# Engineering alloys for 3D printing

## A transformation path opens up novel alloy design

**The alloys used nowadays for metal-based additive manufacturing – colloquially termed 3D printing – are mostly based on compositions inherited from conventional production techniques. The strong anisotropy exhibited by alloys that solidify with cubic lattices (e.g. conventional compositions of Ni- or Ti-based alloys) represents a deep-rooted drawback during AM. The reason is that thermo-mechanical processing as implemented in traditional manufacturing for breaking up anisotropy, as well as controlling grain size and texture, is not considered in AM owing to the attractiveness of near net-shape fabrication. In this work, a phase transformation path opens up an alternative to avoid the typical coarse anisotropic microstructures obtained upon AM of titanium alloys and provides new windows for alloy design of other metallic systems.**

Metal-based additive manufacturing (AM) is resulting in a paradigm change across multiple industries such as the aerospace, biomedical and automotive sectors. One of its key strengths is the fabrication of near net-shape metallic components with complex geometries providing e.g. inner channels for cooling fluids, or bionic and load-optimised structures of minimal weight not achievable by conventional production methods like casting or machining. Layer-by-layer AM production from a 3D computer-aided design provides design freedom, increased product customization and shorter time to market. For Ti-based components, these advantages account for estimated production savings up to 50 %, by basically missing out exorbitant machining costs and material loss. In aerospace, AM is capable to reduce buy-to-fly ratios from 40:1 or 20:1 to 1:1 [1].

Nowadays, the strong anisotropy exhibited by alloys that solidify with fcc or bcc primary phases (e.g. conventional compositions of Ni- or Ti-based alloys) represents a critical issue for acceptance as well as certification of AM parts. This is a consequence of the steep, directional thermal gradient in the molten metal pool, which prevents nucleation ahead of the solidification front provoking epitaxial growth across solidified layers [2]. For instance, severe texture associated with anisotropic structural properties usually remains upon AM and even after post-processing. This effect is particularly relevant for powder-bed AM techniques such as selective laser melting (SLM, shown in Fig.1a), and well-known to occur in the popular Ti-6Al-4V alloy, which accounts for more than 50 % of the titanium market (Fig. 1b).

During AM of Ti-alloys, the strong texture of the bcc β-phase <100> oriented along the SLM building direction, is transmitted to the strengthening hcp α-phase by satisfying the Burgers orientation relationship (OR) {002}α || {110}β. Our approach aims at tackling anisotropy by exploring alternative paths of α formation altering the regular Burgers-related β → α transformation. The solute α-stabiliser lanthanum (La) is added to commercially pure titanium (CP Ti) to exploit metastability around liquid-solid and solid-solid states during

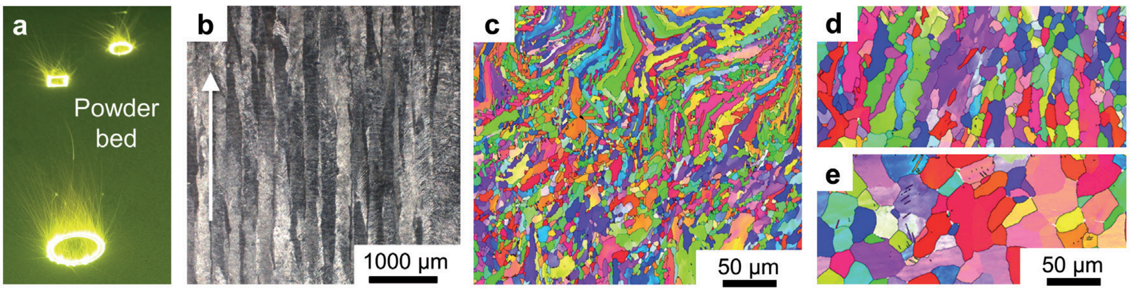


Figure 1

a) Selective laser melting (SLM) is a powder bed-based additive manufacturing process where alloys undergo series of sharp thermal cycles tracing fast heating (~$10^6$ – $10^7$ K/s) and cooling rates (~$10^3$ – $10^8$ K/s). b) Common microstructure obtained after SLM of Ti-6Al-4V showing epitaxially grown prior grains of β phase. c) SLM of Ti-2La leads to texture reductions along the SLM building direction pointed by the arrow in b), owing to the formation of small equiaxed grains of α phase with multiple orientations. Post thermal treatment of the SLM as-built condition in c) by cooling with d) 100 °C/min and e) 5 °C/min from 950 °C ($L_1$+β field) down to room temperature, results in the formation of new α grains of smaller size with increasing cooling rate and extensive globularization.

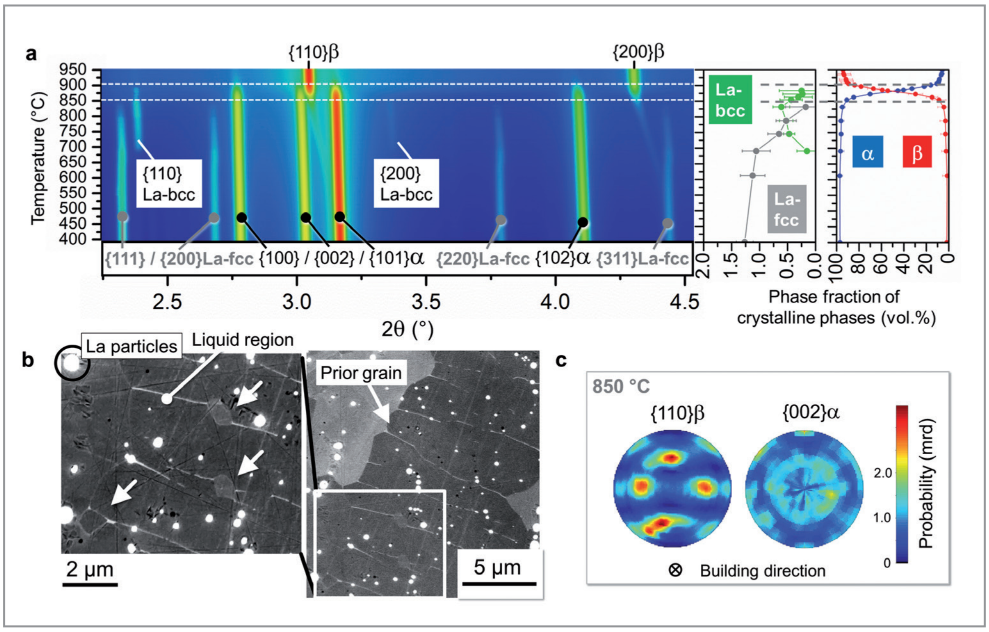


**Figure 2**

Phase transformation kinetics in the SLM Ti-2La alloy. a) Colour-coded 2D plot of the evolution of {hkl} reflections of α, β, La-bcc and La-fcc for a representative 2θ range of 2.25° – 4.55°, combined with the simultaneous evolution of volume fractions of phases during continuous cooling from 950 °C down to 400 °C with 20 °C/min. b) α particles (pointed by arrows) formed at prior β/$L_1$ interfaces in a microstructure quenched from 950 °C. c) Normalized pole figures of {110}β and {002}α at 850 °C indicating that the α phase does not fully inherit the texture of the parent β phase. The transformation β →α is reflected in the rapid increase in the volume fraction of α between 900 – 850 °C shown in a).

SLM. Besides tortuous grains, the microstructure obtained upon SLM of a Ti-2 wt.% La alloy ('Ti-2La') consists in extensive distributions of fine equiaxed α grains (Fig. 1c). These microstructural features are not characteristic of typical transformation mechanisms usually observed in CP Ti or α+β Ti-alloys, namely neither displacive nor diffusive nucleation and growth leading to parent β grains filled with α+β Widmanstätten structures [3].

Upon cooling of the Ti-2La SLM as-built state from 950 °C ($L_1$+β field) down to room temperature with 100 °C/min and 5 °C/min (i.e. thermal conditions closer to thermodynamic equilibrium than SLM, shown in Fig. 1d and 1e, respectively), formation of new α grains and extensive globularisation takes place resulting in recrystallised-like microstructures that do not inherit the usual SLM-induced texture of the parent β phase. Also, grain refinement of α grains is obtained with increasing cooling rate.

The phase transformation kinetics during post-thermal treatment of the SLM as-built state was investigated by *in situ* high energy synchrotron X-ray diffraction (HEXRD) at the P07-HEMS beamline of PETRA III. A rapid transformation β → α takes place between 900 °C and 850 °C (Fig. 2a). At the beginning of the transformation, $L_1$, β and α are present, while La reflections are absent. As was also directly confirmed by the raw diffraction images, this points to formation of α phase prior to the peritectic $L_1$+β →La-bcc reaction given by the Ti-La equilibrium phase diagram [4] starting after about 50 % completion of the diffusive β → α transformation (Fig. 2a). Metallographic analysis of the SLM Ti-2La alloy quenched from 950 °C ($L_1$+β) shows small α particles (pointed by arrows) at β/$L_1$interfaces (Fig. 2b). This, together with the results obtained from *in situ* HEXRD, suggests that nuclei of α form at β/$L_1$ interfaces via the peritectic path $L_1$+β → α, expanding during the subsequent β → α transformation.

The pole figures in Fig. 2c for {002}α and {110}β at 850 °C, i.e. at the end of the β → α transformation, clearly show that to a large extent α does not inherit the texture of β within this temperature range. Thus, the usual Burgers OR typical for a β → α transformation (and inheritance of texture by α) is partially avoided.

We have discovered a transformation path that offers significant texture reduction as well as equiaxed microstructures for a model Ti-2La alloy produced by SLM. This approach can be extended to Ti-alloys with α+β microstructures as proved for a Ti-1.4-Fe-1La alloy and represents a step-forward towards a next generation of titanium alloys for AM.

Moreover, the approach shown in our investigations to adapt alloys to AM using a peritectic reaction opens up windows for target oriented alloy design in other alloy systems.

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## Original publications

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