Binder Jetting 3D Printing of Titanium Aluminides Based Materials: A Feasibility Study

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This study offers the ability to fabricate nearly dense titanium aluminides-based structures using a hybrid method that encompasses binder jetting 3D printing (3DP) of Ti–6Al–4V followed by pressureless ex situ infiltration with Al. Microstructure characterization and phase analysis are performed by scanning electron microscopy equipped with energy dispersive spectroscopy and X-ray diffraction, respectively. The microstructure of the samples fabricated by means of pressureless ex situ infiltration at different temperatures and with various durations is studied and discussed. The nearly dense titanium aluminides-based composites show a Young’s modulus of ≈145 GPa, a compressive strength of ≈1.4 GPa and a bending strength of ≈483 MPa. To demonstrate technological capability of this hybrid approach, complex near-net-shaped objects are fabricated.

1. Introduction

Due to the superior properties over conventional Ti alloys, titanium aluminides have potential applications in the fields of aerospace and automotive industries.1,2 Titanium aluminides (Ti₃Al₆) have low density (3.9 g cm⁻³), good resistance to oxidation, and high strength at elevated temperature. Therefore, the applications of titanium aluminides are not only limited to the aerospace and automotive industries but also recently, porous Ti₃Al₆ is used as gas and liquid filters at elevated temperatures.3

Higher production costs hinder the use of conventional processing routes such as casting, powder metallurgy, investment casting, and ignot forging for fabrication of Ti₃Al₆.2 Also, the brittleness of the Ti₃Al₆ makes them difficult to machine materials. Therefore, the need for near-net-shape processing route is vital.4 Morsi et al.,4,5 and Fu et al.6 reported the hot extrusion route for the fabrication of Ti₃Al₆. This process has been proven as a suitable method for the fabrication of near-net-shaped Ti₃Al₆—materials with limited porosity. Elemental powder processing route has been studied over the years for the fabrication of intermetallic compounds. In this route, a powder blend comprised of elemental powders (Ti and Al) is prepared, consoli-dated and post-processed through reactive sintering synthesis. During reactive synthesis, Ti₃Al₆ is fabricated via diffusion of Al atoms in Ti. But due to Al diffusion, a Kirkendall porosity forms, which leads to bloating of product formed.6

During liquid-state reactive sintering of solid Ti and liquid Al, it was observed that it gave rise to two exothermic peaks at 520–570 and 660–700°C, respectively.7,8

The second exothermic peak is caused by the expansion of the sample. The resulting sample was so fragile that it could not be used for further mechanical testing. The intermetallic compound, which forms at a temperature above the melting point of Al, is Ti₃Al₆ due to the exothermic reaction between solid Ti and liquid Al.9 The intermetallic compound Ti₃Al₆ shows minimum free energy of formation among the intermetallic compounds such as TiAl, Ti₃Al, and TiAl₃ in the temperature range of 273–1473 K.10

The additive manufacturing provides an advantageous edge over conventional techniques due to its capability to fabricate complex structures from computer-aided design (CAD) file. Recently, a lot of work has been done on fabricating of complex Ti₃Al₆-based parts using selective laser melting (SLM) and electron beam melting (EBM).11,12 However, many problems can occur in these processes, such as solid-state cracks, residual thermal stresses due to repeated rapid melting and solidification nature of the fabrication.11,13 In contrast, binder jetting 3DP works on the principle of the layer-by-layer printing, in which the binder ink is distributed on the powder layer. The green parts are then further heat-treated and post-processed.13,14 The detailed review on binder jetting 3DP can be found in ref. [15]. Not much work has been reported on binder jetting 3DP of Ti₃Al₆-based materials. Thus, in the present work an additional approach to the above-mentioned SLM and EBM methods was investigated. We propose a feasible processing route for Ti₃Al₆-based parts using additive manufacturing technique and reactive melt infiltration. It is well known that pressure-assisted or pressureless reactive and nonreactive infiltration of porous preforms by a
liquid metal is one of the preferred techniques of fabricating metal matrix composites (MMC) and ceramic/metal composites. This approach for certain materials compared with some other processing methods can be more economical. The purpose of this work is to fabricate dense Ti$_x$Al$_y$-based composites using indirect 3DP of Ti–6Al–4V porous preforms followed by pressureless ex situ infiltration with Al. The specific objectives are: 1) printing of Ti–6Al–4V preforms by variation of printing conditions, 2) fabrication of dense materials by post-pressureless vacuum infiltration with Al, 3) evaluation of phase composition, microstructure, and mechanical properties of such composites and 4) fabrication of near-net-shaped parts composed of Ti$_x$Al$_y$–based material.

2. Results and Discussion

2.1. Pressureless Ex Situ Melt Infiltration

The TiC/Ti6Al4V crucible-shaped samples were sintered at 1500 °C for 4 h, as this leads to lower open porosity and enhanced mechanical properties. It shall be noted that the crucible-like structure is better for easy reactive melt infiltration, as it can hold the liquid melt for full infiltration. The mechanical properties and phase evolution at the sintering conditions are already discussed in the previous work.

It was observed that Al (calculated according to the porosity of the sintered crucible) fully infiltrated in the porous crucible at 850 °C for 1 h, and no dimensional change or distortion of the crucible were observed. Thus, this pressureless ex situ infiltration of the crucible is a near-net-shape technique for fabrication of Ti$_x$Al$_y$. The presence of different phases such as Ti, TiC, TiAl$_3$, and TiAl$_2$ was confirmed by X-ray diffraction (XRD) spectrogram as shown in Figure 1. The presence of 26 wt% residual carbon content after pyrolysis at 500 °C results in the formation of TiC phase after solid-state sintering at 1500 °C for 5 h. The

![Figure 1. XRD spectrogram of Ti–6Al–4V samples infiltrated with Al chips at 850 °C for 1 h.](image)

![Figure 2. SEM images for Al-infiltrated samples kept at 850 °C for a) 1 h, b) 5 h, and c) 10 h.](image)
wt% of residual carbon after pyrolysis was confirmed and reported in previous study.\cite{20}

### 2.2. Post Heat Treatment of Infiltrated Samples

To study the microstructural stability and evolution of the pressureless ex situ infiltrated samples, the infiltrated samples were subjected to elevated temperatures 850, 1000, and 1150 °C with dwell time 1, 5, and 10 h, respectively.

Scanning electron microscopy (SEM) images of infiltrated samples subjected to 850 °C for 1, 5, and 10 h are shown in Figure 2. It was observed that five different layers could be observed after infiltration at 850 °C for 1, 5, and 10 h. A reduction in Al amount from the dark TiAl$_3$ matrix over the gray outer layer (TiAl$_2$, TiAl, Ti$_3$Al) to the inner Ti–6Al–4V core was observed. As discussed earlier, the diffusion of liquid aluminum in Ti is faster than Ti into liquid Al. As the dwell time increases, the liquid Al diffuses inward, and different Ti–Al intermetallic layers widen (comparing a, b, and c in Figure 2).

The formation of different layers due to variation in Al composition can be explained by the following equation

$$\text{Ti} + \text{Al} = \text{TiAl}_3 \rightarrow \text{TiAl}_2 \rightarrow \text{TiAl} \rightarrow \text{Ti}_3\text{Al}$$  \hspace{1cm} (1)

To study the effect of temperature and time on the microstructural stability, the samples were subjected to 1000 °C for 1, 5, and 10 h. The SEM images are shown in Figure 3. Different layers due to the compositional variation of Al can be observed. The width of each layer composed of TiAl, TiAl$_2$, and Ti$_3$Al increases, as the dwell time is extended. Due to insufficient dwell time, we could not observe the homogenization of the composition throughout the particle. Therefore, it can be concluded that with temperature and time, the microstructure is still evolving with the diffusion of Al inward.

When the pressureless ex situ melt infiltrated samples were heat-treated at 1150 °C for 1, 5, and 10 h, it could be observed that there was a homogenization throughout the inner core area, which was Ti–6Al–4V particle prior to infiltration (Figure 4). The intermetallic compounds Ti$_3$Al and TiAl are present throughout the particle. The presence of TiC phase can also be seen in Figure 4d. The bright spot in the center of particles is vanadium. It is interesting to notice that as the Al diffuses inward and forms an intermetallic compound, vanadium starts to segregate in the center of the particle. This is due to lower solubility of vanadium in intermetallic compounds compared with high solubility in beta Ti phase. It is important to note that the samples were further heat treated at 1250 °C for 5 h, but no significant change in phases observed. Therefore, it can be concluded that the phases are thermally stable.

The XRD analysis of the phases formed after heat treatments at 1150 °C for 1, 5, and 10 h is shown in Figure 5. Only TiAl and Ti$_3$Al as intermetallic compounds are observed. Along with the TiAl intermetallic compound, we could also detect the presence of initial TiC and Al$_{10}$V phases, which matches the explanation of segregation of V in the particle. The presence of TiAl, TiC, Ti$_3$Al, and Al$_{10}$V phases was also confirmed through energy dispersive spectroscopy (EDS) and XRD spectrogram as well (Figure 5).

![Figure 3. SEM images for Al-infiltrated samples kept at 1000 °C for a) 1 h, b) 5 h, and c) 10 h.](image-url)
To study the influence of elevated temperatures on the microstructure evolution and distribution of Ti, Al and V elements, energy-dispersive X-ray (EDX) mapping was performed. Figure 6 shows the EDX mapping of infiltrated samples after an additional heat treatment at elevated temperatures of 850, 1000, and 1150°C for 10 h. Through color contrast, it can be noticed that with increasing temperatures Ti (blue) and Al (red) is more uniformly dispersed compared with 850°C, whereas the vice versa happens with vanadium. As shown in Figure 6h, i, vanadium segregates in the center of the particle due to its low solubility in synthesized titanium aluminides.

2.3. Mechanical Properties

Here, we presented the mechanical properties of the thermally stable pressureless ex situ infiltrated samples heat treated at 1150°C for 10 h. The porosity of the crucible sintered at 1500°C for 4 h was 18%. Based on the volume of open porosity, the mass of the required Al was calculated. After the infiltration at 850°C for 1 h, the open porosity of the infiltrated crucible was calculated by the Archimedes principle. It was observed that the crucible was completely infiltrated with melt Al. The rectangular samples with a dimension of 45 × 4 × 3 mm³ were cut out of the infiltrated crucible for further mechanical testing. The surface of rectangular bars was polished. The mechanical properties of the infiltrated samples heat treated at 1150°C for 10 h are listed in Table 1. The Young’s modulus of 145 GPa, compressive strength of 1.30 GPa, Vickers hardness (HV10) of 3.74 GPa, and bending strength of 483 MPa were measured. Titanium aluminides-based materials fabricated in this work exhibited mechanical properties in the same range as presented in previous studies. The presented mechanical properties are significant, which allows fabricating near-net-shape complex objects with superior mechanical properties. The other main advantage of combining
3DP technique with ex situ melt infiltration is that nearly dense products can be derived. During infiltration, it was observed that there was no deformation of the samples, which was optimal for near-net-shaping process.

2.4. Pressureless Ex Situ Infiltration of Complex Structures

To demonstrate the capability of the described approach, complex-shaped parts were fabricated. The generation of the parts via a 3DP, pressureless reactive infiltration, and heat treatment is shown in Figure 7. After infiltration and heat treatments at 1150 °C, all details of the parts were maintained and dimensional change was barely observable compared with

Table 1. Mechanical properties of the ex situ infiltrated samples heat treated at 1150 °C for 10 h.

| Property                   | Infiltrated samples |
|----------------------------|---------------------|
| Young’s modulus [GPa]      | 145.28 ± 5.6        |
| Compressive strength [GPa]| 1.3 ± 0.57          |
| Bending strength [MPa]     | 482.91 ± 20.5       |
| Hardness [GPa]             | 3.74 ± 0.25         |
| Density [g cm⁻³]           | 3.84                |

Figure 6. Comparison of EDX mapping for infiltrated samples kept at 850, 1000, and 1150 °C for 10 h where a–c) red denotes aluminium, d–f) blue denotes titanium, and g–i) green denotes vanadium.

Figure 7. Titanium aluminides-based gears fabricated by hybrid method.
printed parts. Mechanical properties of the printed and sintered body are sufficient to handle it safely during post-infiltration. During infiltration with Al, the geometrical shape of the part is preserved and no further dimensional change takes place.

3. Conclusion

In this study, nearly dense titanium aluminides-based materials were fabricated by means of binder jetting 3DP using Ti–6Al–4V powder and ex situ reactive melt infiltration. In infiltrated samples, layer-wise titanium aluminide phases (surrounding the initial Ti–6Al–4V powder particles) with different compositions were observed depending on infiltration temperature and duration. The amount of Al decreased from the outer layer to the inner Ti–6Al–4V core. The diffusion of Ti in the liquid Al was slower as compared with diffusion of liquid Al to Ti. When subjecting the infiltrated samples to higher temperatures for a long time, it was observed that the layer-wise structure of titanium aluminides (surrounding Ti–6Al–4V particles) with various Al content were barely observable; i.e., post heat treatment of infiltrated samples, a chemical homogenization of different elements was achieved, and a vanadium-rich core was observed in the center of the original Ti–6Al–4V powder particles due to the poor solubility of V in Ti₆Al₄ phases. The infiltrated samples showed Young’s modulus of approximately 145 GPa, compressive strength of approximately 1.4 GPa, and bending strength of approximately 483 MPa. Combining 3DP technology with post-reactive melt infiltration resulted in the fabrication of dense and near-net-shaped complex structures. Therefore, the proposed approach, which combines binder jetting 3DP and reactive ex situ infiltration, can be considered as a possible additional processing route for the fabrication of complex structures from materials based on titanium aluminides.

4. Experimental Section

Starting Materials and Powder Preparation: For pressureless ex situ melt infiltration, a powder blend was prepared by mixing a spherical argon gas-atomized Ti–6Al–4V alloy powder of grade 23 quality with a particle size distribution of 45–105 μm (TLS Technik GmbH & Co. Spezialpulver, Bitterfeld, Germany) with Dextrin ((C₆H₁₀O₅)n, n = 10–20, molecular weight 1600–32 000 g mol⁻¹, Superior Gelbmittel F, Suedstaerke, Schrobenhausen, Germany) in 90:10 vol% ratio in deionized water, where dextrin acts as binder. Slurry was prepared with distilled water. The prepared slurry was ball milled in tumbling mixer (Turbula, Willy A. Bachofen AG, Switzerland) with Al₂O₃-milling balls for 24 h and then freeze-dried (Delta 2-24, Christ, Osterode/Harz, Germany). The freeze-dried mixture was additionally milled in a tumbler mixer for another 24 h to get a homogeneous powder-binder mixture. The mixed powder was then sieved through 160 μm mesh to get rid of bigger particles (>160 μm) and agglomerates as narrow particle size distribution and sphericity are essential parameters for 3DP.

Printing and Post Processing: The part geometry was designed using a conventional CAD-program (Solid Edge v.17/academic, PLM Solutions, Huntsville/AL, USA). 3DP was performed on a Z-printer 310 (Z-Corporation, Burlington/MA, USA) using a water-based printer solution of H₂O and glycerol with 70 ma.%:10 ma.% ratio. For pressureless ex situ melt infiltration, porous Ti–6Al–4V crucibles with dimensions of 49 × 30 × 4 mm³ were printed. During 3DP, layer thickness was 0.15 mm, shell and core saturation level were kept at 100%. Prior to dedusting, samples were kept in the powder bed for 24 h. The crucibles for ex situ melt infiltration were heat treated in a resistance-heated tube furnace (HTTRH 100300/18 by Hochtemperaturöfen GmbH, Neuhausen) in flowing argon as follows: 25–500 °C at 5 °C min⁻¹, 500–1500 °C at 5 °C min⁻¹. The crucibles were held at 500 °C and at 1600 °C for 1 and 4 h, respectively. The cooling rate down to room temperature was 5 °C min⁻¹.

The sintered crucibles were then infiltrated in the same furnace with Al (mass of Al was calculated based on the open porosity of the sintered crucibles) at 850 °C for 1 h in Ar. Small Al chips (high purity aluminum foil, 0.25 mm thick, Puratronic, Alfa Aesar, Germany) were used for ex situ reactive infiltration instead of Al powder, as the powder is more prone to oxidation. The amount of the Al chips was calculated based on the open porosity of the sintered crucibles.

The heating and cooling rates were 5 °C min⁻¹. To study the microstructural evolution, the crucibles were then cut to the bar-shaped samples with dimensions of 45 × 5 × 4 mm³ and heat treated in flowing Ar at 850, 1000, and 1150 °C for 1, 5, and 10 h, respectively. For all post-heat treatments, the aforementioned tube furnace was used. The heating and cooling rates were 5 °C min⁻¹.

Characterization: Microstructural analysis of powders and samples was carried out on a SEM equipped with dispersive energy analysis EDS, Quanta 200, FEI Ltd, Hillsboro, OR, USA. The samples for SEM analysis were mechanically polished to a 1 μm diamond finish prior to sputtering with gold. The samples were characterized using the X-Ray diffractometer (XRD, Kristalloflex D500, Siemens, Mannheim, Germany) for phase analysis. Open porosity was measured based on Archimedes principle, and density was calculated using the He-pycnometer.

Mechanical properties such as bending strength and compressive strength were measured using four-point bending of bars with dimensions of 45 × 4 × 3 mm³ and spans of 10 and 20 mm according to DIN EN 843-3, as well as compression of samples with dimensions of 8 × 4 × 4 mm³ according to DIN EN 843-2 on the universal testing machine (Instron 5565, Instron Corporation, Canton, USA). The tensile surfaces of the samples were polished to a 6 μm diamond finish prior to bending. Vickers’ hardness (Zwick 3212, Zwick, Ulm, Germany) test in accordance with DIN EN 843-4 was performed with a 98.1 N load applied for 15 s. Average values of bending strength, compressive strength, and hardness were calculated from at least six and twenty measurements, respectively. The effective Young’s modulus of samples was measured with an ultrasonic measuring device (USD10, Krautkrämer, Hürth, Germany) according to DIN EN 843-2.

Conflict of Interest

The authors declare no conflict of interest.

Keywords

metal-matrix-composites, titanium 6–4, titanium aluminides, 3D printing

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[1] G. Welsch, R. Boyer, E. Collings, Materials Properties Handbook: Titanium Alloys, ASM International, Cleveland, OH 1993.
[2] F. Appel, J. D. H. Paul, M. Oehring, Gamma Titanium Aluminide Alloys: Science and Technology, John Wiley & Sons, Weinheim, Germany 2011.
[3] P. Tan, Z. JL, C. Li, Mater. Trans. 2009, 50, 2484.
[4] K. Morsi, M. McShane, M. McLean, J. Mater. Sci. Lett. 1998, 17, 1621.
[5] K. Morsi, T. Fujii, H. McShane, M. McLean, Scr. Mater. 1999, 3, 359.
[6] E. Fu, R. Rawlings, H. McShane, J. Mater. Sci. 2001, 36, 5537.
[7] G.-X. Wang, M. Dahms, Powder Metall. Int. 1992, 24, 219.
[8] G.-X. Wang, M. Dahms, G. Leitner, S. Schultrich, J. Mater. Sci. 1994, 29, 1847.
[9] A. Lawley, JOM 1990, 42, 12.
[10] T. B. Massalski, Binary Alloy Phase Diagrams, Vol. 1, American Society for Metals, Metals Park, OH 1986.
[11] L. Loeber, S. Biamino, U. Ackelid, S. Sabbadini, P. Epicoco, P. Fino, J. Eckert, in Proc. of the Solid Freeform Fabrication Symp., Austin, TX, USA, 2011.
[12] L. E. Murr, S. M. Gaytan, A. Ceylan, E. Martinez, J. L. Martinez, D. H. Hernandez, B. I. Machado, D. A. Ramirez, F. Medina, S. Collins, Acta Mater. 2010, 58, 1887.
[13] I. Gibson, D. W. Rosen, B. Stucker, Additive Manufacturing Technologies: Rapid Prototyping to Direct Digital Manufacturing, Springer, New York 2010.
[14] H. Miyanaji, S. Zhang, A. Lassell, A. Zandinejad, L. Yang J. Miner. Met. Mater. Soc. 2016, 11, 1543e851.
[15] N. Travitzky, A. Bonet, B. Dermeik, T. Fey, I. Filbert-Demut, L. Schlier, T. Schlordt, P. Greil, Adv. Eng. Mater. 2014, 16, 729.
[16] T. W. Clyne, Encyclopaedia of Materials: Science and Technology 2001.
[17] P. Kumar, N. A. Travitzky, P. Beyer, K. H. Sandhage, R. Janssen, Scr. Mater. 2001, 44, 751.
[18] N. Travitzky, Adv. Appl. Ceram. 2012, 111, 286.
[19] N. A. Travitzky, Mater. Lett. 1998, 36, 114.
[20] P. Yadav, T. Bock, Z. Fu, H. Lorenz, I. Gotman, P. Greil, N. Travitzky, Adv. Eng. Mater. 2019, 21, 1900336.
[21] Y. W. Kim, JOM 1994, 46, 30.