An innovative approach to enhancing strength and ductility in cold spray 3D printing through engineered heterogeneous laminate microstructures

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Abstract: Achieving an ideal balance of strength and ductility in 3D-printed low-pressure cold spray materials is highly desirable yet remains a significant challenge. This paper introduces a dual heterogeneous laminated Cu/CuCrZr composite structure, characterized by varying properties between a soft and hard domains, manufactured through low-pressure cold spray followed by heat-treatment. The tailored heterogeneous Cu/CuCrZr microstructure features alternating coarse and fine grains, resulting in a hetero-deformation-induced hardening, caused by the mechanical incompatibility between the coarse grain Cu and fine grain CuCrZr layers, leading to an improvement of work hardening and increase of ductility. This performance is largely attributed to the well-bonded particles and hetero-deformation-induced (HDI) strengthening during plastic deformation. The strengthening effect is due to the accumulation of a substantial number of geometrically necessary dislocations (GNDs) at the heterogeneous interface, which enhances work-hardening and simultaneously boosts both the strength and ductility of the layered structure. The engineered laminate showed 205% and 115% improvement in strength and ductility compared to Cu and 10% and 28% improvement when compared to CuCrZr.

Keywords: Cold spray, heterogeneous structure, laminate architecture, hetero-deformation-induced strengthening

1. Introduction

Cold Spray Additive Manufacturing (CSAM) is a solid-state deposition technology capable of producing freestanding components, thick surface coatings, and structural repairs [1]. In CSAM, metal powders are accelerated by compressed gases, typically nitrogen, helium, or a mixture of both, and directed at a substrate at velocities beyond sound velocity in air. Upon impact, the particles undergo severe plastic deformation and bond to the substrate or previously deposited layers without melting. This sub-melting-point deposition distinguishes CSAM from fusion-based additive manufacturing techniques, offering advantages in thermal control and material preservation. Moreover, CSAM has demonstrated the ability to fabricate dense, high-strength structures with superior deposition rates and scalability compared to laser-based approaches. However, a critical limitation remains: CSAM-deposited materials typically exhibit poor ductility in the as-sprayed state, largely due to severe plasticity, interfacial defects and weak particle bonding introduced during deposition [2].

To address the long-standing strength–ductility improvement in materials processed via thermomechanical treatments, powder metallurgy, and surface engineering techniques, numerous studies have focused on designing heterogeneous microstructures that enable simultaneous improvements in both strength and ductility [3]. Among various hetero-structured designs, laminated architectures have proven particularly effective in balancing strength, ductility, and electrical conductivity. You et al. [4] developed a dual heterogeneous laminated (DHLed) Cu/CuCrZr composite via accumulative roll bonding (ARB) followed by annealing, achieving an impressive combination of high strength (563 MPa), elongation (~16.2%), and electrical conductivity. Ma et al. [5] studied Cu/bronze laminates fabricated by ARB and annealing, revealing that reducing interface spacing increased both strength and ductility through GND pile-up and enhanced back stress. These findings reinforce that interface design and mechanical contrast in laminated metals can significantly enhance the synergistic response of strength and ductility.

While extensive research has been conducted on hetero structures in conventionally processed materials, limited attention has been paid to their development in CSAM. To further explore the potential of engineered heterogeneity in CSAM, we present the first successful fabrication of a dual-laminated heterogeneous microstructure using cold spray additive manufacturing. Pure Cu and CuCrZr powders with microcrystalline structures were deposited using nitrogen as the processing gas to build a multilayered architecture composed of alternating coarse- and fine-grained layers. Flat freestanding tensile specimens were extracted from the builds for analysis. In this study, samples with varying layer counts and interface spacing were fabricated and subjected to post-deposition heat treatment. Detailed characterization was performed to evaluate porosity, microstructure, hardness, and mechanical properties. Furthermore, loading-unloading-reloading (LUR) tensile experiments were carried out to assess back stress evolution, enabling deeper insight into the role of heterogeneity in enhancing the mechanical response of CSAM-fabricated materials. Given the precipitation and dispersion strengthening effects imparted by Cr and Zr in Cu alloys, and the challenges of traditional metallurgical methods, CSAM presents a promising alternative.

2. Materials and methods

The experiment employed gas-atomized pure copper powder (99.9% purity) supplied by Metalpine GmbH (Austria), and a Cu–0.45 wt% Cr–0.05 wt% Zr alloy powder sourced from EOS North America Inc. Both powders had a particle size distribution ranging from 15 µm to 45 µm. Pure Cu and CuCrZr alloy powders exhibited a mix of fine particles surrounding larger ones. The samples were fabricated using the low-pressure commercial SST Series P Cold Spray System, manufactured by Centerline Ltd. in Windsor, Canada. Fig. 1a and b show images of CSAM laminated samples consisting of 7 and 14 layers, respectively, fabricated from alternating layers of CuCrZr and pure Cu powders. The fabrication process involved sequential deposition of CuCrZr as the first layer, followed by Cu as the second, repeated to build up the desired number of layers. No spalling occurred at the interface between the aluminum substrate and the deposited layers, and no cracks were observed within the material. Following deposition, the cold-sprayed parts were detached from the substrate and machined into tensile specimens using electrical discharge machining (EDM). The specimens followed a sub-sized flat tensile geometry with a gauge length of 17.48 mm, width of 6 mm, and thickness of 2 mm. The tensile axis was aligned with the gun traverse direction (0° orientation). To improve the mechanical properties of the cold-sprayed laminated materials, solution annealing (SA) was performed by heating the samples to 950 °C for 30 minutes, followed by water quenching. The solution-annealed specimens were then subjected to age hardening at 480 °C for 30 minutes. The microstructure of the samples was characterized using an optical microscope (Olympus BX41). Microhardness measurements were conducted using a Vickers hardness tester with a 200 g load and a 15-second dwell time. The reported hardness values represent the average of 20 measurements per sample. Tensile tests were carried out at room temperature using an Instron 8874 servo-hydraulic testing machine with a 25 kN load capacity. Testing was performed under displacement control at a rate of 0.05 mm/min, and strain data were captured using a GOM ARAMIS 3D digital image correlation (DIC) system equipped with a 5-megapixel camera and a maximum frame rate of 15 fps. Each tensile test was repeated at least three times under identical conditions, and the average values were reported. To evaluate back stress during tensile deformation, LUR tests were performed. Specimens were unloaded at specific strain levels using load-control mode, with an unloading rate of 200 N/min, until the applied load reached 20 N. The samples were then reloaded to the same load level and continued to the next unloading strain. The same specimen geometry was used as in the monotonic tensile tests.

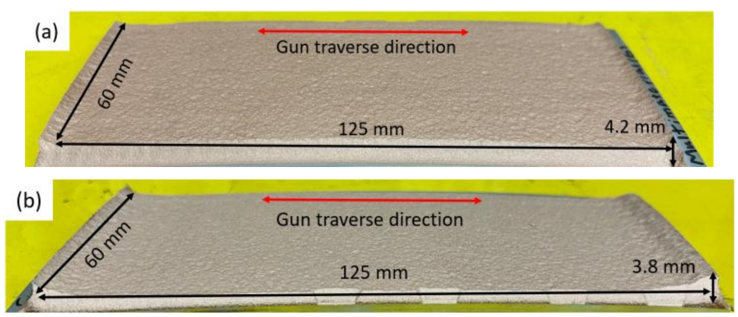

Figure 1. Macro images of laminated Cu/CuCrZr materials with different layer configurations: (a) 7-layer laminate and (b) 14-layer laminate.

3. Results and discussion

3.1. Microstructure

Figs. 2a and b display the microstructure of the of laminated cold-sprayed samples after solution annealing at 950 °C for 30 minutes, followed by water quenching and subsequent age hardening at 480 °C for one hour. The micrographs clearly present the well-defined laminated architecture with varying layer thicknesses and interface spacing. The brighter regions correspond to the Cu layers, while the darker areas represent the CuCrZr layers. The microstructure reveals a mixture of fine and coarse recrystallized grains, as well as distinct annealing twins indicated by blue arrows. Figs. 2c and d further present the recrystallized microstructures of pure Cu and CuCrZr, respectively, at higher magnifications. The optical micrographs reveal a significantly higher porosity in the heat-treated cold-sprayed pure Cu sample compared to the CuCrZr counterpart. This disparity can be attributed to several fundamental differences in their microstructural evolution during post-processing. The higher work-hardening of CuCrZr facilitate more intense plastic deformation upon impact during cold spray, leading to better mechanical interlocking and metallurgical bonding, which improves particle bonding. Pure Cu, on the other hand, deforms more uniformly with less fragmentation, resulting in less effective mechanical bonding. This result in a denser, more cohesive microstructure in CuCrZr, while the pure Cu sample retains residual porosity even after solution annealing and age hardening. During solution annealing at 950 °C and subsequent age hardening, pure Cu undergoes recrystallization and extensive grain growth, resulting in the complete disappearance of the original splat boundaries and the formation of an equiaxed grain structure. In contrast, CuCrZr, being an alloy containing solute atoms of Cr and Zr, exhibits different behavior. These solute atoms contribute to Zener pinning, where fine Cr-Zr precipitates hinder grain boundary motion and retard grain growth [6]. As a result, even after heat treatment, full boundary migration is restricted in CuCrZr, leading to the preservation of the original splat morphology.

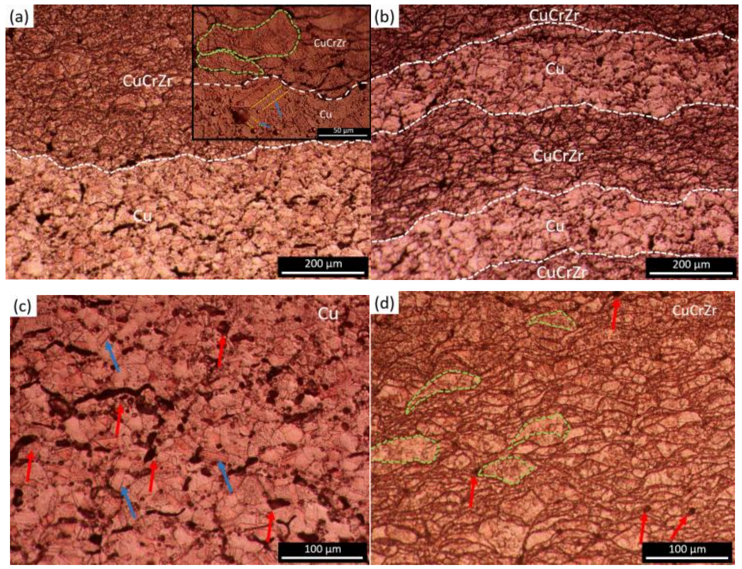

Figure 2. Optical micrographs of solution annealed+ age hardened hetero-structured laminated Cu–CuCrZr samples with (a) 7L and (b) 14L. Images (c) and (d) show the microstructures of the heat-treated Cu and CuCrZr layers individually at higher magnifications. Blue arrows highlight annealing twins, red arrows indicate porosity and unbonded particle interfaces, and green ellipses highlight individual splats that have retained their morphology after heat treatment.

3.2. Mechanical properties

As illustrated in Fig. 3a, prior to heat treatment, the microhardness of the Cu and CuCrZr layers are measured to be 132 ± 5 HV and 170 ± 6 HV, respectively. Following solution annealing and age hardening (SA+AH), a noticeable reduction in hardness is observed, with Cu decreasing to 95 ± 3 HV and CuCrZr to 145 ± 4 HV. This decline is primarily attributed to stress relaxation and recrystallization and grain growth, diminishing the dislocation density in CS parts, which softens the microstructure. Fig. 3b presents the cross-sectional microhardness profile across the 7 layers of Cu/CuCrZr interfaces of 7L and 14L laminated materials. A distinct and abrupt transition in hardness is evident at the interfaces, shifting from the softer Cu to the harder CuCrZr alloy.

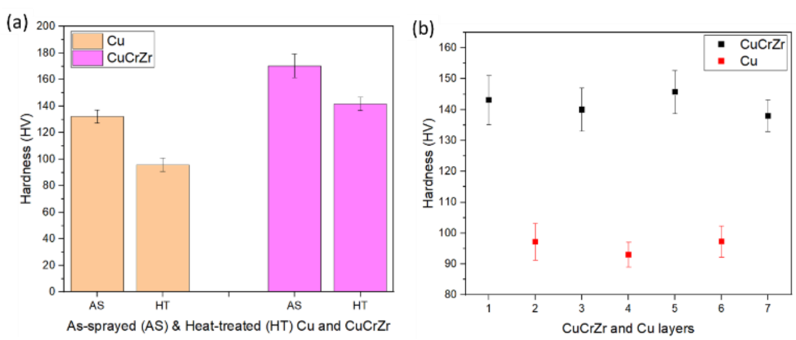

Figure 3. (a) Microhardness of Cu and CuCrZr layers before and after heat treatment; (b) Micro-hardness in both the heat-treated Cu and CuCrZr layers for the first 7 layers averaged over 7L and 14L samples.

These sharp structural and mechanical contrasts across suggests a substantial degree of mechanical incompatibility, which is likely to induce back-stress hardening, a mechanism that can enhance both strength and ductility during plastic deformation [7]. Fig. 4a displays the engineering stress–strain curves of heat-treated samples, including pure Cu, pure

CuCrZr, and Cu–CuCrZr laminates with 7 (7L) and 14 (14L) layers, alongside predicted curves based on the rule of mixtures (ROM) for the laminated samples. The discrepancy in flow stress between the experimentally measured and ROM-predicted curves reaches 56 MPa for the 7L sample and 85 MPa for the 14L sample, accounting for 24.7% and 34.8% of the total flow stress, respectively. The deviation of experimentally measured values from ROM highlights the contribution of hetero-deformation-induced (HDI) strengthening due to the interface effects, as discussed and suggested in [8]. In terms of ductility, the uniform elongation increases from 5.2% (pure Cu) and 8.64% (CuCrZr) to 10.3% and 11% for the 7L and 14L laminates, respectively, representing improvements of approximately 98% and 111.5% over pure Cu, and 19% and 28% over CuCrZr. The experimentally measured ductility values for the 7L and 14L samples exceed the ROM-based predictions by 3% and 3.9%, respectively. Fig. 4b present the enlarged true stress–strain responses obtained from LUR tests on the two laminated 7L and 14L samples. The laminated structures exhibit broad and pronounced hysteresis loops, indicating a strong Bauschinger effect [9]. The Bauschinger effect refers to the reduction in yield strength when a material is unloaded after prior plastic deformation, due to internal back-stresses. There is a notable anelastic recovery strain (ε_{ae}) during unloading in the laminates, likely resulting from rapid plastic yielding initiated during reverse loading. This behavior suggests the presence of hetero-deformation-induced (HDI) stress (back-stress), which becomes more prominent as the number of interfaces increases.

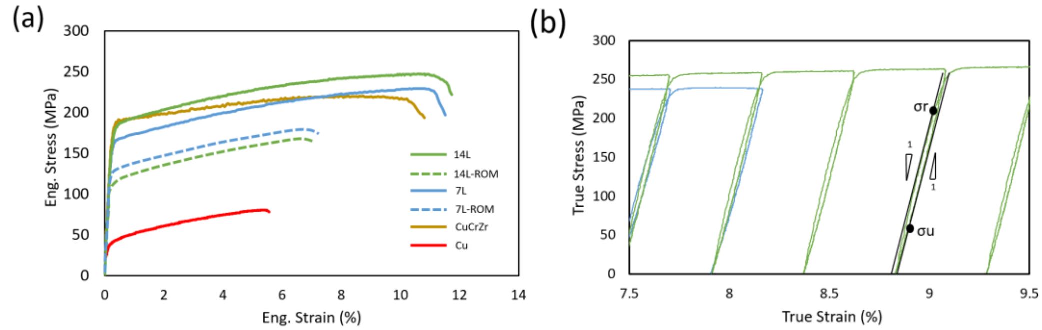

Figure 4. (a) Engineering stress–strain curves of heat-treated Cu–CuCrZr laminated alloys with 7 layers and 14 layers, alongside pure CuCrZr and pure Cu for comparison, (b) Enlarged LUR curves showing the hysteresis loops for laminates.

4. Conclusion

In summary, differences in stacking fault energy, grain size, strength, and alloying content between the Cu and CuCrZr layers lead to mechanical incompatibility during deformation. Nevertheless, the two layers are constrained to deform cohesively, resulting in stress gradients near the interface to accommodate the mismatch in deformation across the boundary. In heterogeneous materials, greater mechanical contrast between constituent layers tends to prolong the elastic–plastic transition, enhancing strain accommodation. Accordingly, the higher interface density in the 14L laminate compared to the 7L structure contributes to a more extended transition regime.

5. Acknowledgments

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