

Article

Laser Additive Manufacturing of Layered Zr-Based Bulk Metallic Glass Composite

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Abstract: As a potential functional material, much effort has been devoted to enhancing the mechanical properties of bulk metallic glass composites (BMGCs). Among them, layered BMGCs are regarded as effective for achieving a strength–ductility synergistic effect. However, it is difficult with the existing metallic glass (MG) preparation technologies to obtain a decent layered structure. In addition, the fragile interface between layers formed using the traditional fabricating method always exacerbates the deterioration of mechanical properties, which restricts the wide application of layered BMGCs. In the case of laser additive manufacturing (LAM), the cooperation of coarse grains in the hot affected zone (HAZ) and fine grains in the remelting zone induced by a unique thermal history is of key importance in eliminating the fragile interface and therefore overcoming premature cracking. Thus, we successfully synthesized Nb–Zr₄₈Cu_{46.5}Al₄Nb_{1.5} layered material with a yield strength of 1332 (±91) MPa and a compression ductility of 4.17 (±0.14)% via LAM. The results of the compressive curves of Nb and BMGC prepared by LAM decisively demonstrate that the layered material obtains a certain degree of plasticity while maintaining relatively high strength. This remarkable mechanical property is mainly attributed to the asynchronous deformation and the interaction of the adjacent Nb and MG layers. It is worth emphasizing that a distinctive round-way crack extension is discovered during the deformation process, which plays a significant role in breaking through the strength ductility trade-off. In addition, the source of yield strength is calculated theoretically using the rule of the mixture and the dislocation strengthening principle. The results indicate that the strength contributed by geometrically necessary dislocations is around 101.7 MPa. In addition, the strength calculated by the rule of the mixture is ~1201.9 MPa. This work offers a new paradigm for BMGCs with excellent strength and ductility as practical engineering materials.

Keywords: laser additive manufacturing; metallic glass composite; layered structure; strength–ductility synergy



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1. Introduction

The trade-off between strength and plasticity is an unavoidable problem in the field of materials [1,2]. In order to adapt to the rapid development of industrialization, breaking the trade-off between the strength and plasticity of materials is an inevitable trend [2]. Extensive investigation over the past few years has shown that the strength of metallic glass (MG) is particularly prominent due to its unique disordered atomic structures [3–7]. In addition, metallic glass lacks the traditional defects, such as dislocations, that endow advantages, and which are not available to conventional crystal alloys [3–17]. Therefore, metallic glass has received wide attention for the application of structural material deriving from its satisfying mechanical properties, such as high hardness, large elastic strain limits, and ultra-high-yield strengths [5–10]. Unfortunately, the inferior tensile ductility of MG impedes its widespread proliferation as a practical engineering material [7,8]. During the deformation process, the infertile plasticity of the amorphous alloy is mainly attributed to the cooperative shear displacement of atomic clusters (shear transformation zones, STZ) rather than dislocations [9–14]. The STZ will evolve into a shear zone with the

applied load, and further expand into fracturing at the extreme limit of homogeneous-to-inhomogeneous flow transition [10–12]. To overcome this dilemma, a second phase is often introduced into amorphous alloys to form amorphous composites and enhance plasticity [12–14]. Among them, the ZrCu-based MG has received extensive interest from the material science field. As reported by Wu et al., B2 phases were introduced into an amorphous matrix to enhance the plasticity of ZrCu-based metallic glass composites utilizing the transformation-induced plasticity (TRIP) effect, obtaining a work-hardening phenomenon [15]. Wu et al. successfully fabricated a $\text{Zr}_{48}\text{Cu}_{46.5}\text{Al}_4\text{Nb}_{1.5}$ bulk metallic glass composite with a strength of 1200 MPa and plasticity of 19.2% by copper casting [5]. Sun et al. analyzed the serration and shear avalanches of a ZrCu-based bulk metallic glass composite in the process of deformation by trajectory convergent evolution of the dynamics during plastic deformation and concluded that the martensitic transformation of the B2 phase can effectively induce multiple shear bands that enhance mechanical properties [6]. Although amorphous composites can improve ductility to some extent due to the introduced soft phase facilitating the nucleation of multiple shear bands to restrain further propagation into cracks. However, the volume fraction of the second phase easily exceeds the percolation threshold of three-dimensional materials for achieving the desired plasticity, which will substantially sacrifice the excellent properties of amorphous alloys [13–16]. By the micro-mechanical investigation of BMGCs, Wang et al. found that the volume fraction of the crystal phase should reach the percolation threshold to significantly improve the ductility of BMGCs. Therefore, they provided an amorphous honeycomb model and proved that the performance of amorphous honeycomb composites is better than that of crystal free-growth BMGCs based on simulation and research into the amorphous alloy percolation threshold [13]. Therefore, the heterostructure of BMGCs is considered to be a valid quality to improve the plasticity of BMGCs without sacrificing the excellent properties of amorphous alloys [13,18].

As reported by Be'chir Che'hab et al., layered steel can achieve enhanced mechanical properties compared to conventional steel because each layer has a unique Young's module [14]. Inspired by their work, the use of layered amorphous composites can be regarded as an effective strategy to realize the synergistic effect of strength and plasticity [19,20]. Wang et al. reported that the nanocrystalline Cu and nanoscale Cu/Zr glass nanolaminate samples fabricated by magnetron sputter deposition were equipped with high flow stress (1.09 ± 0.02 GPa) and tensile strain ($13.8 \pm 1.7\%$) [12]. However, the magnetron sputtering method cannot meet the dimensional requirements of structural materials. In addition, it is difficult to achieve an accurate design for lamellar composites using the traditional preparation methods of amorphous alloys [21,22]. Although copper casting can attain the requirements for a cooling rate that forms amorphous alloys, it is difficult to obtain and modulate heterogeneous structures. Furthermore, in view of the enormous difference in thermal expansion coefficient between soft and rigid layers, the interface bonding strength is undesirable, which is extremely unfavorable for the mechanical properties. As reported by Amy Wat et al., typical interfacial binding voids arise in the Al_2O_3 -Zr-based MG ceramics prepared by pressure-free osmosis. Therefore, a novel preparation method of laminar amorphous composites is critical to bring into play the synergistic effects of strength and plasticity [23].

Laser additive manufacturing (LAM) technology is a reliable method that can fabricate different microstructures due to its unique local melting and solidification process [20,24–31]. This point-by-point approach has the potential to successfully fabricate layered materials. For instance, Guan et al. manufactured a laminated $\text{CrMnFeCoNi}/\text{AlCoCrFeNiTi}_{0.5}$ high-entropy alloy using LAM technology, which obtained a desirable strength–plasticity synergy [20]. In the same way, Cai et al. also prepared a $\text{FeCoCrNi}/\text{FeCoCrNiAl}$ laminated high-entropy alloy using laser melting deposition (LMD) [26]. LAM can achieve an ultra-high cooling rate that satisfies the formation conditions of amorphous alloys [27–30]. In addition, each cooling point will be affected by the adjacent cooling points during the process of LAM and form an annealing zone, namely the so-called heat-affected zone

(HAZ) [28,29]. Meanwhile, a thin remelting zone will be formed between the molten pool and the HAZ [30,31]. In the remelting zone, there is an obvious phenomenon of fine grain strengthening to improve the strength and prevent a sudden change of modulus between the hard layer and the soft layer and eliminate stress concentration at the interface [32]. In the case of fabricating soft-hard layered heterogeneous materials, the HAZ and remelting layer will evolve into a gradient fine crystal transition zone, playing a role in a smooth transition between soft and hard layers to prevent premature cracking caused by the difference of thermal expansion coefficient, which also provides a vital opportunity to fabricate layered amorphous composites using LAM technology [33–38]. Meanwhile, the cooling rate of LAM can reach 10^4 K/s, which can satisfy the requirement of MG formation. Thus, Zhang et al. have successfully fabricated crack-free Zr-based metallic glasses with scaffold structure [28]. In addition, Pauly et al. prepared a $\text{Zr}_{52.5}\text{Cu}_{17.9}\text{Ni}_{14.6}\text{Al}_{10}\text{Ti}_5$ metallic glass with a nearly fully amorphous state [36].

Herein, we prepared Nb- $\text{Zr}_{48}\text{Cu}_{46.5}\text{Al}_4\text{Nb}_{1.5}$ layered structure materials utilizing LAM technology. Nb with high ductility metal is selected as the soft layer for matching the $\text{Zr}_{48}\text{Cu}_{46.5}\text{Al}_4\text{Nb}_{1.5}$ amorphous alloy. The Nb layer completely isolates the amorphous layer and prevents the main shear band from penetrating the material during the deformation process. In addition, the asynchronous deformation of soft and hard layers piles up a large number of geometrically necessary dislocations (GND) at the interface to induce the fragmentation and proliferation of shear bands through the action of normal stress and back stress, endowing plasticity for laminated composites. Thus, the Nb- $\text{Zr}_{48}\text{Cu}_{46.5}\text{Al}_4\text{Nb}_{1.5}$ layered material with a yield strength of 1332 (± 91) MPa and a compress ductility of 4.17 (± 0.14)% is nicely achieved via LAM. We also calculated the yield strength through both the rule of the mixture and the GND strengthening theory to further explore the strengthening mechanism of the layered material. As a result, the strength contributed by geometrically necessary dislocations is around 101.7 MPa and the strength calculated by the rule of mixture is ~ 1201.9 MPa. Our research provides a new solution for the design of controllable layered bulk metallic glass composites.

2. Experiment

Nb- $\text{Zr}_{48}\text{Cu}_{46.5}\text{Al}_4\text{Nb}_{1.5}$ layered structure materials were performed with a laser melting deposition additive manufacturing system (RC-LDM-8060 from Nanjing Raycham in Nanjing, China) with a maximum power of 6000 W. The overall schematic of the experimental process was shown in Figure 1. The titanium alloy was selected as the substrate, blue and silver parts were Nb layer and metallic glass layer, respectively. A water-cooled copper plate was inserted between the substrate and the worktable to obtain the rapid cooling velocity. The $\text{Zr}_{48}\text{Cu}_{46.5}\text{Al}_4\text{Nb}_{1.5}$ powders in the size range of 45 μm to 105 μm were obtained by atomisation and the Nb powder in the size range of 80 μm to 125 μm was prepared by plasma spheroidisation (TekSphero spheroidization system from Tekna Plasma System Inc., Sherbrooke, Canada). As shown in Figure 1, the Nb powder was almost spherical, while a small amount of planetary powder appeared in the SEM figure due to the viscosity of the metallic glass. The spherical $\text{Zr}_{48}\text{Cu}_{46.5}\text{Al}_4\text{Nb}_{1.5}$ MG powders and the Nb powders stored in two powder-feeding cylinders were delivered by coaxial nozzles under the protection of argon gas. By adjusting the rotation speed of the powder feed plate, the quality of the powder feed can be subtly controlled, thus the ratio of the MGCs layer to the Nb layer can be adjusted. In this work, the feed quality of $\text{Zr}_{48}\text{Cu}_{46.5}\text{Al}_4\text{Nb}_{1.5}$ was 10.6 g/min, while the Nb powder was 10.4 g/min. Therefore, the thickness of each layer was 0.5 mm, and alternate deposition of Nb and $\text{Zr}_{48}\text{Cu}_{46.5}\text{Al}_4\text{Nb}_{1.5}$ layer. Moreover, the dye-penetrant inspection was sprayed to detect the cracks. In an attempt to reduce the impact of the heat flow input from the laser on the macroscopic morphology and microstructure of the material, the manufacturing procedure adopted a four-layer cyclic fabricating method in which each layer had a different starting and ending point. The specific process parameters were shown in Table 1. To ensure the formability and good bonding of the material, the laser power of the MGC and Nb layers was determined as

1600 W and 2400 W with a scanning speed of 600 mm/min. Therefore, the ratio of Nb powder to $\text{Zr}_{48}\text{Cu}_{46.5}\text{Al}_4\text{Nb}_{1.5}$ powder was approximately 1:1.

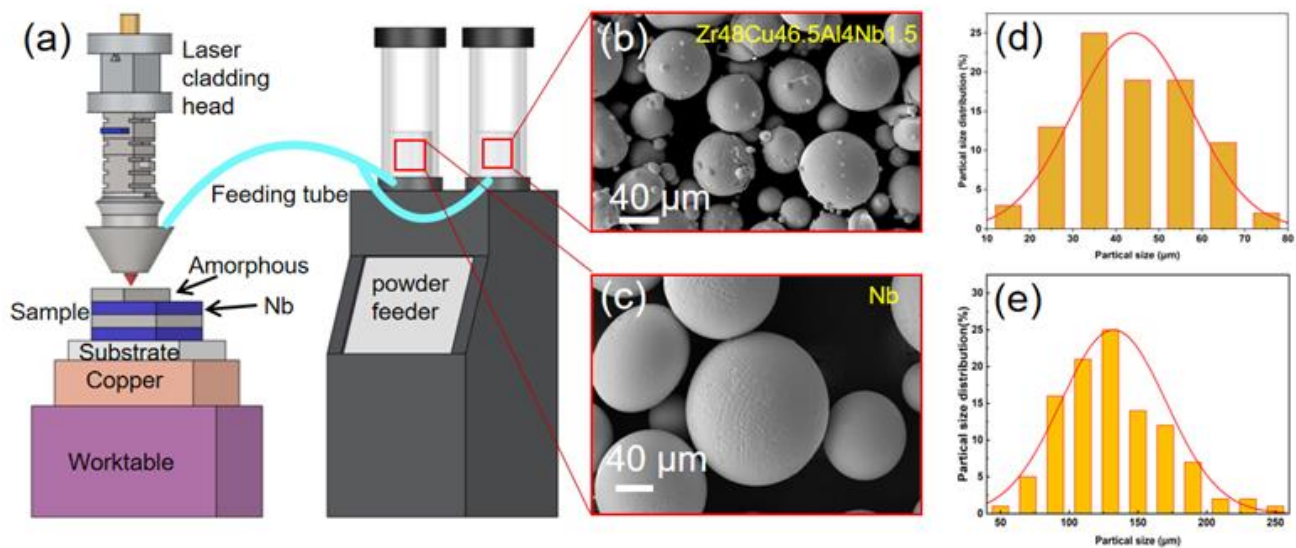


Figure 1. (a) Schematic diagram of laser additive manufacturing equipment. (b,c) SEM figure of the $\text{Zr}_{48}\text{Cu}_{46.5}\text{Al}_4\text{Nb}_{1.5}$ and Nb powders. (d,e) Size distribution of the $\text{Zr}_{48}\text{Cu}_{46.5}\text{Al}_4\text{Nb}_{1.5}$ and Nb powders.

Table 1. Specific process parameter of the LAM layered material.

Powder	Size (μm)	Rotational Rate (n/min)	Powder Mass (g/min)	Laser Power (W)	Scanning Rate (mm/min)
MG	45–105	1.1	10.6	1600	600
Nb	80–125	0.9	10.4	2400	600

The phase composition of the layered structure materials was characterized by X-ray diffraction (XRD, Panalytical Empyrean from Almelo, Netherlands). The micro-structure characterization of the deposited specimens was investigated using a scanning electron microscope (SEM, Zeiss Supra 55 from Carl Zeiss, Oberkochen, Germany) equipped with the electron backscattered diffraction (EBSD) and Transmission Electron Microscope (TEM, JEM 2100F from JEOL, Tokyo, Japan).

3. Result and Discussion

Figure 2a shows the XRD patterns of the powders and the deposited Nb-MGC layered material. Clearly, the XRD pattern of the initial $\text{Zr}_{48}\text{Cu}_{46.5}\text{Al}_4\text{Nb}_{1.5}$ powder depicts a broad maximum containing one faint crystalline Bragg peak, which can be identified as the B2-CuZr phase. For the Nb-MGC layered material fabricated by the LAM, more other crystal Bragg peaks appear on the XRD pattern, indexing to the Nb, B2, B19', $\text{Cu}_{10}\text{Zr}_7$, and CuZr_2 phases. The B2 phase is regarded as a high-temperature metastable phase generated during the cooling process of the amorphous matrix. At the same time, the appearance of the B19's phase indicates that the martensitic transformation from B2 to B19' has been induced by the thermal stress generated during the LAM process. In addition, a small amount of $\text{Cu}_{10}\text{Zr}_7$ and CuZr_2 are classified as crystallization products after the cooling process of amorphous alloys.

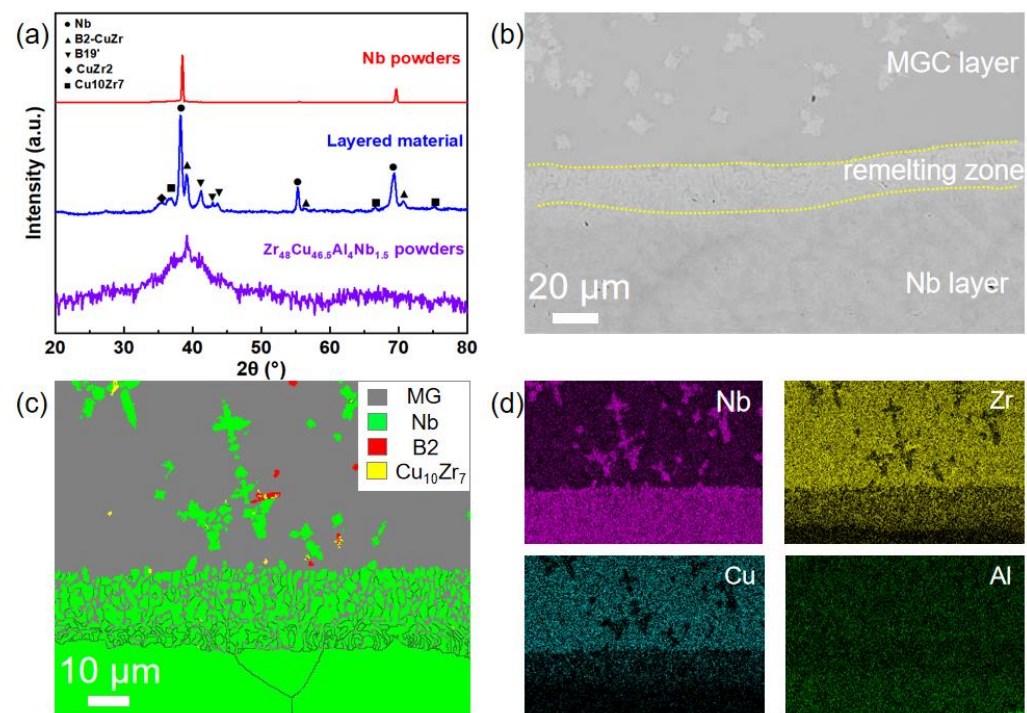


Figure 2. (a) The XRD pattern of the deposited Nb-Zr₄₈Cu_{46.5}Al₄Nb_{1.5} layered material. (b) The SEM morphology of the layered materials. (c) The EBSD phase mapping between the Nb layer and amorphous layer. (d) The in-situ EDS mapping of (c).

To explore the layer structure, the microstructures of the deposited layer material are characterized in Figure 2b–d. As shown in Figure 2b, the layered structure can be obviously perceived. An overlapping transition zone between the amorphous layer and the Nb layer is also observed. In order to further clarify the microstructure of the layered material, the phase map of EBSD and in-situ EDS mapping are shown in Figure 2c,d, respectively. Because of the disordered atomic structures [3–19], the amorphous layer exhibits an unresolvable state, in which the dendrites are presented. The area fraction of the unresolvable zone is calculated as 45.08% according to the EBSD analysis results. The main reason for the composition deviation of the layered material is the supersaturated precipitation of Nb and a small amount of crystallization. The appearance of Cu₁₀Zr₇ and CuZr₂ is due to a decrease of the cooling rate due to the increase of laser power, which is responsible for the crystallization of the metallic glass matrix and the separation of Cu₁₀Zr₇ and CuZr₂ intermetallic compounds. In addition, crystallization also occurs in the HAZ. It also can be inferred from the results of Figure 2c,d that the major composite of the dendrites is the Nb element, which can be attributed to the diffusion and participation of the remelting Nb. From the view of thermodynamics, Nb of the remelting zone will spontaneously diffuse into the amorphous layer. Nb is regarded as a high melting point phase (2468 °C) and is easier to be preferentially precipitated. Thus, in the process of fabricating the MGC layer, the high temperature causes the Nb layer to diffuse towards the MGC layer, resulting in local supersaturation and dispersion of precipitated dendrites Nb in the MGC layer. Meanwhile, the appearance of the Nb fine-grain in the remelting zone is derived from the lack of crystal growth time under high cooling velocity. However, the coarse grain in the HAZ is mainly ascribed to the fact that the annealing effect provides the advantage condition for the solid phase transformation of the Nb layer. The heterogeneous structure of crystal morphology provides a gradient transition of Young's module, which effectively eliminates the stress concentration caused by the non-uniformity of the components. Thus, the gradient structure can not only effectively prevent the material from cracking in advance, but also induces the shear band fragmentation and proliferation at the interface, which is conducive to the improvement of mechanical properties.

To verify the influence of the designed structure on the mechanical properties, the quasi-in-situ compress test results are shown in Figure 3. For comparison, the compress stress-strain curves of the $\text{Zr}_{48}\text{Cu}_{46.5}\text{Al}_4\text{Nb}_{1.5}$ BMGC and Nb fabricated by LAM are concluded in Figure 3a. The compress stress-strain curve of the Nb-MGC layered material indicates that the fracture strength of the sample is $1332 (\pm 91)$ MPa, while the ductility appears to be $4.17 (\pm 0.14)\%$, breaking the strength-ductility tradeoff for the $\text{Zr}_{48}\text{Cu}_{46.5}\text{Al}_4\text{Nb}_{1.5}$ BMGC (1836 MPa, no plasticity). In terms of the Nb fabricated by LAM, the yield strength is $683 (\pm 45)$ MPa and the engineering strain is $30.6 (\pm 0.37)\%$ (for comparison, we just take the 10% of the engineering strain of the compression curve for Nb fabricated by LAM). Quite evidently, the laminated material has relatively high strength and decent plasticity compared to the Nb and MGCs fabricated by LAM. Moreover, the deposited layer material exhibits an overall strain softening during the stretching process, which is derived from the synergistic effect of soft and hard layers. To demonstrate the mechanical behavior of the layered material, the different strain state of the compressing process is marked by b, c, and d, respectively. The corresponding microstructure of the layered material is shown in Figure 3b–d. As shown in Figure 3b, the loading stress is insufficient to stimulate obvious deformation between the soft layer and the hard layer at the elastic stage. With the continuous increment of the compress stress, the slip band begins to occur in the Nb layer until the yield stage, as shown in Figure 3c. It is well-documented that the appearance of slip bands is one of the prominent features of the massive proliferation of dislocations [32]. The splendid interfacial bonding contributed by the participation of remelting zone promotes the transference of the stress from Nb layer to MGC layer. Therefore, it can be indicated that quantities of dislocation accumulations occur in the Nb layer, while the shear bands are just activated in the amorphous layer. Specifically, the extensive dislocations and shear-band branching appear at the remelting zone, resulting in additional ductility compared with the traditional homogeneous metallic glass. It should be noted that a small amount of shear bands reside in the amorphous layer due to the martensitic transformation of B2 phase, acting as the auxiliary carrier of plasticity. B19' phase, the product of TRIP effect of B2 phase, provides the work-hardening effect [5]. After deformation, the hardness of the amorphous matrix is significantly lower than that of the B19' phase, which leads to the failure of the shear band to penetrate the crystal phase [27,28]. The inhomogeneity of Young's modulus caused by martensitic transformation promotes the fragmentation and proliferation of shear bands. However, the Nb layer as the main source of plasticity of the layer material endures the load in deforming, while the amorphous layer limits the deformation of the soft layer. The asynchronous deformation leads to the GND in Nb grains and local stress concentration of amorphous at the interface. The stress concentrations between the soft and hard layers are limited to non-percolating regions in the remelting zone. As the local stress exceeds the limit of the amorphous matrix, the shear band will be activated at the interface and is continuously expanded. With the further increment of deformation into 3.9% (Figure 3d), the layered material begins to enter the over-yield stage. The proliferation of the shear bands and the TRIP effect serve to enhance the ductility until the micro-cracks are stimulated by the approaching of the critical shear offset of the dominant shear band. It can be convincingly illustrated that the Nb fine crystals of the remelting zone block the extension of cracks. Thus, the engineering strain of the laminar material can be further increased to 4.17%. Of particular interest is that the crack propagation is from the MGC layer to Nb layer, which is completely opposite to the prior plastic deformation. To further investigate the mechanism of Nb- $\text{Zr}_{48}\text{Cu}_{46.5}\text{Al}_4\text{Nb}_{1.5}$ layered material breaking through the strength-plasticity trade-off, the theoretical yield strength of the material is calculated. The strength contributed by geometrically necessary dislocations can be estimated by an empirical relationship $\delta_{\text{DS}} = \alpha M G b \rho^{0.5}$, where δ_{DS} is the strength contributed by geometrically necessary dislocations (MPa), M is the Taylor factor of the *bcc* structure, α is the correction constant of *bcc* structure, G is the shear modules of *bcc* Nb (~ 38 GPa) and ρ is the density of dislocations calculated by EBSD mapping [39].

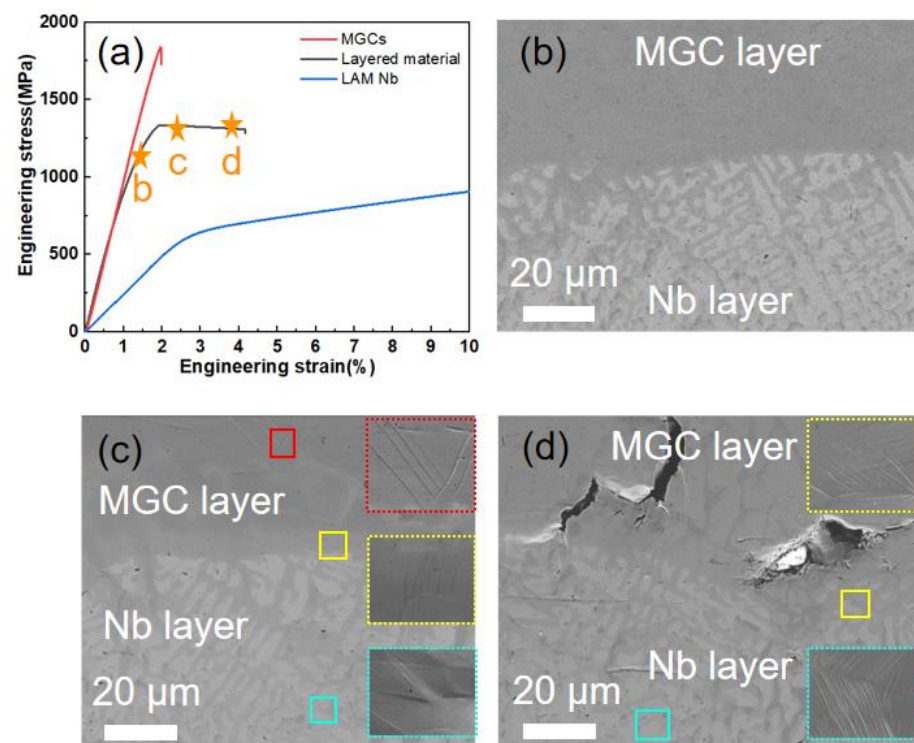


Figure 3. (a) The compress stress-strain curves of the layered material, Nb and MGCs fabricated by LAM. (b–d) The SEM macroscopic features of b, c, and d point in (a).

In addition, the classical rule of mixture is also applicable to layered materials [37,40]. Thus, the yield strength of the layered materials can be regarded as the sum of δ_{ROM} and δ_{DS} ($\delta_y = \delta_{ROM} + \delta_{DS}$), where δ_y is the yield strength of the layered materials and δ_{ROM} is the yield strength of the layered material calculated by the rule of mixture [41]. The average dislocation density can be calculated from the EBSD data by the equation ($\rho = \frac{2KAM_{ave}}{\mu b}$), where KAM_{ave} is the average of the kernel average misorientation, μ is the step size of the EBSD scanning, and b is the Burgers vector of Nb. Moreover, the KAM_{ave} can be calculated by the equation ($KAM_{ave} = \frac{\sum_{i=1}^n x_i y_i}{\sum_{i=1}^n y_i}$). In order to eliminate the impact of sample preparation process, we opted for the range of misorientation from 0 to 3 for the calculation of KAM_{ave} . Therefore, the calculated ρ and δ_{DS} of the layered material are 0.91 m^{-2} and 101.7 MPa, respectively. According to the volume fraction of Nb and the rule of mixture ($\delta_{ROM} = \delta_{Nb0.2} \times V_{Nb} + \delta_{MGC} \times V_{MGC}$), the calculated δ_{ROM} is approximately 1201.9 MPa. It can be seen that the calculated results are close to the experimental results, the yield strength of layered material is mainly composed of two parts, namely the theoretical strength provided by the rule of mixture and the additional yield strength provided by dislocation strengthening.

The schematic of the peculiar deformation for the Nb-MG laminar material is summarized in Figure 4. The plastic incompatibility arises between the Nb and MGC layers during the deformation process, thus the GND is activated to achieve a strength-plasticity synergistic effect. The MGC layer restricts the deformation of the Nb layer, while the Nb layer blocks the propagation of the shear bands and cracks, collectively improving the yield strength and compress ductility.

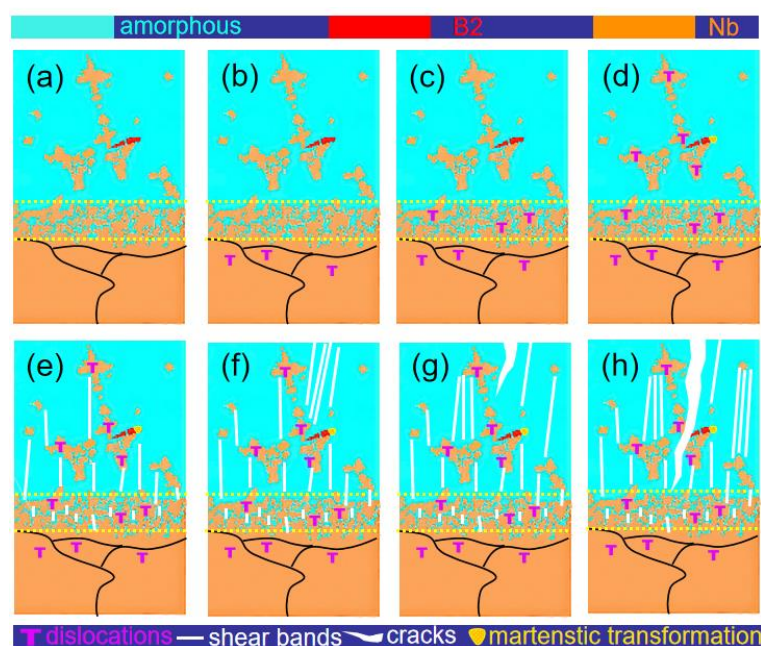


Figure 4. (a–h) Schematic of the deformation process of the layered material.

4. Conclusions

In summary, the Nb-Zr₄₈Cu_{46.5}Al₄Nb_{1.5} layered metallic glass composite is successfully synthesized by LAM. The layered materials show a splendid yield strength of 1332 (±91) MPa with an excellent compress ductility of 4.17 (±0.14)%. Based on the comparison with the Nb and BMGC, it can be concluded that the layered material prepared by LAM has a certain high yield strength on the premise of obtaining plasticity, which breaks through the strength ductility trade-off of the BMGC. We also discovered that the source of the relatively high yield strength is mainly composed of two components: the strength calculated by the traditional rule of mixture, i.e., 1201.9 MPa, and the strength provided by the geometrically necessary dislocation reinforcement due to the heterogeneous structure, i.e., 101.7 MPa. The enhanced strength-plasticity synergy is derived from the asynchronous deformation and the interaction of the adjacent layers. Therefore, the GND accumulated at the interface induces the splitting and proliferation of shear bands. Meanwhile, the Nb layer cuts off the amorphous layer, resulting in the failure of the shear band to rapidly penetrate the entire material. Our findings provide a new idea of breaking through the strength-ductility trade-off of traditional functional materials. Moreover, our work demonstrates that it is an effective method to design and prepare controllable layered metallic glass composites through laser additive manufacturing.

Author Contributions: H.M.: Literature search, figures, data collection, data analysis, and writing; D.Q.: Data analysis, and editing; C.S.: Study design, and editing; Y.L.: Study design, data analysis, and editing. All authors have read and agreed to the published version of the manuscript.

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Data Availability Statement: The data that support the findings of this study are available from the corresponding author upon reasonable request.

Conflicts of Interest: The authors declare no conflict of interest.

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