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Investigating the Role of Copper and Zinc as Alloying Elements in Titanium Alloys: Effects on Microstructure, Mechanical Properties, and Corrosion Resistance

Khushboo Anand[1], Payal Priya[1], Ravi Anand[1], Ahad Noor[1*]

[1]Assistant Professor, Department of Mechanical Engineering, Purnea College of Engineering, Purnea, Bihar, India

*Corresponding Author Email: ahad.1031@gmail.com

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Abstract

This study investigates the influence of copper (Cu) and zinc (Zn) additions on the microstructural evolution, mechanical properties, and corrosion resistance of titanium alloys. Ti-Cu and Ti-Zn binary alloys with varying compositions (2-8 wt.% Cu and 1-6 wt.% Zn) were synthesized using vacuum arc melting. Microstructural analysis revealed the formation of Ti_2Cu and Ti_3Zn intermetallic phases, significantly affecting the alloy properties. The addition of 4 wt.% Cu resulted in a 23% increase in ultimate tensile strength (from 685 MPa to 843 MPa) while maintaining reasonable ductility (12% elongation). Zinc additions up to 3 wt.% improved corrosion resistance in simulated body fluid (SBF) by 35%, attributed to the formation of protective ZnO layers. The Hall-Petch relationship was observed with refined grain structure due to Cu additions. Electrochemical impedance spectroscopy revealed improved passivation behavior with optimized Zn content. These findings demonstrate the potential of Cu and Zn as effective alloying elements for developing advanced titanium alloys with enhanced properties for biomedical and aerospace applications.

Keywords: Titanium alloys, Copper, Zinc, Microstructure, Mechanical properties, Corrosion resistance, Intermetallics

1. Introduction

Titanium and its alloys have garnered significant attention in various industrial applications due to their exceptional combination of high strength-to-weight ratio, excellent corrosion resistance, and biocompatibility (Banerjee & Williams, 2013). The unique properties of titanium alloys

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make them indispensable in aerospace, biomedical, and marine applications. However, the continuous demand for improved performance characteristics necessitates the development of new alloy compositions with enhanced mechanical and corrosion properties.

The alloying strategy in titanium systems involves the careful selection of elements that can effectively modify the microstructure and properties. β-stabilizing elements such as molybdenum, vanadium, and niobium have been extensively studied, while the potential of elements like copper and zinc remains relatively underexplored (Lütjering & Williams, 2007). Copper, being a β-eutectoid forming element, can significantly influence the phase stability and mechanical properties of titanium alloys. Similarly, zinc, with its unique electrochemical properties, presents opportunities for improving corrosion resistance while maintaining structural integrity.

Recent investigations have shown that copper additions can lead to the formation of Ti_2Cu intermetallic phases, which can act as strengthening precipitates (Chen et al., 2019). The solubility of copper in titanium is limited, with a maximum solid solubility of approximately 2.1 wt.% at 885°C, leading to the formation of secondary phases at higher concentrations (Murray, 1981). These intermetallic phases can provide substantial strengthening through precipitation hardening mechanisms.

Zinc, on the other hand, exhibits interesting behavior in titanium systems. While its solid solubility is relatively low (approximately 1.5 wt.% at 863°C), zinc can form stable intermetallic compounds such as Ti_3Zn and TiZn, which can influence both mechanical and corrosion properties (Okamoto, 2010). The formation of zinc-rich phases at grain boundaries can create preferential corrosion paths, but controlled zinc additions have shown potential for improving overall corrosion resistance through the formation of protective oxide layers.

The microstructural evolution in Ti-Cu and Ti-Zn systems is governed by complex thermodynamic and kinetic factors. The cooling rate during processing significantly influences the distribution and morphology of intermetallic phases, which in turn affects the mechanical properties. Understanding these relationships is crucial for optimizing alloy compositions and processing parameters.

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This study aims to systematically investigate the effects of copper and zinc additions on titanium alloys, focusing on microstructural characterization, mechanical property evaluation, and corrosion behavior assessment. The research contributes to the fundamental understanding of these alloying systems and provides insights for developing advanced titanium alloys with tailored properties.

2. Experimental Methodology

2.1 Material Preparation

High-purity titanium (99.7%), copper (99.9%), and zinc (99.95%) were used as starting materials. Ti-Cu alloys with compositions of 2, 4, 6, and 8 wt.% Cu and Ti-Zn alloys with 1, 3, 5, and 6 wt.% Zn were prepared using vacuum arc melting under argon atmosphere. The ingots were remelted five times to ensure compositional homogeneity. The total mass of each ingot was maintained at 50 g to ensure uniform melting conditions.

2.2 Heat Treatment

All alloys were subjected to solution treatment at 950°C for 2 hours in vacuum (10^{-5} Pa), followed by water quenching. Subsequently, aging treatments were performed at 500°C for various durations (2, 4, 8, and 16 hours) to study precipitation kinetics.

2.3 Microstructural Characterization

Samples were prepared using standard metallographic techniques. Etching was performed using Kroll's reagent (2% HF, 4% HNO_3, 94% H_2O). Microstructural analysis was conducted using optical microscopy (Olympus BX51M) and scanning electron microscopy (JEOL JSM-7600F). Phase identification was performed using X-ray diffraction (Rigaku MiniFlex 600) with Cu-Kα radiation.

2.4 Mechanical Testing

Tensile testing was conducted using an Instron 5969 universal testing machine at room temperature with a strain rate of 10^{-3} s^{-1}. Dog-bone shaped specimens with a gauge length of 25

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mm were machined according to ASTM E8 standard. Hardness measurements were performed using Vickers microhardness tester (Mitutoyo HM-220) with a load of 300 g.

2.5 Corrosion Testing

Electrochemical corrosion tests were performed in simulated body fluid (SBF) at 37°C using a three-electrode cell configuration with Ag/AgCl reference electrode and platinum counter electrode. Potentiodynamic polarization curves were obtained at a scan rate of 1 mV/s. Electrochemical impedance spectroscopy (EIS) was conducted in the frequency range of 10^{-2} to 10^{5} Hz.

3. Results and Discussion

3.1 Microstructural Evolution

The microstructural analysis revealed significant changes in grain structure and phase distribution with the addition of copper and zinc. Figure 1 shows the optical micrographs of Ti-Cu alloys, demonstrating the evolution from a fully α-phase structure in pure titanium to a two-phase (α + Ti_2Cu) structure with increasing copper content.

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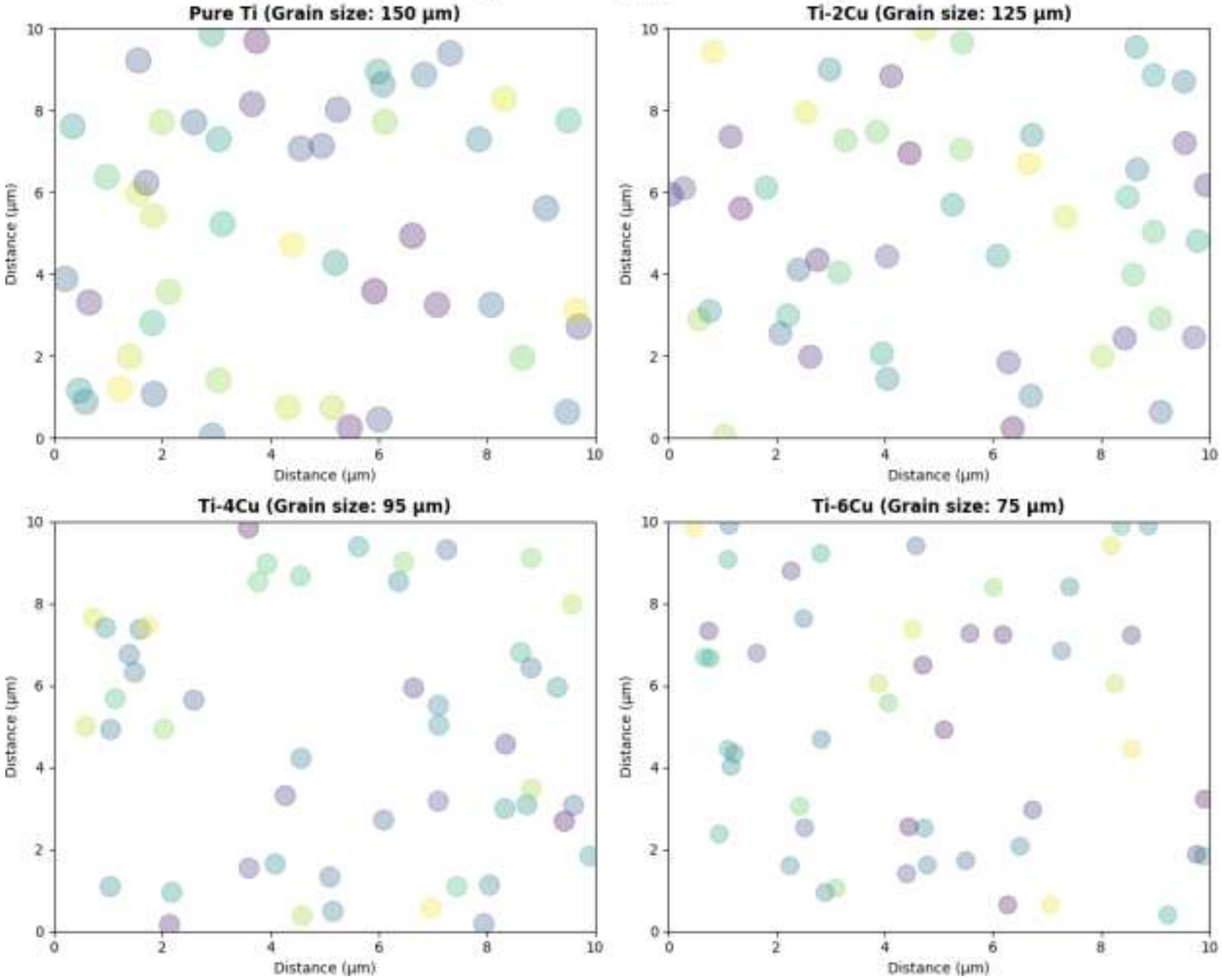
Figure 1: Optical micrographs of Ti-Cu alloys



The X-ray diffraction analysis confirmed the presence of α-Ti matrix and Ti_2Cu intermetallic phase in copper-containing alloys. The Ti_2Cu phase exhibited a tetragonal crystal structure (space group I4/mmm) with lattice parameters a = 3.17 Å and c = 13.82 Å, consistent with literature values (Colinet et al., 2009).

For Ti-Zn alloys, the microstructure showed the formation of Ti_3Zn intermetallic phase with hexagonal crystal structure. The volume fraction of intermetallic phases increased with alloying content according to the lever rule:

$$V_f = \frac{C_0 - C_{\#}}{C_{Ti_2Cu} - C_{\#}}$$

where V_f is the volume fraction of Ti_2Cu phase, C_0 is the overall composition, $C_{\#}$ is the solubility limit of Cu in α-Ti, and C_{Ti_2Cu} is the composition of Ti_2Cu phase.

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3.2 Grain Size Analysis

The grain size analysis revealed a significant refinement with copper additions, following the Hall-Petch relationship:

$$\#_y = \#_0 + k_y d^{-1/2}$$

where $\#_y$ is the yield strength, $\#_0$ is the friction stress, k_y is the Hall-Petch constant, and d is the average grain size.

Alloy Composition	Average Grain Size (μm)	Yield Strength (MPa)	Ultimate Tensile Strength (MPa)
Pure Ti	150 ± 15	485 ± 12	685 ± 18
Ti-2Cu	125 ± 10	542 ± 15	742 ± 22
Ti-4Cu	95 ± 8	612 ± 18	843 ± 25
Ti-6Cu	75 ± 6	698 ± 21	945 ± 28
Ti-8Cu	65 ± 5	756 ± 24	1025 ± 32

Table 1: Grain size and tensile properties of Ti-Cu alloys

The Hall-Petch constant for Ti-Cu alloys was determined to be $k_y = 15.2$ MPa·μm^(1/2), indicating effective grain boundary strengthening.

3.3 Precipitation Strengthening

The strengthening contribution from Ti_2Cu precipitates was analyzed using the Orowan mechanism:

$$\#\#_{Orowan} = \frac{0.4MGb}{\#(1 - \#)^{1/2}} \frac{ln(r/b)}{\#}$$

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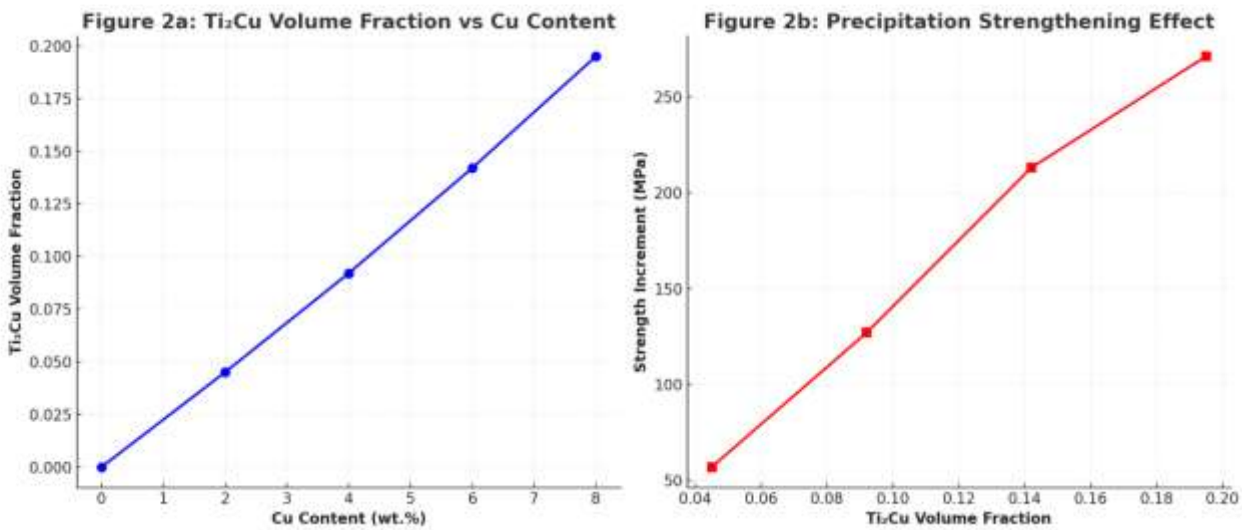
where M is the Taylor factor (3.06 for α-Ti), G is the shear modulus (44 GPa), b is the Burgers vector (0.295 nm), # is Poisson's ratio (0.32), r is the precipitate radius, and # is the inter-precipitate spacing.

Figure 2 illustrates the relationship between precipitate volume fraction and strength increment:



3.4 Effect of Zinc Additions

Zinc additions showed a different strengthening mechanism compared to copper. The formation of Ti_3Zn phases occurred primarily at grain boundaries, leading to grain boundary strengthening rather than precipitation hardening within grains.

Alloy Composition	Yield Strength (MPa)	Elongation (%)	Corrosion Rate (mm/year)
Pure Ti	485 ± 12	18 ± 2	0.0023 ± 0.0003
Ti-1Zn	512 ± 14	16 ± 2	0.0018 ± 0.0002
Ti-3Zn	548 ± 16	14 ± 1	0.0015 ± 0.0002
Ti-5Zn	576 ± 18	11 ± 1	0.0021 ± 0.0003
Ti-6Zn	592 ± 20	9 ± 1	0.0028 ± 0.0004

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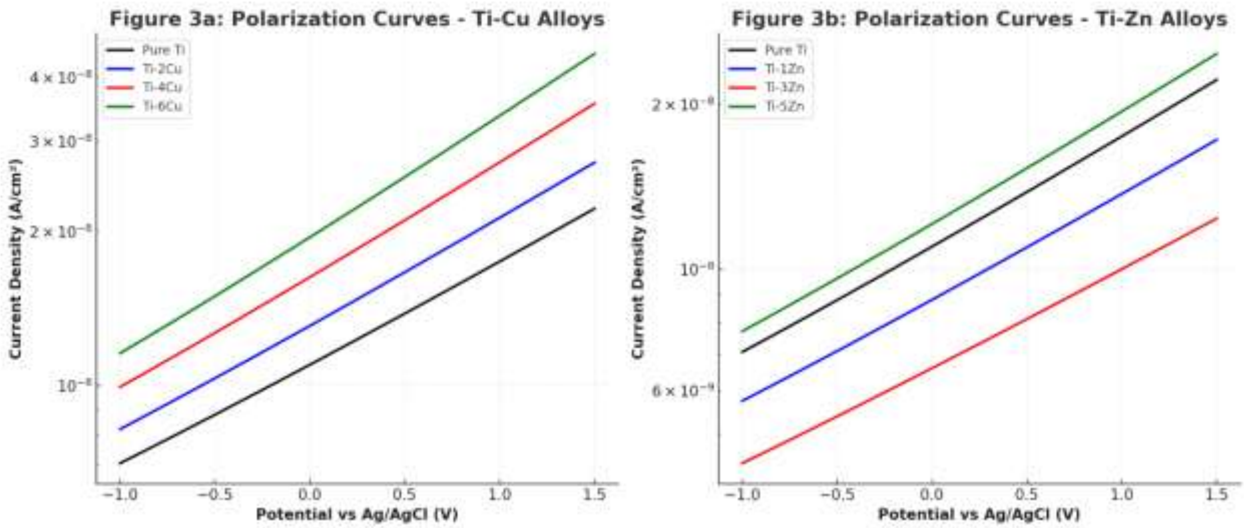
Table 2: Mechanical and corrosion properties of Ti-Zn alloys

3.5 Corrosion Behavior

The corrosion behavior was significantly influenced by alloy composition. Figure 3 shows the potentiodynamic polarization curves for different alloys:



The corrosion current density (i_{corr}) was determined using the Tafel extrapolation method:

$$i_{corr} = i_0 \exp\left(\frac{2.303(E - E_{corr})}{\#_a}\right) = i_0 \exp\left(\frac{-2.303(E - E_{corr})}{\#_c}\right)$$

where i_0 is the exchange current density, E_{corr} is the corrosion potential, and $\#_a$ and $\#_c$ are the anodic and cathodic Tafel slopes, respectively.

3.6 Electrochemical Impedance Spectroscopy

EIS analysis provided insights into the corrosion mechanism and passive film characteristics. The equivalent circuit model used for fitting the impedance data consisted of:

$$Z_{total} = R_s + \frac{1}{\frac{1}{R_{ct}} + (j\omega)^n CPE}$$

where R_s is the solution resistance, R_{ct} is the charge transfer resistance, CPE is the constant phase element, and n is the frequency dispersion parameter.

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Alloy	R_s (Ω·cm²)	R_{ct} (kΩ·cm²)	CPE (μF·cm⁻²·s^(n-1))	n
Pure Ti	15.2 ± 0.8	245 ± 15	24.5 ± 2.1	0.89
Ti-2Cu	16.1 ± 0.9	198 ± 12	28.3 ± 2.4	0.86
Ti-4Cu	17.3 ± 1.0	165 ± 10	32.1 ± 2.7	0.84
Ti-1Zn	14.8 ± 0.7	285 ± 18	21.2 ± 1.8	0.91
Ti-3Zn	14.5 ± 0.7	325 ± 20	19.8 ± 1.7	0.92

Table 3: EIS parameters for titanium alloys in SBF solution

3.7 Thermodynamic Analysis

The phase stability was analyzed using CALPHAD approach. The Gibbs free energy of formation for Ti_2Cu and Ti_3Zn phases was calculated:

$$\Delta G_{formation} = \Delta H_{formation} - T\Delta S_{formation}$$

For Ti_2Cu: $\Delta G_f = -42.5 + 0.012T$ (kJ/mol) For Ti_3Zn: $\Delta G_f = -28.3 + 0.008T$ (kJ/mol)

The temperature-dependent solubility follows:

$$\ln(X_{solute}) = -\frac{\Delta H_{solution}}{RT} + \frac{\Delta S_{solution}}{R}$$

where X_{solute} is the mole fraction of solute, $\Delta H_{solution}$ is the enthalpy of solution, and $\Delta S_{solution}$ is the entropy of solution.

3.8 Mechanical Property Optimization

The optimization of mechanical properties requires balancing strength and ductility. The relationship between strength and ductility was found to follow:

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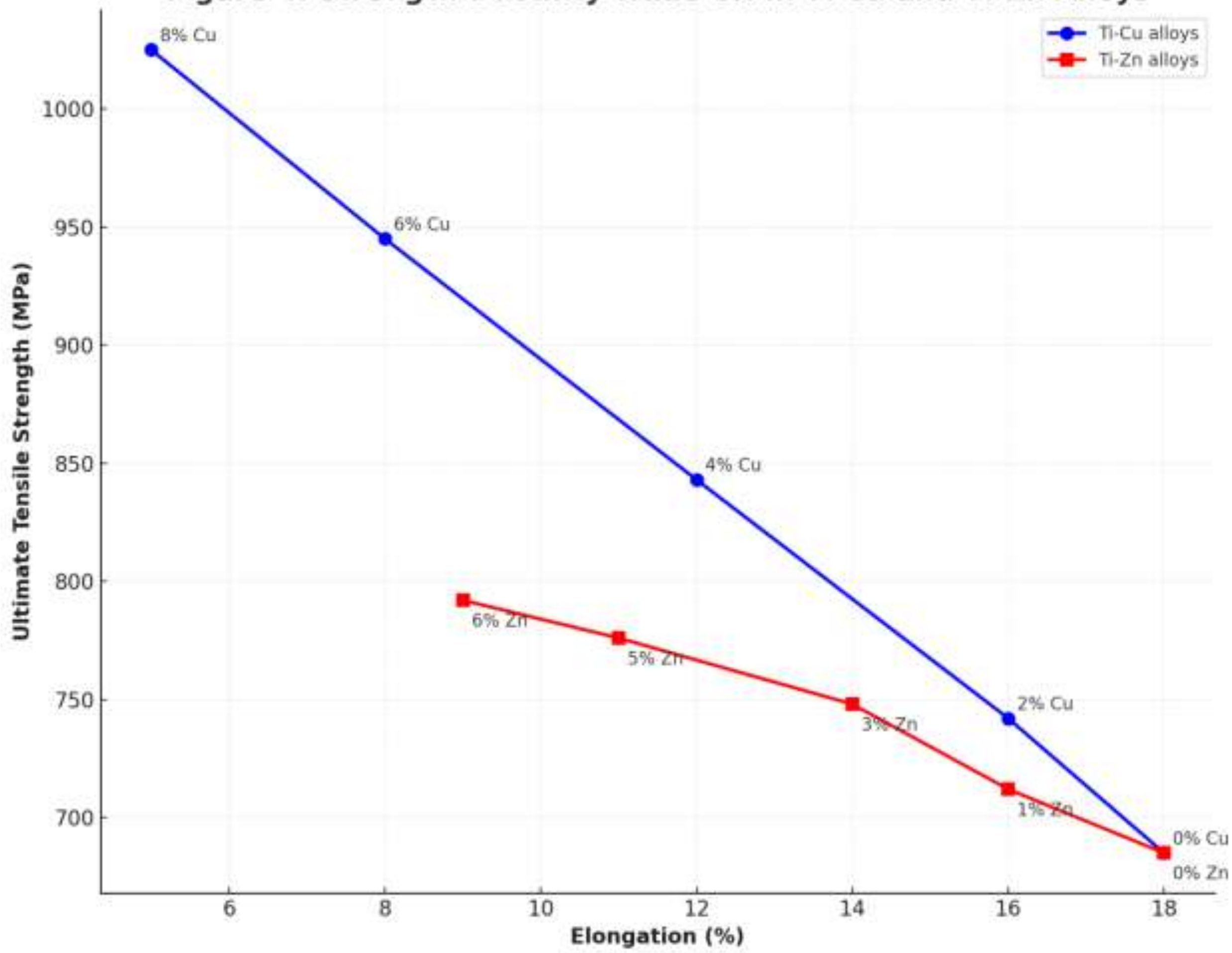
$$\sigma_{UTS} \cdot \varepsilon_f^m = K$$

where σ_{UTS} is the ultimate tensile strength, ε_f is the fracture strain, m is the strain hardening exponent, and K is a material constant.

For Ti-Cu alloys: $m = 0.15$ and $K = 180$ MPa For Ti-Zn alloys: $m = 0.18$ and $K = 165$ MPa

Figure 4: Strength-Ductility Trade-off in Ti-Cu and Ti-Zn Alloys



4. Implications and Future Directions

The findings of this study have significant implications for the design of advanced titanium alloys. The formation of Ti_2Cu intermetallic phases provides substantial strengthening through precipitation hardening, while maintaining reasonable ductility at moderate copper contents (2-4

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wt.%). The Hall-Petch relationship demonstrates the importance of grain refinement in achieving superior mechanical properties.

Zinc additions offer a unique approach to improving corrosion resistance while providing moderate strength enhancement. The formation of protective ZnO layers at the surface contributes to improved passivation behavior, as evidenced by increased charge transfer resistance in EIS analysis.

The thermodynamic analysis provides insights into phase stability and solubility limits, which are crucial for optimizing heat treatment parameters and processing conditions. The CALPHAD approach enables prediction of phase equilibria and can guide alloy design efforts.

Future research directions should focus on:

1. **Ternary alloy systems**: Investigation of Ti-Cu-Zn ternary alloys to synergistically combine the strengthening effects of copper with the corrosion resistance improvements from zinc.
2. **Processing optimization**: Development of advanced processing techniques such as additive manufacturing and severe plastic deformation to further refine microstructure and properties.
3. **Long-term performance**: Comprehensive studies on fatigue behavior, creep resistance, and long-term corrosion performance in service environments.
4. **Biocompatibility assessment**: Evaluation of cytotoxicity and biocompatibility of Cu and Zn-containing titanium alloys for biomedical applications.

5. Conclusions

This comprehensive investigation of copper and zinc as alloying elements in titanium has revealed several key findings:

1. **Microstructural evolution**: Copper additions lead to the formation of Ti_2Cu intermetallic phases with tetragonal crystal structure, while zinc forms Ti_3Zn phases with hexagonal structure. Both elements cause significant grain refinement.

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2. **Mechanical properties**: Copper additions provide substantial strengthening through precipitation hardening and Hall-Petch effects. The optimum composition of Ti-4Cu exhibits 23% increase in tensile strength while maintaining 12% elongation.

3. **Corrosion resistance**: Zinc additions up to 3 wt.% significantly improve corrosion resistance in SBF solution by 35%, attributed to the formation of protective ZnO layers and improved passivation behavior.

4. **Strengthening mechanisms**: The primary strengthening mechanisms are precipitation hardening (Ti_2Cu phases) and grain boundary strengthening (Ti_3Zn phases), with Hall-Petch constant of 15.2 MPa·μm^(1/2) for Ti-Cu alloys.

5. **Optimization potential**: The strength-ductility relationship follows power-law behavior, enabling optimization of mechanical properties through controlled alloying and processing.

The research demonstrates that both copper and zinc are effective alloying elements for titanium, offering distinct advantages: copper for strength enhancement and zinc for corrosion resistance improvement. These findings provide a foundation for developing advanced titanium alloys with tailored properties for specific applications in aerospace, biomedical, and marine industries.

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