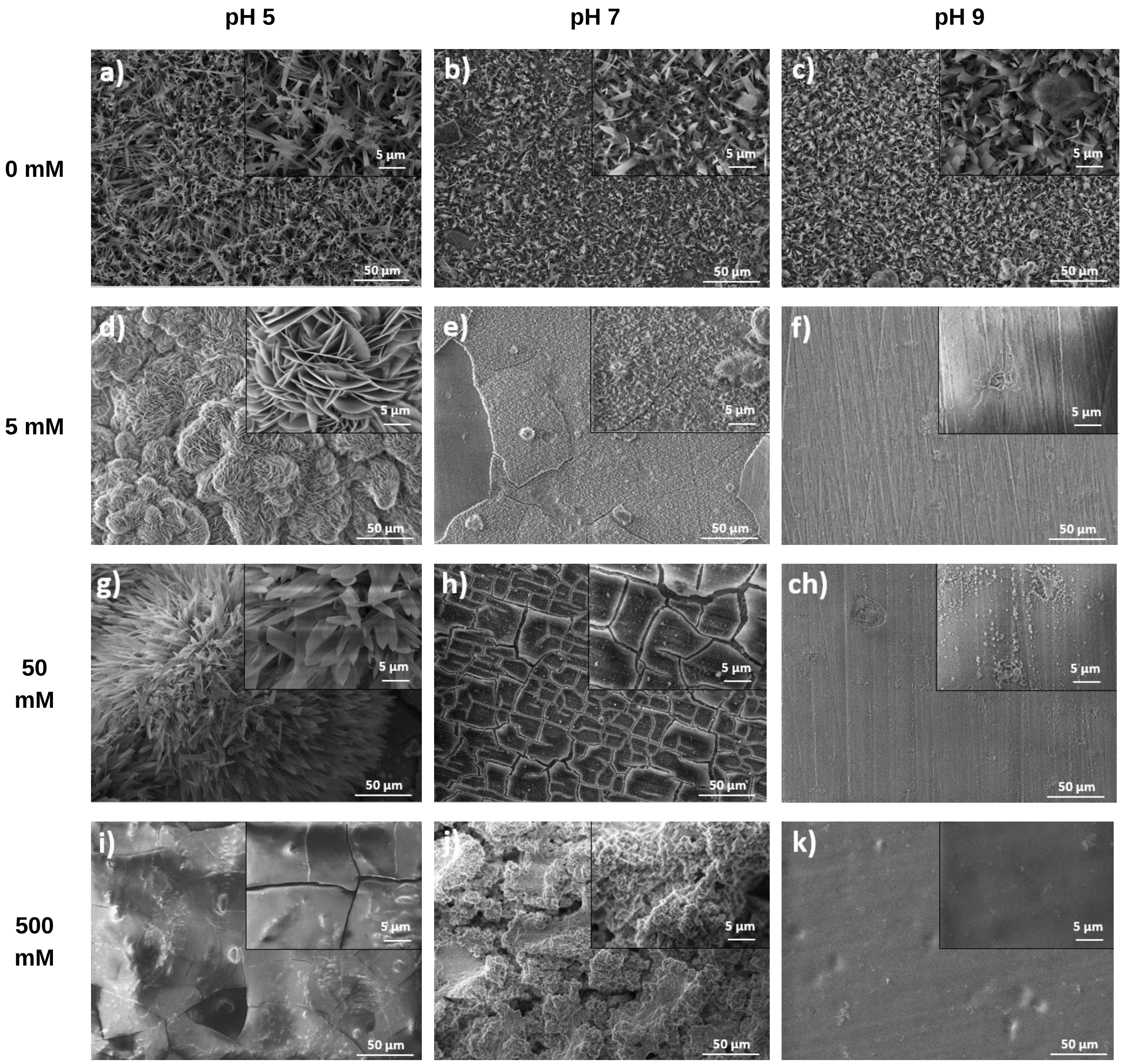

Figure 2 Surface morphology of prepared CaP coatings

Table 1 EDS analysis of layers prepared at pH 5, 7 and 9 without citric acid

pH	Ca	P	O	Other elements
5	20.39	13.98	61.79	3.84
7	22.91	15.58	57.21	4.30
9	22.67	15.82	56.93	4.58

In order to estimate the formation of CaP phases on the Mg surface, a simulation of possible chemical equilibria was performed using Hydra-Medusa software. According to the Hydra-Medusa software, DCPD; HAp with HPO_4^{2-},$H_2PO_4^-$ (in mixture); and HAp with HPO_4^{2-} (in mixture) are formed at pH 5, 7, and 9 respectively under equilibrium conditions (**Figure 3a**).

It can be due to the fact that the Hydra-Medusa software indicates the presence of only stable phases. Deposition of CaP coatings takes place under non-equilibrium conditions, which can lead to the formation of unstable phases like TCP, OCP (octacalcium phosphate), etc. According to the diagram from Hydra-Medusa software (**Figure 3a-d**), the deposited coating at pH 7 and 9 should consist of HAp phase. As described above the OCP phase is not recorded in the diagram due to equilibrium conditions.

By the addition of 5 mM of citric acid into the reaction mixture with pH 5, a coating consisting of approx. 30 µm globular formations were deposited on the substrate surface (**Figure 2d**). These formations did not cover the entire surface. Structural defects, mostly cracks, could be observed. From the detail, it is clear that these globular formations have a lamellar substructure. At pH 7, the formed coating was very thin (**Figure 2e**). From the macroscopic point of view, cracks in the coating and local peeling of parts of the coating are evident. At a closer look, the layer is composed of fine lamellae. From a macroscopic point of view, no formed coating can be observed on the substrate deposited at pH 9 (**Figure 2f**). EDS analysis of all deposited coatings prepared by addition of 5 mM of citric acid is summarized in **Table 2**. Probably at higher pH value, the HAp particles were already precipitated in the reaction mixture and were not deposited on the Mg substrate.

Table 2 EDS analysis of layers prepared at pH 5, 7 and 9 and concentration of citric acid 5 mM

pH	Ca	P	O	Mg	C	Other elements
5	20.88	18.70	60.42	0.00	0.00	0.00
7	19.36	15.09	61.78	3.22	0.00	0.55
9	0.00	0.29	62.56	33.09	3.85	0.21

Increasing the concentration to 50 mM resulted in a change of structure. The coating deposited at pH 5 (**Figure 2g**) formed globular formations similar to the formation in the case of 5 mM of citric acid (**Figure 2d**). However, at closer look shows that the substructure of the globular formations is different. The globular formations did not form a uniform coating on the surface of the substrate. The surface between the globular formations is covered by a thin film that is severely disturbed by cracks. The deposited coating at pH 7 formed a fine, strongly cracked film that covered the substrate surface (**Figure 2h**). At pH 9 (**Figure 2ch**), as in the previous case (pH 9, 5 mM of citric acid), no coating was formed.

According to the EDS results (**Table 3**), at pH 5, the coating is not formed by CaP, because the analysis did not detect the presence of P. Higher content of carbon was also detected. According to the Hydra-Medusa diagram, at pH 5, under equilibrium conditions, more citrate compounds (probably calcium citrate) should be formed in the mixture, but also the DCPD phase. It can be assumed that there was a formation of citrate on the surface. Based on EDS analysis of the deposited coating at pH 7 it was determined that the deposited coating is composed of the DCPD phase or a mixture of DCPD and OCP. According to Hydra-Medusa (**Figure 3c**), citrate, and HAp should be formed at pH 7 and 9. The presence of citrate may be due to the higher carbon content.

Table 3 EDS analysis of layers prepared at pH 5, 7 and 9 and concentration of citric acid 50 mM

pH	Ca	P	O	Mg	C	Other elements
5	13.68	0.00	46.46	0.00	39.86	0.00
7	15.00	12.13	53.39	7.35	10.80	1.33
9	0.00	0.11	64.79	34.69	0.00	0.41

Increasing the concentration of the addition of the chelating agent citric acid to 500 mM led to a change in the morphology of the deposited coating (**Figure 2**). The coating deposited at pH 5 formed a smooth film (**Figure 2i**). No distinct substructure of the deposited coating can be observed from the detailed image and the coating may be formed on an organic basis based on its appearance. The SEM images revealed distinct structural cracks. The deposited coating at pH 7 (**Figure 2j**) was roughened and formed by cracks and pores. The coating formed at pH 9 (**Figure 2k**) was very thin. There was minimal overlap of the grooves from the ground Mg substrate. Considering the results of the EDS analysis (**Table 4**), the deposited coating is mainly composed of calcium citrate phase and possibly a small amount of Hap (**Figure 3d**).

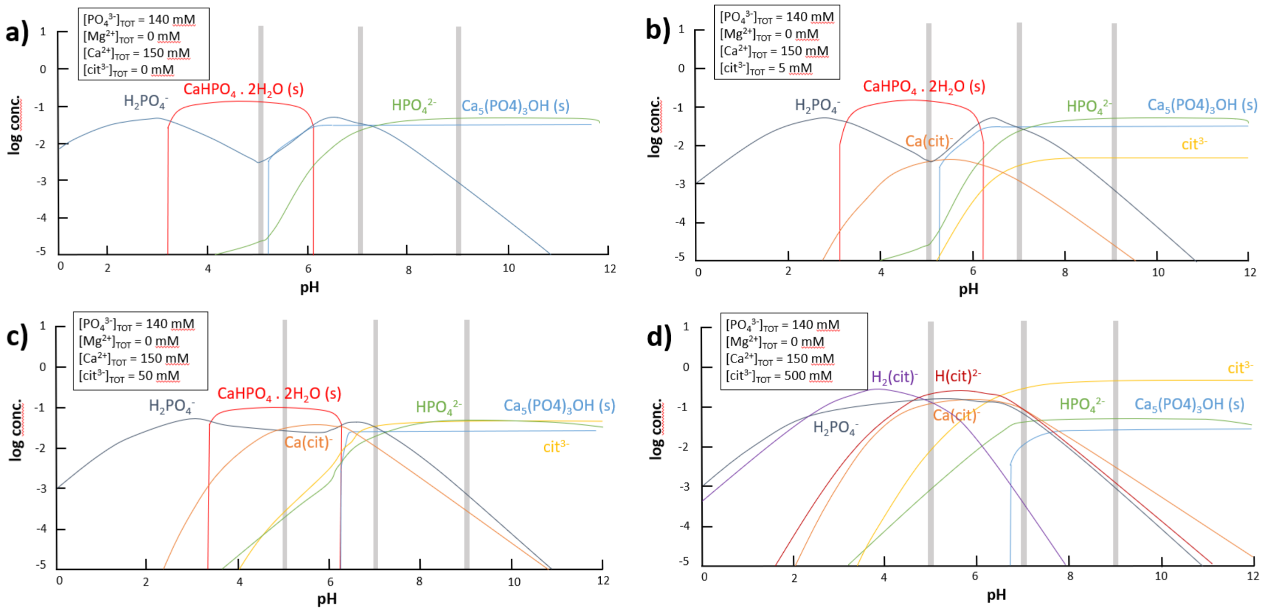

Figure 3 Thermodynamic calculations from Hydra-Medusa chemical equilibrium software

Table 4 EDS analysis of layers prepared at pH 5, 7 and 9 and concentration of citric acid 500 mM

pH	Ca	P	O	Mg	C	Other elements
5	7.41	5.36	50.25	0.50	30.01	6.47
7	10.96	5.21	50.10	0.63	23.77	9.33
9	2.21	1.50	49.98	0.31	29.11	16.89

4. CONCLUSION

Based on the above presented findings, the following conclusions can be drawn:

- Citric acid, as a chelating agent, affects the structure and composition of deposited coatings - without the addition of the chelating agent, the deposited CaP coatings consisted of lamellar crystals.
- The addition of 5 mM citric acid in the reaction mixture led to a change in the structure of the CaP coatings. The original lamellar formations gave rise to coarser and denser globular formations consisting of a plate-like substructure at pH 5. At pH 7, a coating with a very fine substructure was formed, but defects - cracks, flaking - were observed in this coating.
- Concentrations of 50 and 500 mM citric acid in the reaction mixture did not lead to the formation of a homogeneous coating without structural defects at all. The deposited coatings were not continuous, they were formed by cracks and peeling occurred. Moreover, it was shown that a higher concentration of citric acid in the reaction mixture led to the formation of citrate on the surface.
- The addition of a chelating agent caused that at pH 9 no coating at all was formed on the surface of the Mg substrate due to the precipitation of CaP already in the reaction mixture.

- The coatings deposited at pH 5 and 5 mM citric acid concentration in the reaction mixture showed the most compact structure and can be expected to have the best corrosion properties and biodegradable behavior.

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