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Design of Heterogeneous Structured Al Alloys with Wide Processing Window for Laser-Powder Bed Fusion Additive Manufacturing

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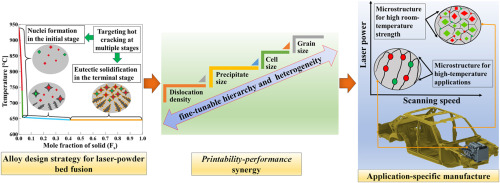
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# Abstract

Required microstructural attributes of an alloy vary with structural applications. The microstructural fine-tuning capability of laser-powder bed fusion (L-PBF) additive manufacturing (AM) enables application specific manufacture of the components. Such manufacture with L-PBF AM requires alloys that exhibit wide processing window and are amenable to multiple deformation mechanisms. However, high hot cracking susceptibility of Al alloys poses a barrier to such printability-performance synergy. In this work we show that an integration of, a) *grain refinement through heterogeneous nucleation,* and b) *eutectic solidification*, leads to crack-free parts at wide range of process parameters, microstructural heterogeneity, and hierarchy in the Al-Ni-Ti-Zr alloy. Such an integration targets hot cracking at multiple stages of solidification in L-PBF as opposed to the contemporary alloy design strategies that target hot-cracking at only specific stages of solidification. The Al-Ni-Ti-Zr alloy exhibits excellent printability and a high as-built tensile performance. Due to the wide processing window and amenability to multiple deformation mechanisms, the alloy microstructure and subsequently the performance, can be fine-tuned. Such strategy opens the gateway for application-specific manufacture of Al alloys with L-PBF AM and establishes a fundamental shift in current methodologies for design of these alloys for L-PBF AM.

# Graphical Abstract



# Keywords

Al alloys, Heterogeneous microstructure, Laser-powder bed fusion additive manufacturing, Alloy design, Solidification

# 1. Introduction

Historically, the manufacture of structural metallic components has involved long supply chain networks. Which manufacturing process would be a part of the supply chain is decided by the desirable microstructural attributes and mechanical properties, alongside the geometrical complexity of the final component. Consider the example of a car where an engine cylinder head that is geometrically complex and requires high creep resistance, is manufactured by casting, whereas the vehicle frame, that requires high strength, is usually manufactured by forming processes. Naturally, the microstructural requirements for both the components are different. Laser-powder bed fusion (L-PBF) additive manufacturing (AM) promises to disrupt the current supply chain network with its unprecedented capabilities of microstructural fine tuning and producing geometrically complex parts. In L-PBF, the alteration of process parameters, such as, laser power and laser scanning speed, allows control of solidification parameters, namely thermal gradient (G) and growth rate (R). G and R, in turn, have decisive influence on the scale and morphology of the microstructure. The process parameters-based control of microstructure in L-PBF thus allows application specific, on-demand manufacture of the components and thereby promises to disrupt the long conventional supply chain networks. Further, at a given set of process parameters, the G and R vary across a small melt pool volume [1], [2]. Therefore, the microstructure of an L-PBF processed alloy may consist of domains of fine and coarse grains (heterogeneous grain structure (HGS)) [3], [4], [5], [6], [7], [8]. Also, if the alloy composition allows, then different phases, and hierarchical features that span across multiple length scales, e.g., solute atoms, precipitates, dislocations, cell walls and cells, grain boundaries and domain boundaries of fine and coarse grains, may exist within the as-built microstructure. Such microstructural hierarchy and heterogeneity are crucial for activating multiple deformation mechanisms, achieving high strength-ductility combination, and thus, the alloy performance [2], [9], [10], [11], [12], [13]. Despite these advantages, currently the potential of L-PBF in processing Al alloys is not exploited to the fullest due to their high hot cracking susceptibility (HCS) and thus, poor printability. Their high HCS is further aggravated at L-PBF process parameters that promote columnar growth and so, the current Al alloys may only be processed at a limited set of parameters. Note that the columnar growth leads to an aggravated HCS because of the poor strain accommodation capability of columnar grains and their low liquid permeability [2], [14], [15]. Essentially, high HCS of Al alloys narrows their processing window and hampers their application specific manufacture with L-PBF. Therefore, there is a need for alloy design strategies for L-PBF that can produce Al alloys with a) wide processing window ***and*** b) microstructural hierarchy and heterogeneity and thus, improved performance. The microstructural hierarchy and heterogeneity makes the alloy amenable to multiple deformation mechanisms [2], whereas a wide processing window allows fine tuning of these microstructural features and thus, the alloy performance. Such a synergy of wide processing window and amenability to multiple deformation mechanisms is referred to as ***printability-performance synergy*** in this work.

Interestingly, non**-**equilibrium cooling rates, and large variation in G and R across the melt**-**pool [16], which result in varying degrees of microstructural hierarchy and heterogeneity in L-PBF, may also result in hot cracking and thus poor printability in Al alloys [2]. To reduce the HCS of Al alloys, researchers have so far implemented either the strategy facilitating grain refinement (as seen in Zr**-** and Sc**-**containing Al alloys [6], [7], [17], [18]) or that facilitating eutectic**-**like solidification in the terminal stage (as seen in Si**-** and Ce**-**containing Al alloys [19], [20], [21], [22]). In alloys that use the grain**-**refinement strategy, a high probability of columnar growth still exists during L-PBF AM [23], [24]. The reasons for high predisposition to columnar growth during L-PBF of such alloys include inherently low efficiency of the process of heterogeneous nucleation, well-directed and high thermal gradients, and formation of remelting zones within the melt pool [2], [25]. For alloys that rely upon grain refinement strategy, such columnar growth, whenever it may occur, would suffer from high HCS in the terminal stage of solidification [2]. Further, only a specific set of L-PBF process parameters facilitate columnar to equiaxed transition (CET), while cracking-susceptible columnar growth may prevail at other parameters [26]. Therefore, using the grain refinement strategy does not lead to Al alloys with a crack-resistant microstructure and a wide processing window [27], thus hampering their application specific manufacture with L-PBF. However, one advantage of grain refinement strategy is that it may lead to HGS and thus, improved mechanical properties at certain process parameters where HCS is minimized [3], [24]. An example of Al alloy that uses grain-refinement strategy and manifests HGS, yet a narrow processing window with L-PBF is, Al-Mg-Sc-Zr alloy. Despite containing grain refiners in the form of Sc and Zr, the Al-Mg-Sc-Zr may exhibit coarse columnar grains along with fine equiaxed grains, and thus, may exhibit HGS as shown by Gu et al. [24]. However, at certain L-PBF process parameters, the presence of microcracks has been established within the Al-Mg-Sc-Zr alloy [27]; this indicates a narrow processing window of the alloy. Conversely, although using the eutectic solidification strategy leads to excellent printability through liquid feeding and minimal thermal strains in the terminal stage, only homogeneously fine or homogeneously coarse grain structure can be obtained (depending on the process parameters) [28]. In either case, strength**-**ductility trade-off impales the material; such behavior is common in Al-Si [19], [20], [21] and Al-Ce [29] alloys. It is therefore evident that the current strategies for designing Al alloys for L-PBF lead to a trade**-**off between alloy printability and performance [2]. This work proposes a strategy that integrates grain refinement and eutectic solidification for design of Al alloys for L-PBF. The resulting alloy may consequently exhibit a wide processing window and thus, excellent printability, alongside an HGS and hierarchical as**-**built microstructure. Fig. 1 summarizes how L-PBF can be used for application specific manufacture of such Al alloys.

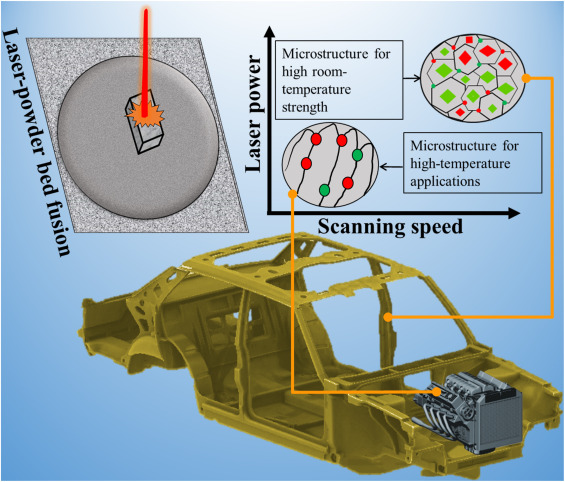


Fig. 1. Achieving application specific manufacture with L-PBF. An alloy that exhibits wide processing window with L-PBF and allows formation of heterogeneous and hierarchical features, can be used to manufacture different components with varying microstructural requirements. Illustration shows how the microstructural requirements for different components within a product may vary: engine components require thermally stable, coarse-grained microstructure, attainable at small laser power and slow scanning speed, whereas the vehicle frame requires fine-grained microstructure, for enhanced room-temperature strength, attainable at high laser power and fast scanning speed.

# 2. The alloy design strategy

Addition of elements that: **a)** can aid in heterogeneous nucleation of fine**-**equiaxed α**-**Al grains, *and* **b)** can form a terminal eutectic with Al, may assist in developing an Al alloy with synergistic printability and performance [2]. Grain refinement would occur within the melt pool only at those sites where primary grain refining phases are present and/or where favorable G to R ratios for CET exist. Note that the primary grain refining phases may “decorate” only specific sites in the as**-**built microstructure due to formation of the remelting zones [17], [18], [30]. Therefore, the formation of fine-equiaxed grains occurs only at specific microstructural sites. Now, due to high predisposition to columnar growth in L-PBF, remainder of the microstructural sites where grain refinement does not occur, would still solidify into coarser columnar grains with high HCS. However, invoking eutectic solidification at the terminal stage of solidification, may reduce the HCS of columnar grains. This is because a terminal eutectic would provide ample liquid for backfilling of cracks. Further, the alloy facilitating a terminal eutectic would solidify at a close-to-zero freezing range at the terminal stage thus, leading to minimal thermal strain and strain rate. Therefore, a crack-free microstructure containing precipitates, fine-equiaxed grains and coarse columnar grains would be obtained in as-built condition, i.e., a hierarchical and heterogeneous microstructure with excellent printability. Such microstructure is expected to exhibit high tensile strength and ductility.

Alloying additions of transition metals such as Ti and Zr in Al, form metastable, coherent L12 trialuminides that may act as sites for heterogeneous nucleation and aid in formation of fine-equiaxed grains [31], and thus, a crack-free microstructure. Furthermore, precipitation strengthening could also be achieved with these trialuminides [31]. Therefore, Ti and Zr alloying elements meet the alloy design requirement of design of an age-hardenable Al alloy. Alloying quantities of Ti and Zr are determined based on the design considerations pertaining to alloy freezing range, and solid solubility limits of Ti and Zr in Al under conditions of rapid solidification [42] (see Section S1, Supplementary information). Although such grain-refinement and precipitation strengthening effects can also be achieved with Sc-containing Al alloys, Sc is a scarce and very expensive element and hence adds to alloy costs. To facilitate eutectic solidification at the terminal stage, Ni has been added, which at ~6 wt%, forms an Al-Al3Ni eutectic. Considering the hot susceptibility index (HSI) [2], [6], [7], critical temperature range (CTR) [2], [7] (both calculated from Scheil-Gulliver solidification simulations (SGSS)) and enhanced solid solubility in rapid solidification, an Al-3Ni-1Ti-0.8Zr (wt%) composition, hereinafter referred to as Al-Ni-Ti-Zr alloy, was finalized and gas-atomized. Further details on alloy design considerations are provided in Section S1 of Supplementary information of this article.

# 3. Materials and methods

SLM 125HL equipped with a continuous wavelength Yb fiber laser was used to perform L-PBF of the gas-atomized alloy powder (average size ~45 µm). Fifteen combinations of laser power (*P)* and scanning-speed (*v*) were examined for parametric optimization (see Table 1). Hatch width, layer thickness and scanning strategy were kept constant at 0.13 mm, 0.03 mm, and stripes strategy with 67° interlayer-rotation, respectively. Substrate temperature was set at 100 °C and the spot size was ~70 µm. Further, relative densities of printed specimens were determined using ASTM B962 standard method for Archimedes’ principle-based relative density measurements. The *P-v* combination resulting in maximum relative density was used to print a rectangular block of dimensions 100 × 25 × 50 mm3. Subsequent microstructural and mechanical characterization was performed on specimens extracted from this block.

Table 1. L-PBF process parameters used for parametric optimization and their corresponding OM numbers.

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| ***P* (W)** | ***v* (mm/s)** | **OM number** | **hatch width (*W*, mm)** | **Layer thickness (*t*, mm)** | **Volumetric energy density (**PvWt**, J/mm3)** |
| **200** | 100 | 1 | 0.13 | 0.03 | 512.8 |
|  | 200 | 2 |  |  | 256.4 |
|  | 300 | 3 |  |  | 170.9 |
|  | 400 | 4 |  |  | 128.2 |
|  | 600 | 5 |  |  | 85.5 |
|  | 800 | 6 |  |  | 64.1 |
|  | 1000 | 7 |  |  | 51.3 |
| **350** | 400 | 8 |  |  | 224.4 |
|  | 600 | 9 |  |  | 149.6 |
|  | 800 | 10 |  |  | 112.2 |
|  | 1000 | 11 |  |  | 89.7 |
|  | 1200 | 12 |  |  | 74.8 |
|  | 1400 | 13 |  |  | 64.1 |
|  | 1600 | 14 |  |  | 56.1 |
|  | 1800 | 15 |  |  | 49.9 |

X-ray microscopy was performed using Zeiss X-radia Versa520 and the voxel size was set to ~1 µm. Dragonfly software was used for reconstruction of the X-ray microscope (XRM) dataset. Samples for electron microscopy were prepared by first, mechanically polishing to 1 µm surface finish and then, by electrochemical polishing using Struers LectroPol equipment. A mixture of ~33% nitric acid and ~67% methanol (vol%) stored at − 30 °C was used as an electrolyte and the voltage was set to 18 V. Electron backscatter diffraction (EBSD) map and backscattered electron (BSE) images were acquired using FEI NOVA scanning electron microscope (SEM) equipped with Hikari camera. Transmission electron microscope (TEM) specimen was extracted via focused ion beam milling performed using FEI Nova NanoLab 200™. TEM was performed using FEI Tecnai F20-FEG™. The TSL OIM™ and TEAM™ software were used for analysis of data obtained from EBSD and energy dispersive X-ray spectroscopy (EDS), respectively. Three mini tensile specimens, each from the as-built and aged conditions, with gage length 5 mm, width 1.25 mm and thickness 1 mm, were tested at room temperature and 10−3 s−1.

# 4. Results and discussion

Fig. 2(a) shows the temperature (T) vs mole fraction (Fs) of solid curve and the solidification path obtained from SGSS of Al-Ni-Ti-Zr alloy. Formation of Al3Ti and Al3Zr precipitates is suggested in the initial stages of solidification; these precipitates are believed to provide sites for heterogeneous nucleation of α-Al grains and result in fine-equiaxed grains. In the terminal stage of solidification, which is most susceptible to hot cracking [14], the solidification path predicted the formation of Al3Ni phase at ~640 °C, the temperature at which Al-Al3Ni eutectic also forms. The formation of eutectic phase starting from when mole fraction of solid (Fs) is just ~0.4 through the terminal stage of solidification, has two implications. First, it implies that ample liquid is available for crack-backfilling and second, a large portion of solidification (including terminal solidification) occurs at zero freezing-range thus producing minimal thermal strains. Furthermore, Ni has low solid solubility in Al, hence despite the high solidification rates in L-PBF, there is high probability that Ni will be rejected in the liquid in interdendritic regions. The fine-equiaxed grains and zero terminal freezing-range has following implications. As solidification proceeds, solidification shrinkage and thermal contraction induce tensile stress/strain on the mushy zone. The high HCS of terminal stage further aggravates when the mushy zone consists of columnar-dendritic grains [2], [32] and/or when the alloy spends longer time in the terminal stage of solidification where shrinkage strains have detrimental impact on the HCS due to reducing liquid availability [2], [33]. Note that the deformation in mushy zone happens by intergranular slide and thus, less number of grain boundaries in case of columnar-dendritic grains reduces the ductility of the mushy zone [14], [32]. On the contrary, presence of fine-equiaxed grains (facilitated by potent primary phases in this alloy) would make the mushy zone more ductile. Additionally, a zero CTR, which is the difference between temperatures corresponding to Fs values of 0.95 and 1, is facilitated by Al-Al3Ni eutectic in this alloy. A zero CTR would result in minimal thermal strains in the terminal stage of solidification and thus, inhibit hot cracking [2]. Fig. 2(b) shows T-(Fs)1/2 curve used for determining the HSI of Al-Ni-Ti-Zr alloy. HSI is defined as the slope of T-(Fs)1/2 curve near Fs = 1 [6], [7]. An HSI of less than 1 is suggested; such low HSI indicates occurrence of grain bridging to resist cracking [34]. Since grain refinement is expected to occur at only specific sites in the microstructure, remaining sites are expected to solidify into crack-free, coarse-columnar grains. Hence, the as-built Al-Ni-Ti-Zr alloy is expected to exhibit a wide processing window alongside microstructural hierarchy and HGS, i.e., a synergy between excellent *printability* and *performance*.

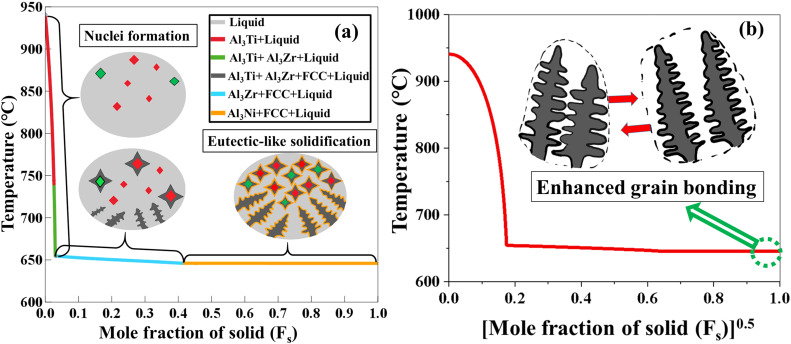


Fig. 2. Scheil-Gulliver solidification behavior of Al-Ni-Ti-Zr alloy. (a) T-Fs curves for the Al-Ni-Ti-Zr alloy. Illustrations depict the sequence of solidification events as predicted by the T-Fs curves. (b) T-(Fs)0.5 curves for the Al-Ni-Ti-Zr alloy. Illustration depicts that a low HSI facilitates enhanced grain bonding.

Fig. 3(a) shows optical micrographs (OMs), from longitudinal (XZ) and transverse (XY) planes, of specimens printed at different combinations of laser-power (*P*) and scanning-speed (*v*)*.* The numbers on OMs correspond to specific combinations of *P-v* as summarized in Table 1. The rather remarkable absence of cracks at all *P-v* combinations represents wide processing-window of the Al-Ni-Ti-Zr alloy, its excellent resistance to hot cracking and thus excellent printability. However, a large number of spherical pores at higher energy densities points towards the formation of keyhole pores [35]. Fig. 3(b) and (c) represent the relative Archimedes densities of Al-Ni-Ti-Zr alloy printed at different *P-v* combinations and suggest that for a given *P*, maximum consolidation occurred at higher values of *v*, i.e., at lower energy densities. Formation of a high mole fraction of low melting point Al-Al3Ni eutectic (Fig. 2(a)) is believed to prevent lack of fusion (LOF) defects at lower energy densities and hence to result in maximum part-consolidation at these energy densities. Thus, the alloy consumes less energy while printing, i.e., the L-PBF of Al-Ni-Ti-Zr alloy is more economical. Maximum relative density of ~99.8% is obtained at 350 W-1400 mm/s; therefore, the microstructural and mechanical characterization was performed on the specimen printed at this *P-v* combination. A magnified-reconstructed XRM image displays distribution of pores within the specimen printed at 350 W-1400 mm/s (Fig. 3(d)). Image analysis reveals a porosity vol% of ~0.1% at ~1 µm voxel size; few round-shaped defects yet no cracks are visible. Such low porosity content further establishes excellent printability of the Al-Ni-Ti-Zr alloy.

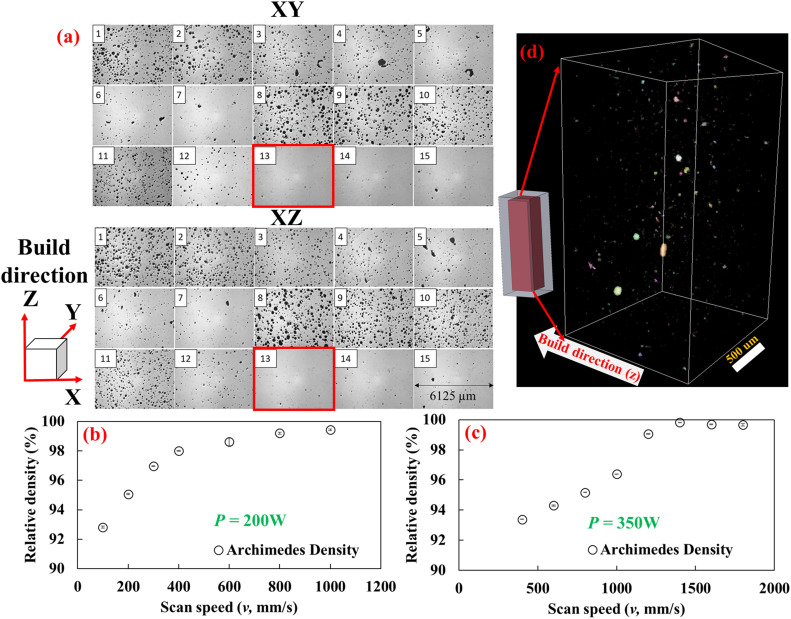


Fig. 3. Wide processing window of the Al-Ni-Ti-Zr alloy with L-PBF. (a) OMs from transverse (XY) and longitudinal section (XZ). The highlighted OM corresponds to the specimen used for further microstructural and mechanical characterization in this work. Relative densities vs v for specimens printed at (b) 200 W and (c) 350 W. Relative density of each specimen in (b) and (c) was measured three times. (d) Reconstructed 3D XRM image representing porosity distribution within as-built Al-Ni-Ti-Zr alloy specimen corresponding to OM number 13.

Fig. 4(a) represents a low magnification EBSD inverse pole figure (IPF) map from longitudinal plane of the as-built Al-Ni-Ti-Zr alloy. Image analysis revealed that ~65% of the as-built microstructure solidified into fine-grained (F.G.) regions comprising equiaxed grains of size ~0.4–5 µm. The remainder solidified into cellular dendritic coarse-grained (C.G.) regions of grain length and width ~5–40 µm and ~1–15 µm, respectively. BSE micrographs in Fig. 4(b–d) show the equiaxed F.G. and dendritic C.G. regions. Generally, coarse cellular dendritic grains are highly susceptible to hot cracking during L-PBF [2]. However, in the Al-Ni-Ti-Zr alloy, crack-free coarse dendritic grains form an integral part of the HGS and represent the crack resistance of the alloy. Careful observation of Fig. 4(d) reveals precipitates in the F.G. region as indicated by the white dashed curve. Altogether, Fig. 4(a–d) establish an overall HGS and hierarchical microstructure of the Al-Ni-Ti-Zr alloy in as-built condition. A high-angle annular dark-field scanning-transmission electron microscope (HAADF-STEM) image from a region near melt-pool boundary, confirms cuboidal precipitates of edge length ~100 nm, in the middle of the grains (Fig. 5(a)). EDS maps obtained from TEM (Fig. 5(b–d)) suggest that these are Ti- and Zr-containing precipitates surrounded by α-Al grains. Altogether, Fig. 5(a–d) indicate that heterogeneous nucleation of α-Al grains occurred on these precipitates. Considering the solidification path shown in Fig. 2(a) and the high potency of primary Al3(Ti,Zr), these Ti- and Zr-containing precipitates are believed to be primary Al3(Ti,Zr). Smaller nano-scaled Ti-rich precipitates are also seen in Fig. 5(c). These smaller precipitates, combined with the larger nucleant precipitates, contribute to the microstructural hierarchy of the as-built Al-Ni-Ti-Zr alloy. While wide processing window of the alloy enables printing at high *P* and *v* (small *G* to *R* ratio) where equiaxed growth is favored, primary Al3(Ti,Zr) (Fig. 2(a)) provide heterogeneous nucleation sites and further facilitate CET, thus generating a high area fraction of fine equiaxed grains in the as-built microstructure. On the other hand, the absence of primary Al3(Ti,Zr) precipitates from specific locations within a melt pool, contributes to formation of coarse columnar grains at those locations. Notably, the formation of potent nucleants in an early stage of solidification, as suggested by the SGSS (Fig. 2(a)), is important from the perspective of design of alloys with a higher area fraction of equiaxed grains in that the nucleants will simply witness more liquid. Further, in LPBF-AM, due to well defined direction of maximum thermal gradient, columnar grains outgrow their equiaxed counterparts in a growth competition [2]. However, formation of potent nucleants in the early stages facilitates formation of equiaxed grains before the effects of thermal gradients could take over to produce a columnar grains-dominant microstructure [2].

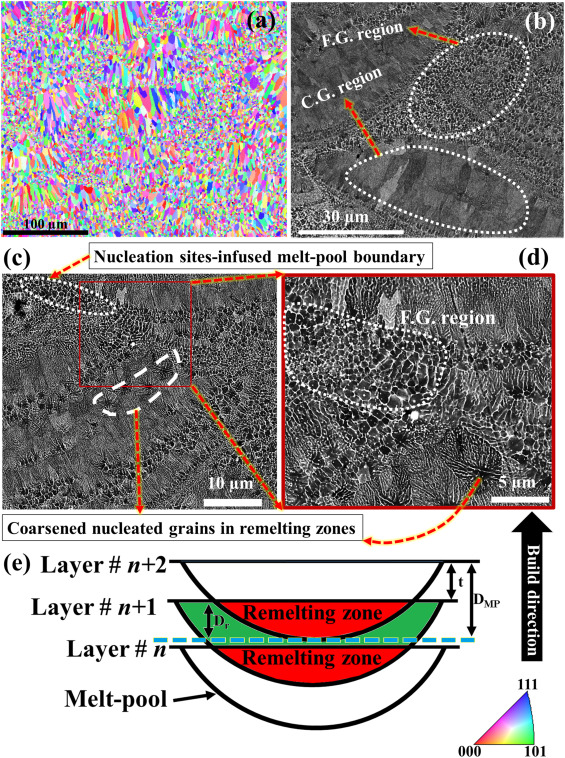


Fig. 4. Microstructural heterogeneity and hierarchy in as built Al-Ni-Ti-Zr alloy. (a) EBSD IPF map for as-built Al-Ni-Ti-Zr alloy (see bottom right corner for color key). (b–d) BSE micrographs representing various features in as-built Al-Ni-Ti-Zr alloy. (e) A schematic of remelting zones within a melt-pool. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

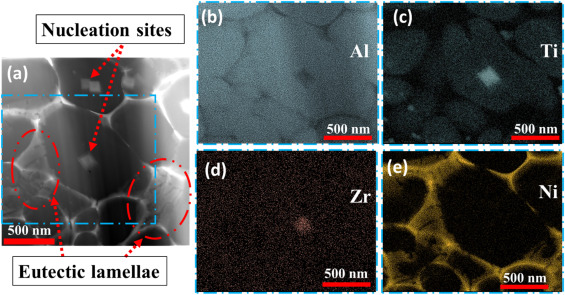


Fig. 5. HAADF-STEM image and EDS maps for as-built Al-Ni-Ti-Zr alloy depicting the occurrence of heterogeneous nucleation and eutectic solidification during L-PBF. (a) HAADF-STEM image and (b–e) corresponding EDS maps of as-built Al-Ni-Ti-Zr alloy.

A trend suggesting higher fraction of finer grains near the melt-pool boundaries (Fig. 4(c and d)) follows from a higher population density of Al3(Ti,Zr) nucleants at these locations compared to that within the melt-pool. Distinctive process dynamics in L-PBF including formation of remelting zones contribute to this trend. Partial remelting of the previously solidified melt pool is necessary to attain a printed part free of LOF defects in L-PBF. Such partial remelting results in formation of remelting zones within the melt pools. Temperature in a remelting zone, represented by red-colored zone between layer # *n* and layer # *n + 1* in Fig. 4(e), reaches values higher than that in the green-colored zone [30]. Now, at higher temperature, *either* **a)** dissolution of Al3Ti and Al3Zr nucleants may occur thus resulting in lesser number of potent nucleants for nucleation of α-Al grains *or* **b)** coarsening of α-Al grains previously nucleated on these nucleants may occur (Fig. 4(c and d)). In either case, coarser grains will prevail within these remelting zones. Conversely, nucleants may not dissolve within the green-colored zone and thus, several heterogeneously nucleated fine equiaxed α-Al grains may sustain in this zone.

While G/R affects grain morphology, cooling rate, represented by G×R, affects size. Cooling rates at different locations in the melt-pool were calculated using Eq. (1) [36],

(1)

where is cell size (μm) and  is cooling rate (K s−1). Cell size is calculated from high-magnification micrographs using the line-intercept method; one such micrograph is shown in Supplementary Fig. S1.  varied within the melt-pool (Supplementary Table 1); the average  of ~(2.86 ± 0.32)× 105 K s−1 was obtained. At such high non-equilibrium cooling rates, the higher quantity of metastable L12 Al3Ti and Al3Zr precipitates are likely to form thus assisting in heterogeneous nucleation of α-Al grains.

An Al-Ni-rich lamellar structure in the intergranular region (Fig. 5(a) and (e)) suggests a terminal Al-Al3Ni eutectic and explains hot cracking-resistance of columnar grains during L-PBF of Al-Ni-Ti-Zr alloy. Formation of this terminal eutectic reduces the HCS of the most cracking-susceptible stage of solidification, i.e., the terminal stage. Reduced HCS of the terminal stage allows printing at wide range of process parameters, including higher *v* (Fig. 3(a–c)), which, in turn, results in formation of a relatively shallower and overall smaller melt-pool [37]. Notably, SGSS also predicted excellent hot cracking resistance of Al-Ni-Ti-Zr alloy due to formation of Al-Al3Ni eutectic at the terminal stage of solidification. Now, for a given layer-thickness (*t*, µm), a smaller melt-pool depth (*DMP*, µm) also means smaller remelting zone depth (*Dr*, µm, Fig. 4(e)) (Eq. (2)),

(2)

Smaller values of  would mean greater numbers of Al3Ti and Al3Zr nuclei could survive resulting in relatively higher fraction of F.G. region as compared to when the  is higher. Therefore, eutectic solidification and heterogeneous nucleation work in tandem to produce a crack-free as-built microstructure with HGS. Notably, the current alloy design strategy targets hot cracking at multiple stages in solidification. In the initial stages, the potent primary nuclei promote equiaxed growth and prevent the overcrowding of microstructure by cracking-susceptible columnar grains, whereas in the terminal stage, the formation of eutectic leads to efficient crack backfilling and minimal thermal strains. An alloy with wide processing window is thus obtained. Such alloys allow microstructural fine-tuning by allowing printing at different process parameters wherein different G and R may be obtained. Hence, the current alloy design strategy opens the path for application-specific manufacture of Al alloys with L-PBF, in that the alloy microstructure may be controlled to obtain required mechanical properties.

Fig. 6(a) represents engineering tensile stress-strain curves for as-built and aged (400 °C-4 h) mini tensile specimens of Al-Ni-Ti-Zr alloy. Tensile properties are tabulated in Table 2. An increase in yield strength (YS) upon aging confirms the presence of solid solution in as-built condition as well as the precipitation hardenability of the novel Al-Ni-Ti-Zr alloy (Supplementary Fig. S2). In addition to exhibiting precipitation strengthening, Hall-Petch strengthening, and dislocation strengthening, the as-built alloy is believed to exhibit back-stress-induced strengthening due to its HGS. The materials processed with L-PBF often contain high densities of geometrically necessary dislocations (GND) that increase with increasing cooling rates [38]. Since the cooling rate varies within the melt-pool, as shown in Supplementary Table 1, varying densities of GND must be present. Additionally, varying cooling rate also results in varying sizes of Ti- and Zr-containing precipitates in both F.G. and C.G regions (Figs. 4(d) and 5(c)) and varying cell size in the C.G. region (Table S1). Thus, the HGS in as-built Al-Ni-Ti-Zr alloy is supplemented by a hierarchy in GND density, precipitate size, and cell size. This microstructural heterogeneity and hierarchy result in numerous obstacles to dislocation motion within the as-built microstructure. The effectiveness of a microstructure in obstructing dislocation motion depends inversely on distance between two adjacent obstacles (obstacle interspacing) [13]. In an alloy with microstructural hierarchy and heterogeneity, several obstacles with varying degrees of effectiveness exist, in that the obstacle interspacing varies depending on obstacle type. For example, within the F.G. region, the distance between two adjacent Al3(Ti,Zr) precipitates is much smaller as compared to the distance between two adjacent grain boundaries within the C.G. region. This varying obstacle interspacing creates hard and soft regions within the microstructure, and thus, creates deformation gradients during deformation [2]. Such deformation gradients are accommodated by GND accumulation. Further, as GNDs accumulate, they produce a long-range stress, called back-stress, and inhibit further slip; this leads to high synergistic strength and ductility [2], [12], [13], [39]. The tensile properties of Al-Ni-Ti-Zr alloy are compared to other homogenous grain-structured additively manufactured Al alloys (Fig. 6(b)) [19], [20], [28], [40], [41]. The high performance of the reported alloy is attributed to very low porosity content and activation of multiple deformation mechanisms. It is worth noting that due to its wide processing window and ability to produce microstructural heterogeneity and hierarchy, the performance of Al-Ni-Ti-Zr alloy may be fine-tuned as per the requirements of the structural application.

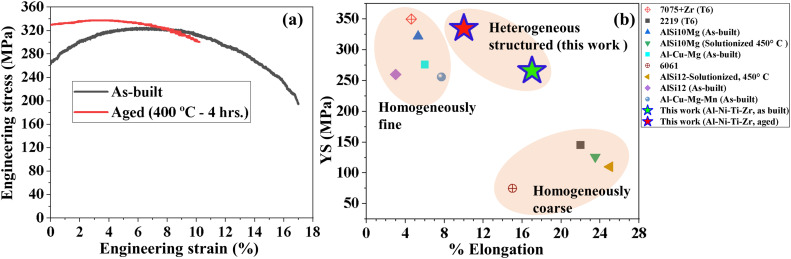


Fig. 6. Tensile performance of Al-Ni-Ti-Zr alloy. a) Engineering stress vs. engineering strain curves for Al-Ni-Ti-Zr alloy, and b) comparison of tensile properties of Al-Ni-Ti-Zr alloy with other additively manufactured Al alloys.

Table 2. Tensile properties of Al-Ni-Ti-Zr alloy.

|  |  |  |  |
| --- | --- | --- | --- |
| **Alloy condition** | **YS (MPa)** | **Ultimate tensile strength (UTS, MPa)** | **% elongation** |
| **As built** | 266 ± 1 | 331 ± 9 | 17 ± 1 |
| **Aged, 400 °C-4 h** | 335 ± 10 | 345 ± 7 | 10 ± 3 |

# 5. Conclusions

In this work, we have shown that an alloy design strategy, which integrates a) *grain-refinement through heterogeneous nucleation* and b) *eutectic solidification* leads to a wide processing window, microstructural heterogeneity, and hierarchy, i.e., a synergy between printability and performance. An Al-Ni-Ti-Zr alloy is designed based on these premises. Upon L-PBF, this alloy exhibits fine equiaxed grains that nucleate on Al3(Ti,Zr) precipitates, and coarse columnar grains with enhanced cracking resistance due to a terminal Al-Al3Ni eutectic. The subsequent heterogeneous grain structure, solute atoms, precipitates, phase boundaries, cell boundaries, and grain and domain boundaries constitute the microstructural heterogeneity and hierarchy within the as built alloy and signify its amenability to multiple deformation mechanisms. As a result, the alloy exhibits high tensile performance in as built condition (yield strength of 266 MPa and % elongation of 17%). Furthermore, the wide processing window of the Al-Ni-Ti-Zr alloy with L-PBF would allow fine-tuning of the as-built microstructure and thus, the mechanical properties of the alloy. The reported alloy design strategy is believed to open the gateway for application-specific manufacture of Al alloys with L-PBF and lead to a fundamental shift in how these alloys are currently designed for L-PBF.

# CRediT authorship contribution statement

**Saket Thapliyal:** Conceptualization, Methodology, Investigation, Data curation, Formal analysis, Writing - original draft. **Shivakant Shukla:** Methodology, Writing - review & editing. **Le Zhou:** Methodology, Writing - review & editing. **Holden Hyer:** Methodology, Writing - review & editing. **Priyanshi Agrawal:** Methodology, Writing - review & editing. **Priyanka Agrawal:** Methodology, Writing - review & editing. **Mageshwari Komarasamy:** Methodology, Writing - review & editing. **Yongho Sohn:** Funding acquisition, Conceptualization, Supervision, Resources, Writing - review & editing. **Rajiv S. Mishra:** Funding acquisition, Conceptualization, Supervision, Resources, Writing - review & editing.

# Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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