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To cite this article: Chunlei Qiu & Xu Chen (2024) Dislocation network mediated grain boundary engineering in an additively manufactured titanium alloy, Materials Research Letters, 12:11, 797-805, DOI: [10.1080/21663831.2024.2385969](https://doi.org/10.1080/21663831.2024.2385969)

To link to this article: <https://doi.org/10.1080/21663831.2024.2385969>



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# Dislocation network mediated grain boundary engineering in an additively manufactured titanium alloy

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## ABSTRACT

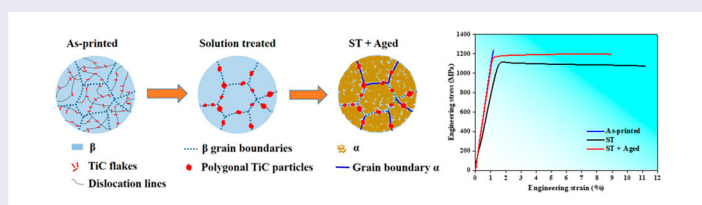
Continuous grain boundary  $\alpha$  (CGB- $\alpha$ ) usually causes degradation of mechanical properties in titanium alloys. Here, we propose to employ dislocation network in an additively manufactured titanium alloy for GB engineering to suppress CGB- $\alpha$ . A C-bearing titanium alloy was selectively laser melted to produce homogeneously distributed TiC flakes and a dislocation network that links them to GBs. Upon solution treatment, the dislocation network promotes dissolution of intragranular carbides and formation of discrete GB TiC particles. These GB carbides suppress the formation of CGB- $\alpha$  during ageing treatment, which together with the formation of high-density intragranular  $\alpha$  leads to excellent strength-ductility synergy.

## ARTICLE HISTORY

Received 23 May 2024

## KEYWORDS

Titanium alloys; selective laser melting; grain boundary engineering; microstructure; tensile properties



## 1. Introduction

Grain boundaries (GBs) are well known to play an important role in mechanical property development in polycrystalline metallic materials. At low temperatures, they act as a natural effective dislocation motion barrier or sink and constitute as an important strengthening mechanism. At high temperatures, they are rapid atomic diffusion paths that greatly affect high-temperature properties such as creep [1]. GBs are also the sites that are liable for elemental micro-segregation and accumulation during materials processing or heat treatment, which could be highly influential to the processability and precipitation behavior of a material. For example, the micro-segregation of B, Si and O at GBs during additive manufacturing of highly-alloyed nickel-based superalloys could lead to hot tearing [2–4]. In titanium alloys, accumulation of  $\alpha$ -forming elements such as O and Al at GBs can result in the formation of GB  $\alpha$  during heat treatment that could be detrimental to mechanical properties [5–8]. GB engineering is necessary for development of a

good combination of mechanical properties in a metallic material.

In titanium alloys, GB  $\alpha$  can exist in two morphologies, i.e. continuous and discontinuous. It is well established that continuous GB  $\alpha$  is particularly deleterious to fracture-related properties because its presence can cause strain accumulation and localization during deformation that could lead to lower crack initiation and propagation resistance and thus intergranular fracture [5–9]. Consequently, ductility and fatigue properties are usually compromised by the presence of continuous GB  $\alpha$  [5–7]. Meanwhile, the rejection of  $\beta$  stabilizers, which could be caused by the formation of GB  $\alpha$ , may result in the formation of precipitate-free zones (PFZs) [10,11]. The plasticity incompatibility due to the strength difference between the PFZs and precipitate zones (PZs) inside  $\beta$  grains could lead to the intercrystalline fracture as well [10,11]. In contrast, the presence of discontinuous GB  $\alpha$  could reduce the strain accumulation at the prior- $\beta$  grain boundaries during the

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Supplemental data for this article can be accessed online at <https://doi.org/10.1080/21663831.2024.2385969>.

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deformation process and inhibit the crack propagation along the GBs.

The formation and morphology of GB  $\alpha$  in Ti alloys are affected by a range of factors, such as cooling rate, annealing temperature, GB structure and  $\alpha$  variant selection during  $\beta \rightarrow \alpha$  transformation [12–18]. For instance, slow cooling from the  $\beta$  phase field, which allows for sufficient time for solute atomic diffusion to GBs, could easily lead to the formation of GB  $\alpha$  [11]. Continuous GB  $\alpha$  was found to preferentially nucleate and form at the high-angle grain boundaries (HAGBs) of the  $\beta$  phase [13–15]. Moreover, when GB  $\alpha$  follows the Burgers orientation relationship (BOR)  $(0001\alpha // 110\beta)$  and  $\langle 11\bar{2}0\rangle\alpha // \langle 1\bar{1}1\rangle\beta$  with both adjacent  $\beta$  grains, which constitutes the lowest interfacial energy configuration, the formation of continuous GB  $\alpha$  is favored [16,17]. This criterion applies when the angular deviation of the two adjacent grains is below  $10^\circ$  [17]. The GB  $\alpha$  habit plane (HP) inclination relative to the grain boundary plane (GBP) could also influence the GB  $\alpha$  morphology [16,18]. When the inclination angle is small ( $\sim 0^\circ$ ), *i.e.* their HPs are nearly parallel to the GBP, continuous GB  $\alpha$  forms due to the decrease of the strain energy and interfacial energy [16,18]. To promote formation of discontinuous GB  $\alpha$  in titanium alloys, it requires either special design of heat treatment or stringent control on heat treatment parameters [12,19]. Selective laser melting (SLM), as a powder-bed additive manufacturing (AM) technology, shows extremely rapid cooling after melting ( $10^4$ – $10^6$  °C/s) which can fully suppress the formation of GB  $\alpha$  in titanium alloys [20–22]. Nonetheless, this also usually leads to the formation of non-equilibrium microstructure in the alloys, for example, acicular  $\alpha'$  martensite in SLM-processed Ti-64. The necessary use of post-process heat treatment to achieve equilibrium microstructure for balanced mechanical properties inevitably leads to the formation of GB  $\alpha$ , very often in a continuous form [6,19,23–25]. Moreover, this usually leads to coarsening of intragranular  $\alpha$  or  $\alpha'$  that causes significant reduction in strength [22,23,26–28]. Qu *et al.* [29] performed HIP plus high temperature–short time heat treatment on as-printed Ti-64 which not only significantly reduces porosity and obtains ultrafine martensitic structure but also fully suppresses the formation of GB  $\alpha$ , leading to greatly improved fatigue properties. However, the elongation is still low due to the presence of ultrafine  $\alpha'$ . In general, up to date, the focus has been on AM process and heat treatment optimization for titanium alloys, but continuous GB  $\alpha$  is still difficult to be fully suppressed or eliminated simply through process control in many cases [7,23–26]. Moreover, a stringent control over manufacturing processes and heat treatments leaves highly limited room and freedom for tailoring other

microstructural features such as intragranular  $\alpha$  precipitates. Thus, in this study, instead of simply resorting to process optimization, we propose to introduce discrete particles such as carbides to the GBs in titanium alloys to produce discontinuous GB  $\alpha$  or  $\alpha$ -free GBs by taking advantage of the well-developed dislocation network formed within SLM-processed titanium alloys. Specifically, a C-containing titanium alloy (Ti-6Mo-5.5Cr-1Co-0.1C, wt%) is SLM-processed to produce homogeneously distributed TiC flakes and a complex dislocation network that links TiC flakes to the GBs. Upon solution treatment, the dislocation network acts as rapid diffusion pipes to promote dissolution of TiC flakes and allow C to diffuse to the GBs to form TiC particles decorating the GBs. The pre-existing GB TiC particles effectively suppress the formation of continuous GB  $\alpha$  during the subsequent ageing treatment. Our results show that an ultrahigh yield strength and a good uniform elongation have been achieved in the titanium alloy through this approach.

## 2. Materials and methods

The material used in the present study is Ti-6Mo-5.5Cr-1Co-0.1C (wt%). The material was synthesized by mixing argon atomized pure Ti, Cr and Co powder particles (15–53  $\mu\text{m}$ ) with pure Mo and  $\text{Cr}_3\text{C}_2$  powder particles which have an average diameter of 1  $\mu\text{m}$  and 2.5  $\mu\text{m}$ , respectively, followed by selective laser melting. The mixing was conducted with a shaft rotation speed of 600 rpm for 30 minutes in an argon atmosphere by using a horizontal cylindrical ball mill [30]. A ball-to-powder weight ratio of 4:1 and balls with a diameter of 5 mm were used for the powder mixing. The mixed powder was then processed under a modulated pulsed laser mode using a Renishaw AM400 system equipped with a ytterbium fiber laser. Samples with dimensions of  $60 \times 10 \times 12 \text{ mm}^3$  were fabricated in an argon atmosphere for microstructural characterization and tensile testing. A Meander scanning strategy was used for hatch scanning on each layer. After each layer, the scanning direction was rotated by  $67^\circ$ . The samples were fabricated at 400 W with a laser exposure duration of 80  $\mu\text{s}$ . A powder layer thickness of 30  $\mu\text{m}$ , a point distance of 60  $\mu\text{m}$  and a hatch distance of 60  $\mu\text{m}$  were used in the current study. The moving speed of laser exposure from one point to another adjacent point was set to be 5000 mm/s for all the sample fabrication. Some of the as-fabricated samples were sealed in argon-filled glass tubes and subjected to solution treatment (ST) at 850°C (above the  $\beta$  transus) for 40 minutes, followed by water quenching (WQ). Some of the samples were further aged at 600°C for 3 h followed by air cooling.

The as-printed and SLM + heat-treated samples were then longitudinally sectioned by electrical discharge machining (EDM) and ground using SiC papers from 200 grit up to 4000 grit before being polished using 3  $\mu\text{m}$  diamond suspension and then colloidal silica suspension (or OPS solution). The samples were then etched in a solution containing 50 mL distilled water, 25 mL  $\text{HNO}_3$  and 5 mL HF for microstructural characterization using scanning electron microscopy (SEM). A Zeiss SUPRA55 SEM microscope was used for the microstructural characterization. Transmission electron microscopy (TEM) study was also performed on some of the as-printed samples. Disc specimens with 3 mm in diameter were machined out of the samples and ground into a thickness of 60–90  $\mu\text{m}$  using 800–1200 grit silicon carbide papers and then electro-polished to perforation using a twin-jet electropolisher (RL-1). A polishing solution containing 5% perchloric acid and 95% ethanol was used to electro-polish the samples. The TEM experiments were carried out at an accelerating voltage of 200 KV using a FEI TecnaiF20 FEG TEM microscope.

Tensile test was performed on the as-printed and SLM + heat-treated samples. Tensile specimens with a gauge length of 23 mm and a reduced section diameter of 4 mm were machined out of the horizontally built samples. The tests were conducted in air at a nominal strain rate of  $5 \times 10^{-4}/\text{s}$  using a Zwick/Roell Z100 universal material testing machine. After the tensile test, the fracture surfaces of the specimens were examined using SEM and their deformation structures investigated using TEM.

### 3. Results and discussion

Figure 1 shows the microstructure of the as-printed Ti-6Mo-5.5Cr-1Co-0.1C alloy. It is clear that the matrix is decorated by homogeneously distributed disc-like precipitates which show an average thickness of around  $24 \pm 7$  nm and an average diameter of  $207 \pm 76$  nm with the majority of them being below 250 nm in diameter. Point EDS analysis on one of the precipitates shows that these precipitates are enriched in Ti and C; see Supplementary Figure 1. According to the high-resolution TEM (HRTEM) micrograph of one of these precipitates and its Fast Fourier Transformation (FFT) pattern (Figure 1(f)), the precipitates are identified to be face-centred cubic (FCC) TiC flakes. Each of them was found to be surrounded by a cluster of dislocations; see Figure 1(c–e). This could be due to the high stress/strain accumulation at the  $\beta/\text{TiC}$  interfaces incurred by the high lattice mismatch between the two phases during rapid cooling upon SLM. To be noted, these precipitates are interconnected with each other by dislocations and are

linked to GBs via dislocations, too, leading to the formation of a highly complex dislocation network; see Figure 1(d–e). It is well known that SLM, due to its steep thermal gradients within small melt pools and rapid cooling rates [31,32], can develop high residual stresses and a high density of dislocations in the matrix. Upon ST, the intragranular TiC flakes together with the complicated dislocation network all disappear and instead near-spherical or elongated elliptical particles form at GBs; see Figure 1(g–i). These GB particles were found to be enriched in Ti and C according to the TEM-EDS mapping analysis shown in Supplementary Figure 2 and are identified to be TiC particles based on the analysis of the diffraction pattern from one of these particles as shown in Figure 1(i). These particles are highly homogeneously distributed along the GBs and the grain interior is almost free of precipitates. This is in sharp contrast with previous studies on conventionally manufactured C-containing titanium alloys where TiC precipitates are usually homogeneously distributed within the  $\beta$  matrix upon heat treatment [33,34]. The difference could be due to the sophisticated dislocation network present in the current SLM-processed material which should have promoted dissolution of TiC flakes in the  $\beta$  matrix during ST. It is well established that dislocations can significantly reduce the diffusion activation energy and enhance diffusivity of interstitial atoms [35–37], which probably makes them become rapid atomic diffusion pipes and expedites the diffusion of C from the TiC flakes leading to dissolution of the TiC flakes. Meanwhile, GBs can act as traps for interstitial atoms such as C and retard its diffusion [35], which causes accumulation of C at the GBs and promotes the formation of GB TiC particles. Dark-field TEM micrograph reveals the formation of a high density of athermal  $\omega$  particles in the grain interior after ST and WQ; see Supplementary Figure 3.

Further ageing treatment leads to a burst formation of  $\alpha$  precipitates in the material which mainly exist as short laths with a length of  $\sim 330$  nm and a width of  $\sim 140$  nm; see Figure 1(j–l). While  $\alpha$  also form along the GBs, they are interrupted and separated by GB TiC particles (Figure 1(j–k)), leading to suppression of formation of continuous GB  $\alpha$ . This could be beneficial to mechanical properties given that continuous GB  $\alpha$  network is usually harmful for mechanical properties [5–9]. That the GB  $\alpha$  is interrupted by the presence of GB TiC particles is further verified by the TEM examination results as shown in Figure 2(a). Moreover, it is noted that the GB  $\alpha$  is extremely thin with a thickness of merely 37 nm. There are even a certain number of GBs which are completely free of  $\alpha$  phase (Figure 2(a)). It seems that the presence of TiC tends to suppress the formation of  $\alpha$  or at least interrupt their growth. According to previous study [38],

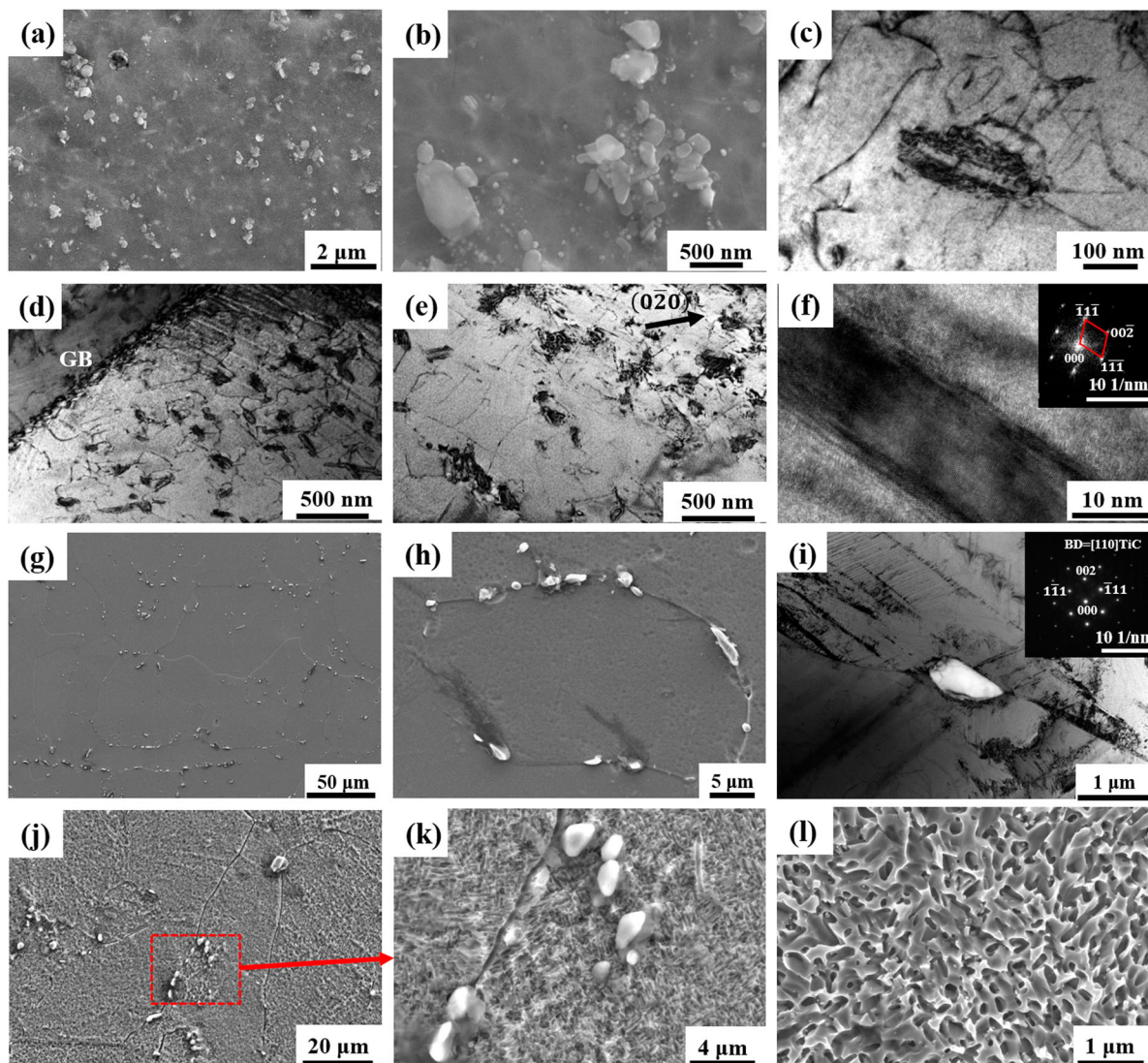


**Figure 1.** (a,b) SEM micrographs and (c–f) TEM micrographs showing the microstructure in the as-printed Ti-6Mo-5.5Cr-1Co-0.1C alloy; (g,h) SEM micrographs and (i) TEM micrograph showing the microstructure in the SLM-processed and solution-treated sample; (j–l) SEM micrographs showing the microstructure in the SLM + ST + Aged sample.

TiC acts as an effective O (which is a strong  $\alpha$  stabilizing element) absorber. As such, the presence of TiC at the GBs would help reduce O content there and suppress the formation and growth of GB  $\alpha$ . Figure 2(c,d) show the distribution of  $\alpha$  laths in the solution-treated and aged sample. It is clear that these precipitates are homogeneously distributed in the  $\beta$  matrix.

Figure 3 shows the tensile engineering stress–strain curves, true stress–strain curves and strain hardening rate–true strain curves. The as-printed Ti-6Mo-5.5Cr-1Co-0.1C sample shows a high ultimate tensile strength (UTS,  $\sim 1236$  MPa) but no yield strength (YS) or elongation (EL), indicating that it is highly brittle, probably due to the overwhelming presence of TiC flakes throughout the matrix that have embrittled the material. The TiC flakes may have made dislocation motion extremely

difficult during deformation due to their morphology and brittle nature. ST significantly enhances the YS ( $\sim 1100$  MPa) and EL ( $\sim 10\%$ ), which could be due to the removal of intragranular TiC flakes which allows dislocations to move freely in the matrix during deformation. The high density of ultrafine athermal  $\omega$  particles (Supplementary Figure 1) would have made a significant contribution to the ultrahigh YS of the SLM + ST sample. Ageing treatment further elevates YS ( $\sim 1170$  MPa) and UTS (1199 MPa) but leads to a small decrease in EL ( $\sim 8\%$ ); see Figure 3(a). Nonetheless, the uniform EL increases significantly from less than 2% in the ST state to around 8% after ageing treatment; see Figure 3(b). The SLM + ST sample shows strain hardening rates as high as 800–1000 MPa between 2.5% and 10% true strains. Ageing increases remarkably the strain hardening rates to

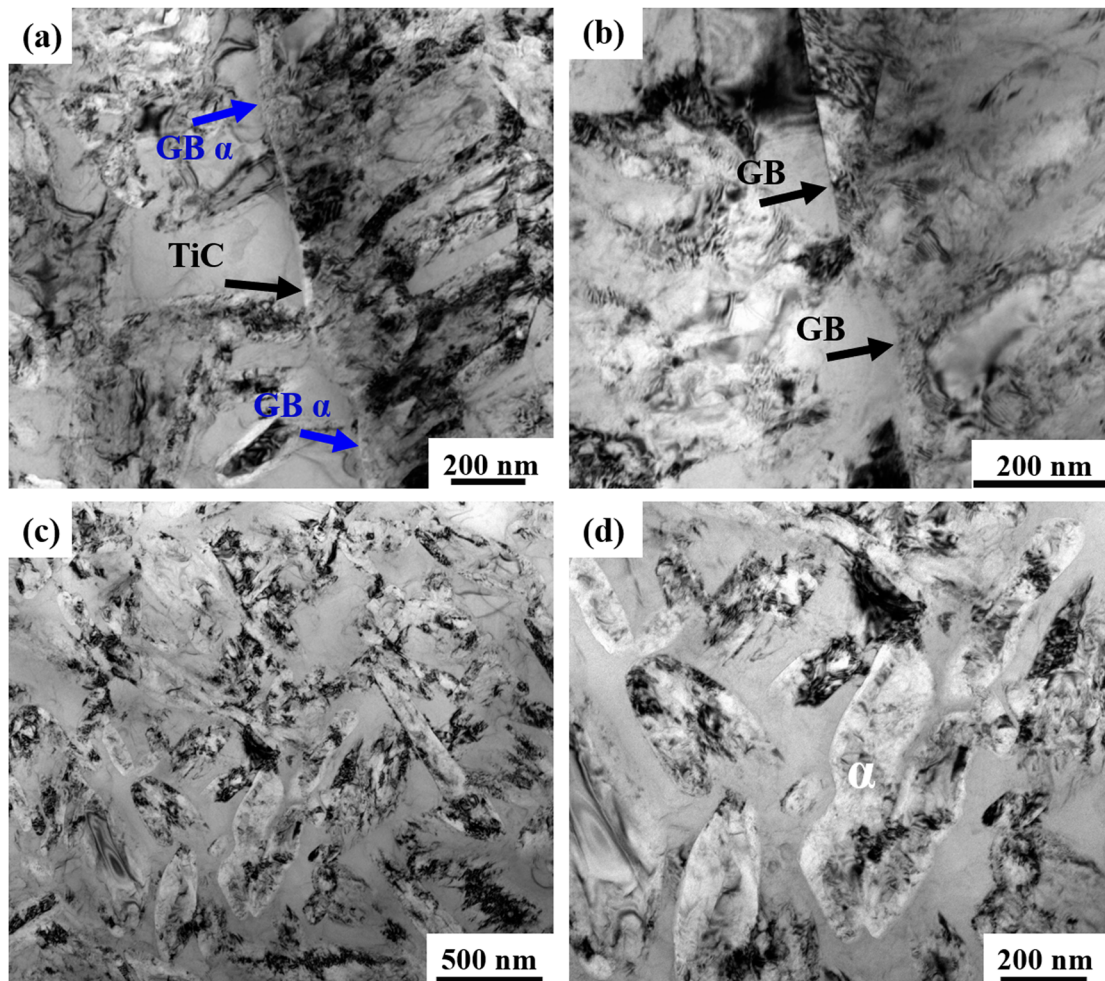


**Figure 2.** TEM micrographs showing the microstructure in ST and aged Ti-6Mo-5.5Cr-1Co-0.1C, (a) thin and discontinuous grain boundary  $\alpha$  phase (marked by blue arrow) disrupted by TiC particles (marked by black arrow); (b)  $\beta$  grain boundary depleted in  $\alpha$  phase; (c, d) Bright-field TEM micrographs showing the intragranular  $\beta$  matrix and  $\alpha$  precipitates.

1.5 ~ 2.5 GPa. Since the main microstructural difference between the ST sample and the ST and aged sample lies in whether there are  $\alpha$  precipitates or not, the mechanical property results suggest that the  $\alpha$  precipitates have played an essential role in elevating strain hardening rates and uniform EL. Similarly, the samples containing  $\alpha$  precipitates (as-printed and ST + aged samples) both show higher elastic modulus than the sample free of  $\alpha$  phase (ST), indicating that  $\alpha$  precipitates are crucial for enhancement of elastic modulus. With the presence of  $\alpha$  precipitates, the titanium alloy may be harder and stiffer leading to higher elastic modulus.

To better understand the origin for the mechanical property development in these samples, the fracture surfaces of the tensile tested specimens have been investigated by SEM. It is shown that the fracture surface of the as-printed sample contains a number of cleavage facets (Figure 4(a)), indicating that the sample has failed in a highly brittle way, which accounts for its poor ductility.

Both the SLM + ST sample and SLM + ST + Aged sample show highly dimpled fracture surfaces (Figure 4(b,c)), indicating that the two types of samples are highly ductile. SEM examination on the longitudinal section of the SLM + ST + Aged and tensile-tested sample reveals that the sample has experienced a mixed fracture mode (transgranular + intergranular fracture modes), as evidenced by the propagation path of a secondary crack which has crossed through both the interior of a grain and a GB; see Figure 4(d). Moreover, it is noted that when a crack propagates along a GB, its propagation path can be deviated by the presence of TiC particles and its tip can become blunted when encountering TiC particles; see Figure 4(d-f). In this sense, GB TiC particles are effective in impeding crack propagation and thus should be beneficial to the ductility and fracture toughness of the material. This is in sharp contrast against the continuous crack propagation in the titanium alloys containing continuous GB  $\alpha$  which normally

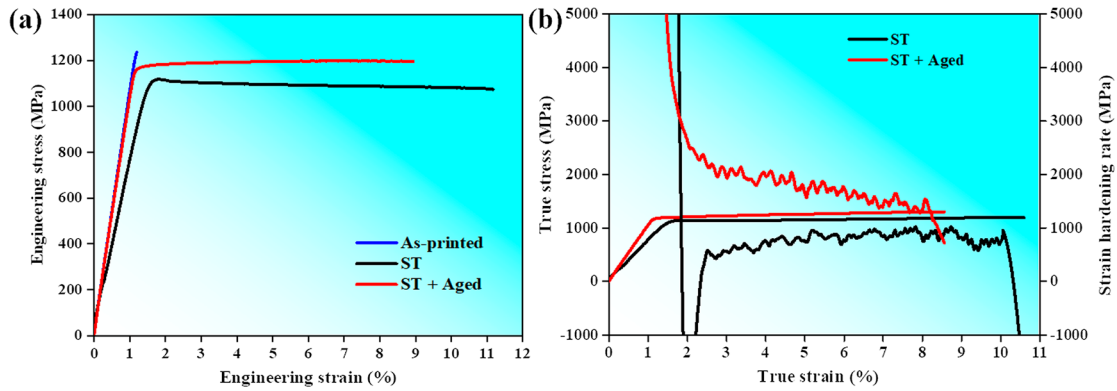


**Figure 3.** (a) Tensile engineering stress-strain curves and (b) true stress-strain curves and strain hardening rate-true strain curves of the ST and aged Ti-6Mo-5.5Cr-1Co-0.1C samples.

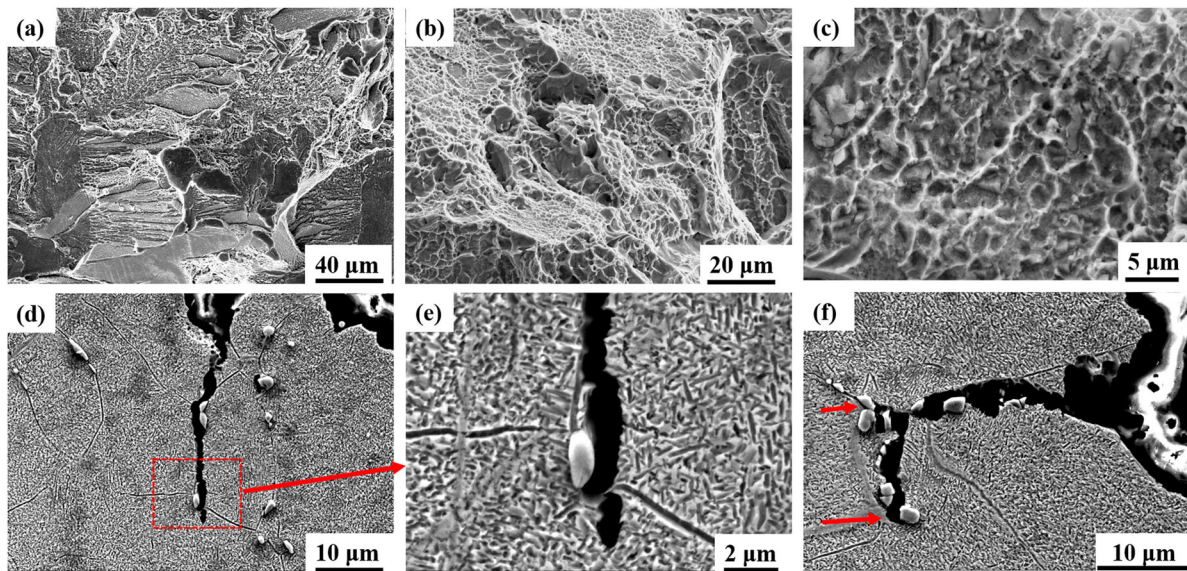


**Figure 4.** SEM micrographs showing the tensile fracture surfaces of (a) SLM-processed, (b) SLM + Solution-treated and (c) SLM + ST + Aged Ti-6Mo-5.5Cr-1Co-0.1C samples, respectively; (d-f) the secondary crack propagation paths of a ST and aged sample.

demonstrate straight cracking path along the GBs and show sharp crack tips during fracture [8,24]. In addition, discontinuous GB  $\alpha$  and  $\alpha$ -free GB does not lead to the formation of the mechanically constrained plastic zone, which avoiding the premature formation of cracks [6,7,25,29].

Figure 5 shows the deformed substructures in the SLM-processed and ST Ti-6Mo-5.5Cr-1Co-0.1C sample and the SLM + ST + aged sample after tensile test. It is clear that dislocation slip has dominated in the SLM-processed and ST sample, which accounts for the significant improvement in YS and EL after ST. In the deformed ST and aged sample, a high density of dislocations accumulates around the  $\alpha$  precipitates (Figure 5(a,b)) and meanwhile a number of dislocations are observed to be present within the  $\alpha$  laths, indicating that dislocations have slipped through both  $\beta$  matrix and  $\alpha$  precipitates. Obviously, dislocation slip has become

the dominant deformation mechanism in these samples. As compared with the simply ST sample which is free of  $\alpha$  precipitates, the ST + aged sample shows higher UTS, strain hardening rates and uniform elongation. This could be mainly attributed to the presence of  $\alpha$  precipitates. On one hand, these precipitates can effectively impede dislocation motion, as evidenced by the accumulation of high-density dislocations at the  $\alpha/\beta$  interfaces, leading to enhanced strain hardening rates, UTS and uniform EL. On the other hand, the  $\alpha$  precipitates can be sheared through by dislocations, which allows plastic deformation to proceed without too early failure. This together with the discontinuous GB  $\alpha$  guarantees acquisition of decent total EL. The current finding is not inconsistent with previous studies on many high-strength titanium alloys where ultrafine  $\alpha$  precipitates were all reported to cause significant strengthening to the materials [39–42].

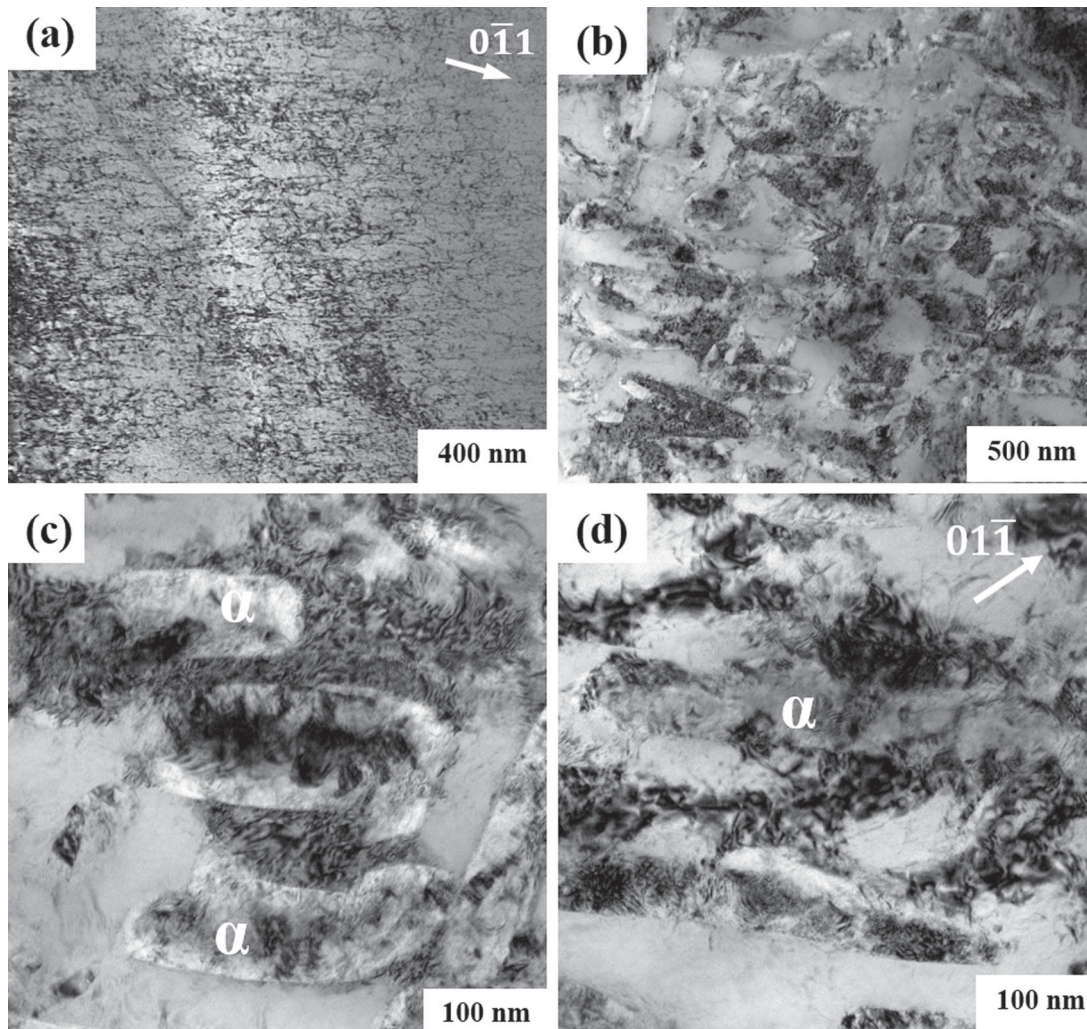


**Figure 5.** TEM micrographs showing the deformed substructures in (a) the SLM-processed and solution-treated sample and (b–d) the SLM + ST + Aged sample after tensile test.

In general, the present study has demonstrated a dislocation network mediated grain boundary engineering approach in an additively manufactured titanium alloy. The approach successfully suppresses the formation of continuous GB  $\alpha$  in the titanium alloy and leads to combination of an ultrahigh yield strength and a good uniform elongation. The approach can be translated to other additively manufactured titanium alloys which contain precipitate-forming elements or are doped with additive particles. The findings also pave the way for microstructural control in additively manufactured materials by taking advantage of the complicated dislocation network.

### Disclosure statement

No potential conflict of interest was reported by the author(s).

### Funding

This work was supported by the Aeronautical Science Foundation of China [grant number 20220042051001], the Science

Centre for Gas Turbine Project [grant numbers P2023-B-IV-001-001, P2022-DB-IV-001-001] and the National Key Research and Development Program from the Ministry of Science and Technology of the People's Republic of China [grant number 2018YFB0703400].

### Data availability

The data that supports the findings of this study are available from the corresponding author upon request.

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