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Influence of foaming agents on laser based manufacturing of closed-cell Ti foam

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Abstract

Titanium offers a high specific strength, low density, and excellent corrosion resistance. It finds application in many fields like automotive, aerospace, drilling, and biomedical industries. To improve the adherence of bone cells on implants a rough surface can be of advantage. Such a surface is featured by a foamed structure. For achieving a foamed Ti structure, laser induced foaming was used. In this case, Ti powder is pre mixed with foaming agents. The foaming agents are degraded by laser induced energy and produce gaseous products like carbon dioxide, while the Ti powder is molten by the laser. Due to the fast cooling rate carbon dioxide forms gaseous bubbles in the solidifying material. Mandatory for the foaming agents is that they are biocompatible. Previous studies using the foaming agents $CaCO_3$, $MgCO_3$, $MgTiO_3$, and $MgTiO_3$ mixed to Ti powder resulted in a porosity of up to 0.3. By varying the content of the foaming agent porosity and pore diameter of the samples were adjusted.
It is expected that an increased porosity could be achieved by mixing the foaming agents among each other. The influence of the specific foaming agents and their mixtures on the porosity is presented in this work. By mixing the foaming agents together and adding them to the powder, the porosity of the samples was increased compared to only adding one foaming agent to the powder.

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*Keywords:*Ti Foam; Foaming agents; Laser based foaming; Ti implants; Nanoindentation

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1. Introduction

Processing of metallic foams is investigated at the Laser Zentrum Hannover e. V. (LZH) since 1999 (Haferkamp et al. (1999)). Very interesting as metallic foam for implants is a Ti foam. Ti offers particularly a great biocompatibility (Higuchi et al. (2005), Maekawa et al. (2005), Sakamoto et al. (2005), Bannon and Mild (1983)). A laser based process offers itself for application to make a Ti foam. By conventional methods Titanium and its alloys are difficult to machine and the processing causes high tool wear (Weinert and Petzoldt (2004), Hohenhoff et al. (2005)). Using a laser based process titanium foam structures with dense, closed outer skin can be realized. The porous foamed core is generated by adding foaming agents to the titanium powder. A structure comparable to cancellous bone should be realized. To allow implants for different bone types, a wide range of foaming agents were chosen and even mixed with each other. To generate such foams near net shape would allow for application in medicine. An advantage is a rough but closed outer skin of the foamed structures allowing for good cell adherence on the implant (Diefenbeck et al. (2011)). The laser based foaming of titanium is presented in this contribution.

2. Experimental

To machine the Ti foam a diode laser system at a laser power of 350 watts was chosen. The laser diameter at its focus was 860 nm, the wave length was 940 – 980 nm. The process was performed in a reaction chamber under Ar as inert process atmosphere. The setup of laser head and shielding box is depicted in Fig. 1. A special powder reservoir with five grooves for the Ti powder was placed in the reaction chamber (Fig. 2). In each groove 2.5 g powder of the same mixture was deposited to achieve five samples for analysis in one processing step.

As powder Ti with a particle size between 75 µm and 100 µm was mixed with the respective foaming agents. For the foaming agents the decomposition temperatures were chosen to be lower than the melting temperature of Ti with 1,933 K. Each of the foaming agents dissociates at a specific temperature. The specific decomposition temperatures are for:

- calcium carbonate ($CaCO_3$) 1,181 K (Wiberg (1971))
- magnesium carbonate ($MgCO_3$) 813 K (Wiberg (1971))
- magnesiumtitanate ($MgTiO_3$) 1,813 K (Wechsler and Navrostsky (1984))

The foaming process leaded to a lot of smog that was removed by a suction placed close to the reaction chamber. After processing, the welding beads were cleaned from residual particles in a ultrasonic bath. To measure the porosity a pycnometer was used. Next the welding beads were cut and polished for optical evaluation. The Ti matrix was inspected by energy-dispersive X-ray spectroscopy (EDX). To achieve the hardness and Young's Modulus of the Ti Matrix, nanoindentation techniques were used.

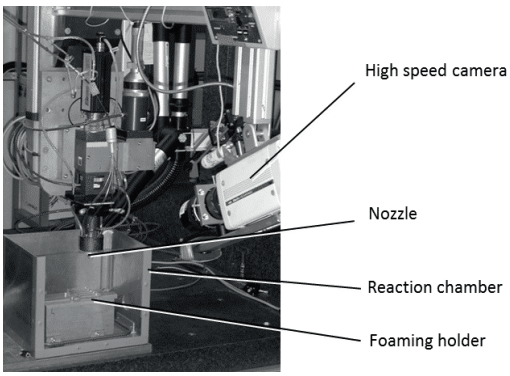


Fig. 1. Setup for Ti foaming

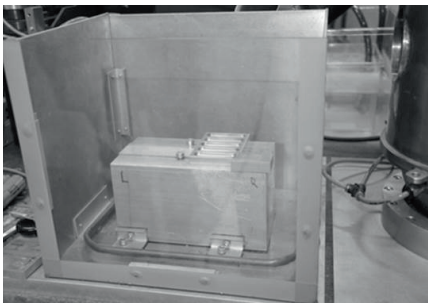


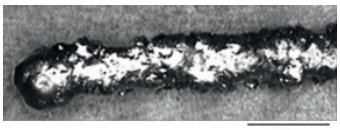
Fig. 2. Powder reservoir in reaction chamber

3. Results and discussion

The foaming process could be established with the presented setup. By the laser induced energy Ti was molten and the foaming agent dissociated. In the process, the molten Ti and gaseous bubbles agglomerated on solidified material and a porous sample could be achieved. Exemplary welding beads foamed with 0.7% $CaCO_3$ and 1.9% $CaCO_3$ are depicted in Fig. 3. The concentration of the foaming agent has a significant influence on the porosity. If a high amount of foaming agent is added, the pores are too big, the foam collapses.

Thus, for the specific foaming agents a working area was defined. At a concentration of foaming agent between 1.0% and 1.3% best results were achieved. For this work the values with a concentration of 1 % foaming agent were considered. Applying $CaCO_3$ as foaming agent the biggest pores were realized. With an increased content of $CaCO_3$ as foaming agent the foam collapsed. The highest porosity could be achieved by inserting $MgCO_3$ as foaming agent. With a high content of foaming agent the foam collapsed, too. In case of $MgTiO_3$ as foaming agent a porosity of 0.26 could be established (Fig. 4). For this foaming agent the foam was stable even for higher contents of foaming agent. In case of $MgTiO_3$ as foaming agent additional carbon was added to improve the reaction to gaseous carbon. A slightly increase of porosity could be achieved for this foaming agent by addition of carbon. The process was reproducible for all foaming agents. The specific foaming characteristics of the foaming agents can be corresponded to their specific decomposition temperatures and the specific kinetics of their foaming processes. The achieved porosities at 1% of foaming agent concentration are depicted in Fig. 5. Fig. 6 shows cross sections of samples foamed with 0.4% and 1% $MgCO_3$ as foaming agent. The influence of the increased content of foaming agent to the pore size is obvious.

a) 0.7% $CaCO_3$



b) 1.9% $CaCO_3$

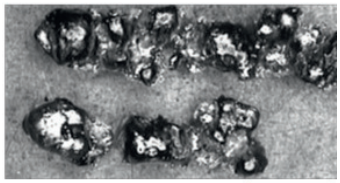


Fig. 3. Foamed welding beads: a) foamed with 0.7% $CaCO_3$, b) foamed with 1.9 % $CaCO_3$

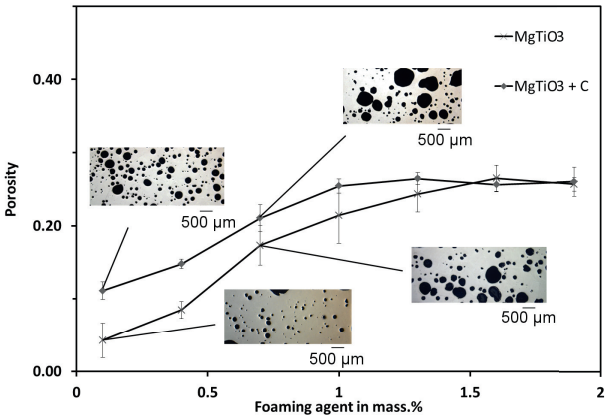


Fig. 4. Porosities for Ti foam foamed with $MgTiO_3$ and $MgTiO_3$+ C as foaming agent

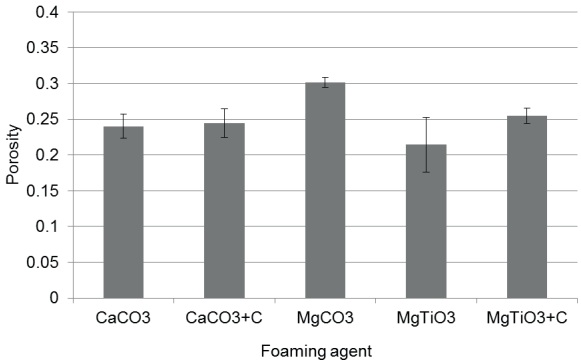


Fig. 5. Porosities for Ti foam foamed with 1 % of foaming agent

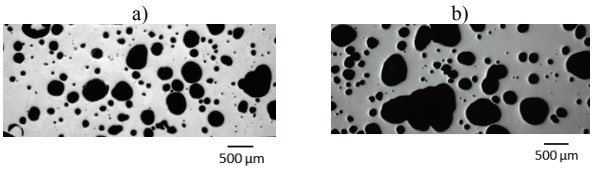


Fig. 6. Cross sections for Ti foam samples with: a) 0,4%, b) 1% $MgCO_3$ as foaming agent

The highest porosities could be achieved by mixtures of foaming agents. The foaming agents were mixed to the Ti powder that at total a foaming agent concentration of 1% could be achieved. Fig. 7 depicts the porosities (measured with pycnometer) of samples foamed with mixtures of foaming agents. The mixture of $MgCO_3$ and $MgTiO_3$ as foaming agents (each with a concentration of 0.5% in the powder) had the lowest porosity with a value of 0.25. In this case a mixture shows no improvement of the porosity. By mixing $CaCO_3$ and $MgTiO_3$ as foaming agents the porosity was increased to a value of 0.33. A mixture of $CaCO_3$ and $MgCO_3$ as foaming agents had a porosity of 0.34. In case of mixing $CaCO_3$, $MgCO_3$, and $MgTiO_3$ as foaming agents (each with a concentration of 0.33% of the powder) a porosity of 0.36 was realized. The addition of carbon brought no advantage in this case. Exemplary a µ-CT (micro-X-ray computed tomography) scan of a sample foamed with a mixture of $MgCO_3$, $CaCO_3$, and $MgTiO_3$ is depicted in Fig. 8. For this sample the measured porosity on the cut-through was 54%. Energy-dispersive (EDX) X-ray spectroscopy was conducted on foamed samples to analyze for contaminations of the Ti matrix. For all samples the matrix shows no content of foaming agent. At the pore wall the content of contaminations was below 0.02% for all samples. This value is within the EDX threshold.

To evaluate exactly the mechanical properties of the thin walls of Ti foam, it is mandatory to use a system allowing for a displacement in the range a few ten nm to a few microns and with a precision in the nm range. A system lending itself for application is a nanoindentation system. This is commonly used to measure hardness and Young's modulus of thin diamond-like carbon (DLC) coatings and thin layers (Pape and Gatzen (2008), Pape (2011)). The mechanical properties of the Ti matrix allow judging the influence of the foaming process and foaming agents on the Ti matrix. A load between 1 µN and 10 mN and a displacement of up to 5 µm could be realized by the test system. On a sample 80 indents were performed in the Matrix on a foam wall. A load of 5 mN was chosen, for measurement a Berkovich tip with 80 nm tip radius was applied. The Young's Modulus and hardness were evaluated by the method of Oliver and Pharr (Oliver and Pharr (1992)). The hardness was 4,6 GPa with a derivation of 1,2 GPa, the Young's Modulus was 132,9 GPa with a derivation of 6,4 GPa. The measured data are slightly higher than values reported in literature (Mante et al. (1999), Tam et al. (2009)).

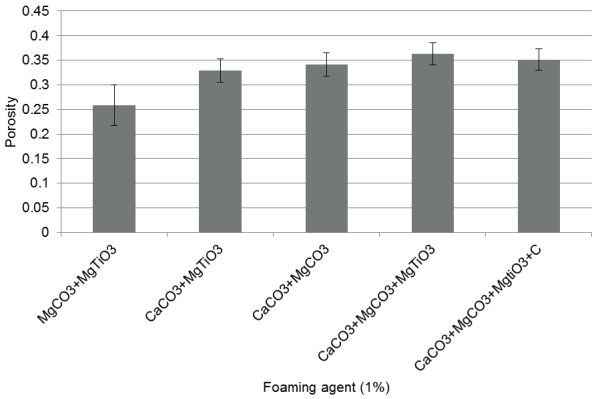


Fig. 7. Porosities for Ti foam foamed with mixtures of foaming agents (measured with pycnometer)

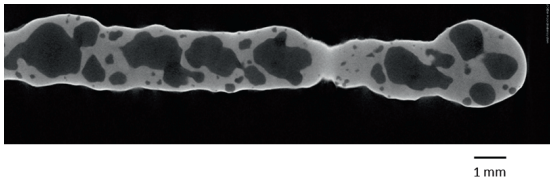


Fig. 8. Micro-CT image of foamed titanium specimen, foamed with mixture of $CaCO_3$, $MgCO_3$, and $MgTiO_3$

4. Conclusions

For all foaming agents a stable foaming process could be established. In the process and for the samples each foaming agent shows its own characteristics. This effect can be referred to the various decomposition temperatures and the specific reaction kinetics. Thus a mixture of the foaming agents allowed for obtaining an increased porosity, as the gaseous bubbles react at different temperature stages. For further investigations, foaming agents with a higher decomposition temperature like lithium carbonate or strontium carbonate should be investigated next. Finally it's planned to realize higher amounts of foam by stacking layer by layer of the welding beads. So far, the highest porosity in laser induced foam samples could be obtained for a sample foamed with a mixture of foaming agents. By mixing the foaming agents $MgCO_3$, $CaCO_3$, and $MgTiO_3$ (altogether 1% concentration) a porosity of 0.36 (measured by a pycnometer) was reached. The samples itself show a closed metal foam with a completely molten and dense matrix. Only a small amount of foaming agents could be detected using EDX analysis at the pore walls. It could be shown by nanoindentational measurements, that the Ti matrix has the mechanical properties as pure Ti.

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References

Bannon, B. P., Mild, E. E., 1983. Titanium Alloys for Biomaterial Application: An Overview. Titanium Alloys in Surgical Implants, editors Luckey, H. A., Kubli, F.

Diefenbeck, M., Mueckley, T., Schrader, C., Schmidt, J., Zankovych, S., Bossert, J., Jandt, K.D., Faucon, M., Finger, U., 2011. The effect of plasma chemical oxidation of titanium alloy on bone-implant contact in rats. Biomaterials 32, 8041-8047.

Haferkamp, H., Burmester, I., Herzog, D., Ostendorf, A., 1999. Laser Beam Welding of Metal Foams. Presented at the International Conference on Lasers LASERS'99.

Haferkamp, H., Ostendorf, A., Goede, M., Bunte, J., 1999. Potential of Laser Welding of Metal Foams. Presented at the International Conference on Cellular Metals and Metal Foaming Technology.

Higuchi, Y., Ohashi, Y., Nakajima H., 2005. Biocompatibility of Lotus-type Porous Metals in Alveolar Bone. Proceedings of the 4th International Conference on Porous Metals and Metal Foaming Technology MetFoam05, Kyoto, Japan.

Hohenhoff, G. et al., 2005. Rapid prototyping of articular metallic endoprostheses with adapted elasticity. Presented at International SFB Colloquium Hannover.

Maekawa, K., Hayashi, T., Hanyu, K., Umeda, K., Murakami, T., 2005. The Spark Plasma Sintering Method using Laminated Titanium Powder Sheet for Fabricating Porous Biocompatible Implants. Proceedings of the 4th International Conference on Porous Metals and Metal Foaming Technology MetFoam05, Kyoto, Japan.

Mante, F.K., Baran, G.R., Lucas, B., 1999. Nanoindentation studies of titanium single crystals. Biomaterials. 20, 1051-1055.

Oliver ,W.C., Pharr, G.M., 1992. An improved technique for determining hardness and elastic modulus using load and displacement sensing indentation experiments. Journal of Materials Research 7, 1564 - 1583.

Pape, F., Gatzen, H.H., 2008. Tribological Behavior of Multilayer Diamond-like Carbon (DLC) Coatings. Porceedings, GFT Tribologie Fachtagung , Vol. I, Goettingen, Germany, 9/1-9/10.

Pape, F., 2011. Mikrotribologische Untersuchungen an Wälzlagern mit polymeradditiver Fettschmierung. Thesis, Leibniz Universitaet Hannover.

Sakamoto, Y., Asaoka, K., Kon, M., Matsubara, T., Yoshida, K., 2005. Porous Titanium Compacts as Biomaterials for Hard Tissue Replacement. Proceedings of the 4th International Conference on Porous Metals and Metal Foaming Technology MetFoam05, Kyoto, Japan.

Tam, E., Petrzhik, M., Shtansky, D., Delplancke-Ogletree, M.-P., 2009. Combination of Instrumented Nanoindentation and Scanning Probe Microscopy for Adequate Mechanical Surface Testing. Journal of Materials Science &Technology 16, 2129.

Wechsler, B.A., Navrostsky, A., 1984. Thermodynamics and structural chemistry of com-pounds in the system $MgOTiO_2$. Journal of Solid State Chemistry 55, 165-180.

Weinert, K., Petzoldt, V., 2004. Machining of NiTi Based Shape Memory Alloys. Materials Science and Engineering, Part A 378, 180-184.

Wiberg, E., 1971, Lehrbuch der anorganischenChemie, Hollemann-Wiberg, Walter de Gruyter& Co.