学 位 論 文 要 約

氏　　名　Mwangi Peter Ndung'u

題　　目　Development of novel oxygen-containing titanium alloys with enhanced strength and ductility

Environmental concerns regarding carbon dioxide (CO_2) emissions necessitate the development of lightweight structural materials to enhance aircraft and automobile fuel efficiency. Commercially pure titanium (CP-Ti) demonstrates exceptional potential for structural applications across automotive, medical, and aerospace sectors, due to its high specific strength, corrosion resistance, and biocompatibility. However, the inherent strength limitations of CP-Ti restrict its applications where mechanical performance is paramount. Current enhancement strategies encompass alloying with aluminum (Al), vanadium (V), iron (Fe), zirconium (Zr), oxygen (O), and nitrogen (N), complemented by post-processing methods including rolling and swaging. While these approaches augment strength, they typically deteriorate ductility. Among available options, Ti-6Al-4V dominates commercial applications due to its optimal strength-ductility balance. However, biocompatibility concerns regarding Al and V toxicity, coupled with economic constraints of V, limit broader implementation. Alternative approaches utilizing cost-effective elements, particularly O, demonstrate significant strength enhancement but compromise ductility. This study systematically investigates novel Ti alloy development through three critical objectives: (i) identification and optimization of cost-effective, non-toxic alloying elements for concurrent strength-ductility enhancement, (ii) microstructural control through optimized manufacturing processes, and (iii) quantification of synergistic effects between alloying elements and processing methods on mechanical properties.

Chapter 1 establishes the foundational understanding of Ti and Ti-based alloys, emphasizing their distinctive properties. Despite the attractive mechanical, chemical, and biomedical attribute, CP-Ti is unsuitable for load-bearing applications due to its low strength. Current enhancement methodologies encompass alloying and post-processing techniques, with alloying facilitating strength improvement through solid solution strengthening and grain refinement, albeit at the expense of ductility. Post-processing methods, particularly heat treatment, enhance ductility but introduce challenges in microstructural control and interstitial contamination. Microstructural characteristics, determined by alloying and post-processing methods, fundamentally influence mechanical properties. Laser powder bed fusion (LPBF) processes generate columnar grains which are undesirable for structural applications and rapid cooling rates promote formation of martensitic phases which are detrimental to ductility.　Elements with high growth restriction factors facilitate grain refinement. Within this context, Cu and O emerge as promising candidates for grain refinement, potentially enhancing strength while minimizing anisotropic properties in LPBFed Ti alloys. Additionally, incorporation of high Cu contents induces antibacterial properties. LPBF presents optimal characteristics for Ti-Cu-O alloy fabrication, while first-principles calculations

based on density functional theory provide theoretical framework for atomic-level interactions analysis.

In Chapter 2, investigation of LPBF-fabricated Ti-Cu-O alloys demonstrated substantial improvements in microstructure and mechanical properties compared to CP-Ti. Cu and O addition induced significant grain refinement, transforming coarse columnar grains into fine acicular grains. Additionally, microstructural characterization revealed fundamental alterations in crystallographic texture and grain boundary characteristics. As revealed by the pole figure analysis, CP-Ti exhibited strong crystal texture along the {0001} basal plane with a maximum intensity of 43.59. However, in the case of Ti-Cu-O samples, the {0001} plane was changed into various orientations with maximum intensities of Ti-0.8Cu-0.35O and Ti-1.6Cu-0.55O samples decreasing to 12.54 and 9.62, respectively, which are much lower than that of CP-Ti. The texture weakening was attributed to the formation of multiple variants during $\beta \rightarrow \alpha$ transformation. The refined microstructure observed in Ti-Cu-O alloys was due to the combined effects of growth restriction factor (Q), freezing range (ΔT), and drag effects on the migration of grain boundaries. The grain size reduction, consequently, resulted in increased length fraction of high angle grain boundaries (HAGBs). Resultant mechanical properties exhibited remarkable enhancement: Ti-0.8Cu-0.35O achieved 815 MPa yield strength with 27.1% elongation, while Ti-1.6Cu-0.55O demonstrated ultra-high yield strength of 1036 MPa maintaining 20.3% elongation. These improvements stemmed from synergistic effects of grain refinement, solid solution strengthening, and multi slip system activation evidenced by elevated work hardening rates. Fractographic analysis revealed mixed-mode fracture mechanisms with dominance of ductile failure.

Chapter 3 documented a comprehensive analysis of LPBFed Ti-Cu-O alloys, revealing significant progress in addressing the strength-ductility trade-off challenge. Through detailed microstructural and mechanical analyses, the study identified and characterized multiple strengthening mechanisms. It was established that grain refinement and solid solution strengthening from interstitial oxygen atoms were the predominant factors enhancing strength. The analysis of strengthening mechanisms revealed that contribution of O to yield strength was 327 MPa in Ti-1.6Cu-0.55O samples, markedly exceeding the 50.6 MPa contribution from Cu. The observed exceptional ductility was attributed to three primary mechanisms: multiple slip system activation, enhanced <c+a> dislocation slip activity, and increased *c/a* lattice parameter. The reduction $CRSS_{Pyramidal}/CRSS_{Prismatic}$ and $CRSS_{Basal}/CRSS_{Prismatic}$ ratios with increasing O contents increased the probability of activating pyramidal and basal slip systems during tensile deformation. Consequently, this promoted non-prismatic slip system activation, particularly prominent in grains exhibiting high Schmid factor values. Detailed quantitative analysis revealed a substantial increase in pyramidal <a> slip activity from 8% in CP-Ti to approximately 30% in Ti-Cu-O samples, underscoring the significant impact of modified CRSS ratios on deformation behavior. Importantly, the activation of pyramidal slip systems along <c+a> played a crucial role in accommodating slip along the *c*-axis and thus enhancing ductility. These discoveries represent a major advancement in understanding deformation mechanisms in Ti-based alloys and highlight the effectiveness of strategic alloying in LPBF manufacturing processes.

In Chapter 4, first-principles calculations elucidated oxygen interstitial site preferences and their effects on Ti-O alloy properties. Oxygen atoms preferentially adopted symmetrical configurations with titanium atoms, inducing lattice expansion. Octahedral sites exhibited optimal stability with minimum formation enthalpy, preserving the hexagonal close-packed (hcp) structure. Under rapid solidification conditions, oxygen atoms predominantly occupied octahedral sites, with minor crowdion site occupation, resulting in the non-equilibrium α' phase. Elastic constants analysis via Pugh's criterion demonstrated superior ductility in mixed octahedral-crowdion (O-C) configurations compared to octahedral-only arrangements. Density of states (DOS) analysis confirmed crowdion occupancy's role in mitigating oxygen-induced embrittlement, with increased states near the Fermi level indicating enhanced metallic bonding. Higher oxygen contents shifted the pseudo-gap toward the Fermi level, indicating enhanced covalent bonding a sign of high strength properties.

Chapter 5 expanded upon the Ti-O supercell structures developed in Chapter 4 by incorporating Cu atoms. Through first-principles calculations and density functional theory (DFT) analysis, critical insights were gained regarding the interactions among titanium, copper, and oxygen atoms in Ti-Cu-O alloys. The introduction of Cu and O into Ti resulted in significant modifications to both structural and elastic properties. Analysis of lattice constants demonstrated a reduction in lattice parameter a and variations in lattice parameter *c*, attributed to the combined effects of substitutional Cu atoms and interstitial O atoms. Structural investigations crowdion interstitial site occupancy by O atoms had a higher impact on crystal structure distortion than substitutional Cu atoms. Computational analysis of elastic properties indicated that Cu addition enhanced the ductility of Ti-O alloys, evidenced by an increased Pugh's ratio (*B/G*). This finding correlated directly with the improved mechanical performance of LPBFed Ti-Cu-O alloys observed in Chapter 2. Supporting evidence from density of states (DoS) analysis revealed elevated electronic states near the Fermi level in Cu-containing alloys, characteristic of enhanced metallic bonding. Additionally, the shift of the pseudo-gap toward the Fermi level in Ti-Cu-O alloys suggested covalent bond formation, contributing to increased strength. These computational results aligned with experimental observations, providing insight into the atomic-scale mechanisms responsible for enhanced mechanical properties in Ti-Cu-O alloys.

Chapter 6 examined the influence of increased Cu content (3 wt%) on the microstructure and mechanical properties of LPBFed Ti-Cu-O alloys. XRD analysis demonstrated complete solid solution of Cu and O into Ti during the LPBF process, while simultaneously confirming the presence of Ti_2Cu phases in LPBFed Ti-3Cu-xO samples. This formation of intermetallic compound was found to be directly proportional to the elevated Cu concentrations, a phenomenon attributable to the limited solubility of Cu in Ti (maximum 2.1wt%). Furthermore, despite the rapid cooling and solidification rates inherent to the LPBF process, the thermal cycling induced by laser irradiation facilitated the eutectic $\beta \rightarrow \alpha + Ti_2Cu$ transformation. The resultant microstructure displayed characteristic fine acicular grains, attributed to the synergistic effects of growth restriction factor (Q) and freezing range (ΔT) arising from Cu and O contents. Microstructural characterization identified predominantly high-angle grain boundaries (HAGBs) exceeding 82% length fraction which were attributed to grain refinement. Mechanical characterization through uniaxial tensile testing demonstrated significant property enhancement upon exceeding the Cu solubility limit. The Ti-3Cu-0.38O composition achieved optimal mechanical properties, exhibiting a yield strength of 1049±7 MPa and ultimate tensile strength of 1110±2.5 MPa. A comparative analysis of solute effects revealed that Cu additions imposed more ductility penalties relative to O content, manifested by total reduction in elongation from 27% to 9.8% as Cu content increased from 1.6 wt% to 3 wt%. This ductility deterioration was correlated with the Ti_2Cu intermetallic phases which are formed at elevated Cu contents. The magnitude of ductility reduction contrasts with first-principles calculations presented in Chapter 5, where more Cu contents enhanced ductile properties of Ti. This divergence arises because elastic properties derived from first-principles calculations are based on a perfect crystal model devoid of the defects that inherently exist in processed materials.

This research investigated the development of high-performance titanium alloys through incorporation of Cu and O using laser powder bed fusion (LPBF) process. The Ti-Cu-O alloys exhibited significant microstructural refinement, transforming from coarse columnar grains to fine acicular morphologies with random crystal orientations, thereby mitigating anisotropy. Mechanical characterization through tensile tests of Ti-Cu-O alloys demonstrated notable improvements in strength and ductility, successfully overcoming the strength-ductility trade-off.

These findings establish that controlled Cu and O additions, combined with LPBF processing, effectively produce titanium alloys with superior strength-ductility balance for structural applications.