Degradable silver-based alloys
Resorbierbare Silberlegierungen

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Noble metals solved in iron implants are effective cathodes, which can suit to accelerate the corrosion rate of the base material. In terms of its antibacterial behavior as well as lower costs in comparison with gold or platinum, silver seems to be an attractive candidate to adapt the corrosion rate of implants to the medical requirements. However, the degradation of silver in human bodies is a time-consuming process, and is controversially discussed due to the unknown long-term effect of silver on the human organism. Alloying silver with chemical elements less resistant to corrosion in aqueous mediums, particularly, in simulated body fluid, can improve the degradability of silver. Therefore, the current study addresses the design of adapted silver alloys exhibiting improved degradability in comparison with pure silver. Pure silver and binary silver alloys containing silicon, magnesium and calcium are studied in terms of their microstructure, open-circuit potential and degradation rate.

Keywords: Silver alloys / alloy-design / biomedical application / open-circuit potential / degradability

Edelmetalle, die in eisenbasierten Implantaten gelöst sind, wirken als effektive Kathoden und können die Korrosionsrate des Grundwerkstoffs beschleunigen. In Bezug auf sein antibakterielles Verhalten sowie die niedrigeren Kosten im Vergleich zu Gold oder Platin, ist Silber ein attraktives chemisches Element, um die Korrosionsrate von eisenbasierten Implantaten an die medizinischen Anforderungen anzupassen. Der Abbau von Silber im menschlichen Körper ist jedoch ein zeitaufwändiger Prozess und wird aufgrund der noch nicht eindeutig geklärten Langzeitwirkung von Silber auf den menschlichen Organismus kontrovers diskutiert. Legieren von Silber mit chemischen Elementen, die weniger korrosionsbeständig in wässrigen Medien, insbesondere in simulierter Körperflüssigkeit, sind, kann die Resorbierbarkeit von Silber begünstigen. Daher befasst sich diese Studie mit dem Design von adaptierten Silberlegierungen, die im Vergleich zu reinem Silber eine verbesserte Resorbierbarkeit aufweisen. Reinsilber und binäre Silberlegierungen, die Silizium, Magnesium und Calcium enthalten, werden hinsichtlich ihres Gefüges, des freien Korrosionspotenzials und der Degradationsrate untersucht.

Schlüsselwörter: Silberlegierung / Legierungsentwicklung / Biomedizinische Anwendung / Freies Korrosionspotenzial / Resorbierbarkeit

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1 Introduction

Conventional inert biomaterials, such as stainless steels or titanium alloys, exhibit the necessary combination of high strength and ductility as well as an excellent corrosion resistance and thus, can be used as permanent implants. However, implants, which do not inherit the particular function of the organism permanently but temporarily support the healing process of the tissue, organ or bone for a limited time, should dissolve in the human body afterwards [1].

Under such circumstances, magnesium-, zinc- and iron- based degradable biomaterials gain significant attention. Although appropriate alloying concepts to improve the low yield strength of magnesium alloys are a focal issue in scientific research, still the very fast degradation rate due to the low standard potential (−2.37 V) as well as the significant release of hydrogen gas during the degradation restrict the application for magnesium alloys [2, 3]. Zinc, for example, has a more positive standard potential (−0.76 V), which results in a lower degradation rate in comparison with pure magnesium. During corrosion only little amount of hydrogen gas is released [3, 4]. However, in higher amounts, zinc ions can be toxic for the organism, and the mechanical properties of pure zinc are not sufficient for vascular applications [2, 5]. With an excellent combination of mechanical properties, mainly a high strength combined with a high ductility, iron is a material of choice for vascular applications [6]. The main drawback of iron is the relatively low degradation rate in comparison with magnesium- or zinc-based alloys due to its high standard potential (−0.44 V). However, this drawback can be eliminated with the help of appropriate alloying elements, like manganese, increasing the corrosion rate while simultaneously maintaining the necessary combination of the mechanical properties [7]. Nonetheless, small additions of carbon further improve the strength without deteriorating the formability [8]. Here, the degradation rate of iron-manganese steel containing 21 wt.% of manganese and 0.7 wt.% of carbon is up to 30 % higher than that of pure iron. Nevertheless, during the degradation of these alloys in simulated body fluids, the formation of surface oxidation layers occurs, which is known to limit further degradation of the material [9].

In order to minimize this passivation and simultaneously improve the degradability of iron and its alloys, the addition of noble metals, such as gold, palladium, platinum, and silver, was proposed by different researchers [10–14]. Noble metals have positive standard potentials resulting in a high potential difference with iron and thus, act as cathodes accelerating the degradation of the iron matrix in corrosive environment. Due to its anti-bacterial behavior as well as low costs in comparison with other noble metals, silver seems to be the optimal candidate for alloying iron alloys in order to adapt their degradability to the medical requirements.

However, iron and silver are not dissoluble and therefore, iron alloys containing silver cannot be produced via conventional casting [15]. Thus, such alloys can only be manufactured by means of powder metallurgy, including mechanical alloying with subsequent sintering or powder-based additive manufacturing, in particular laser powder bed fusion [16, 17].

The main issue remaining on the way of commercialization of iron based alloys containing silver is the inert behavior of silver particles released during the degradation of the iron matrix. The optimal size of powder for laser powder bed fusion amounts to 10 μm–65 μm, whereas the diameter of blood vessels can be lower than 3 μm [18]. Under such circumstances, the silver particles, which have slow degradation, particularly, due to formation of silver-oxide and silver-chloride layers on the surface, pose a risk of blockage of vessels [19].

The potential candidates for silver alloying are elements, which:

→ are essential trace elements in sufficient amount in order to reduce the risk of over dosage during degradation;

→ are dissoluble with silver in order to enable casting of silver alloys;

→ have a lower standard potential in comparison with silver and form less noble intermetallic phases, which could be potentially more prone to corrosion in body fluid than pure silver;

→ form eutectic phases with silver to reduce the size of silver particles that remain after dissolution of alloying partner.

From the variety of potential candidates, which fulfil these requirements, silicon, magnesium, and calcium were chosen to investigate their influence on degradability of silver, Table 1 [3, 20, 22].

Therefore, the aim of the current work addresses the design of adapted silver alloys with silicon, magnesium and calcium, which exhibit an improved degradability in comparison with pure silver. Hence, the
effect of the amount of the alloying elements on the degradation rate of the designed alloys in terms of microstructure and phase composition is investigated.

2 Materials and experimental details

2.1 Melting experiments

The alloying elements, silver (99.99 %), calcium (99.99 %), magnesium (99.9 %) and silicon (99.999 %), were used in form of pellets with a size ranging from 5 mm to 10 mm. Silver pellets were acquired from ESG Edelmetall-Service GmbH & Co. KG, Germany, whereas the other alloying elements were obtained from HMW Hauner GmbH & Co. KG, Germany. The nominal chemical compositions of the designed alloys were chosen in order to achieve, Table 1:

| Alloying system | Silver | Silver-silicon | Silver-magnesium | Silver-calcium |
|-----------------|--------|----------------|------------------|----------------|
| Alloy Ag        | 0      | 0              | 0                | 0              |
| Silver in wt.%  | 100    | 96             | 93               | 86             |
| Alloying element in wt.% | 0 | 4 | 7 | 14 |

1. Eutectic mixtures of silver with alloying element [15];
2. specific intermetallic phases or mixtures of intermetallic phases [15].

Prior to the melting experiments, the pellets mixed in the desired proportion were placed into separate steel crucibles with a diameter of 16.5 mm. The inner surface of each crucible was coated with 3 M™ boron nitride to prevent a reaction of the alloying elements, particularly silicon, with the steel surface. Subsequently, the crucibles were placed in a water-cooled copper coil and heated by applying an alternating current to the coil, Figure 1. Simultaneously, argon gas was supplied from the top side of the crucible in order to avoid oxidation of the alloying elements, particularly, magnesium and calcium. The heating temperature for each investigated alloy amounted 1050 °C and was controlled using a pyrometer, which was attached to the outer surface of the crucible. The dwell time after reaching the heating temperature was 5 minutes. Afterwards, the crucible was removed from the copper coil and quenched in water.

2.2 Microstructure and chemical composition

Due to the high brittleness of alloys with higher amounts of calcium and magnesium, the alloys
were embedded in epoxy resin in order to prevent fracture during sampling. From each alloy, four samples with a height of 1 mm were cut and mechanically ground, Figure 2.

The homogeneity of the chemical composition was analyzed using the top and bottom samples 1 and 4 of the ingot. Then, sample 1 was polished and consistently etched in solutions according to Table 3.

To characterize the microstructure, the etched samples were examined with the optical microscope Keyence VHX 5000 in combination with the scanning electron microscope Zeiss Ultra Plus. The scanning electron microscope was operated at an acceleration voltage of 20 kV, using a secondary electron detector. Furthermore, the general chemical composition of the alloys as well as the local chemical composition of phases revealed in the microstructure were investigated with energy dispersive spectroscopy.

2.3 Open-circuit potential measurements and immersion tests

The open-circuit potential of the investigated alloys was measured in 5 % sodium chloride dissolved in deionized water using an MLab 100 potentiostat from Bank Elektronik with a scan rate of 1 scan/s for 300 s. Apart from that, the open-circuit potential of iron-manganese steel (XIP1000), which was used in previous investigations as base material for an iron-silver alloy, was measured as reference [17].

The immersion tests were carried out in glass beakers filled with 100 ml of Ringer’s lactate solution (131.00 mmol/l sodium, 5.40 mmol/l potassium, 1.80 mmol/l calcium, 112.00 mmol/l chloride, 28.00 mmol/l lactate) for 72 days. All beakers were placed on a smooth shaking plate to guarantee a steady moving of the test solution, Figure 3. The shaking plate was equipped with a heater and thus, to simulate the temperature of blood in the human body, the immersion tests were performed at a constant temperature of 37 °C ± 2 °C. Finally, air was pumped in each beaker to avoid a depletion of oxygen in the Ringer’s lactate solution.

In the beginning, the test solution was changed after the first and third day. With ongoing time, the solution was changed every seventh day. Parallel, every specimen was dried and weighted (XP205 DeltaRange, Mettler Toledo). After 72 days of immersion time, all specimens were cleaned with acetone, followed by a subsequent ultrasonic cleaning in an acetone bath for 5 min. Afterwards, the specimens were weighted and investigated via scanning electron microscopy.

Table 3. Etching solutions used for the microstructural investigations.

| Solution     | Chemicals                        | Ratio | Etching time       |
|--------------|----------------------------------|-------|--------------------|
| 1            | Aqueous ammonia solution (25 %)  | 1 : 5 | 5 s–60 s, depending on alloy |
|              | Aqueous hydrogen peroxide solution (35 %) |       |                     |
| 2            | Deionized water                  | 10 : 1| 5 s–60 s, depending on alloy |
|              | Aqueous hydrochloric acid (37 %) |       |                     |
3 Results

3.1 Melting experiments

The melting of silver alloys containing magnesium or calcium, especially in case of higher contents of the alloying elements, is a challenging task due to the high affinity of both elements, magnesium and calcium, to oxygen at elevated temperatures. When the surface of molten alloy is in contact with air, what occurs during melting without applying inert gas atmosphere or due to insufficient supplement of inert gas in case of casting, these alloying elements bind silver and oxygen in temperature stable complex oxides, which cannot be molten further, Figure 4a. Although the vacuum melting can solve the oxidation issue, it facilitates the formation of gas pores, Figure 4b. The formation of gas pores can be explained by insufficient vacuum degassing of glass chamber, which results in diffusion of remained gases into molten metal during heating stage with subsequent release during solidification. The negative pressure of vacuum facilitates formation of the pores.

In order to prevent the segregation of alloying elements during cooling, the crucible with the molten metal was quenched in water. However, the high temperature gradient between crucible wall and center results in the formation of shrinkage in the ingot, Figure 4c. The slow gradual dipping of the crucible in water allowed the casting of ingots without inner shrinkage.

Therefore, all melting experiments were performed under argon atmosphere with the solidification of the metal in the melting crucible in order to prevent a reaction of the metal with oxygen. Subsequent cooling was performed with the help of a slow gradual dipping of the crucible into water. This procedure resulted in ingots with the necessary homogeneity regarding the chemical composition, and without gas cavities or inner shrinkage, Table 4. The ingots were then prepared for further investigations.
3.2 Microstructure and local chemical composition

3.2.1 Pure silver and silver alloyed with silicon

The silver ingot consists preferably of large equiaxed grains with a grain size between 500 μm and 2000 μm, Figure 5a. Detailed investigation of the microstructure employing scanning electron microscope (not presented) has not revealed any additional information.

Alloying of silver with silicon results in a significant grain refinement, Figure 5b. The microstructure consists preferably of a eutectic mixture of silver plates (grey) divided by black silicon laths, which is confirmed by the mapping using energy dispersive spectroscopy, Figure 5c–e. Gen-

Table 4. Homogeneity of the chemical composition of the ingots.

| Alloy     | Ag | Ag-4Si | Ag-7Mg | Ag-14Mg | Ag-7Ca | Ag-14Ca | Ag-25Ca |
|-----------|----|--------|--------|---------|--------|---------|---------|
| Content of alloying element in wt.% | Sample 1 | 0 | 4.27 | 5.96 | 13.66 | 7.96 | 12.98 | 24.43 |
|           | Sample 4 | 0 | 3.73 | 6.04 | 13.83 | 7.58 | 13.31 | 25.5  |

Figure 5. Cross section micrographs of pure silver and a silver-silicon alloy: overview of the microstructure of pure silver a) and silver-silicon b) from optical microscopy; c) and d) magnified scanning electron microscopy images showing the microstructure of the silver-silicon alloy; e) distribution of silicon in the microstructure from the element mapping using energy dispersive spectroscopy in accordance with the micrograph d). (Etching procedure – Table 3).

Bild 5. Mikroskopische Aufnahmen von reinem Silber und einer Silber-Silizium-Legierung: Lichtmikroskopische Übersicht über die Mikrostruktur von reinem Silber a) und Silber-Silizium b); c) und d) vergrößerte rasterelektronenmikroskopische Aufnahmen der Silber-Silizium-Legierung; e) Verteilung des Siliziums in der Mikrostruktur aus dem Mapping der chemischen Elemente unter Zuhilfenahme von energiedispersiven Röntgenspektroskopie gemäß Aufnahme d). (Ätzverfahren - Tabelle 3).
eraly, the thickness of silicon laths amounts to 200 nm up to 300 nm, whereas a few laths with a thickness of few microns can be observed. Simultaneously, interlamellar spacing of silver between silicon laths amounts to approximately 3 μm.

### 3.2.2 Silver alloyed with magnesium

The microstructure of silver alloyed with 7 wt.% of magnesium is dendritic with local contents of magnesium of up to 7.7 wt.%, Figure 6a, b. The assumed precipitation of the second phase on the grain boundaries of dendrites can be observed. This phase exhibits a higher magnesium content than the matrix and is likely presented in form of eutectic mixture.

A further increase of magnesium results in the formation of two phases with different magnesium contents, Figure 6c. The precipitates with a low magnesium content (up to 1.3 wt.%) are embedded in the matrix, which consists of a higher magnesium content (up to 23.4 wt.%), Figure 6d.

### 3.2.3 Silver alloyed with calcium

The microstructure of silver alloyed with 7 wt.% of calcium is predominantly represented by a phase containing 11.6 wt.% Ca, Figure 7a, d. This phase appears in form of laths with a length between 100 μm and 300 μm and a width ranging from 30 μm to 50 μm. The second phase with lower calcium content occurs in separate thin laths, which are finer than that of first phase.

An increasing calcium content up to 14 wt.% results in a mixture of two phase, Figure 7b, e. The non-porous phase contains approximately 14 wt.% calcium. The laths of this phase have similar length as the embedding phase in the alloy with 7 wt.% Ca, but they are much thinner: Their maximal width amounts to 10 μm. The second phase is porous and contains up to 17.7 wt.% calcium.

The alloy with the highest calcium content consists of an eutectic mixture (bright areas) embedded in the matrix phase (dark areas), Figures 7c, f. The laths of the matrix phase are less elongated than those in the alloys with containing less calcium. The width of the laths in the eutectic mixture amounts to 200 nm–300 nm. In comparison with

![Figure 6. Images of silver alloyed with magnesium from scanning electron microscopy: a) and b) Ag-7Mg; c) and d) Ag-14Mg. The numbers in brackets represent the measured content of magnesium in wt.%. Numbers 1–4: energy dispersive spectrums of corresponding points in figures b) and d). (Etching procedure – Table 3).](image)

**Figure 6.** Images of silver alloyed with magnesium from scanning electron microscopy: a) and b) Ag-7Mg; c) and d) Ag-14Mg. The numbers in brackets represent the measured content of magnesium in wt.%. Numbers 1–4: energy dispersive spectrums of corresponding points in figures b) and d). (Etching procedure – Table 3).

**Bild 6.** Rasterelektronenmikroskopische Aufnahmen der Silberlegierungen mit Magnesium: a) und b) Ag-7Mg; c) und d) Ag-14Mg. Die Zahlen in Klammern stehen für den gemessenen Magnesiumgehalt in Gew.-%. Nummern 1 bis 4: Energiedispersive Röntgen-Spektrometrien der entsprechenden Punkte in den Aufnahmen b) und d). (Ätzverfahren – Tabelle 3).
the eutectic mixture the laths of the intermetallic phase exhibit significantly higher calcium content (35.2 wt.% compared to 25.1 wt.%).

3.3 Measurements of open-circuit potential

In comparison with silver alloys, pure silver reveals the highest open-circuit potential, Table 5. Independent of the alloying elements, an increasing content of the alloying element shifts the open-circuit potential to lower values. Although the silver alloyed with 7 wt.% of calcium and silver alloyed with 7 wt.% of magnesium exhibit almost similar open-circuit potential, an increase of calcium and magnesium content up to 14 wt.% results in different effects on the open-circuit potential in both alloys: silver alloyed with 14 wt.% of calcium has an open-

Table 5. Open-circuit potentials of the investigated alloys.

| Alloy       | Ag  | Ag-4Si | Ag-7Mg | Ag-14Mg | Ag-7Ca | Ag-14Ca | Ag-25Ca | XIP1000** |
|-------------|-----|--------|--------|---------|--------|---------|---------|-----------|
| open-circuit potential, mV | –243 | –358   | –357   | –680    | –401   | –1155   | –1355   | –828 (5)  |

*iron-manganese steel, which potentially can be used as a base material for biodegradable implants.

*Eisen-Mangan Stahl, der potenziell als Basismaterial für bioresorbierbare Implantate verwendet werden kann.
circuit potential up to 2 times more negative than silver alloyed with 14 wt.% of magnesium. The most negative open-circuit potential exhibits the alloy with 25 wt.% calcium. The iron-manganese steel shows an open-circuit potential of -828 mV, which is lower than the open-circuit potential of silver alloyed with 14 wt.% of magnesium but higher than the open-circuit potential of silver alloyed with 14 wt.% of and 25 wt.% of calcium.

3.4 Degradation during immersion tests

The samples alloyed with 25 wt.% of calcium corroded completely during the first day of immersion in Ringer’s lactate solution, Figure 8.

All other alloys withstand the whole test period of 72 days and exhibit a downward character of the mass loss during the test period, Figure 9. Furthermore, all alloys except silver alloyed with 14 wt.% calcium reveal the highest mass loss rate during the initial test period.

Alloying of silver with silicon does not significantly change the mass loss rate in comparison with pure silver – the curves exhibit similar character. After 23 days, the mass loss rate of both alloys decreases below 0.1 mg·cm⁻²·d⁻¹. During the next 49 days, it further decreases to 0.03 mg·cm⁻²·d⁻¹.

The alloys with 7 wt.% magnesium or calcium exhibit almost the same mass loss rate during test. The mass loss rate of both alloys after 72 days amounts to approximately 0.05 mg·cm⁻²·d⁻¹.

A further increase of the magnesium or calcium content results in a mass loss rate of 0.08 mg·cm⁻²·d⁻¹ (magnesium) and 0.27 mg·cm⁻²·d⁻¹ (calcium) after 72 days of immersion respectively. Both alloys also exhibit the highest degradation rate in comparison with the other alloys. Furthermore, a fracture of the sample with 14 wt.% calcium can be clearly observed. For the first time, the origin of this fracture, occurring as small crack, was observed after 9 days of immersion.

Although the accuracy of the measurements of objects smaller than 1 μm or chemical elements such as oxygen using energy dispersive spectroscopy is limited, it is sufficient to determine a qualitative difference between the chemical compositions of the different surface features observed during analysis in scanning electron microscope.

During immersion tests, all investigated alloys formed oxide layers, Figure 10. These oxide layers almost completely cover the surfaces of pure silver and the silver-silicon alloy. Simultaneously small areas with not oxidized base material interrupting the oxide layer are also observed. All alloys containing magnesium exhibit oxide layers, which cover completely the sample surface. In comparison with the layer formed on the surface of pure silver and silver alloyed with 4 wt.% of silicon, this layer is more heterogeneous and consists of sublayers exhibiting different oxygen contents. For silver alloyed with 14 wt.% of calcium, the oxide layer seems to have only weak bond with the base material, due to cracks, which formed during immersion on the boundaries of the intermetallic phases, Figures 7b, 10f. Simultaneously, the oxide layer in the sample with 7 wt.% calcium can still be observed on the surface.

4 Discussion

4.1 Silver alloyed with silicon

According to the phase diagram alloying of silver with 4% silicon results in the formation of a eutectic mixture of silicon and silver with a small amount of silicon, which is proved by the analysis of the microstructure, Figures 5b–d, 11a. The observed microstructure is also in agreement with re-
results of a previous study focusing on a similar alloy composition [23].

A grain refinement facilitates the corrosion rate of materials in corrosive environment due to local formation of galvanic coupling between grains and grain boundaries [24]. Small additions of silicon significantly refine the grain size of silver, whereas silicon itself has a negative standard potential in comparison with silver (−0.15 V vs. 0.8 V) [3]. Furthermore, the measured open-circuit potential of silver–silicon is also more negative than that of pure silver, Table 5. Regardless of the presented results,

Figure 9. Average mass losses of the investigated alloys and pure silver during the immersion test and images of samples prior and after 72 days of immersion: a) Ag; b) Ag-4Si; c) Ag-7Mg; d) Ag-14Mg; e) Ag-7Ca; f) Ag-14Ca. The number below the capture “72 days” represents the degradation rate based on the average mass loss from day 1 to day 72.

Bild 9. Durchschnittliche Masseverluste der untersuchten Legierungen und des reinen Silbers während des Immersions-tests und Aufnahmen von Proben vor und nach 72 Tagen im Immersionstest: a) Ag; b) Ag-4Si; c) Ag-7Mg; d) Ag-14Mg; e) Ag-7Ca; f) Ag-14Ca. Die Zahl unter der Beschriftung “72 Tage” steht für die Degradationsrate basierend auf dem durchschnittlichen Masseverlust von Tag 1 bis Tag 72.
alloying of silver with silicon does not improve its degradation rate. Due to silver laths within the observed eutectic mixture in this alloy, it is expected that the oxide layer observed on the surface of silver alloyed with 4 % of silicon after immersion has a similar protective nature like the oxide layer observed on the surface of pure silver. Thus, the formation of the protective oxide layer results in the

Figure 10. Images of samples after immersion tests from scanning electron microscope: a) Ag; b) Ag-4Si; c) Ag-7Mg; d) Ag-14Mg; e) Ag-7Ca; f) Ag-14Ca. (The numbers in the magnified sections represent the oxygen content in the corresponding areas based on measurements using energy dispersive spectroscopy.

Bild 10. Rasterelektronenmikroskopische Aufnahmen von Proben nach Immersionstests: a) Ag; b) Ag-4Si; c) Ag-7Mg; d) Ag-14Mg; e) Ag-7Ca; f) Ag-14Ca (Die Zahlen in den vergrößerten Ausschnitten stehen für den Sauerstoffgehalt in den entsprechenden Bereichen basierend auf Messungen unter Zuhilfenahme von energiedispersiver Röntgenspektroskopie.

Figure 11. Phase diagrams of the investigated silver alloys adapted from [15]: a) silver-silicon; b) silver-magnesium; c) silver-calcium. The alloys in italics are given in accordance with chemical composition measured using energy dispersive spectroscopy, Table 4.

Bild 11. Phasendiagramme der untersuchten Silberlegierungen adaptiert von [15]: a) Silber-Silizium; b) Silber-Magnesium; c) Silber-Calcium. Die Legierungen in kursiver Schrift beziehen sich auf die chemischen Zusammensetzungen, die bei den entsprechenden Messungen unter Zuhilfenahme von energiedispersiver Röntgenspektroskopie ermittelt wurden, Tabelle 4.
same degradation rate as that of pure silver, Figure 9a, b.

### 4.2 Silver alloyed with magnesium

Alloying of silver with 7 wt.% and 14 wt.% magnesium should result in the formation of the intermetallic phase Ag₃Mg and a mixture of the intermetallic phases Ag₅Mg and AgMg, Figure 11b. The silver alloyed with 7 wt.% of magnesium consists of dendritic grains containing 7.7 wt.% magnesium and a eutectic mixture precipitated on the grain boundaries, containing 10.8 wt.% to 16.3 wt.% magnesium, Figure 6. It can be assumed that the microstructure of this alloy consists of a solid solution of magnesium in silver (dendrites) and an eutectic mixture. The eutectic mixture presumably consists of a silver solid solution and the intermetallic phase AgMg. The phase Ag₃Mg is a result due to an ordering of the silver solid solution (Ag) proceeding at a relatively slow cooling rate of 30 °C/hour in the temperature interval from 386 °C to 389 °C [25]. Since the cooling rate during quenching of the crucible in water is 3 to 4 orders higher than the cooling rate mentioned above, the phase Ag₃Mg is not evolving in the microstructure.

High magnesium content in the matrix phase as well as very low magnesium content in elongated precipitations of the silver alloyed with 14 wt.% of magnesium indicate the presence of the intermetallic phase AgMg as well as a solid solution of magnesium in silver. The low magnesium content in the silver solid solution can be attributed to a non-equilibrium solidification due to water quenching of the crucible, which results in inhomogeneous redistribution of magnesium during cooling.

Generally, the silver alloyed with 14 wt.% of magnesium exhibits a more preferable microstructure for the origin of local galvanic couplings attributable to both, higher amounts of grain and phase boundaries as well as likely higher differences of the standard potentials between the phases due to their varying magnesium content.

Based on the obtained data, an increase of magnesium in silver results in a gradual increase of both, the negativity of the open-circuit potential and the degradation rate, whereas the degradation rate of silver alloyed with 7 wt.% and 14 wt.% of magnesium is correspondingly 47 % and 55 % higher than that of pure silver.

### 4.3 Silver alloyed with calcium

In accordance with the observed microstructure and measured chemical composition of the evolved phases, the silver alloyed with 7 wt.% of calcium consists of an intermetallic matrix Ag₉Ca₂, in which presumably thin laths of Ag₅Ca₂ are embedded, Figures 7a, 11c. A further increase of calcium up to 14 wt.% results in the formation of the porous intermetallic phase Ag₅Ca with a higher calcium content, in which thin laths of the non-porous phase Ag₅Ca₂ are observed. The eutectic mixture detected in silver alloyed with 25 wt.% of calcium exhibits a lower Ca content than the matrix phase. Thus, the alloy presumably consists of the intermetallic phase AgCa and an eutectic mixture of this phase with the intermetallic phase Ag₅Ca embedded in an AgCa matrix.

Analogous to silver alloys containing magnesium, an increase of calcium shifts the open-circuit potential to values that are more negative. Furthermore, the degradation rate of these alloys is higher, which is in agreement with a previous study [26]. Although silver alloys with 7 wt.% magnesium or 7 wt.% calcium exhibit a similar open-circuit potential as well as a comparable degradation rate, an increase of calcium up to 14 wt.% results in a more negative open-circuit potential (−1155 mV vs. −680 mV). Therefore, the degradation rate is significantly higher (590 μm·year⁻¹ vs. 18 μm·year⁻¹). This can be attributed to both, weak bonding between oxide layer and base material as well as by corrosion induced crack formation on the phase boundaries between Ag₅Ca and Ag₅Ca₂ during immersion.

### 4.4 Future work

In terms of potential implementation of degradable silver alloys, the following aspects are to be considered:

→ In order to allow the formation of galvanic coupling between the silver alloy and the iron-manganese steel, the silver alloy should have a more positive standard potential, i.e. open-cir-
circuit potential, than the iron-manganese steel, i.e. higher than −828 mV;

→ The degradation rate of the silver alloy should be significantly higher than that of pure silver (11.6 μm·year⁻¹, Figure 9a) but, simultaneously, lower than that of iron-manganese steel (130 μm·year⁻¹, according to [9]) in order to prevent premature dissolution of silver particles.

Therefore, under consideration of these aspects, silver with a magnesium content of 14 wt.% seems to be the most appropriate alloy.

In future work, the alloys with a calcium content between 7 wt.% and 14 wt.% are to be studied more detailed. They can potentially exhibit a degradation rate, which lays between that of the already investigated silver-calcium alloys. Furthermore, alloys with a magnesium content of 15 wt.% to 18.5 wt.% are promising candidates. According to the phase diagram, the microstructure of these alloys should be a single AgMg phase, which could allow a uniform degradation of the alloy in comparison with the degradation of a multiphase microstructure.

Independent on the chosen alloy composition, the interaction of the particles of the silver alloy with iron-manganese steel during processing via additive manufacturing, i.e. laser powder bed fusion is mandatory to address. Besides this, the corrosion mechanism of iron-manganese steel with particles of the silver alloy as well as absorption of released silver particles by organism, which take place during the degradation of the implant in the body, represent a central questions for future work.

5 Conclusions

In the current work, the effect of silver alloyed with silicon, magnesium and calcium on the resulting microstructure and (bio-)degradability was investigated.

Generally, alloying silver results in a significant grain refinement independent on the alloying element. Here, the most pronounced refinement exhibits for silver containing 4 wt.% silicon. Detailed analysis of the microstructure as well as of the local chemical composition of the evolved phases allowed the evaluation of the phase composition for the investigated alloys. Principally, the identified phases coincide with the data given in the corresponding phase diagrams.

Although alloying silver with silicon reduced the open-circuit potential compared with pure silver, it did not facilitate the degradation rate due to the formation of a dense oxide layer protecting the base material.

Oxide layers were also observed for silver alloys with calcium and magnesium. In contrary to silver-silicon, the protective effect of these layers is less detrimental in terms of degradation: the degradation rate increases in comparison with pure silver. Furthermore, higher contents of the alloying elements strengthen this effect.

However, as it was observed for silver-calcium with 14 wt.% calcium and more, a too high content of the alloying element can be detrimental. On the one hand, the open-circuit potential becomes too low and therefore, the alloy is less noble than that of the potential counter partner (iron-manganese steel), which is designed as base material for biodegradable implants. Here, the acceleration of the degradation due to galvanic coupling between particles of the silver alloy and the steel matrix is questionable. On the other hand, the degradation rate becomes higher than that of iron-manganese steel, which could result in an earlier dissolution of the silver alloy compared to the iron-manganese steel. Such behaviour of silver alloys with high Ca- and likely high Mg-content can potentially be used for the development of a separate class of degradable alloys with degradation rates between iron- and magnesium based alloys.

Under consideration of the presented aspects as well as in terms of the resulting degradation rate, a silver alloy with about 14 wt.% magnesium seems to be the most appropriate candidate for a suitable iron-manganese-silver alloy as implant material in order to facilitate the degradation in the human body. Therefore, in future work, silver alloys with a calcium content between 7 wt.% and 14 wt.% as well as alloys with a magnesium content between 15 wt.% to 18.5 wt.% will be investigated more detailed. Here, the heat treatment of all promising alloys will be investigated in terms of adjustment of microstructure exhibiting a preferably uniform degradation behaviour.

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