

Article Adjustment of AgCaLa Phases in a FeMn Matrix via LBM for Implants with Adapted Degradation

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Abstract: For many applications, implants overtake body function for a certain time. Bioresorbable implants reduce patient burden as they prevent adverse consequences due to remaining implants or operations for removal. Such materials are in clinical use but do not fulfill the requirements of all applications. Iron (Fe) is promising to develop further bioresorbable materials as it offers biocompatibility and good mechanical properties. Alloying, e.g., with manganese (Mn), is necessary to adapt the mechanical behavior and the degradation rate. However, the degradation rate of FeMn is too low. The creation of phases with high electrochemical potential evokes anodic dissolution of the FeMn, increasing the degradation rate. Therefore, silver (Ag), which is insoluble with Fe, has high potential, is biocompatible, and offers antibacterial properties, can be used. Powder-based processes such as laser beam melting (LBM) are favorable to process such immiscible materials. A degradable Ag alloy has to be used to enable the dissolution of Ag phases after the FeMn. This study reports first about the successful processing of FeMn with 5 wt.% of a degradable Ag–calcium–lanthanum (AgCaLa) alloy and enables further targeted adaption due to the gained understanding of the effects influencing the morphology and the chemical composition of the Ag phases.

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Citation: Krüger, J.T. Adjustment of AgCaLa Phases in a FeMn Matrix via LBM for Implants with Adapted Degradation. *Crystals* **2022**, *12*, 1146. https://doi.org/10.3390/cryst12081146

Academic Editors: Bolv Xiao and Kay-Peter Hoyer

Received: 26 July 2022 Accepted: 12 August 2022 Published: 15 August 2022

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Copyright: © 2022 by the author. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). **Keywords:** silver alloys; corrosion; biomedical application; laser beam melting; bioresorbable metal; iron alloys

1. Introduction

To enable the treatment of diseases and injuries with implants, suitable implants with properties adapted for each application are necessary. This forms a need for new materials with adapted properties. Thus, new materials are developed to improve the quality of patients' lives and reduce patients' burdens. [1–3] All materials for implants need to be biocompatible, which describes the absence of any adverse consequences including inflammatory, toxicity, carcinogenic properties, etc. The most currently used materials guarantee biocompatibility due to inert material behavior. However, the application of not inert materials enables the utilization of beneficial features of materials for implants, such as the antibacterial effect of released ions [1,2,4,5]. In the actual research e. g. bioresorbable materials to prevent adverse consequences by remaining implants and operations for removal of implants or materials with antibacterial properties preventing implant infections are addressed [3,5–7].

Magnesium (Mg)-based materials or polymers are already applied successfully as degradable implants [1,5,8,9], but currently available materials are not suited for all possible applications because of reduced mechanical properties compared to conventional iron (Fe)-based implant materials [2,8,10]. Thus, further degradable materials need to be developed. Due to good mechanical properties and biocompatibility, Fe alloys are promising as degradable materials. Hence, the presented investigation aimed to develop a bioresorbable Fe-based material with antibacterial properties [5,8,11–13]. Alloying of Fe is required to obtain suited mechanical properties and adapted degradation behavior,

as pure Fe degrades too slowly [3,5,14,15]. Manganese improves the mechanical properties due to its twinning-induced plasticity (TWIP) and degradation rate, as it reduces the electrochemical potential. In addition, segregations of Mn lead to differences in the local electrochemical potential. As a material with lower electrochemical potential is increasingly attacked by corrosion, local differences improve the anodic dissolution of areas with low potential [12,15–19]. For such FeMn alloys, promising results regarding biocompatibility have been obtained [16,20–24].

Probably due to the formation of degradation inhibiting layers, the degradation rate of FeMn is for nearly all applications too low and the material has to be further adapted [13,20,22,25]. The creation of targeted noble phases within a FeMn matrix is an approach resulting in the increased anodic dissolution of the FeMn matrix [25–28]. When two metals with different electrochemical potentials are in contact and an electrolyte is present, the atoms of the less noble material are more likely to be dissolved than when without contact with a more noble material. Due to their high electrochemical potential, noble elements are well suited to create noble phases. In particular, Ag is promising to form noble phases within FeMn as it is insoluble with Fe, biocompatible, and has antibacterial properties [26,29–31]. This immiscibility enables the existence of noble phases in an unchanged FeMn matrix, which makes it well suited apart from its low degradation rate. Enhanced degradation due to the addition of Ag is reported by a few studies [12,26,29,32,33]. The addition of 5 wt.% Ag was selected for the presented investigations as it enables suited properties regarding mechanical behavior, biocompatibility, and degradation behavior [26,29,34,35]. However, this is a guess and it might be necessary to adapt the amount of Ag, based on further investigations of the material, but 5 wt.% is promising. Furthermore, the Ag has to be adapted by alloying as it would remain after degradation of the matrix and could cause adverse consequences. For example, the Ag particles could be transported to sensitive organs in the human body such as the brain or the lung [36-38]. Thus, biocompatible and degradable Ag alloys are required to substitute for the pure Ag. The electrochemical potential of these alloys is still high enough to evoke anodic dissolution of the FeMn, but they enable the dissolution of the Ag phases after the matrix material [31,39–41]. In the presented investigations a degradable AgCaLa alloy with 12 wt.% Ca and 5 wt.% La, developed by Krüger et al. [31], was utilized.

For the successful realization of the FeMn–AgCaLa material concept, dispersed Ag-CaLa phases in the FeMn matrix have to be evoked. To process such immiscible materials and obtain an adapted morphology of Ag phases is challenging [42,43]. Powder-based metallurgical processes such as laser beam melting enable the processing of such materials, as mechanically mixed powders can be used [29,44,45]. Due to the small melt pool, strong melt flow, as well as rapid melting and solidification, homogenous and adaptable Ag phases in an iron-based matrix can be obtained via LBM [26,35,46,47]. Apart from the morphology of the Ag phases, the chemical composition has to be addressed. To achieve the required chemical composition might be a concern, as between immiscible materials distinctive diffusion of alloying elements might occur [35,48]. Thus LBM is a promising technique, as the short time at high temperatures reduces the time for diffusion. However, even for the processing of FeMn with pure Ag via LBM, distinctive diffusion of Mn from the matrix to the Ag is observed [35]. Thus, an adaption of the LBM strategy has to address a reduced diffusion of alloying elements as well as the morphology of the Ag phases since the chemical composition of Ag phases is important for the electrochemical potential and the degradation performance [31,39–41]. LBM strategies with reduced energy input are favorable as they reduce the time at high temperatures, but for these strategies, a certain porosity has to be accepted [35].

However, the uptake of Ca and La by the FeMn matrix is not critical as both elements can be used as deoxidizers [49,50]. Thus, diffusion of Ca and La is acceptable as long as the Ag phases remain degradable. A diffusion of Mn from Fe into Ag reduces the Mn content within the matrix material, whereby the matrix would keep the austenitic structure and the TWIP effect even if the Mn content is reduced by 2 wt.% [19]. On the one hand, Mn might

contribute to the degradation of the Ag phases after the dissolution of the matrix, but on the other hand, the uptake of Mn reduces the electrochemical potential of pure Ag [35]. In summary, the diffusion of alloying elements is noncritical for the matrix material. The same can be assumed for the AgCaLa alloy. For this alloy, an impact on the degradability and electrochemical potential will also be present, but this should be acceptable since the diffusion is not too pronounced.

Furthermore, the mechanical properties are decisive for the intended application. Due to its immiscibility, the inclusions of Ag do not have a direct connection to the FeMn and act like pores concerning the load capability, but the mechanical properties are still satisfying as the ductile character of FeMn enables the reduction of tension peaks [26,35]. Strategies are being investigated to obtain a bone-like stiffness via targeted porosity to avoid stress shielding; thus, the Ag phases might address this concern by the way [51,52].

However, to develop a suited material, the Ag phases need to be adapted and, therefore, knowledge of the interaction of both melts throughout the LBM process, respectively, and the mechanisms responsible for the generation of the Ag inclusions are mandatory to enable a targeted adaption. Gaining knowledge regarding the influencing physical effects during LBM to enable the targeted adaption is the focal point of current research [53–56]. As the physical effects cannot be observed directly, the resulting microstructure and properties of the processed material are investigated, knowledge concerning the physical effects is transferred, and the melt pools are observed to generate models of the LBM process [53,57–59].

The laser radiation causes the continuous formation of bulk material due to sequential proceeding sub-processes. The most decisive sub-processes depending on further physical effects and interactions with each other are the absorption of laser radiation, melting and consolidation, melt flow, heat dissipation, and solidification [53,55,57,59]. Further effects such as spattering or chemical reactions are caused by the sub-processes [55,57,60,61], whereby, e.g., the adsorption depends not only on the absorptivity of the solid and liquid material as an eventually formed keyhole, reflection within the powder bed, and deflection by the vapor plume, etc., but influence the energy intake, too [54,62,63]. A depression is formed if the recoil pressure of vaporized material is high enough to displace molten material against surface tension [64–66]. As the laser is reflected within a depression it further increases energy absorption and more material evaporates. Thus, the depression supports itself and once a threshold value of energy input is exceeded, a keyhole is formed [64,67]. Due to increased energy absorption in the so-called keyhole welding mode, the size of the melt pool can increase [64,68]. As the addition of alloying elements with high vapor pressure supports the formation of a keyhole, they can lower the energy input needed for the keyhole welding mode [65–67].

Furthermore, the spattering influences the final structure and composition of the mixed material as spattering depends on the material properties as well as process characteristics such as energy density [57,60,69,70]. Ejections of liquid material mainly result from recoil pressure and Marangoni forces, respectively, and instabilities of the melt flow [60,71], whereby a keyhole significantly contributes to spattering [57,60,70]. The intensity of effects causing spattering depends, e.g., on the viscosity of the melt and the surface tension [54,57,60,71]. Aside from the ejection of molten material, the non-molten powder is ejected due to an upward gas flow resulting from heating and vaporization in the laser spot. Additionally, the material-dependent evaporation can cause a bow-off impulse, accelerating powder particles from the surrounding powder bed [57,70,72].

Aside from the physical effects, the chemical properties of the reactivity of the processed material influence the LBM process, as elements with high reactivity can react with each other or with the remaining oxygen within the building chamber [73–75]. As the reactivity increases with temperature, the chemical reactions can be so distinctive that developed oxides deteriorate the connection between adjacent and superimposed melt tracks [73,74,76,77]. Additionally, slag positioned on the top can be incorporated into the bulk material, deteriorating the mechanical properties [74,78,79].

Thus, manifold interacting physical effects depending on the material properties and process conditions have to be considered to develop a model that explains the continuous melting process and structure of the manufactured parts. Therefore, at first, the main influencing variables, which are the surface tension and the recoil pressure, have to be incorporated. Following this, further effects can be integrated to improve the model [53,54,57]. However, the evaporation is decisive for the welding mode as well as consequently the appearance of the melt pool. Thus, via the shape of the melt pool, the welding mode can be identified. Flat melt pools are characteristic of the conduction welding mode with heat transfer mainly by conduction. Deep and narrow melt pools arise from the beforementioned keyhole welding mode with heat transferred by convection. A transition mode with proportions of both modes is defined between the other modes [53,80,81].

Based on the before-mentioned knowledge from the literature, and by the results presented in this study, a model was developed to explain the interaction of both melts and enable targeted adaption. As this model is based on the results gained for processing of FeMn with pure Ag by Krüger et al. [35], the main statements relevant to the present study are briefly summarized as following, beginning with separation of a melt pool into three sections where different physical effects are decisive [53]. The first part of the melt pool is predominantly influenced by the recoil pressure causing depression, which provokes the transition welding mode and melt flow due to displacement. As the recoil effect acts similarly regarding FeMn and pure Ag, it causes the emergence of Ag into the melt pool, which supports the diffusion of alloying elements from one metal into another metal.

For the morphology of the Ag phases, the tail end and transition section determined by surface tension are decisive, since during solidification the position of Ag is defined and the location in the moment of solidification is defined by the former melt flow. The surface tension leads to the accumulation of Ag on the top as this arrangement requires the lowest surface energy. Since accumulation reduces the surface, it minimizes the surface energy. Due to the lower surface tension of Ag compared to FeMn, a surface of Ag on the top requires less energy than a surface of FeMn on the top would require. Thus, once Ag reaches the top surface it is trapped there. The Ag is especially positioned at the flanks of the melt pools as an outward-directed vortex because the Marangoni force transports Ag to the melt pool sides.

2. Experimental Procedures

The production, preparation, and investigation of the samples were almost identical to the methods applied in Krüger et al. [35]. Thus, the results of both studies are well comparable.

Argon-gas-atomized FeMn powder (nominal composition: 22 wt.% Mn, 0.6 wt.% C, Fe bal.; Nanoval GmbH & Co. KG, Berlin, Germany) and AgCaLa powder (Nanoval GmbH & Co. KG, Berlin, Germany) were used in this study. To measure the chemical composition of the AgCaLa powder, inductive coupled optical emission spectroscopy (ICP-OES) was deployed. Feedstock for the AgCaLa powder was an alloy with 12.9 wt.% Ca and 5.7 wt.% La (ICP-OES). The particle size distribution (PSD) was determined with a Mastersizer 2000 (Malvern Panalytical GmbH, Kassel, Germany). An HL-2000-HP-FHSA (Ocean Optics, Inc., Orlando, FL, USA) was utilized to determine the absorption of the powder bed.

The FeMn was mixed with 5 wt.% of AgCaLa with a drum hoop mixer (30 min at 60 rpm) using half-filled powder containers. To guarantee a humidity of less than 5%, the powder was vacuum dried. With an SLM 280^{HL} 2.0 (SLM Solutions Group AG, Lübeck, Germany) the powder was processed in an inert gas atmosphere (argon (4.6), oxygen level < 0.03%). Based on previously unpublished work, the parameters were selected (Table 1). All samples (cubes: $10 \times 10 \times 10 \text{ mm}^3$, cylinders for computer tomographic (CT) analysis: \emptyset 5 × 10 mm³, blocks for tensile specimens: $13 \times 36 \times 10 \text{ mm}^3$) were produced in one built-job. According to the density and the achieved AgCaLa phase content, the samples were designated as "HD" for high density, "LD" for low density, and "LSC" for samples with low silver content.

Strategy	HD	LD	LD-2	LSC	LSC-2
Slicing in µm	50	50	50	50	50
Scanning velocity in mm/s	850	900	900	700	700
Laser power in W	260	220	220	300	280
Hatching in µm	150	190	130	110	110

Table 1. Parameters conducted for processing via LBM.

The scanning direction was rotated 67° between the following layers. To reveal an idea of the melt pool appearance, some samples without rotation were fabricated as well. These samples are indicated by a "-0" at the end of the enumeration, e.g., HD-0.

Miniature dog-bone specimens were prepared for the tensile tests (measuring length: 8 mm, width: 3 mm, thickness: 1.5 mm, radius: 2 mm). The shapes of the specimens followed DIN EN ISO 6892-6 but were not in accordance with the criteria of proportional specimens. The specimens were eroded out of bulk material (HD) manufactured horizon-tally aligned and ground up to the final step P2500 with silicon carbide (SiC) paper.

Grinding up to P4000 was conducted iteratively for the preparation for the microstructural investigations. To avoid the impact of edge effects, 1 mm or more material was removed. A mixture of 50% corrosion inhibiting lubricant (CUTLUB (diluted, 3%), Cloeren Technology GmbH, Wegberg, Germany) and silica polishing suspension (grit size: 50 nm, Cloeren Technology GmbH, Wegberg, Germany) was used for final vibration polishing for 12 h. Selected samples were etched with 0.5% HNO₃ acid from 30 s up to 150 s.

An Axiophot (Carl Zeiss AG, Oberkochen, Germany) and a Keyence VHX5000 digital microscope (KEYENCE Corporation, Osaka, Japan) were applied for light microscopy (LM). A Zeiss Ultra Plus (Carl Zeiss AG, Oberkochen, Germany) field emission scanning electron microscope (FE-SEM) with secondary electron (SE) and backscatter electron (BSE) detectors was used for further investigation. The electron backscatter diffraction (EBSD) detector DIGIVIEW 5 (AMETEK, Berwyn, PA, USA) enabled the investigation of the grain structure, whereas the chemical composition was detected with an energy-dispersive X-ray spectroscope (EDS) detector Octane Pro (AMETEK, Berwyn, PA, USA). All EBSD-data presented in the Results Section were not cleaned. The micro-CT SkyScan 1275 (Bruker Corporation, Billerica, MA, USA) enabled the three-dimensional observation of the structure of the Ag phases. Via wavelength dispersive X-ray analysis (WDX) with a Jeol JXA-8100 (Jeol Denshi K.K., Akishima, Tokyo, Japan), the content of elements of the AgCaLa within the matrix was determined.

An MTS 858 Table Top System (MTS Systems Corporation, Eden Prairie, MN, USA) was used to perform quasi-static tensile tests with a testing velocity of 0.13 mm/min (strain rate less than 0.0025 1/s). The tests were performed following DIN EN ISO 6892-6 and an extensometer was used.

3. Results and Discussion

As the feedstock properties are crucial for the LBM process, the powder used was characterized in a first step. Both powders had a suited particle size distribution (PSD) (Figure 1a); the morphology of the AgCaLa powder was appropriate as it consisted mainly of spherical particles with only a few satellites (Figure 1d). The same applied to the FeMn powder [35]. The AgCaLa powder feedstock contained 12.4 wt.% Ca, 5 wt.% La, 0.3 wt.% O, and Ag bal. measured via ICP-OES. Thus, the chemical composition met the intended content of alloying elements (12 wt.% Ca, 5 wt.% La) and the powder took up only a little O during gas atomization despite the high reactivity of Ca and La. The surface structure of the AgCaLa particles confirmed the achievement of a capable AgCaLa feedstock, as a lamellar structure was present, as observed for the conventionally cast alloy [31]. The addition of AgCaLa influenced the absorption of the laser radiation, as for FeMn adsorption of 69.3% was determined in contrast to 61.8% for FeMn with AgCaLa. However, sufficient



adsorption can still be expected. Thus, the feedstock was well-suited to obtain a material with the intended properties.

Figure 1. (**a**) PSD of powder feedstock; (**d**,**e**) SEM-SE: gas-atomized AgCaLa particles; (**b**) processing via LBM with different parameter settings; (**c**,**f**,**g**) LM: cross-section of samples with varying AgCaLa content in the bulk material process strategies: (**c**) LD-2, (**f**) LSC-2, (**g**) LSC.

Since the process parameters significantly influence the behavior of the AgCaLa during the LBM process, differences in smoke evolution, sample top surfaces, and bulk material were observed. Some samples comprised metallic blanc as-built top surfaces while others were matt (Figure 1b). This matt surface might be due to the formation of slag, as well as the deposition of welding spatter. This hypothesis is substantiated by the increased deposition of smoke marks near the samples with matt surfaces. Crosssections confirmed differences, as the top surface of matt samples was significantly rougher (Figure 1c,f,g). On top of all samples, some AgCaLa phases were deposited, but the AgCaLa phases were more distinctive for samples with matt surfaces. However, the distribution of AgCaLa in the bulk material differed more significantly as in some samples nearly no AgCaLa was incorporated, whereas other samples contained well-dispersed AgCaLa phases connected to some porosity. The lack of AgCaLa in some of the samples was not caused by inhomogeneous deposition of the powder feedstock, as the AgCaLa depositions on the top of these samples proved. Additionally, the good distribution of both components in the powder bed was confirmed by investigations of the chemical distribution [35]. Thus, the incorporation of AgCaLa into the bulk material strongly depended on the process parameters. This can be utilized to manufacture material with a graded distribution of AgCaLa, as demonstrated further in Figure 5. The settings used for the sample shown in Figure 1g were applied to obtain areas without AgCaLa.

As a surface like the final top surface was remelted with the manufacturing of each following layer, the upper surface was characterized by its morphology as well as its chemical composition. The as-built top surface was enriched with Ag and depleted of Fe (Figure 2a), confirming the formation of an AgCaLa layer on the top of samples containing AgCaLa in the bulk material, whereby some of the areas with a high Fe content were due to non-molten particles adhering to the top surface. These particles are transported to the melt pool behind the interaction zone with the laser by the inward gas flow [60–62,82]. Consequently, these powder adhesions do not originate out of the melt pool, and the AgCaLa layer formed by the melting process is more distinctive.

7 of 22



Figure 2. Corresponding SEM-SE and SEM-EDS of as-built surfaces (HD): (**a**) top surface with enrichment of Ag and O, (**b**) side surface.

The inhomogeneous distribution of Ca, Mn, and La together with O on the top surface indicates the formation of slag on the top surface containing various chemical compounds of the alloying elements and O. This surface composition explains the observed matt surface appearance and smoke evolution (Figure 1b). Thus, chemical reactions between alloying elements and remaining oxygen occur during the LBM process.

The side surface was characterized by adhering powder particles from the adjacent powder bed and enrichment of Ag, as well as an inhomogeneous distribution of the alloying elements and O, like on the top surface, but less distinctive. The adhering FeMn particles covered some underlying Ag, and thus the enrichment of Ag was more distinctive. Hence, AgCaLa was more likely positioned on the top and at the sides of a sample and chemical compounds were present on the top as well as at the side of the as-built samples.

Cross-sections verified the enrichment of AgCaLa on the top surface (Figure 3), but the AgCaLa layer was inhomogeneous as the layer was partly thin and elsewhere the AgCaLa was extended deep into the material. These deep incisive AgCaLa phases were positioned at the flanks of single melt pools, respectively, between adjacent melt tracks, as demonstrated by samples built without any rotation of the direction of scanning (Figure 3c,d). The deposition at the flanks of the melt pools was more distinctive for samples with a low density. Thus, AgCaLa agglomerated in the upper part of the samples, and the AgCaLa phases in the bulk material originated from these agglomerations. For scanning without any rotation of the direction between neighboring melt tracks was nearly lost and the material was not suited for the intended application (Figure 3d). This effect was not observed if a rotation was conducted (Figure 3b).



Figure 3. LM of etched cross-sections of top surfaces with enrichment of AgCaLa: (**a**) HD, (**b**) LD, (**c**) HD-0, AgCaLa phases between adjacent melt pools, narrow shape of melt pools, (**d**) LD-0.

Compared to samples with a high density (Figure 3a), the enrichment of AgCaLa on the upper surface, and in particular the deep incisive phases, was less distinctive for samples manufactured with the LD strategy. Thus, the conducting of the LD strategy and acceptance of a certain porosity reduces the enrichment of AgCaLa in the upper part and consequently seems to facilitate the incorporation of AgCaLa.

The observed AgCaLa phases did not have the bright appearance which is typical of Ag. Consequently, these phases did not match the observed slag on the top surface. Thus, the slag was a thin layer on the AgCaLa phases, but not a voluminous layer. As the EDS measurements reflected the chemical composition near the surface, including the slag, an even more distinctive enrichment of AgCaLa under the slag can be assumed than indicated by the EDS measurement in Figure 2a.

Aside from the observation of the morphology of the AgCaLa phases, the appearance of the melt pools was identifiable. The melt pools indicated in Figure 3a,c for the HD strategy had a relatively narrow and deep shape. In contrast, the melt pools resulting from the LD strategy were less deep and narrow (Figure 3b,d). Furthermore, the LBM-typical columnar dendritic structure of solidification was identifiable [83].

Investigations of the morphology of the AgCaLa phases within the bulk material demonstrated that the observed deep incisive AgCaLa phases at the side of melt pools continued into the bulk material, as the cross-sections of the bulk material without any rotation show aligned AgCaLa phases (Figure 4a). These AgCaLa phases were positioned between adjacent melt pools confirmed by the distribution of AgCaLa at the edge of the samples (Figure 4m). Additionally, the slightly visible grain structure confirmed the position between the melt pools in the bulk material as the grains grew from the side to the center of the melt pools, as indicated by arrows in Figure 4i [63,84]. An alignment along the melt tracks was also indicated by a section perpendicular to the building direction (Figure 4e). The positioning between adjacent tracks was more distinctive for material processed with the LD-0 strategy (Figure 4c,g,k,o). These samples had an almost continuous Ag layer at the edge of each melt track. However, these distinctive AgCaLa layers did not occur for the HD-0 strategy. For the HD-0 strategy, the AgCaLa was divided into separated phases (Figure 4a,e,i,m). This effect was more pronounced for the strategy HD with rotation of the scanning direction, as this material was characterized by homogenous AgCaLa phases with a compact shape (Figure 4b,f,j,n).



Figure 4. SEM-SE: morphology of AgCaLa phases in a FeMn matrix: (**a**,**e**,**i**,**m**) HD-0, AgCaLa phases positioned between adjacent melt pools; (**b**,**f**,**j**,**n**) HD, homogeneously distributed AgCaLa phases; (**c**,**g**,**k**,**o**) LD-0, distinctive deposition of AgCaLa phases between adjacent melt tracks with a weak connection between single tracks; (**d**,**h**,**l**,**p**) LD, AgCaLa phases aligned along the melt tracks, separated by the deep center of the melt pool of the following layer.

The intensive deposition of AgCaLa at the sides of the melt tracks matched the increased amount of Ag detected at the sides of as-built samples (Figures 2b and 4m,n,p). Distinctive AgCaLa layers in the bulk material were only observed for the LD-0 strategy and not for samples produced with the LD strategy with rotation of the scanning direction (Figure 4d,h,l,p). The AgCaLa phases of LD samples revealed regular structures and the phases were separated by continuous lines of FeMn. As the AgCaLa was preferred deposited at the side of melt tracks and these structures had an angle of 67°, corresponding to the rotation of the scanning direction, these phases were divided into smaller fractions by the deep center of the melt tracks of the following layers (Figure 4h,l).

Apart from the morphology, a porosity was specifically observed in samples produced with the LD and LD-0 strategies, whereby even samples with HD-0 and HD strategies exhibited a certain porosity. The pores were preferably located near the AgCaLa phases or within the AgCaLa phases. Aside from the porosity, further inclusions were present in most of the AgCaLa phases. These inclusions were in samples with high as well as low density.

Three-dimensional investigations of the morphology of AgCaLa in the bulk material confirmed a homogenous distribution for HD and LD samples within the whole volume (Figure 5d,e). For samples built with the LD strategy, the porosity was significantly pronounced. The acceptance of this certain porosity enabled the adjustment of smaller AgCaLa phases (Figure 5e). Thus, taking into account the previous results, well-dispersed AgCaLa phases could be obtained via LBM and the adjustment of regular AgCaLa phases was possible.



Figure 5. 3D-distribution of AgCaLa phases analyzed via μ-CT: (**a**) size distribution of AgCaLa phases; (**d**) HD, homogenous distribution of AgCaLa phases; (**e**) LD, homogenous distribution of AgCaLa phases and pores; (**b**,**c**,**f**) samples with a graduated distribution of AgCaLa phases by variation of LBM parameters; (**g**) schematic illustration of the parameter variation used for samples (**b**,**c**,**f**).

However, for both materials, some AgCaLa phases were significantly larger than the initial powder particles, indicating agglomeration of AgCaLa. These agglomerations confirmed the formation of the AgCaLa phases from the enrichment of AgCaLa in the upper part of the LBM manufactured parts (Figure 5a). Thus, the AgCaLa phases in the bulk did not originate from single powder particles.

As Figure 1g depicts, it was possible to produce samples without AgCaLa in the bulk material with LSC parameters. If these LSC parameters were applied for the center parts, an AgCaLa-free center could be obtained. Figure 5g demonstrates the applied hatchings schematically. HD and LSC parameters with an overlap resulted in an almost AgCaLa-free center and homogenously dispersed AgCaLa phases in the outer area (Figure 5b). Similar results were obtained when the HD parameters were used for several circular counter-paths in combination with LSC parameters for the center (Figure 5c,f). For the counter-paths, the stripe-like hatching is displaced by several circles (Figure 5g). This strategy resulted in AgCaLa phases aligned along the circular melt tracks comparable to the HD-0 structure (Figure 4e). In summary, it was possible to obtain well-dispersed AgCaLa phases in the outer area while the center was almost free of AgCaLa with both hatching strategies. Thus, the targeted adjustment of the homogenous distribution of AgCaLa phases was possible. Furthermore, an adaption of the morphology and size distribution was possible, as the different particle sizes of LD and HD parameter settings prove. As reported by Krüger et al. [35], further parameters such as layer thickness can be applied for further adaptions if the results of degradation tests, investigations of biocompatibility, etc., make adaptions necessary.

The corresponding investigation of the grain structure and distribution of the chemical elements point out the embedding of the AgCaLa phases in an austenitic matrix, which is typical for this material processed via LBM (Figure 6a). The columnar dendritic structure of solidification was detectable in the EBSD data and the associated segregations of Mn were slightly visible (Figure 6b) [35,83]. Segregations of Mn occurred on a larger scale, e.g., along the melt pool boundaries, as identified in Figure 6a [35,85].



Figure 6. Microstructure of the FeMn matrix and AgCaLa phases: (**a**) SEM-EBSD with corresponding SEM-EDS: HD, austenitic matrix with AgCaLa phases; (**b**) SEM-EBSD with corresponding SEM-EDS: HD, columnar dendritic structure with segregations; (**c**,**e**) SEM-SE: HD, water-free prepared AgCaLa phases in the FeMn matrix; (**d**) SEM-EDS: HD, water-free prepared inhomogeneous distribution of alloying elements and O in an AgCaLa phase.

As expected and intended, the alloying elements Ca and La were detected within the Ag-rich areas, whereas Mn was detected within the matrix material (Figure 6a). However, it must be considered that the preparation might influence the chemical composition due to the reactivity of the alloying elements. Particularly, the final vibration polishing for 12 h might be crucial. Thus, for the investigation of the structure of the AgCaLa phases, all samples were solely ground to a grid size of 2500 using ethanol as a cooling lubricant. These samples showed less porosity and various inclusions in the AgCaLa phases instead of the porosity observed after the water-based preparation route (Figure 6c,e). The inclusions were enriched with Ca, O, and partially La (Figure 6d) and might be oxides of Ca. As a similar chemical composition was detected for the slag on the as-built top surface, these phases might be slag incorporated into the AgCaLa phases during LBM. The dissolution of these inclusions during preparation with water was conclusive since Ca forms hydroxides which are dissolvable in water but insoluble in alcohol [86]. Thus, the observed porosity (Figure 4) was due to the dissolving of Ca- and O-rich inclusions, and the real structure in the bulk material was better preserved in water-free prepared samples (Figure 6d). Additionally, to the Ca- and O-rich areas, small inclusions of FeMn were dispersed in the AgCaLa phases. However, between these inclusions, wide Ag-rich areas containing Ca and La were detected, as intended for the AgCaLa phase.

The preparation routine also influenced the O distribution significantly as O was mainly detected in the AgCaLa phases after the water-free preparation and in the area of bulk

material after the water-based preparation. Thus, during a water-based preparation, oxides were formed in the area of the FeMn while the O-rich regions of AgCaLa were dissolved and the O distribution shown in Figure 6a was less representative than in Figure 6d.

For the AgCaLa phases of water-free prepared samples which were ground to 2500er grid size and subsequently polished with 3 µm water-free suspension, a composition of 75.8 wt.% Ag, 10.6 wt.% Ca, 5.4 wt.% La, 5.2 wt.% Mn, 3.9 wt.% O, and 0.7 wt.% Fe was determined via WDX (average of five particles with 121 measuring points each, outliers excluded). Thus, the alloying elements remained in the AgCaLa and the intended chemical composition of the AgCaLa was almost reached. However, the Ca content was less than in the powder feedstock and less than intended. Additionally, the detected O confirmed the formation of O-containing compounds, and some Mn was taken up from the surrounding matrix by the AgCaLa. The uptake of Mn was more pronounced for the processing of FeMn with pure Ag, as described by Krüger et al. [35], resulting in the chemical composition of 88.3 wt.% Ag, 11.7 wt.% Mn, 0.1 wt.% O, and 0.6 wt.% Fe (WDX).

The lack of any gradual transition of the chemical composition or enrichments of elements at the boundary between AgCaLa and FeMn indicates the lack of any connection or transition zone between both phases. Thus, the AgCaLa phases were present in the matrix without any connection to the matrix.

The fraction area resulting from the quasi-static tensile test confirmed the missing interconnection between the AgCaLa phases and the FeMn matrix since a detachment of AgCaLa, as well as cavities from which AgCaLa was detached, were observed (Figure 7b,c,d). Besides, brittle fractured AgCaLa phases were also present. These fractures occurred probably due to mechanical clamping with undercuts, albeit, even for fractured AgCaLa, a separation from the surrounding material was detected (Figure 7c). As expected and in contrast to the AgCaLa, the FeMn matrix was characterized by a ductile fracture behavior (Figure 7e) [19]. On a larger scale, the fracture was cleaved comparable to the typical behavior of brittle fracture behavior (Figure 7b,d). This structure was conclusive since the AgCaLa phases that did not carry a significant load were the weakest points and the fracture lines proceeded between them.



Figure 7. Results of tensile tests: (**a**) Tension elongation diagram of five samples, each represented by a different color; (**b**–**e**) SEM-SE: fracture area; (**b**,**d**) cleaved fracture, reduced load-bearing cross-section due to AgCaLa phases; (**c**) brittle fraction of AgCaLa phase; (**e**) ductile fraction of FeMn matrix.

The observed fracture surface is conclusive with the mechanical behavior, since after exceeding the yield strength, the material was 10% plastically deformed in agreement with the ductile structure of the matrix, while the failure occurred spontaneously without significant necking (Figure 7b). This failure behavior, which is more likely for brittle materials, was indicated by the lack of regression of tension before failure. Thus, the

FeMn enabled a ductile material behavior, but the notch effect of the AgCaLa phases was comparable to the influence of pores by suppressing necking [19,26,87].

The average ultimate tensile strength was 701 MPa (standard deviation: 29 MPa) and the elongation to fracture was 12.1% (standard deviation: 29 MPa). For some samples, the transition between elastic and plastic elongation was flattened and no distinct yield strength was distinguishable. Thus, a reliable determination of the yield strength was not possible, since the behavior of the samples significantly differed. For the samples with a distinct transition, a yield strength of 475 MPa can be estimated.

The following section aims to understand the influencing parameters regarding the formation and the resulting structure of the AgCaLa inclusions to enable further targeted adaption to create biodegradable Fe-based material. Furthermore, the suitability of the presented material for the intended application is discussed.

3.1. Formation of Insoluble AgCaLa Phases

The results presented demonstrate that a mixture of iron-based matrix material in combination with a degradable Ag alloy can be processed via LBM. A good and adaptable distribution of AgCaLa within the bulk material can be obtained and the chemical composition remains, although some minor changes due to loss and uptake of alloying elements and O occur. This is an outstanding result, as previous investigations revealed intensive interaction and diffusion of alloying elements between insoluble melts of FeMn and pure Ag during LBM [35].

However, the addition of 12 wt.% Ca and 5 wt.% La to Ag significantly influences the LBM process, although these alloying elements result in only 0.85 wt.% of the mixed material. In contrast to the processing of pure Ag with FeMn, where a transition welding mode is identified, a keyhole mode was determined for the present results due to the deep and narrow melt pools [35,62,63,80,81]. Here, the energy introduced with every single track was reduced for HD parameters compared to the parameters for the processing of FeMn, as well as FeMn with pure Ag. The hatch distance and scanning speed were increased while the laser power was decreased [35]. Thus, the different welding mode was not caused by increased energy introduction but by the alloying elements Ca and La. The absorption rate of AgCaLa was not the reason, as the absorption was lower for the processed material with AgCaLa. However, the formation of a keyhole due to vaporization increases the energy absorption. Consequently, the vaporization behavior of the material is decisive [65,66,88]. Ca has a significantly higher vapor pressure than Mn, Ag, Fe, and La [89]. Accordingly, the increasing vaporization and formation of keyholes due to the addition of even small amounts of Ca are conclusive. Additionally, the vapor pressure depends linearly on the mole fraction, so Ca has a decisive influence as the vapor pressure of Ca is at 1000 °C 10,000 times higher than for Mn [89,90]. In addition, the enrichment of AgCaLa in the upper part of the LBM manufactured material increases the influence of Ca. Accordingly, for the LD parameters, less enrichment of AgCaLa on the top was observed and the melt pools were not as deep and narrow.

As the keyhole mode increases the amount of energy available for melting, the melt pool size increases and it is to be expected that a reduced energy density is sufficient for the processing of FeMn with AgCaLa [64,65,67,68,88,91]. Further energy might be released by chemical reactions, indicated by the observed compounds on the top and within the AgCaLa phases [57]. Apart from the changed energy feeding, the heat dissipation might be affected due to differences in heat conductivity, radiation, etc. [53,59,92]. Nevertheless, the main influencing parameter is the high vapor pressure of Ca as it evokes the keyhole mode. Due to this, further minor differences in comparison to the processing of FeMn with pure Ag cannot be identified.

However, apart from the changing welding mode, similar formation of the AgCaLa phases compared to pure Ag phases as described by Krüger et al. [35] can be assumed. Hence, the model of the formation of AgCaLa phases presented in Figure 8 is based on conclusions from the results discussed here and the adaption of information from the

literature, e.g., regarding melt flow and shape of the melt pool. In the first part of the melt pool, the recoil pressure is decisive [53,64,66,80]. The AgCaLa originating from the powder feedstock as well as the enrichment of AgCaLa on the upper surface were melted and emerged into the FeMn (Figure 8b). The emerging is conclusive, as the recoil pressure causes strong melt flow around the keyhole and affects both components similarly [64,71,93]. Additionally, the enrichment of AgCaLa on the top surface in the interaction zone with the laser is implausible, as this would reduce the energy adsorption, since Ag has a high reflectivity. Moreover, the observed diffusion of alloying elements between the liquid components supports the theory of emerging, as the emerging simplifies diffusion due to an increased contact interface.

The surface tension is decisive in the backward part of the melt pool and causes, e.g., Marangoni flow [53,59,80,94]. The results presented reveal that no transition between AgCaLa and FeMn exists. Thus, a phase border with a certain surface tension exists between both melts. Consequently, the AgCaLa coagulates when the floating phases come in contact, as the coagulation reduces surface energy. The position of AgCaLa on the top can be explained by the lower surface tension of AgCaLa compared to FeMn. As less surface energy is necessary to create a top surface of AgCaLa than for a top surface of FeMn, additional energy would be necessary for the incorporation of AgCaLa from the top surface to generate a free top surface of FeMn as well as a new surface between AgCaLa and FeMn. Accordingly, once AgCaLa reaches the surface it is trapped there. The lower surface tension of AgCaLa compared to FeMn is consistent, as the surface tension of Ag can be expected to be lower than that of FeMn [35,95,96]. Additionally, the surface tension of La and Ca is lower than for Ag. Since typically the surface tension of alloys ranges between the surface tension of the single elements, the surface tension of AgCaLa can be assumed to be lower than that of pure Ag [97–99]. Moreover, the position of AgCaLa on the top enables intense contact of AgCaLa with the atmosphere and uptake of O, which results in further reduction of surface tension [95].

AgCaLa reaches the top surface due to the random flow of the floating AgCaLa, as the melt flow is strong enough to keep the AgCaLa floating even against gravity [100,101]. A further effect supports the rising of AgCaLa particles: as the surface tension of the surrounding FeMn decreases with increasing temperature, the surface tension of the FeMn melt is the lowest in the upper and hottest part of the melt pool. Consequently, the FeMn flows under the floating AgCaLa towards higher surface tension, and the AgCaLa is pushed upwards [35,102,103]. Thus, the position of AgCaLa on the top is conclusive.

Another effect results in the position of the AgCaLa between neighboring melt tracks: The temperature depending on the surface tension induces an outward-directed melt flow vortex of the FeMn melt under AgCaLa [71,104–106]. This outward and downward directed flow drags the AgCaLa melt down (Figure 8a). The AgCaLa at the flanks of the melt pools is more easily detectable for the process strategies without any rotation of the scanning direction. The positioning at the sides of the melt pool is significantly more pronounced for AgCaLa than for Ag [35]. This might be due to different melting modes or could be influenced by the different material properties of AgCaLa. The bigger difference in surface tension between AgCaLa and FeMn than between FeMn and Ag could result in a stronger manifestation of the surface tension-driven mechanisms observed for pure Ag. Furthermore, the AgCaLa enables the use of parameters with increased hatch distance compared to a combination of FeMn with Ag [35]. An increased hatch distance enables easier incorporation of the AgCaLa, as the LD parameters prove. With such an LD strategy, a regular structure of AgCaLa phases arranged along the melt track and divided into insular phases by the deep center of the following melt track can be obtained. These unique structures confirm the effects responsible for the formation of the AgCaLa phases. Thus, the presented results match the previous results for the processing of FeMn with pure Ag by Krüger et al. [35], and the more significant morphology of the AgCaLa phases confirms the stated hypotheses regarding the Ag phase formation.



Figure 8. Formation of AgCaLa phases throughout the LBM process, schematic model; melt pool shape and melt flow adapted from [60,64,68,71,93,107]: (**a**) outward directed vortex of FeMn transporting AgCaLa to the flanks of the melt pool; (**b**) emerging of AgCaLa due to keyhole and accumulation on the top in the backward part of the melt pool due to surface tension; (**c**) distribution of AgCaLa in the top of LBM-manufactured material, with remaining AgCaLa phases at the lower end of the melt pools.

As the AgCaLa is transported to the top of the melt pool, the AgCaLa in the upper part of the melt pool is remelted and transported upwards again with the generation of each

new layer. This mechanism leads to an increased amount of AgCaLa in the melt pool. Only AgCaLa phases at the lower end of the melt pool remain in the bulk material during the generation of the next layer. After a few layers, an equilibrium in the addition of AgCaLa from the powder feedstock and the remaining of AgCaLa in the bulk material is achieved. Thus, the AgCaLa phases in the bulk material are remaining parts of the agglomeration of AgCaLa on the top and do not originate from initial powder particles. This agglomeration, mainly caused by surface tension-driven effects, is conclusive with the determined size of the AgCaLa phases (Figure 5a) since some phases are larger than initial powder particles.

3.2. Spattering Causing Graded Distribution of AgCaLa

The model presented cannot explain why in some samples no AgCaLa phases were formed. According to the model, even if the accumulation on the top were more pronounced, after several layers too much AgCaLa would be accumulated and remain in the bulk material. However, less AgCaLa was observed on the top of samples manufactured with LSC parameters. Therefore, the AgCaLa must be removed by other effects. One explanation might be the excessive formation of AgCaLa spatters. As specified in the introduction, the spattering depends, e.g., on the vaporization behavior, viscosity, and surface tension of a material [57,60,72]. Hence, the intensive spattering of AgCaLa due to the high vapor pressure of Ca is conclusive, as the evaporation causes recoil and accelerates the material. Additionally, the reduced surface tension of AgCaLa might simplify the shearing of AgCaLa. However, the significant influence of the material properties on the spattering is observed by Gunenthiram et al. [60].

Apart from ejection from the melt pool, an increased ejection of AgCaLa from the powder bed is possible as evaporation can create a blow-off impulse [57,60,62,70,82]. Since Ca evaporates excessively, an increased blow-off impulse concerning the AgCaLa particles is conclusive. Thus, the preferred ejection of AgCaLa is conclusive but occurs only for parameter settings which lead to a high energy density. A reduced scanning speed and increased laser power (LSC-1 and LSC-2) increase the energy in the melt pool, resulting in increased spattering [57,60,70]. Nevertheless, regarding the scanning speed opposite effects are reported [57,70]. However, in the present study, the LSC parameters led to increased spattering and, as AgCaLa was more likely to be removed from the melt pool, material that did not contain any AgCaLa could be generated. Additionally, some of the effects resulting in increased spattering of AgCaLa might only occur at a higher energy level.

However, the presented results prove the pronounced sensitivity to the process parameters, which can be utilized to create material with graded properties. Thus, it is possible to create components with AgCaLa phases only in the defined areas. To reduce the degradation rate at the beginning, fewer AgCaLa phases in the edged area are beneficial. If instead of the degradable FeMn a not degradable Fe-based matrix material like 316L is used, it would be possible to manufacture implants that release Ag. As Ag acts antibacterially, those implants could prevent implant-related infections [40,45,108,109]. In such material, the mechanical load capability would be less affected due to the lack of AgCaLa in the center. Thus, the results achieved in this study can be applied to other applications of immiscible elements in multi-material systems.

3.3. Generation of Slag and Chemical Composition of AgCaLa

Apart from the possibility to generate a suitable distribution of AgCaLa phases, the chemical composition of the AgCaLa phases has to be discussed critically. The composition is changed by the loss of Ca and the intake of Mn. However, knowing this, a potential loss of Ca can be balanced by an increased content in the feedstock, whereas the intake of Mn is less distinctive than for pure Ag [35]. Thus, the addition of Ca and La reduces the solubility of Mn in Ag. The reduced intake of Mn proves the possibility to prevent the uptake of undesirable elements by the addition of acceptable elements. This option is considerably important for degradable Ag phases within a not degradable matrix, as the intake of, e.g., nickel (Ni) is critical for the human organism.

Apart from the deviation of the overall chemical composition, the inclusion of chemical compounds generated during the LBM process might be a crucial point. The occurrence of such reactions despite the low oxygen content during LBM is a common challenge, specifically for the processing of alloys with reactive elements [73–75,79]. When this slag is incorporated into the material it can weaken the mechanical properties [76,78]. In the present case, the investigated material contained slag only in combination with AgCaLa phases which did not contribute to the load capacity. The incorporation of the slag into AgCaLa is conclusive due to the lower surface tension and melting temperature of AgCaLa. Since the oxides of Mn decompose and melt at high temperatures, incorporation to FeMn with high melting temperature is less probable [46,110,111]. Additionally, the slag is located on the top of AgCaLa, and AgCaLa lies on FeMn; thus, the slag is in contact with AgCaLa and not with FeMn. The low density contributes to the fact that AgCaLa is on the top [100,104]. Anyway, in comparison to the distinctive slag on the top, only a little amount of slag is detected in the bulk material. This might be due to repeated accumulation of slag on the top accompanied by the ejection of oxides with the spatters, the simultaneous oxidation and de-oxidation, as well as vaporization of oxides in the laser spot, which might contribute to the reduced incorporation of slag into the bulk material [69,73,76,112]. Aside from the incorporation of slag, porosity is observed together with the AgCaLa in the bulk material, even for the HD parameter settings. This porosity should be noncritical, as improved osteoconductivity and degradation behavior are reported for targeted porosity [16,113]. Thus, the porosity caused by the AgCaLa might be beneficial.

However, the AgCaLa phases are suited to the intended application despite the deviation in the chemical composition, as Ag-rich areas are present. These regions presumably have a higher electrochemical potential than the surrounding matrix and should therefore cause enhanced anodic dissolution of the FeMn. The inclusions of slag might be dissolved directly after contact with the aqueous environment, as the samples prepared with water reveal. If these inclusions remain, they could enhance the dissolution of the AgCaLa phases due to differences in the electrochemical potential. The intake of Mn might also contribute to the degradation of the AgCaLa phases after the dissolution of the matrix material. Otherwise, Mn reduces the electrochemical potential of the AgCaLa phases. Whether this reduction is critical depends on the extent of the reduction. Therefore, investigations of the degradation behavior are mandatory to determine the influence of the AgCaLa phases, as presented in this study, and enable further defined adaption, e.g., by adjusting the morphology via process conditions and the chemical composition via the feedstock material.

3.4. Mechanical Properties Affected by AgCaLa

Apart from the degradation behavior, the material needs to fulfill the mechanical requirements. The results of the quasi-static tensile test are promising as the yield strength of approximately 475 MPa is only 5% lower than that of additively processed FeMn, and FeMn modified with 5 wt.% pure Ag. The modification with pure Ag impacts the yield strength just slightly. The elongation at break (identical sample shape) of FeMn is between 25% and 45%, and 16% and 24% for FeMn with pure Ag. Thus, the elongation at break is significantly reduced to 12.1% for the modification with AgCaLa [35]. As any deformation of an implant is not acceptable, the elongation at break is not considered to be crucial. However, a certain ductile material behavior is recommended since for a coincidental overload the implant would not break directly. For the ultimate tensile strength, the identical tendency as for yield strength and elongation at break is observed. The ultimate tensile strength is about 1025 MPa for FeMn, 850 MPa for FeMn modified with pure Ag, and 701 MPa for FeMn modified with AgCaLa. Thus, the modification with pure Ag affects the mechanical properties less than the modification with AgCaLa [35]. The volume fraction of AgCaLa is higher than for Ag due to the lower density of AgCaLa and thus the impact of AgCaLa on the load carrying section is increased. Furthermore, the reduction

observed for FeMn with AgCaLa might be due to the porosity observed in combination with the AgCaLa phases, as the load-bearing cross-section is further reduced. Porosity could be related to chemical reactions and slag incorporation since porosity is observed in combination with slag in single-component materials [78]. This increased porosity might also be an explanation for the flattened transition between elastic and plastic deformation. However, the porosity might be beneficial to adapt the stiffness to the stiffness of bones and reduce the stress shielding effect [51,52].

In summary, the quasi-static mechanical properties are promising apart from a few restrictions which can be improved by process adaption to reduce the generation of slag. As fatigue behavior is a decisive factor for medical implants, it has to be investigated additionally. It can be assumed that the notch effect of the AgCaLa phases in combination with pores affects the fatigue behavior more strongly than the quasi-static properties. However, the AgCaLa phases exhibit a globular shape. Together with the ductile behavior of the matrix material, a reduction of tension peaks can lead to an acceptable fatigue behavior.

4. Conclusions

The present study reports on the processing of FeMn with a degradable Ag alloy via LBM for the adaption of the degradation rate. The effects influencing the morphology and chemical composition of the Ag phases are identified to enable further targeted adaption for the application as implant material. Additionally, the suitability of the material as degradable implant material is discussed.

LBM enables the processing of FeMn with degradable AgCaLa alloy. Suited, adaptable morphology and chemical composition of the AgCaLa phases are obtained.

AgCaLa is enriched on the top and between adjacent melt tracks due to surface tension-driven effects.

AgCaLa in the upper part is remelted; only AgCaLa at the lower end of the melt pools remains in the bulk material.

Graded distributions with regular structures and regions without AgCaLa can be achieved as the morphology of AgCaLa phases is sensitive to LBM parameters.

The use of AgCaLa instead of pure Ag significantly influences the LBM process. The high vapor pressure of Ca causes keyhole welding mode.

Slag is generated due to the high reactivity of Ca, La, and Mn. The slag is incorporated into the AgCaLa phases. The Ag phases take up Mn from the matrix.

Suited areas with high Ag content in the AgCaLa phases should enable increased anodic dissolution of the FeMn matrix due to different electrochemical potentials.

Due to the addition of AgCaLa, the yield strength is reduced by only 5% compared to pure FeMn.

As the presented results demonstrate, the chemical composition of an Ag alloy processed via LBM with an iron-based matrix influences the process characteristics and the material properties in many aspects. Thus, all relevant aspects, such as changes in the welding mode, the loss and intake of alloying elements by diffusion, varying saturation concentration, vaporization of alloying elements, or generation of slag have to be considered to generate a biocompatible material with a suited morphology of Ag phases and degradation behavior. However, the material presented in this study reveals promising properties. Investigations of the degradation behavior and biocompatibility are required to enable further targeted adaptions to be made.

Funding: This research was funded by German Research Foundation (DFG) grant number SCHA1484 /44-1.

Acknowledgments: The author gratefully thanks the German Research Foundation (DFG) for financial support. This work results from the project SCHA1484/44-1. Additionally, the author thanks Mirko Schaper and Kay-Peter Hoyer for enabling this work and supervision. Furthermore, the author would like to thank Anatolii Andreiev, Sabrina Beumer, and Lea Kaspersmeier for promoting the production and examination of the tested material.

Conflicts of Interest: The author declares to have no conflict of interest.

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