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REVIEW

Synergistic Enhancement in Strength and Electrical Conductivity of Cu-Ti Alloys: Composition Design, Microstructure, and Processing

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Abstract: Cu-Ti alloys, owing to their excellent mechanical strength, have been widely applied in aerospace, electrical engineering, and rail transit. However, issues including relatively low electrical conductivity (EC), Ti element segregation, oxidation, and discontinuous precipitation have constrained the enhancement of their comprehensive performance and engineering applications. This research reviewed recent progress on the evolution of microstructure and performance regulation of Cu-Ti alloys, with a focus on the analysis of the formation mechanism of precipitates and their influence on the mechanical properties and EC of the alloys. The composition design strategies, advanced preparation technologies, and thermo-mechanical treatment were also summarized. On this basis, it is proposed that constructing a heterogeneous structure with multiscale and multiphase strengthening is a feasible technical path to further improve the yield strength, ultimate tensile strength, and EC of Cu-Ti alloys through improvements in composition design, hot treatment process, and microstructure control. This work is expected to develop copper alloys with good processability, high strength, and high EC to meet the rapid development of high-end manufacturing fields such as electrical engineering and aerospace.

Key words: Cu-Ti alloy; composition design; microstructure; processing technology; properties

1 Introduction

High-strength conductive copper alloys are crucial for advanced applications in aerospace, electrical engineering, and high-speed railways^[1-5]. In general, high-strength conductive copper alloys can be classified into high-strength, high-electrical conductivity (EC) copper alloys and ultrahigh-strength elastic copper alloys. For the former alloys, they possess excellent properties, such as tensile strength exceeding 600 MPa and EC higher than 80% IACS (international annealed copper standard), and their representative systems include Cu-Ni-Si, Cu-Cr-Zr, and Cu-Fe-P. For ultrahigh-strength elastic copper alloys, tensile strengths exceeding

1000 MPa are expected for deployment in specific demanding service environments. Typical examples include Cu-Be, Cu-Ti, Cu-Ni-Sn, and Cu-Ni-Si alloys^[6-8]. Among these alloys, Cu-Ti alloys have gained significant attention due to their excellent mechanical properties, including ultrahigh strength, good ductility, and good workability. Unlike Cu-Be alloys, which exhibit excellent EC but contain toxic beryllium, Cu-Ti alloys are regarded as a promising alternative because of their non-toxic composition and outstanding high-temperature mechanical properties.

Despite their advantages, Cu-Ti alloys face significant challenges, particularly in balancing high strength and EC. Cu-

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Ti alloys are typical spinodal-decomposed copper alloys^[9-13], whose main strengthening mechanism is precipitation strengthening. Nanoscale β' -Cu₄Ti phases form in the copper matrix, significantly enhancing the mechanical properties. However, an increase in Ti content leads to a severe degradation of EC, which is attributed to the presence of excessive solute atoms and intermetallic phases that scatter conduction electrons. Additionally, Ti segregation, oxidation, and the formation of discontinuous precipitates at grain boundaries pose additional obstacles to alloy processing and performance optimization.

To address these challenges, recent studies have explored various approaches, including alloy composition adjustment, heat treatment optimization, and microstructure engineering. The core of these methods is to minimize residual Ti content while maximizing the introduction of strengthening microstructures. Notably, the design of heterogeneous structures has emerged as a promising strategy to achieve simultaneous enhancement of strength and EC in Cu-Ti alloys. Through multiphase synergistic strengthening, these structures introduce a controlled distribution of precipitates, refined grain structures, and improved solute partitioning to optimize the material properties.

This review provided a comprehensive overview of the latest progress in Cu-Ti alloys, focusing on microstructure evolution, strengthening and conduction mechanisms, preparation methods, and heat treatment strategies. Special attention is paid to the design and control of heterogeneous structures to overcome the traditional strength-conductivity trade-off. Finally, the future research directions and potential industrial applications of Cu-Ti alloys were discussed, providing insights for their further development.

2 Microstructure of Cu-Ti Alloys

Cu-Ti alloy is a typical precipitation-strengthened Cu-based

alloy, and its excellent mechanical properties are closely related to its microstructure. Fig. 1 shows the typical morphological characteristics of Cu-Ti alloys at different aging stages. It is worth noting that these micrographs indicate at least two precipitated phases in the alloy: continuous precipitates distributed within the grains and discontinuous precipitates formed near the grain boundaries. The evolution of the size, volume fraction, and distribution of these precipitated phases throughout the heat treatment process has a significant impact on the mechanical properties and EC of the alloy. In addition, the grains of the alloy exhibit an equiaxed morphology, and there is no significant growth during the aging heat treatment. The migration of the interface is more prominently manifested as the continuous invasion of the reaction front of the cellular structure into the parent grains. A stable grain boundary structure is of great significance for the mechanical properties of Cu-Ti alloy at high temperatures, such as excellent stress-relaxation resistance^[15].

Precipitated phases play a crucial role in determining the mechanical and EC properties of aging-hardened Cu-based alloys. According to the binary phase diagram of the Cu-Ti alloy (Fig. 2), various precipitated phases are formed during the solution and aging processes of Cu-Ti alloys, including β' -Cu₄Ti (also known as α -Cu₄Ti) and β -Cu₄Ti. It is worth noting that a crystal-type transformation occurs between 400 and 500 °C, i.e., when the aging temperature is lower than 400 °C, the precipitated phase is β' -Cu₄Ti, and when the aging temperature is higher than 500 °C, β -Cu₄Ti forms. Currently, it is generally believed that during heat treatment, the Cu-Ti alloy undergoes spinodal decomposition and forms a metastable β' -Cu₄Ti phase for strengthening^[16-20]. This coherent phase forms a body-centered tetragonal (bct) structure with lattice constants of $a=b=0.584$ nm and $c=0.362$ nm, and the orientation relationship with the matrix is $(100)_\alpha // (310)_\beta$ and

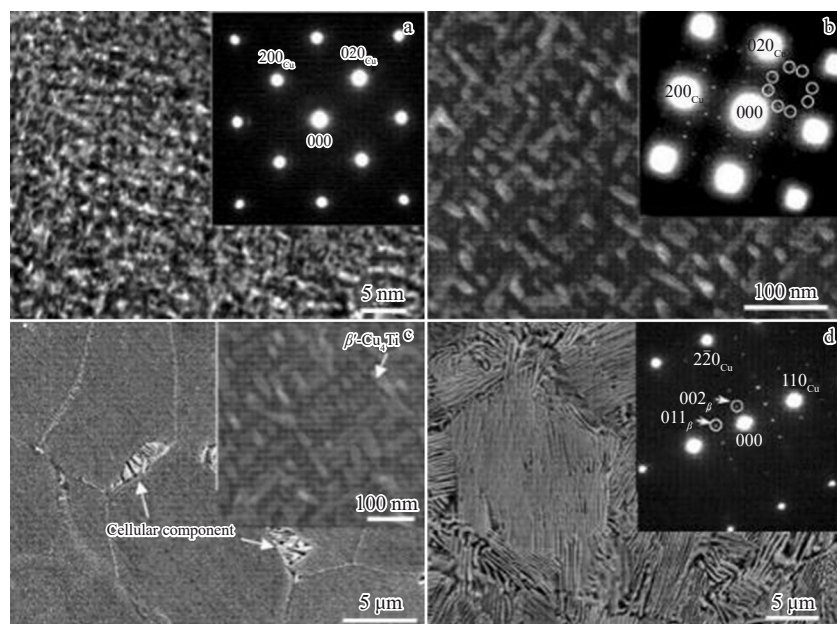


Fig. 1 Morphologies of Cu-4Ti alloy after aging at 450 °C for different time^[14]: (a) 60 min; (b) 180 min; (c) 1440 min; (d) 2880 min

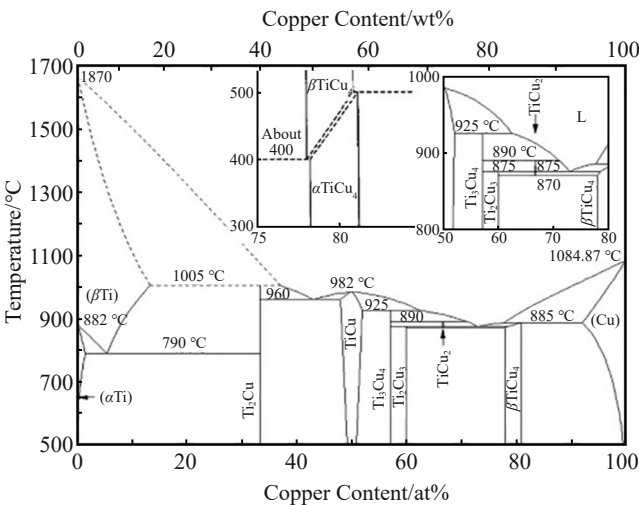


Fig.2 Binary phase diagram of Cu-Ti alloy^[5]

$[001]_a/[001]_b$ ^[19,21]. Meanwhile, it is usually distributed spherically or rod-shaped within the alloy grains, as shown in Fig. 3. At the same time, its distribution in the matrix can consume excessive Ti solute atoms, thereby reducing electron scattering and increasing EC. The volume fraction and size of β' -Cu₄Ti also play a key role in determining the properties of Cu-Ti alloys. Studies show that increasing Ti content promotes the precipitation reaction, resulting in a higher fraction of β' -Cu₄Ti and thus a greater strengthening effect^[22–25]. However, a high Ti content also leads to a sharp decline in EC. It must be admitted that differences in preparation techniques and heat treatment also affect the characteristics of the β' -Cu₄Ti phase. As shown in Table 1, the size and volume fraction of the precipitates are closely related to the composition and heat-treatment process. In general, lower temperatures are more favorable for controlling the precipitate size, while the combination of deformation processing and heat treatment is beneficial for achieving a higher precipitate volume fraction. The size and volume fraction of the β' -Cu₄Ti phase are appro-

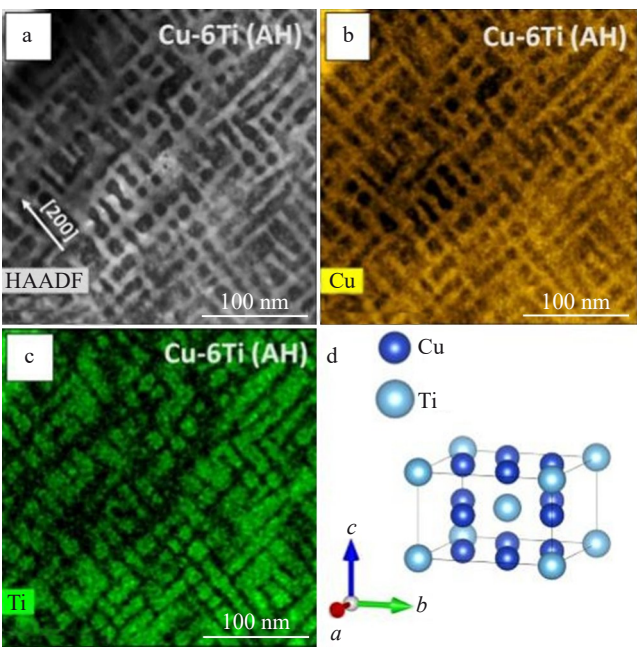


Fig.3 Analysis of β' -Cu₄Ti phase in aged Cu-6Ti (wt%) alloys^[18]: (a) high angle annular dark field (HAADF) image; (b) distribution of Cu; (c) distribution of Ti; (d) schematic diagram of crystal structure

ximately 20 nm and 15%, respectively. For Cu-Ti alloys, the cellular structure at grain boundaries also needs attention, especially under high-temperature or long-term aging conditions. Due to its discontinuous changes in composition and structure relative to the matrix at the interface, it is also referred to as discontinuous precipitates in some studies. The structure and composition of these cellular structures are quite different from the β' -Cu₄Ti phase. It contains the thermodynamically stable β -Cu₄Ti phase and α -Cu phase, with the two phases stacked alternately to form a structure similar to pearlite, as shown in Fig.3d. The β -Cu₄Ti

Table 1 Size and volume fraction of β' -Cu₄Ti phase in different Cu-Ti alloys

Alloy/wt%	Heat treatment process	Size/nm	Volume fraction/%	Ref.
Cu-2Ti	60% cold rolling (CR)+500 °C/1.85 h+60% CR+500 °C/0.74 h	33.4	41	[26]
Cu-2.57Ti-0.35Cr-0.11Mg-0.04Si	85% CR+400 °C/1 h+90% CR+380 °C/6 h+95% CR+360 °C/28 h	20	15.3	[27]
Cu-2.7Ti-0.2Fe	80% CR+450 °C/0.5 h+50% CR+400 °C/0.5 h+50% CR+350 °C/1h	23	16.1	[19]
Cu-2.7Ti-1Fe	80% CR+450 °C/0.5 h+50% CR+400 °C/0.5 h+50% CR+350 °C/1 h	20	12	[19]
Cu-3Ti	95% CR+450 °C/1 h	15	3	[11]
Cu-3Ti-1Cr	50% CR+500 °C/2 h	17	12.6	[28]
Cu-3.2Ti-0.2Fe-0.2V	400 °C/2 h+5% CR+450 °C/4 h	27.1	16.5	[29]
Cu-3.3Ti	400 °C/1 h+70% CR+400 °C/20 h	12	7.49	[30]
Cu-3.5Ti-0.2Fe	450 °C/2 h	3.38	39	[31]
Cu-4.8Ti	20% CR-315 °C/2 h-20% CR-350 °C/2 h	5.1	10.89	[32]
Cu-4.8Ti	20% CR-315 °C/2 h-20% CR-315 °C/2 h	3.8	13.44	[32]
Cu-4.8Ti	20% CR-350 °C/2 h-20% CR-315 °C/2 h	4.3	12.57	[32]
Cu-6Ti	450 °C/2 h	8.6	55	[17]
Cu-6.3Ti-0.34Cr-0.16Mg	60% CR+450 °C/0.5 h	25	47.8	[33]

phase was determined as the orthorhombic structure with lattice constants of $a=0.4528$ nm, $b=0.4345$ nm, and $c=1.2932$ nm, and it exhibits an orientation relationship of $(111)_\alpha // (010)_\beta$ and $[110]_\alpha // [001]_\beta$ with the matrix^[19,24]. Fig. 4 shows the lattice structure of the β -Cu₄Ti phase and its interface with the α -Cu phase. It should be noted that although the β phase maintains a certain coherent relationship with the α phase, the local mismatch (indicated by the yellow arrow) likely acts as a crack initiation site under load, resulting in unsatisfactory mechanical properties^[17]. Therefore, the optimization of the composition of Cu-Ti alloys and the control of heat-treatment parameters usually aim to reduce or suppress the formation of cellular structures. In addition, in some studies, the Ti-rich phase of the cellular structure has also been identified as the β -Cu₃Ti phase, which has an orthorhombic structure with lattice constants of $a=0.517$ nm, $b=0.435$ nm, and $c=0.452$ nm^[25].

More than half a century ago, Sato et al^[34] reported the transformation of spherical particles to a lamellar shape in Cu-Ti alloys. Subsequently, Datta et al^[35] summarized the precipitation sequence of Cu-Ti alloys as follows: supersaturated solid solution $\rightarrow$ wavy spinodal structure $\rightarrow$ β' -Cu₄Ti phase $\rightarrow$ β -Cu₃Ti phase. After high-temperature holding and quenching, the Ti element has no time to precipitate and forms a supersaturated solid solution. After aging at 400–600 °C, Ti gradually aggregates and finally forms a precipitated phase. The precipitation behavior of Cu-Ti alloys mainly involves the periodic aggregation of Ti atoms. In the early stage of aging, Cornie et al^[36] found that Ti atoms aggregated and grew along the $\langle 100 \rangle$ direction of the matrix to form typical wavy stripes, and then the β' -Cu₄Ti phase was formed in situ. Many subsequent studies also reported the spinodal decomposition in Cu-Ti alloys^[9,12,19,37–38]. Semboshi et al^[14] drew the time-temperature transformation (TTT) diagram of Cu-Ti alloys, as shown in Fig. 5. They believed that the decomposition process of Cu-Ti alloys in the temperature range of 400–700 °C follows the following sequence: spinodal decomposition generates Ti-rich regions, needle-like β' -Cu₄Ti

phase is formed, discontinuous precipitates of lamellae containing the β -Cu₄Ti phase occur, and stable equilibrium β -Cu₄Ti phase is formed. However, with the development of detection techniques, new views on the formation mechanism of precipitated phases have emerged. For example, Laughlin et al^[12] observed evidence of spinodal decomposition and ordering in a solution-quenched Cu-5.17Ti (wt%) alloy, but no evidence of ordering was observed in a Cu-3.08Ti (wt%) alloy. Their research shows that when the Ti content in the Ti-rich region reaches a certain level, the ordering transformation is initiated. Batra et al^[39] pointed out that the N_3M phase is formed after spinodal decomposition, which is a transition phase and is replaced by the metastable β' -Cu₄Ti phase during subsequent aging. Wei et al^[40–41] believed that the phase transformation includes two completely different processes: spinodal decomposition and the growth of spinodal structure. In addition, some studies propose a catastrophic nucleation theory to explain precipitation in the early stage of aging in the Cu-0.9Ti (at%) alloy, which is characterized by critical nuclei of several atomic sizes and extremely low nucleation barriers^[42]. Due to the very rapid spinodal decomposition of Cu-Ti alloys, especially those with high Ti content, rapid quenching alone cannot prevent the decomposition. Until now, there is still a lack of in-situ observation of the decomposition process and ordering, and further exploration of the phase transformation process is needed.

3 Strengthening and Conductive Mechanisms of Cu-Ti Alloys

3.1 Strengthening mechanisms

After a series of heat treatments, the yield strength (YS) σ_y of the Cu-Ti alloys will increase significantly, even exceeding 1000 MPa. This strength increase can be attributed to the combined effect of various strengthening mechanisms, including solid solution strengthening ($\Delta\sigma_{ss}$), fine-grain strengthening ($\Delta\sigma_{GB}$), work hardening ($\Delta\sigma_{dis}$), and precipitation strengthening ($\Delta\sigma_{pre}$). The combined effect of the above-mentioned mechanisms increases the mechanical strength of

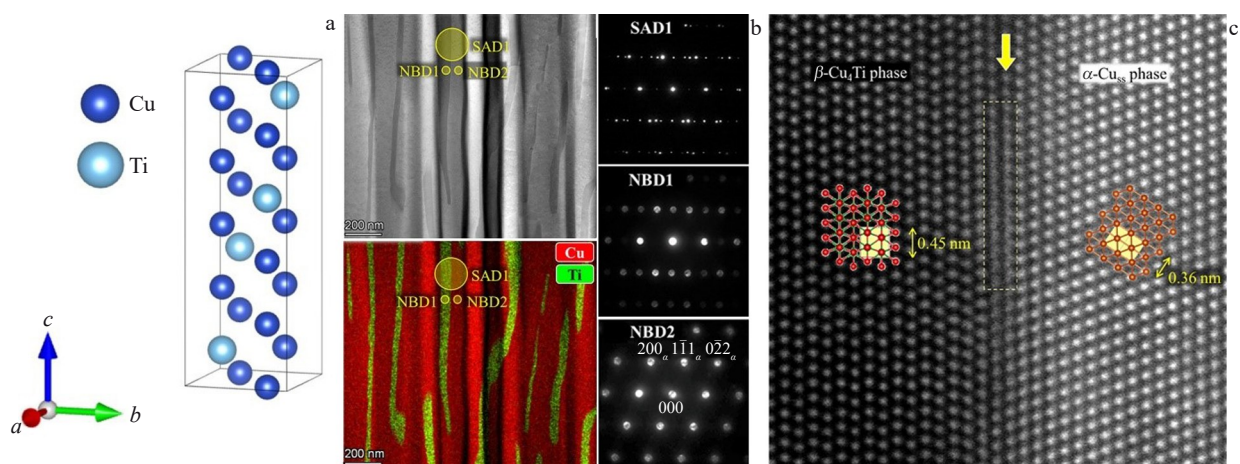
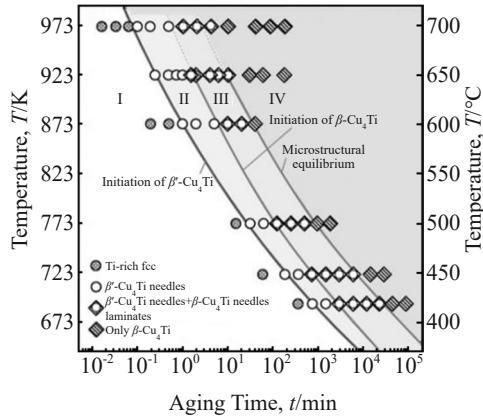


Fig.4 Analysis of β -Cu₄Ti phase in Cu-4Ti (wt%) alloys^[17]: (a) schematic diagram of crystal structure; (b) element distributions; (c) interface between α and β phases

Fig.5 TTT diagram of Cu-4Ti (at%) alloy^[14]

the Cu-Ti alloy, as expressed by Eq.(1)^[5,11,31,43]:

$$\sigma_y = \sigma_0 + \Delta\sigma_{ss} + \Delta\sigma_{GB} + \Delta\sigma_{dis} + \Delta\sigma_{pre} \quad (1)$$

where σ_0 is the strength of the copper matrix (about 60 MPa)^[11,31].

Solid solution strengthening is related to a small number of solute atoms added to the alloy, mainly including unprecipitated Ti atoms and other deliberately added trace elements. Due to the difference in atomic size between the solute atoms and the copper matrix, this mismatch creates lattice distortion and forms a local stress field in the matrix. These stress fields enhance the YS of the alloy by pinning dislocations and increasing the resistance to dislocation movement. However, due to the strong scattering effect of point defects on electrons, the introduction of solid solution atoms will significantly reduce the EC of Cu-Ti alloys. In most cases, the types and amounts of solid-solution elements must be strictly controlled. Commonly used solid solution elements include Mg, Ca, Sn, Cd, Ag, Zn, and Ni. The increase in strength caused by solid solution strengthening can be expressed as the sum of the contributions of different components, as expressed by Eq.(2)^[31,44-46]:

$$\sigma_{ss} = \sum MG \frac{\epsilon_s^2 c^{\frac{1}{2}}}{700} \quad (2)$$

where M is the Taylor factor, G is the shear modulus, ϵ_s is the mismatch strain caused by the lattice distortion of adjacent solutes, and c represents the concentration of solute atoms. For precipitation-strengthened Cu-Ti alloys, the strength increase from solid-solution strengthening is usually only a few dozen megapascals.

Grain refinement strengthening mainly improves the strength of the alloy by increasing the grain-boundary density. Due to the orientation difference on both sides of the interface, dislocations are strongly hindered when passing through the grain boundary, and this manifests as an increase in the strength of the alloy. The strengthening effect of grain boundaries can be described by the Hall-Petch relationship, as expressed by Eq.(3)^[5,31]:

$$\Delta\sigma_{GB} = k_{GB} d^{-\frac{1}{2}} \quad (3)$$

where k_{GB} is the Hall-Petch coefficient (also regarded as the

resistivity of grain boundaries to dislocations); d is the average size of equiaxed grains. Generally, the smaller the grain size of the alloy, the higher the grain-boundary density and the more obvious the strengthening effect. It is worth mentioning that special subgrain boundaries, twin boundaries, and phase interfaces have also been shown to follow the above relationship^[47-50].

Work hardening originates from the dislocations generated during plastic deformation. The dislocations introduced by plastic deformation interact to form complex substructures, including dislocation tangles, dislocation walls, and dislocation cells. These substructures significantly increase the resistance to dislocation movement, making the deformation more difficult and thereby increasing the YS of Cu-Ti alloys, which manifests as the work-hardening effect. However, due to the generation of a high-density dislocation structure, work hardening will lead to a decrease in the plasticity of the alloy. At the same time, due to its unstable high-energy state, the thermal stability of the alloy will also be affected. The contribution of work hardening is directly related to the dislocation density, as expressed by Eq.(4)^[5,11,31]:

$$\Delta\sigma_{dis} = M\alpha G b \rho^{\frac{1}{2}} \quad (4)$$

where α is a constant, and ρ represents the dislocation density. Traditional plastic deformation processes, such as CR and cold drawing, can conveniently and efficiently improve the strength of the alloy, and these processes have almost no impact on the EC of the alloy. Therefore, these strengthening methods have been widely used in industrial production.

Precipitation strengthening is mainly achieved by nano-precipitates formed during the aging process. Excessive Ti atoms are added to pure copper, and after high-temperature solution treatment, quenching treatment is carried out to ensure a supersaturated solid solution. Then, aging treatment is carried out at a lower temperature to form a large number of nanoscale precipitates that are uniformly distributed in the alloy matrix. These nano-precipitates can effectively impede the movement of dislocations and grain boundaries, thus greatly increasing the strength of the alloy. The strengthening effect of the precipitates can usually be explained by the Orowan mechanism, as expressed by Eq.(5)^[31,51]:

$$\Delta\sigma_{pre} = \frac{0.81 M G b}{2\pi(1-\nu)^{\frac{1}{2}}} \times \frac{\ln(d_p/b)}{\lambda} \quad (5)$$

where b is the value of the Burgers vector (0.255 nm for Cu), ν is the Poisson's ratio (0.34), d_p is the average size of the precipitates, and λ represents the distance between the precipitates. Furthermore, considering the shape, structure, and distribution of the precipitates, as well as their orientation relationship with the matrix, the above relationship can be further optimized. For example, Yang et al^[5] calculated the strength changes when disc-shaped precipitates with different thicknesses were parallel or perpendicular to the slip plane, as shown in Fig.6. Precipitate thickness has a significant impact on the strength increase. When the thickness is less than 0.5 nm, the strength increase can exceed 1200 MPa. At the same

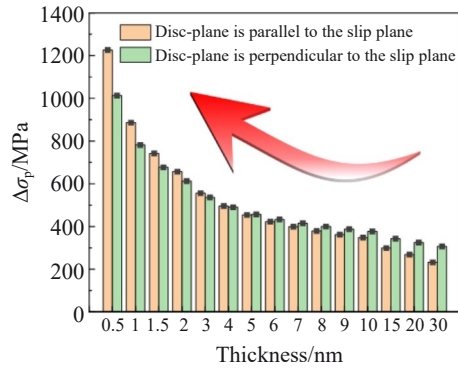


Fig.6 Relationship between YS increment and thickness of disc-like δ -Ni₂Si with different growth ways (d_p and f_v are 8 nm and 0.14%, respectively)^[5]

time, it can also be found that when the thickness is less than 4 nm, the precipitates parallel to the slip plane can provide a greater strength increase than those perpendicular to the slip plane; the opposite occurs when the thickness exceeds 4 nm.

Overall, the abovementioned several strengthening mechanisms quantitatively describe the relationship between the parameters of the microstructure and the strength of Cu-Ti alloys; their essence is that dislocations experience varying resistivity during plastic deformation. Xu et al^[31] studied the aging behavior of the Cu-Ti-Fe alloy and calculated the contribution of each mechanism to YS, as shown in Fig. 7. In the cold-rolled alloy, work hardening is the main strengthening mechanism, accounting for more than 72% of the strengthening effect. For the peak-aged alloy, work hardening still provides approximately 30% increase in strength, and the precipitates with a size of approximately 3.4 nm contribute more than 46% of the peak-aged strength. The combined action of the four strengthening mechanisms increases strength by approximately 980 MPa, which is consistent with the experimental results.

3.2 Conductive mechanism

As a typical face-centered cubic alloy, the plastic deformation mechanism of the Cu-Ti alloy is still mainly dominated by dislocation motion. The essence of various strengthening mechanisms is to introduce a large number of defects to hinder the migration and movement of dislocations by adjusting the alloy composition or microstructure. However, these defects will inevitably lead to an increase in

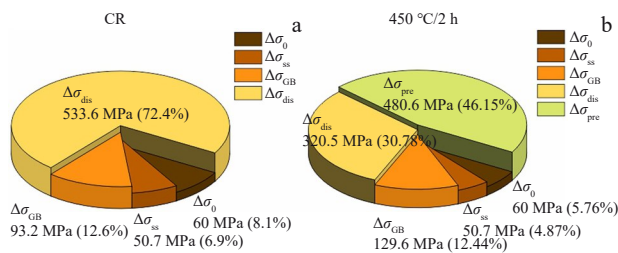


Fig.7 Statistical results of the contribution of different strengthening mechanisms to the strength of Cu-3.5Ti-0.2Fe (wt%) alloy^[31]: (a) CR alloy; (b) alloy after 450 °C/2 h treatment

electron scattering, thus reducing the EC of the alloy. According to Matthiessen's theorem, the total resistivity (ρ_{total}) of Cu-Ti alloys can be calculated by adding the resistivity caused by various defects:

$$\rho_{total} = \rho_0 + \rho_{ss} + \rho_{GB} + \rho_{dis} + \rho_{pre} \quad (6)$$

where ρ_0 is the electrical resistivity of the copper matrix; ρ_{ss} , ρ_{GB} , ρ_{dis} , and ρ_{pre} represent the increase in electrical resistivity caused by solute atoms, grain boundaries, dislocations, and precipitates, respectively.

The increase in electrical resistivity caused by solute atoms is significant. The main reason is that solute atoms disrupt the periodicity of the Coulomb potential field of the metal lattice, becoming the primary source of electron scattering. This effect (ρ_{ss}) can be expressed by Eq.(7):

$$\rho_{ss} = K_{ss}c \quad (7)$$

where c is the solid solution atom concentration; K_{ss} represents the increase in resistivity for every 1at% increase in solid-solution atoms. Studies show that the resistivity of copper alloys has a linear relationship with the solid-solution concentration of alloying elements, as shown in Fig. 8, and that the effects of different elements on resistivity vary significantly. It is worth noting that the Ti has the largest proportionality coefficient (about 160 nΩ·m/wt%)^[27], which means that even trace Ti in solid solution can significantly reduce the EC of Cu alloys. Therefore, in the design and optimization of Cu-Ti alloys, reducing the solid-solution concentration of Ti in the matrix has become a key strategy to improve EC. For example, promoting Ti precipitation through heat treatment or reducing Ti content by controlling composition can effectively reduce the resistivity increase caused by solid-solution Ti atoms.

As a type of defect, grain boundaries also disrupt the periodicity of the copper lattice. Their presence enhances electron scattering and increases the electrical resistivity of alloys. The grain boundary-induced resistivity increment (ρ_{GB}) can be calculated by the following formula:

$$\rho_{GB} = \frac{2}{3} K_{SGB} \frac{S}{V} \quad (8)$$

where K_{SGB} is the resistivity of the grain boundary; S/V represents the surface area of the grain boundary per unit

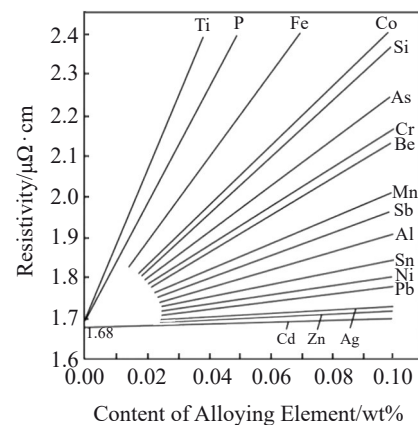


Fig.8 Effect of solute atoms on the resistivity of copper alloys^[52]

volume. The result shows that the resistivity of the grain boundary is inversely proportional to the grain size. The smaller the grain size, the greater the resistivity of the grain boundary. For example, the study found that when the grain size is reduced to tens of nanometers, the resistivity of pure copper increases by at least one order of magnitude^[47]. The influence of the grain boundary on the resistivity is not only closely related to the grain size but also significantly affected by the characteristics of the grain boundary and the direction of electron movement. Specifically, irregular atomic arrangements and changes in chemical composition at the grain boundary, such as solute segregation or impurity enrichment, further enhance the electrons scattering and significantly increase the resistivity. In addition, the grain-boundary resistivity exhibits obvious anisotropic characteristics: when a grain boundary is perpendicular to the electron-flow direction, its contribution to the resistivity is much greater than that of a grain boundary parallel to the electron-flow direction. This is because the perpendicular grain boundary can more effectively disrupt the electron transport path and increase the scattering probability. During the processing, the grain morphology and orientation of the material will further affect the grain-boundary resistivity. For example, in the cold-deformed Cu alloy, the grains are elongated along the processing direction, and the grain boundaries tend to align parallel to the direction of electron movement, thus reducing the contribution of the grain boundary to the resistivity. This phenomenon indicates that by optimizing the processing technique, the adverse effects of the grain boundary on the resistivity can be effectively reduced, and the EC of the material can be improved.

The influence of dislocations on resistivity stems from their scattering effect on electrons. In metals, the movement paths of electrons are disrupted by the local lattice distortion near the dislocation lines, leading to an increase in resistivity. However, compared with two-dimensional defects such as grain boundaries and phase boundaries, dislocations are linear defects. Their local lattice distortion range is relatively small, and the affected area is limited. Therefore, their contribution to electron scattering is weak. In addition, the effect of dislocations becomes more obvious with the increase in density. But due to the possible mutual shielding effect between dislocations, when the density reaches a certain level, the increase in resistivity tends to stabilize. The contribution of dislocations to resistivity (ρ_{dis}) can be calculated by the following formula:

$$\rho_{\text{dis}} = K_{\text{dis}} \rho \quad (9)$$

where K_{dis} is the dislocation resistivity (about $2 \times 10^{-25} \Omega \cdot \text{m}^3$), and ρ is the dislocation density. Actually, the effect of dislocations on resistivity is also related to the distribution morphology of dislocations. Dislocations with high density and uniform distribution may lead to more significant electron scattering, while non-uniformly distributed dislocations may cause enhanced local scattering. Therefore, controlling the dislocation density while ensuring high strength to reduce the

adverse impact on EC is a key issue in the design of Cu-Ti alloys.

The influence of precipitates on the resistivity of Cu-Ti alloys is mainly reflected in two aspects: interfacial electron scattering and changes in solute element concentration. When the content of precipitates is low and the size is small, the resistivity change (ρ_{pre}) can be calculated by Eq.(10)^[53]:

$$\rho_{\text{pre}} = 3nf_v(\rho_{\text{Cu}} + \rho_{\text{pre}}) - 3n^2 f_v^2 \frac{\rho_p(\rho_{\text{pre}} + 3\rho_{\text{Cu}})}{\rho_{\text{Cu}} + 2\rho_p} \quad (10)$$

where f_v is the volume fraction of the precipitated phase, ρ_{Cu} is the resistivity of Cu, ρ_p is the resistivity of the precipitated

phase, and $n = \frac{\rho_p - \rho_{\text{Cu}}}{2\rho_p + \rho_{\text{Cu}}}$. The interface between the

precipitated phase and the matrix will increase electron scattering due to lattice mismatch and chemical discontinuity. At the same time, the formation of the precipitated phase can reduce the solute concentration in the matrix and decrease lattice distortion, thus effectively reducing the electrical resistivity. In fact, since precipitation is a continuous process, it is usually difficult to determine the states of all precipitated phases in experiments^[7], which makes it difficult to directly fit the functional relationship between electrical resistivity and precipitated phases from experimental results. Therefore, subtraction is mostly used in research to determine the effect of precipitated phases on the EC of alloys.

4 Composition Design of Cu-Ti Alloys

Cu-Ti alloys have a wide range of applications in fields such as electronics, aerospace, and power engineering due to their excellent mechanical properties and good EC. However, the EC of Cu-Ti alloys is usually affected by the solid solution effect of the Ti element, which restricts their application in some cases with high EC requirements. In order to optimize the comprehensive properties of Cu-Ti alloys, researchers regulate their microstructure, phase transformation behavior, and mechanical properties by introducing various alloying elements. The effects of different alloying elements on the properties of Cu-Ti-X alloys are summarized in Table 2. Ultimate tensile strength (UTS) of different alloys is also compared. The introduction of these alloying elements exerts a multidimensional regulatory effect on alloy performance. On the one hand, they significantly enhance the mechanical properties of the alloy and balance the strength-plasticity trade-off. On the other hand, Cu-Ti alloys have achieved enhanced EC through compositional regulation. Different alloying elements play distinct roles, including promoting the formation of precipitates, refining grains, inhibiting the formation of discontinuous precipitates, and regulating the phase-transformation behavior of the alloy. By rationally designing the alloy composition, a better balance between mechanical properties and EC can be achieved to meet the needs of different application scenarios.

Although Ti is the primary strengthening element and provides pronounced solid-solution strengthening, its adverse influence on EC cannot be neglected. Table 3 summarizes the

Table 2 Performance comparison of Cu-Ti-X (wt%) alloys

Alloy	Microhardness/HV	YS/MPa	UTS/MPa	Elongation/%	EC/% IACS	Ref.
Cu-6Ti-0.3Fe	350	975	1080	17.0	9.0	[17]
Cu-2.7Ti-1Fe	-	935	1057	2.2	26.4	[19]
Cu-2.7Ti-0.2Fe	-	1068	1127	2.5	20.3	[19]
Cu-4.5Ti-0.5Co	320	710	890	25.0	8.0	[22]
Cu-4.5Ti-0.9Co	310	610	795	19.0	10.0	[22]
Cu-4.5Ti-1.8Co	250	575	745	16.0	14.2	[22]
Cu-3Ti-2Mg	261	-	-	-	12.7	[54]
Cu-3Ti-2Mg	328	-	-	-	16.7	[55]
Cu-3Ti-0.1Zr	266	674	802	29.0	14.1	[56]
Cu-4Ti-0.1Zr	301	741	846	24.0	13.5	[56]
Cu-4Ti-1Al	255	-	-	-	13.0	[57]
Cu-3Ti-2Sn	135	-	-	-	39.8	[58]
Cu-3Ti-0.2Fe-1Sn	310	-	-	-	18.6	[59]
Cu-3Ti-1Cr	339	1033	1292	8.0	12.0	[28]
Cu-3Ti-1Cr	277	721	854	21.0	13.0	[60]
Cu-4.5Ti-1Cr	326	849	968	21.0	9.0	[60]
Cu-3Ti-1Ni	205	-	-	-	18.2	[61]
Cu-3Ti-5Ni	187	-	-	-	31.3	[61]

Table 3 Performance comparison of aged Cu-Ti (wt%) alloys

Alloy	Microhardness/ HV	YS/ MPa	UTS/ MPa	Elongation/ %	EC/% IACS	Ref.
Cu-1.5Ti	210	350	520	23.0	24.5	[62]
Cu-1.5Ti	280	670	760	9.0	26.5	[62]
Cu-2.7Ti	355	950	1000	3.5	12.0	[22]
Cu-3Ti	319	889	969	10.5	12.5	[11]
Cu-3Ti	311	828	895	13.0	13.2	[11]
Cu-3.5Ti	340	-	-	-	13.9	[63]
Cu-4.5Ti	340	700	890	20.0	11.0	[23]
Cu-5.4Ti	455	1400	1450	1.5	4.8	[22]
Cu-6Ti	339	881	1000	17	8.1	[18]

properties of Cu-Ti alloys with varying Ti contents, revealing that improvements in microhardness and strength occur at the expense of EC. Nagarjuna et al.^[64] reported that increasing Ti content markedly enhances both microhardness and UTS, owing to its strong solid-solution strengthening effect. In particular, when the Ti content exceeds 4wt%, higher Ti promotes spinodal decomposition, leading to fine precipitates even in quenched samples and further strengthening the alloy. Furthermore, aged alloys with higher Ti contents achieve peak microhardness more rapidly than those with lower Ti contents, which can be attributed to the accelerated reaction kinetics induced by high Ti concentrations. However, excessive Ti content also leads to the rapid development of discontinuous precipitates^[26,33,58,65], which generally have a detrimental effect on the mechanical properties of the alloys. Liao et al.^[19] also pointed out that the stability of the β' -Cu₄Ti phase decreases with increasing Ti content. When the Ti content reaches or

exceeds 19at%, its stability becomes lower than that of the β -Cu₄Ti phase. This result leads to the dissolution of the metastable phase and the transformation into discontinuous precipitates, making it more difficult to simultaneously improve both the strength and EC of the alloys.

Precipitation strengthening is generally recognized as the primary strengthening mechanism in ultrahigh-strength Cu-Ti alloys, and the coherent β' -Cu₄Ti phase significantly enhances the mechanical properties. To reduce the concentration of Ti in the matrix and to promote the formation of additional precipitated phases, the addition of minor alloying elements has emerged as an effective strategy for performance optimization. In particular, the introduction of Fe into Cu-Ti alloys yields multiple beneficial effects. First, Fe can combine with Ti to form rod-shaped Fe₂Ti phases, which lower the Ti concentration in the matrix and thereby improve the EC of the alloy. Second, during heat treatment, Fe₂Ti phases act as pinning sites for grain boundaries, leading to grain refinement^[20]. Moreover, compared with Ti atoms, Fe has a lower vacancy binding energy, indicating a lower diffusion rate. This reduced diffusivity slows down the diffusion of alloying elements, thereby influencing the precipitation process. In addition, the addition of Fe suppresses the formation of discontinuous precipitates and improves the thermal stability of the alloy^[15,18,33]. Therefore, the presence of Fe contributes to the optimization of microstructure and overall performance of Cu-Ti alloys. Rouxel et al.^[18] reported the influence of minor Fe additions on the microstructure and properties of Cu-6Ti (wt%) alloys. They found that Fe suppressed spinodal decomposition, leading to softening of the solution-treated Cu-Ti-Fe alloy. As shown in Fig.9, the YS of the quenched alloy was only 323 MPa, which was

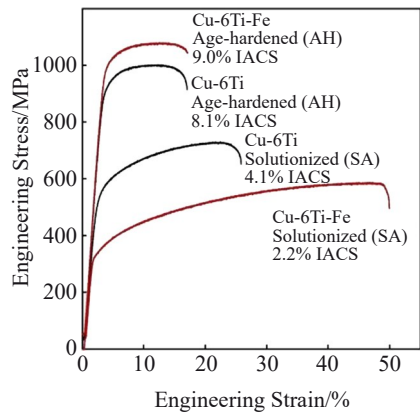


Fig.9 Engineering stress-engineering strain curves of Cu-6Ti-(Fe) (wt%) alloys^[18]

approximately 200 MPa lower than that of the Fe-free alloy, while the elongation reached 48%. After aging treatment, the YS and EC increased to 975 MPa and 9.0% IACS, respectively, which were 80 MPa and 0.9% IACS higher than those of the Fe-free alloy, while the elongation was basically unchanged at 17%. The addition of V and Cr further improved the thermal stability of the Fe_2Ti phase^[66–68], allowing prolonged aging to transform more Ti into the strengthening β' - Cu_4Ti phase. Liu et al^[66–67] also reported that V atoms partially substituted Fe in the Fe_2Ti phase to form $(\text{Fe}, \text{V})_2\text{Ti}$ phase, as shown in Fig. 10. This substitution reduced the binding energy of the precipitates and promoted the formation of fine precipitates. These precipitates served as heterogeneous nucleation sites, refining the as-cast structure during

solidification and suppressing grain boundary migration during heat treatment, and thereby leading to grain refinement. However, the refined grains provided more nucleation sites for discontinuous precipitates. As a result, V addition promoted discontinuous precipitate formation in the early stage of aging, but it strongly suppressed discontinuous nucleation of precipitates at later stages or at higher temperatures, which was attributed to the suppression of Ti diffusion by V^[66]. The combined effects of grain refinement, precipitation strengthening, and suppression of discontinuous precipitates enabled the peak-aged alloy to achieve a UTS of 976.8 MPa and an elongation of 18.8%, exhibiting both high strength and ductility. Zhao et al^[68] reported that Cr, Fe, and Ti formed a $(\text{Fe}, \text{Cr})_2\text{Ti}$ phase, and that Cr promoted precipitate formation and grain refinement, thereby increasing the peak-aged hardness of the Cu-Ti-Fe-Cr alloy. In addition, Markandeya et al^[60,69–70] found that Cr additions enhanced the strength of Cu-Ti alloys but decreased EC. In the Cu-3Ti-1Cr (wt%) alloy, the formation of Cr_2Ti phases improved the strength, while solid-solution strengthening from Cr resulted in reduced EC. Huang et al^[28] also reported that Cr mainly existed in the form of coarse Cr phases, Cr_2Ti phases, and nanosized Cr precipitates in the Cu-3Ti-1Cr (wt%) alloy, as shown in Fig. 11. These precipitates played a crucial role in suppressing the formation of discontinuous precipitates and improving the alloy stability. After aging at 500 °C for 2 h, the Cr-containing alloy exhibited a YS of 1033 MPa, with Cr contributing about 10% of the strengthening effect through both precipitation and solid-solution mechanisms. Minor Mg additions exert little influence on the EC of Cu alloys. Thus, they are often introduced for grain refinement. Previous studies^[54–55,71–72] have

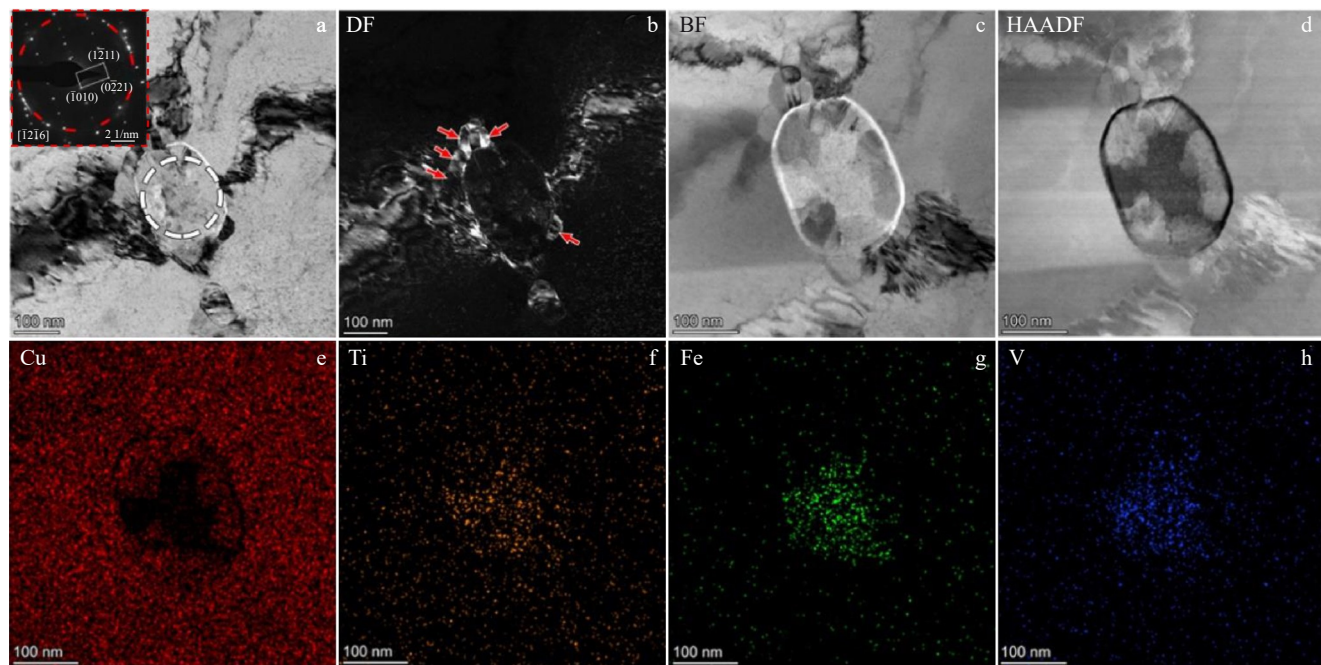


Fig.10 Microstructures and elemental distributions of Laves phases in Cu-3Ti-0.2Fe-0.2V (wt%) alloys^[67]: (a) bright field (BF) TEM image with inset of corresponding selected area electron diffraction (SAED) pattern; (b) dark field (DF) TEM image; (c) magnified BF TEM image; (d) HAADF image; (e–h) EDS mapping results

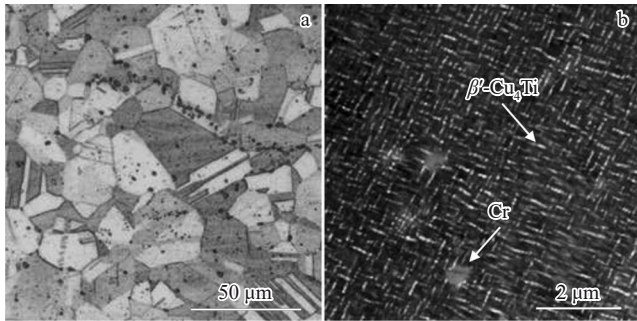


Fig.11 Microstructures of Cu-3Ti-1Cr (wt%) alloy aged at 500 °C for 120 h^[28]: (a) optical image and (b) BF TEM image

investigated the microstructure and properties of Cu-3Ti-2Mg (wt%) alloy. The results show that the addition of Mg significantly improves the hardness and EC of the as-cast alloy. As shown in Fig. 12, after aging at 450 °C for 4 h, Cu₂Mg precipitated from the matrix, resulting in a remarkable increase in hardness and EC. Furthermore, after CR, the grains of the Cu-3Ti-2Mg (wt%) alloy were deformed, and the microstructure became more uniform. After 70% cold reduction and aging at 450 °C for 3 h, the hardness and EC were further increased to 357.6 HV and 18.5% IACS, respectively^[72].

Ni has an atomic radius close to that of Cu and can form various intermetallic compounds with Ti. As shown in Fig. 13, during solidification of the Cu-3Ti-1Ni alloy, NiTi phases form and act as nucleation cores, transforming the as-cast structure from dendritic to equiaxed grains and refining the microstructure. After aging, NiTi, Ni₃Ti, and β'-Cu₃Ti phases are precipitated in Ni-containing alloys, which significantly enhance EC^[73]. High Sn contents tend to cause severe segregation. Lebreton et al^[74] reported that in as-cast Cu-xTi-2.75Sn (wt%) alloys, CuTi₃Sn₃ intermetallic compounds formed in the interdendritic regions, as shown in Fig. 14. Wang et al^[58] suggested that the formation of CuSn₃Ti₃ phases in Cu-Ti-Sn alloys consumes Ti from the matrix, thereby improving the EC of Cu-3Ti-2Sn alloys. After aging at 450 °C for 8 h, the hardness and EC of Cu-3Ti-2Sn alloys reached 134.5 HV and 39.8% IACS, respectively. Jing et al^[59] prepared Cu-3Ti-0.2Fe-1Sn (wt%) alloys and found that after solution treatment, CR, and aging, the peak hardness and EC reached 310.2 HV and 18.6% IACS, respectively. Konno et al^[37] further reported that Al additions enhanced the EC of Cu-Ti alloys but reduced the hardness of aged alloys from 280 HV to

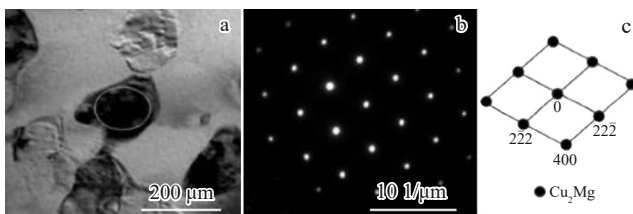


Fig.12 TEM analysis of aged Cu-3Ti-2Mg (wt%) alloy^[71]: (a) TEM image; (b) SAED pattern; (c) schematic diagram

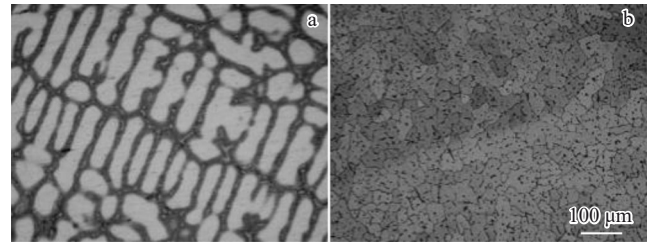


Fig.13 Microstructures of as-cast Cu-3Ti (wt%) alloy (a) and Cu-3Ti-1Ni (wt%) alloy (b)^[73]

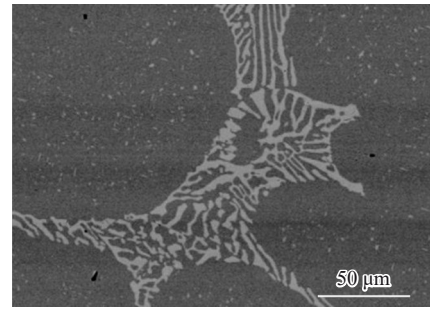


Fig.14 Intermetallic compounds in as-cast Cu-3Ti-2.75Sn (wt%) alloys^[74]

180 HV. During aging, Al formed a cubic AlCu₂Ti phase containing Cu and Ti, which maintained coherent or semi-coherent relationships with the matrix. In addition, Al suppressed spinodal decomposition during the early stages of aging. Cheng et al^[57] studied the phase transformation behavior of Cu-4Ti-1Al (wt%) alloys during aging at different temperatures and concluded that Al additions delayed ordering transformations. However, the AlCu₂Ti phase can be easily coarsened during aging, leading to reduced thermal stability of the alloy.

In addition, the addition of microalloying elements can suppress the formation of discontinuous precipitates, which contributes to the overall properties of Cu-Ti alloys. Nagarjuna et al^[23,75] reported that Co addition refined the grain size of Cu-4.5Ti (wt%) alloys from 75 μm to 20 μm in Cu-4.5Ti-1.8Co (wt%) alloys. During solution and aging treatments, coarse intermetallic compounds such as TiCo and Ti₂Co were formed, which reduced the peak hardness of the alloy. The effect of Co on EC was found: on the one hand, Co in solid solution increased electron scattering, leading to lower EC; on the other hand, with increasing Co content, more Ti was consumed to form intermetallic compounds with Co, thereby reducing the Ti concentration in the matrix and enhancing EC. As a result of these competing effects, the EC of the alloy first decreased and then increased with increasing Co content. At 1.8wt% Co, the EC of the Cu-4.5Ti-1.8Co (wt%) alloy reached 14.2% IACS. Markandeya et al^[56] fabricated Cu-3.0Ti-0.1Zr (wt%) and Cu-4.0Ti-0.1Zr (wt%) alloys and found that the addition of Zr suppressed spinodal decomposition. After solution treatment, single-phase Cu-Ti-Zr alloys were obtained, and the presence of Zr prolonged the time required to reach peak aging from 16 h to 24 h, with β'-Cu₃Ti as the

main precipitate. The peak hardness of Cu-3.0Ti-0.1Zr (wt%) and Cu-4.0Ti-0.1Zr (wt%) alloys reached 266 and 301 HV, with EC of 14.1% IACS and 13.5% IACS, respectively. Furthermore, Yang et al^[38] observed pronounced grain refinement in solution-treated Cu-4Ti-0.12Zr-0.05RE (wt%) alloys, along with suppression of spinodal decomposition. After aging at 420 °C for 6 h, the alloy reached a maximum hardness of 3200 MPa. After aging for 10 h, a lamellar structure consisting of $\alpha + \beta$ -Cu₃Ti phases was observed, as shown in Fig. 15. EDS analysis further revealed Zr enrichment at the interfaces, which effectively suppressed the growth of discontinuous precipitates.

N, B, and C elements exhibit strong affinity for Ti, enabling the formation of stable covalent compounds; therefore, they are employed to optimize the properties of Cu-Ti alloys. Semboshi et al^[76] applied a plasma nitriding process to Cu-4Ti (at%) alloys, producing a nitride layer with several micrometers thick on the surface. This layer, composed of TiN and Cu₃Ti₃O, significantly enhanced the surface hardness and wear resistance of the alloy. Ikeda et al^[77] fabricated Cu-Ti-N alloys with varying N contents, where N reacted with Ti to form TiN, thus reducing the amount of Ti in solid solution. As a result, the EC increased by approximately 5% IACS, albeit at the expense of hardness. Semboshi et al^[78] further investigated the influence of minor B addition (about 0.03at%) on the microstructure and properties of Cu-4Ti (at%) alloy. The boron content is too low to form the TiB₂ phase, but it was found to preferentially segregate at grain boundaries. Although it had little effect on phase-transformation behavior,

it effectively suppressed discontinuous precipitation during the later stages of aging, leading to an increase in hardness by about 50 HV. Moreover, B segregation at grain boundaries improved boundary cohesion, thereby enhancing the elongation of the alloy. Wang et al^[79] synthesized Cu-Ti-C alloys via spark plasma sintering (SPS) and reported that C addition significantly improved the EC of the alloy. As shown in Fig. 16, when the atomic ratio of C/Ti approached 1, the maximum EC reached 81.6% IACS. During sintering and subsequent heat treatment, C reacted with Ti to form TiC, reducing the Ti content in the matrix and improving EC while lowering hardness.

5 Advanced Preparation Technology of Cu-Ti Alloys

Melting is one of the most commonly used methods for preparing copper-based alloys. In this process, different alloying elements are added to the copper matrix, followed by casting to obtain ingots. After that, the alloys are subjected to treatments such as hot working, solution treatment, cold working, and aging, depending on the requirements. However, due to the special physicochemical properties of Ti, the preparation of Cu-Ti alloys faces several challenges. Firstly, Ti is chemically active and readily reacts with oxygen or other impurities during melting, leading to the formation of oxides or nitrides that may cause compositional deviations. Studies^[65,80] have shown that the strength and EC of Cu-Ti alloys are closely related to the Ti content. To precisely control the Ti content, most studies have employed vacuum casting (VC) to fabricate Cu-Ti alloys. Since the density of Ti

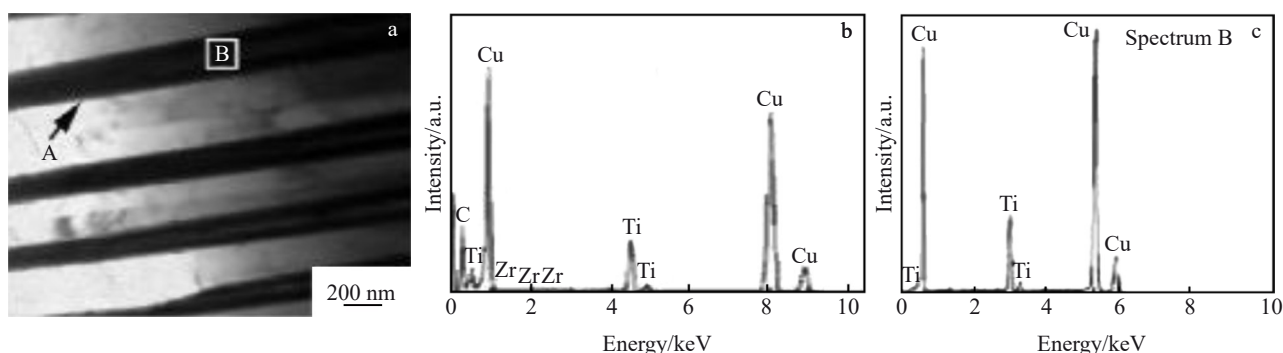


Fig.15 TEM image of over-aged Cu-4Ti-0.12Zr-0.05RE (wt%) alloy (a)^[38]; EDS spectra of point A (b) and region B (c) marked in Fig.15a^[38]

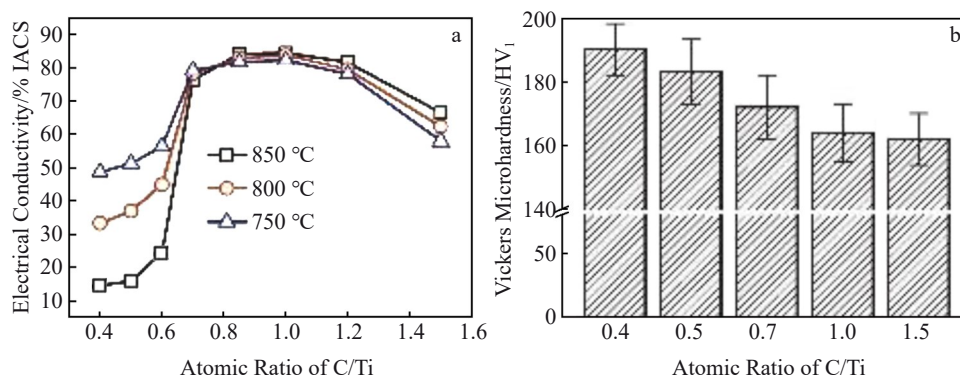


Fig.16 Variation of properties of Cu-Ti-C alloys with atomic ratio C/Ti^[79]: (a) EC and (b) Vickers microhardness

is much lower than that of molten Cu and its melting point is higher, segregation can easily occur during casting, resulting in non-uniform microstructures in the ingots, as shown in Fig. 17. In addition, the poor fluidity of the Cu-Ti melt often causes shrinkage cavities during solidification, which may lead to severe cracking in subsequent processing. Burn-off and segregation of Ti not only increase the difficulty of melting but also reduce the workability, strength, EC, and corrosion resistance of Cu-Ti alloys. Therefore, controlling the melting conditions to obtain alloys with uniform composition and microstructure is a prerequisite for improving the comprehensive performance of Cu-Ti alloys. Nevertheless, compared with conventional continuous casting, VC is characterized by high production costs and low efficiency, making large-scale industrial application a major challenge. This section introduces several preparation techniques of Cu-Ti alloys that have been widely studied in recent years, including non-vacuum melting, mechanical alloying, and powder metallurgy, which aim to optimize ingot quality, improve overall alloy performance, and enhance production efficiency.

5.1 Non-vacuum melting technique

Melting under an inert or protective atmosphere can, to some extent, reduce the Ti oxidation and thereby improve the overall properties of the alloy. However, Ti burn-off during melting remains difficult to avoid. Zhang et al.^[65] prepared Cu-Ti alloys using vacuum arc melting, as shown in Fig. 18. By comparing the designed composition with the measured composition, they found that Ti burn-off occurred during melting, and the burn-off ratio (burn rate) increased as the Ti content decreased. Moreover, due to the limitations of vacuum devices, it is difficult to carry out slag removal and composition analysis during the melting process, making composition control more challenging. In addition, vacuum-melted alloys are generally limited in size, allowing only small-batch production with relatively high cost. To address these issues, in recent years, researchers have attempted to develop non-vacuum melting techniques for Cu-Ti alloys. The main strategies involve the introduction of protective atmospheres or the use of fluxes as surface coverings to

isolate the melt from air. Fu et al.^[11] fabricated Cu-3Ti (wt%) alloy rods in a non-vacuum environment using the heating-cooling combined mold (HCCM) continuous casting process, as shown in Fig. 19, and the mold is composed of a heating section and a cooling section, which generates an extremely large temperature gradient at the interface between the two sections. A certain amount of deoxidizer was added to suppress oxidation during melting. Inductively coupled plasma analysis showed that the Ti content was 2.92wt%, indicating precise compositional control. As shown in Fig. 20, compared with VC alloys, the as-cast HCCM alloys exhibited a columnar grain structure and improved secondary dendrite arm spacing due to the large temperature gradient at the solidification front. Although more pronounced micro-segregation of Ti was observed, these Ti-rich phases were thermodynamically unstable and could be rapidly eliminated during subsequent homogenization treatment. After solution treatment, cold deformation, and aging, the HCCM-processed Cu-Ti alloy exhibited a hardness of 311 HV, YS of 828 MPa, elongation of 13.0%, and EC of 13.2% IACS, comparable to VC alloys, but with a much simpler processing route. In addition, Xie et al.^[81] developed a composite flux containing chloride salts, which reacted with the atmosphere during melting to form HCl, H₂, and Cl₂ gases, thereby retarding oxidation of the copper melt. Zheng et al.^[82] reported a covering agent composed of chlorides and fluorides, which enabled the preparation of Cu-Ti alloys containing 0.01%–5% Ti under non-vacuum conditions, with a Ti burn-off ratio of about 3%. Xiong et al.^[83] used chlorides as fluxes to prepare Cu-Ti alloys with 0.5wt%–3.0wt% Ti. After solution treatment, cold working, and aging, the resulting alloy wires achieved UTS≥750 MPa, EC≥25% IACS, and hardness≥200 HV. Moreover, Chen et al.^[84] introduced Zr during production to protect Ti from oxidation, reducing the Ti burn-off ratio to only 1.4% when the nominal Ti content was 3.0wt%. Compared with vacuum or atmosphere-controlled melting, the addition of fluxes or deoxidizers not only reduces the constraints on melting equipment but also significantly lowers the production cost and complexity, making the process more suitable for large-scale industrial production. However, for

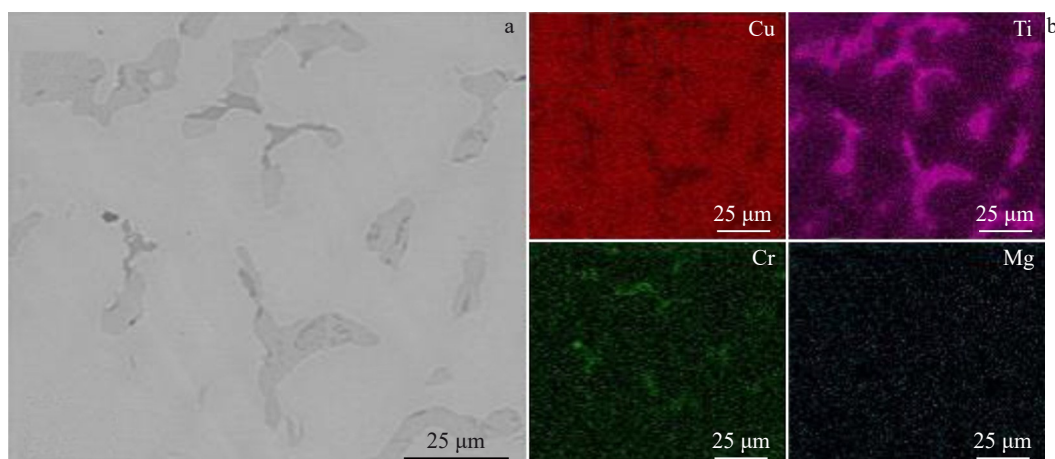


Fig. 17 Distribution of elements in as-cast Cu-8Ti-0.4Cr-0.4Mg (at%) alloy^[33]: (a) SEM image; (b) EDS mapping of Cu, Ti, Cr, and Mg

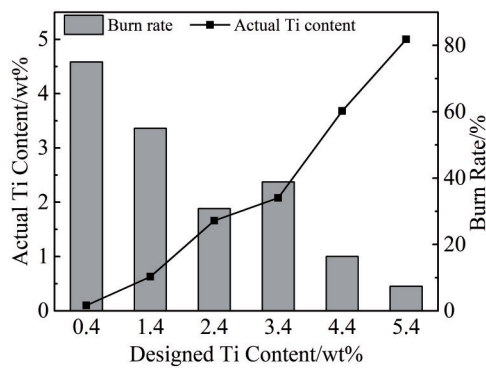


Fig.18 Burning loss of Ti element in vacuum arc melting^[65]

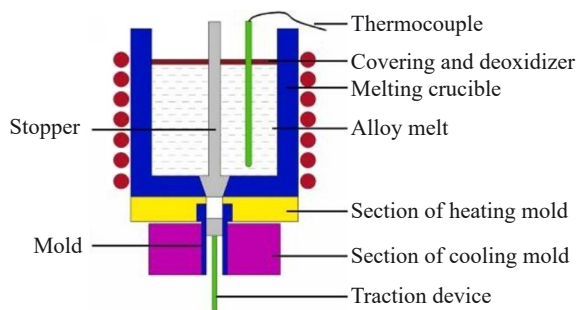


Fig.19 Schematic diagram of HCCM continuous casting process^[11]

optimal protection, the amount of flux must be strictly controlled: an overly thin layer cannot effectively isolate the melt from air, leading to pores caused by gas absorption, while an overly thick layer may result in incomplete flux melting, leaving residues that impair subsequent processing. Furthermore, certain flux components may react with Ti at high temperatures, altering alloy composition and deteriorating properties. Therefore, although flux-assisted non-

vacuum melting improves the quality of Cu-Ti alloys to some extent, its application still requires careful material selection and strict process control.

5.2 Solid-state preparation methods

Mechanical alloying (MA) is a solid-state powder processing technique, where different metal or alloy powders are alloyed through high-energy ball milling. Under strong mechanical forces, powders undergo repeated fracture and welding, eventually forming alloy materials with unique microstructures. The process of MA involves both plastic deformation and elemental diffusion. Fig. 21 shows the MA process for preparing Cu-Ti alloys. During deformation, solute atoms, dislocations, vacancies, and grain boundaries evolve, altering the stress-strain distribution inside the powder. At the same time, the introduction of defects provides more diffusion paths and stable driving forces for alloying. Under continuous impacts from the milling balls, the powders are compacted, and elemental diffusion occurs, leading to a more uniform distribution of alloying elements. In addition, MA is particularly suitable for preparing alloys containing elements that are difficult to process via conventional melting.

Powder metallurgy (PM) is widely used to prepare high-performance Cu-based alloys and is often combined with MA. As shown in Fig. 22, pure elemental or pre-alloyed powders are thoroughly mixed, compacted in molds, and then sintered under high temperature and pressure conditions to form bulk materials. Currently, the main sintering methods for Cu-Ti alloys include hot pressing (HP), hot isostatic pressing, and SPS. Karakulak et al^[85] fabricated Cu-Ti alloys with different Ti contents via HP. Increasing Ti content led to the formation of more Ti-rich particles, which were surrounded by multilayer intermetallic compounds, thereby enhancing hardness and wear resistance. Wang et al^[86-87] prepared Cu-

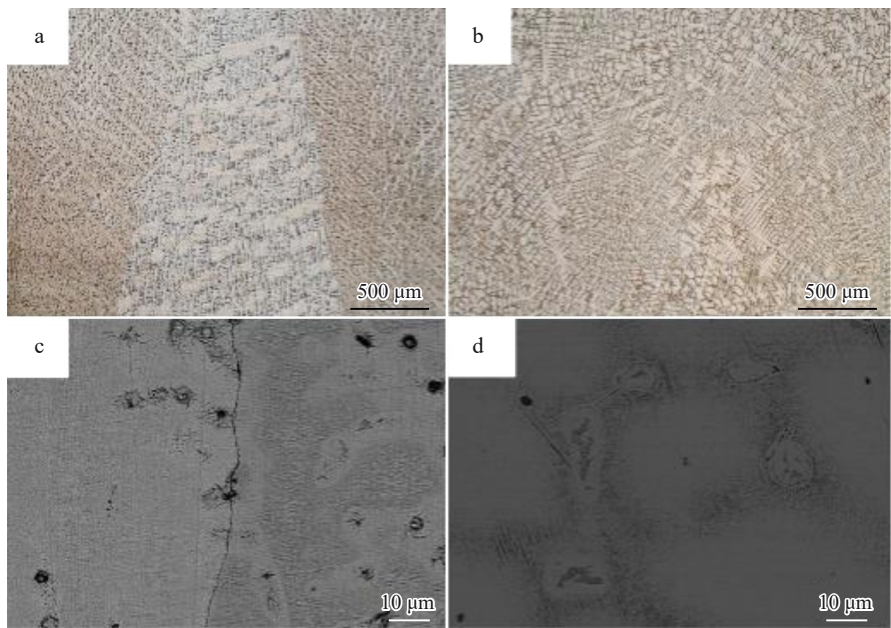


Fig.20 Optical micrographs (a–b) and SEM images (c–d) of as-cast microstructures of Cu-3Ti (wt%) alloys prepared by different processes^[11]: (a, c) HCCM process; (b, d) VC process

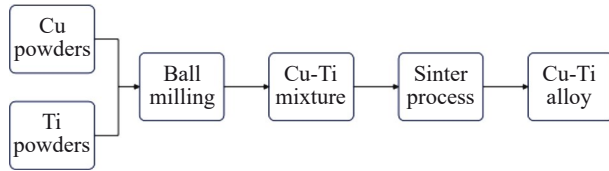


Fig.21 Schematic diagram of MA process for preparing Cu-Ti alloys

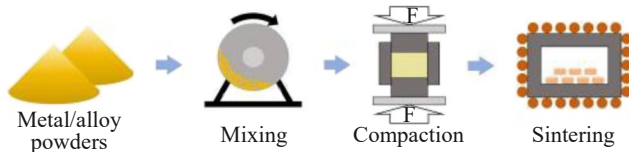
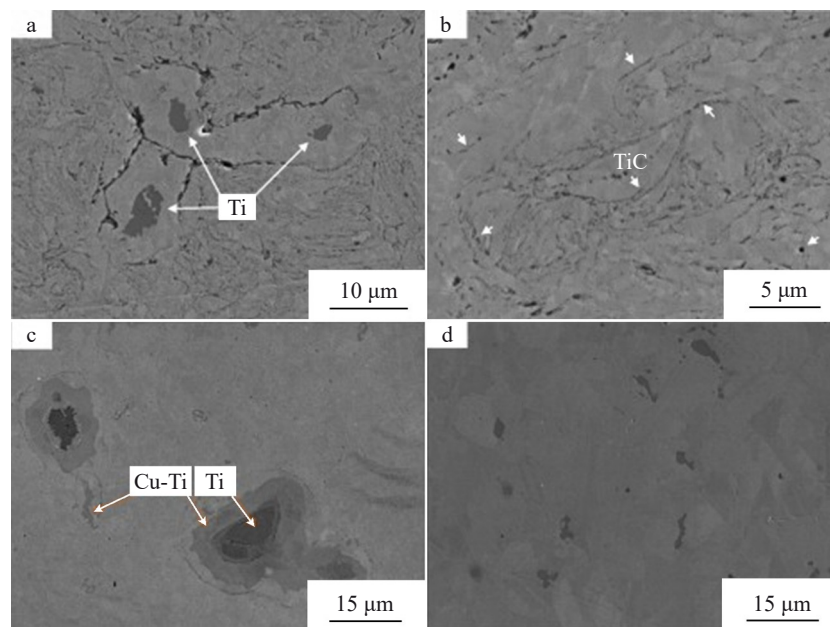
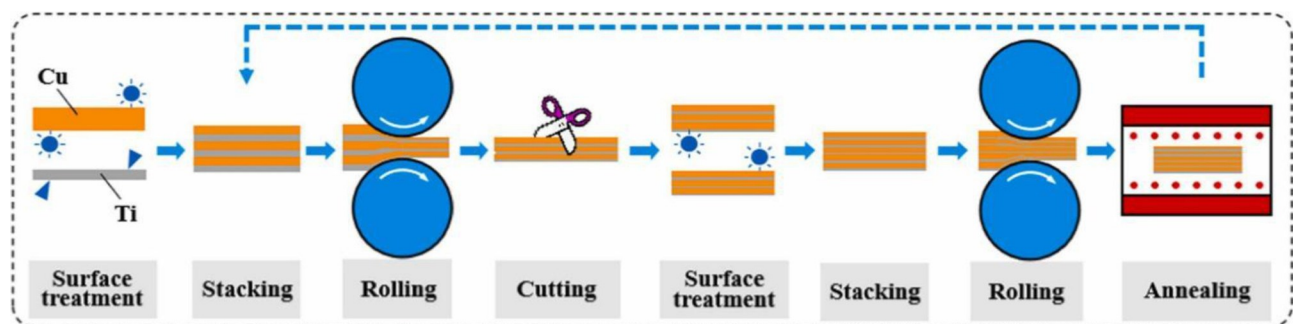


Fig.22 Schematic diagram of PM process

2.5Ti (wt%) and Cu-2.5Ti-0.625C (wt%) alloys using SPS. As shown in Fig.23, in the C-containing alloys, Ti reacted with C during sintering and subsequent heat treatment to form dispersed TiC particles in the matrix. In contrast, the C-free alloys still contained residual Ti particles, though they were refined. Although PM provides better compositional control and enables the design of composites with tailored microstructures, limitations remain, including low

densification of products, process complexity, high cost, and non-uniform microstructures. Therefore, further optimization is still required for large-scale industrial applications.

The advantages of MA are also reflected in accumulative roll bonding (ARB), which is a type of severe plastic deformation technique. The principle of the ARB technique is shown in Fig. 24, which involves repeated stacking, rolling, and restacking, introducing a high level of strain into the material. Tu et al.^[10,32,88] developed an accumulative roll bonding-deformation diffusion (ARB-DD) process, combining repeated deformation with subsequent diffusion annealing for compositional homogenization. During processing, interlocking slip systems promoted the formation of Taylor lattices that sustained high dislocation densities. The defects and internal stresses of high density further accelerated elemental diffusion, ultimately reducing the segregation index of the alloy to below 0.01 and producing homogeneous Cu-Ti billets, as shown in Fig. 25. In addition, multiscale substructures provided favorable nucleation sites and driving forces for Cu,Ti precipitation, thereby improving aging efficiency and mechanical performance. The resulting alloys exhibited a UTS of about 1036 MPa, hardness of 322 HV, and EC of 10% IACS.

Fig.23 Morphologies of Cu-2.5Ti-0.625C (wt%) alloy (a-b) and Cu-2.5Ti (wt%) alloy (c-d) under different processing states^[87]Fig.24 Schematic illustration of principle of ARB technique^[10]

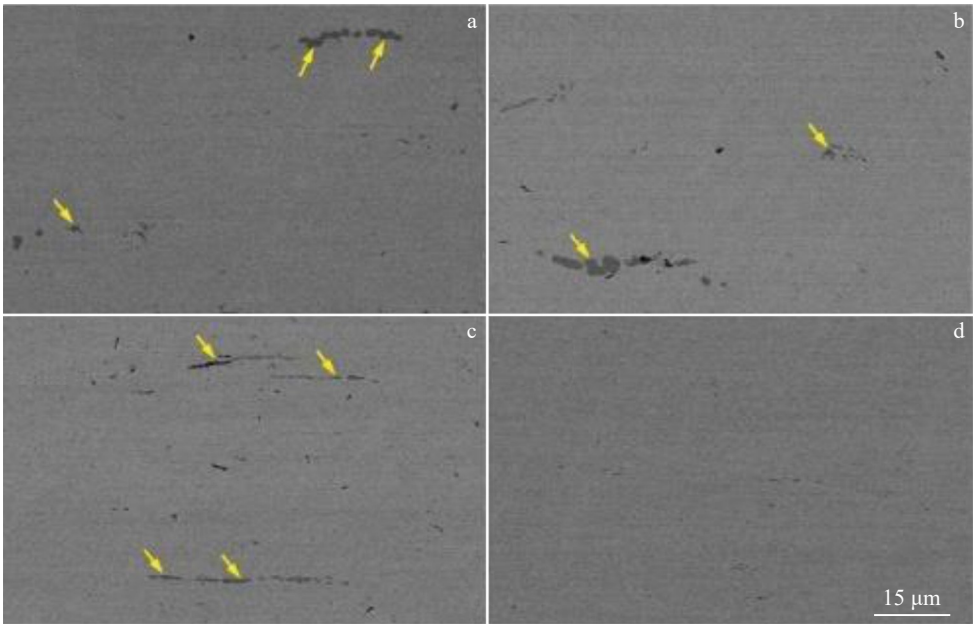


Fig.25 Morphologies of Cu-5Ti (wt%) alloy after different processes^[10]: (a) ARB-20%-800 °C/12 h; (b) ARB-800 °C/10 h; (c) ARB-800 °C/10 h-20%; (d) ARB-800 °C/10 h-20%-800 °C/2 h

6 Heat Treatment of Cu-Ti Alloys

The preparation process of Cu-Ti alloys has overcome the challenge of composition control, ensuring the uniformity and consistency of the initial alloy composition, which lays the foundation for subsequent microstructural optimization. Through rational composition design and optimization, not only can the grain size be refined, but the phase transformation behavior can also be tailored, thereby providing opportunities for performance enhancement. As a key step in property modulation, heat treatments including homogenization, solution treatment, deformation, and aging enable precise control over the microstructural evolution, thus realizing the synergistic improvement of both mechanical strength and EC. Nevertheless, elucidating the coupling relationship between microstructure and properties remains a major focus of current research.

Compared with the solution-treated state, although the aged Cu-Ti alloys exhibit significantly improved overall properties, their EC remains limited to only 10% IACS – 15% IACS, which is much lower than that of Cu-Be alloys. To address the low EC in Cu-Ti alloys, Semboshi et al^[89–96] conducted aging treatments of Cu-3Ti (at%) alloys under a hydrogen atmosphere. The results demonstrated that hydrogen greatly enhanced the EC of the alloys. During the early stages of aging, nanoscale β' -Cu₃Ti precipitates formed, followed by the formation of TiH₂ phases through the reaction between Ti and hydrogen. This process effectively diluted the solute Ti atoms and reduced the lattice distortion in the Cu matrix, thereby improving EC, as shown in Fig.26. Notably, hydrogen addition also suppressed the formation of discontinuous precipitates, enabling the alloy to retain high hardness even after prolonged aging under a hydrogen

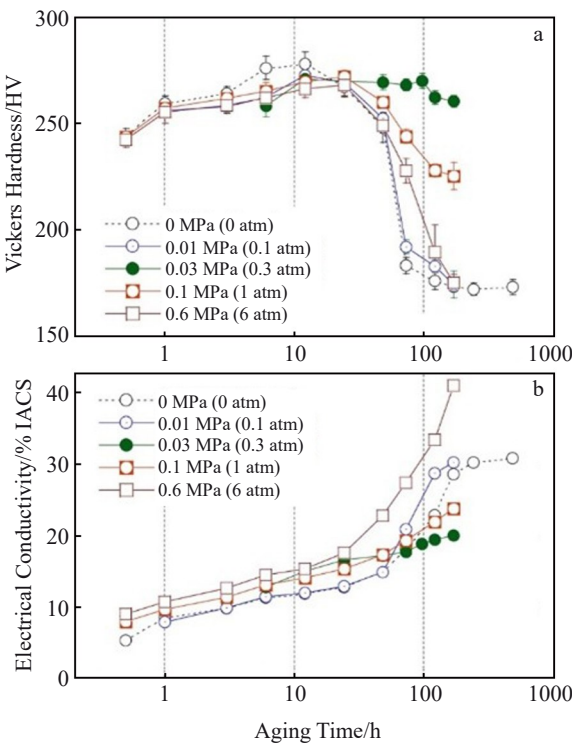


Fig.26 Vickers hardness (a) and EC (b) of Cu-4Ti (at%) alloys aged at 723 K and hydrogen pressures between 0–6 atm^[96]

pressure of 0.03 MPa.

Introducing a certain degree of plastic deformation prior to aging can generate a high density of dislocations and substructures within the alloy. These defects serve as pathways for solute diffusion and preferential nucleation sites for precipitates during subsequent heat treatment, while also providing the necessary energy to accelerate precipitation. Such effects not only shorten the aging time to some extent,

but also promote a more uniform distribution of solute elements, thereby optimizing the microstructure and enhancing the overall properties of the alloy. Nagarjuna et al.^[97] investigated the effect of cryogenic rolling on the microstructure and properties of Cu-1.5Ti (wt%) alloys. Cryogenic rolling markedly increased dislocation density, accelerated precipitation kinetics, and reduced the peak aging temperature. After 90% deformation and aging at 400 °C for 2 h, the hardness, UTS, and YS of the alloy reached 300 HV, 854 MPa, and 824 MPa, respectively, which were significantly higher than those of samples rolled at room temperature. Han et al.^[98] further revealed that pre-deformation altered the precipitation behavior of Cu-Ti alloys, where strain-induced shear bands acted as heterogeneous nucleation sites and simultaneously inhibited the growth of discontinuous precipitates. Semboshi et al.^[93] also reported the aging of pre-deformed Cu-4.2Ti (at%) alloys under a hydrogen atmosphere. Compared with undeformed samples, the cold-rolled samples exhibited higher maximum strength, with both hardness and EC increasing faster and reaching peak values in shorter times. The β' -Cu₄Ti and TiH₂ strengthening phases preferentially nucleated at dislocations and twin boundaries, leading to a remarkable improvement in overall properties, with strength and EC exceeding 1000 MPa and 30% IACS, respectively.

Thermo-mechanical treatment (TMT), which introduces initial deformation and pre-aging steps, exerts a more profound influence on the microstructure and properties of Cu-Ti alloys. Studies have shown that the strengthening effect of the alloy responds differently to each stage of TMT. Therefore, by tailoring the combination of processing parameters, it is possible to obtain unique microstructures and enhanced comprehensive properties. Fu et al.^[26] employed a two-step hierarchical deformation-aging method in a Cu-2Ti (wt%) alloy, achieving nanoscale twins with a spacing of 3.2 nm and precipitates with a spacing of 75–110 nm. As a result, the alloy exhibited a hardness of 356.24 HV, UTS of 1192.22 MPa, and EC of 25.23% IACS. Wang et al.^[27] designed a stepwise-cooling TTT, in which the aging temperature was gradually reduced during multiple CR+aging cycles to achieve long-term aging. After three cycles, excellent overall performance was obtained, with UTS and EC reaching 1144 MPa and 24.1% IACS, respectively. This improvement can be attributed to the interaction between nanoscale precipitates and high-density dislocations.

7 Cu-Ti Alloys with Heterogeneous Structure

In recent years, heterogeneous-structured copper alloys have become a research hotspot, as they can overcome the conventional strength-ductility trade-off of homogeneous materials and provide new pathways to achieve ultrahigh strength with good ductility. For Cu-Ti alloys, mechanical properties and EC can be further improved by rational microstructural design, such as the introduction of discontinuous precipitates, strengthening precipitates, and interface strengthening induced by cold deformation. Liu et al.^[29] applied short-time annealing to a Cu-3.2Ti-0.2Fe-0.2V

(wt%) alloy, obtaining a combination of coarse and fine grains. After subsequent aging at 400 and 450 °C, the alloy exhibited a strength increase of about 120 MPa compared with conventionally annealed coarse-grained samples, reaching 976.8 MPa, while maintaining an elongation of 18.8%. With an additional 5% CR prior to aging at 450 °C, the strength was further enhanced to 1057 MPa, although its elongation decreased to 10.6%. Among these strengthening contributions, a hetero-deformation induced hardening effect of 284.5 MPa was identified as the primary mechanism. Moreover, Yang et al.^[5] designed a heterogeneous structure consisting of hard domains and soft domains in a Cu-3.18Ti (wt%) alloy. The hard domains provided high microhardness, while the soft domains improved EC and ductility. By optimizing the distribution of these two domains, they achieved a desirable balance, with the hard domains contributing to a maximum hardness of 372.8 HV while maintaining an EC of 14.4% IACS.

In Cu-Ti alloys, improving EC relies on creating continuous electron-transport pathways. During aging, Ti atoms segregate to grain boundaries, promoting the transformation of fine, continuous precipitates into coarser, lamellar, discontinuous precipitates. Although discontinuous precipitates may impair mechanical strength, prolonged aging substantially reduces solute Ti from the matrix, thereby improving EC. Semboshi et al.^[48–49] demonstrated that heavy cold drawing enables synergistic optimization of strength and EC in Cu-Ti alloys by restructuring discontinuous precipitates. As shown in Fig. 27, prolonged aging treatment produced a matrix dominated by β -Cu₄Ti, which ensures high EC but limited strength. Subsequent cold drawing refines the lamellar β -Cu₄Ti through bending, fragmentation, and spacing reduction, thereby enhancing precipitation strengthening and dislocation strengthening simultaneously.

Based on the abovementioned analysis, we designed a new synergistic optimization model that employs cold-deformation-induced rearrangement of discontinuous precipitates and a multiscale strengthening strategy combining precipitation strengthening, interface strengthening, and heterostructure-induced strengthening. The corresponding microstructural evolution is illustrated in Fig. 28. Firstly, a lamellar β -Cu₄Ti phase was generated through long-term heat treatment, introducing high-density phase boundaries. Subsequent CR induced twisting and folding of the lamellae, leading to their refinement, and simultaneously, high-density dislocations were generated, thereby significantly enhancing the alloy strength. Finally, secondary aging at relatively low temperature promoted the re-precipitation of dissolved Ti atoms as nano-particles with strong precipitation-strengthening effects. Fig. 29 shows the aging response and mechanical properties of the alloy at different temperatures. With optimized secondary-aging parameters, both the strength and EC of Cu-Ti alloys were further improved. Notably, after aging at 400 °C for 4 h, the alloy achieved a UTS of 989 MPa, an elongation of 8%, and an EC of 34.6% IACS. Such outstanding performance can be attributed to the oriented lamellar discontinuous precipitates and the nanoscale

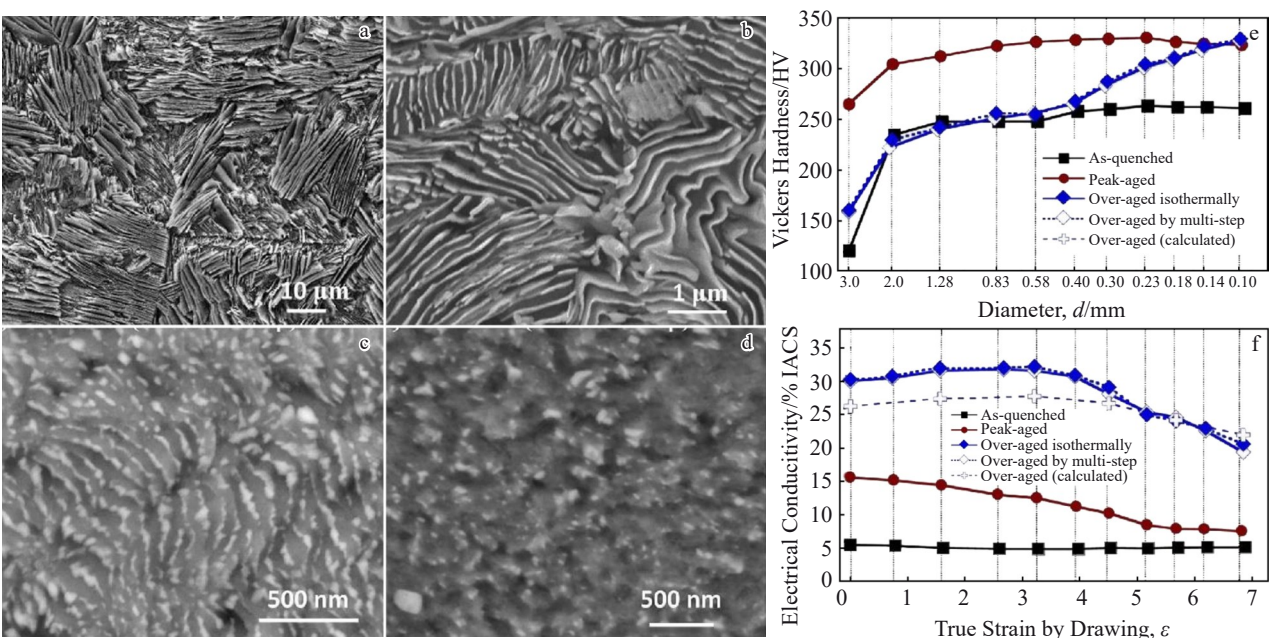


Fig.27 Cross-sectional micrographs of cold-drawn Cu-3.6Ti (wt%) alloy wires with true strains ε of 0 (a), 2.6 (b), 4.5 (c), and 6.2 (d)^[48]; Vickers hardness (e) and EC (f) of cold-drawn Cu-3.6Ti (wt%) alloy wires^[48]

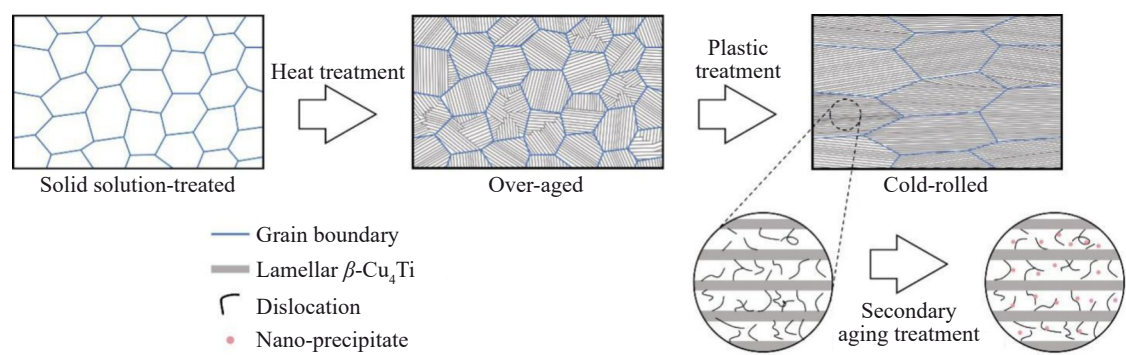


Fig.28 Evolution of structure in multiphase strengthened Cu-3.2Ti (wt%) alloys

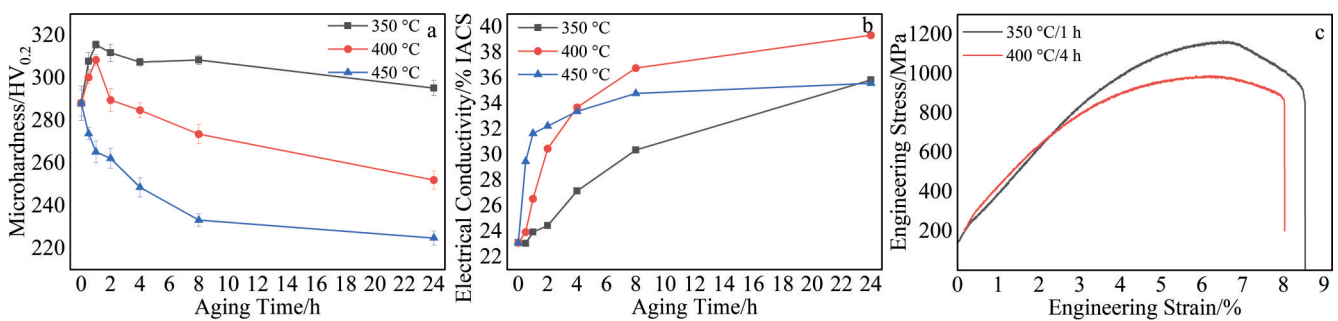


Fig.29 Performances of Cu-3.2Ti (wt%) alloys during aging treatment at different temperatures: (a) microhardness, (b) EC, and (c) engineering stress-engineering strain curves

secondary precipitates. Clearly, compared with conventional homogeneous Cu-Ti alloys, this synergistically strengthened hetero-structured multiphase alloy achieves a remarkable balance between mechanical and electrical properties. The underlying strengthening mechanisms will be discussed in

future work. Furthermore, alloying design may provide additional pathways for microstructural optimization. For example, introducing trace elements such as Co, Mg, or Fe can refine the initial microstructure and promote discontinuous precipitates.

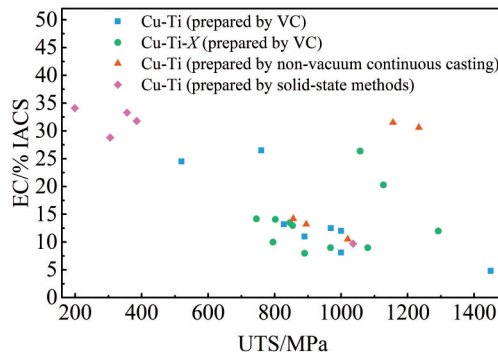


Fig.30 Comparison of Cu-Ti alloys^[10-11,18,20,22-23,28,56,60,62-63,83-84]

8 Summary and Outlook

Precipitation-strengthened Cu-Ti alloys possess ultrahigh strength, excellent workability, superior wear and corrosion resistance, and nontoxic characteristics, making them highly promising for applications in daily life and industrial production. They are considered ideal substitutes for ultrahigh-strength Cu-Be alloys. However, despite the remarkable strengthening effect provided by Ti, challenges such as low EC, complex melting processes, and compositional segregation remain unresolved. With the growing demand for enhanced comprehensive properties, research on Cu-Ti alloys has advanced considerably in recent years. Fig.30 shows the strength and EC of the Cu-Ti alloys. It can be seen that the properties of most Cu-Ti alloys are concentrated in a strength range of 800–1200 MPa and an EC of 5% IACS–15% IACS. The addition of alloying elements can improve the overall performance to a certain extent, and non-vacuum processing routes are also capable of meeting the performance requirements of Cu-Ti alloys. In addition, it is worth noting that Cu-Ti alloys fabricated by solid-state processing methods (such as MA) exhibit the highest EC.

The current development status and future research objectives can be summarized as follows.

1) Solute precipitation and microalloying. Insufficient precipitation of Ti atoms is the primary cause of low EC in Cu-Ti alloys. Microalloying has shown some potential in alleviating this issue, but the limitations remain in balancing strength and EC. Systematic exploration of more alloying elements is required, particularly those strongly interacting with Ti, which promote its full precipitation from the matrix. This strategy could simultaneously improve EC and mechanical properties. Moreover, multi-element alloying deserves attention. Notably, nonmetallic elements such as H, C, and N exhibit strong affinity with Ti, effectively dragging more Ti out of solid solution. By carefully controlling their addition and heat-treatment parameters, the precipitation behavior of Ti and microstructural evolution can be further optimized, enabling the design of Cu-Ti alloys with both ultrahigh strength and high EC.

2) Phase transformation mechanisms. Although significant progress has been made in understanding the phase

transformation behavior of Cu-Ti alloys, with general mechanisms and macroscopic features being widely reported, controversies remain regarding the details of spinodal decomposition, ordering, and discontinuous precipitation. These transformations may exhibit distinct characteristics under different heat treatment conditions and alloy composition. Advanced in-situ experimental techniques are needed for direct observation and clarification. Meanwhile, computational materials science is emerging as a powerful tool for alloy design. Atomistic thermodynamic and kinetic simulations, combined with experimental validation, can help elucidate the fundamental mechanisms of phase transformations and guide the design of next-generation Cu-Ti alloys.

3) Effect of cold deformation. Cold working introduces crystal defects such as dislocations, low-angle grain boundaries, and twin boundaries, significantly altering the mechanical and physical properties of alloys. For Cu-Ti alloys, the challenge is to achieve high strength without sacrificing EC. Thus, cold deformation plays a particularly crucial role. Since strength and EC are generally mutually constrained, microstructural engineering through defect manipulation offers a promising pathway to overcome this trade-off. Precise control of dislocation density and grain boundary distribution can enhance mechanical performance while minimizing EC loss, providing valuable strategies for the development of Cu-Ti alloys with balanced properties.

4) Heat treatment processes. Precipitation strengthening remains the core principle for high-performance Cu-Ti alloys, and precise control of precipitate morphology is highly dependent on heat treatment parameters. TMT has emerged as a particularly promising route. Clarifying the matching of deformation and heat treatment enables the dynamic optimization of precipitates. In addition, the design of multi-stage heat treatment strategies is expected to overcome the limitations of single-step processes in balancing strength and EC. Besides, heat treatment under special atmospheres or external fields (such as electric fields, magnetic fields, and super-gravity fields) also merits further in-depth investigation.

5) Processing techniques. At present, vacuum melting is still the dominant preparation method for Cu-Ti alloys. Although it is effective in ensuring high purity and preventing contamination, this technique faces limitations in large-scale production and the fabrication of complex components. Therefore, developing alternative processing routes is essential. A non-VC process, with improved atmosphere control and cooling techniques, offers a simpler and more cost-effective solution with the potential to optimize alloy properties. Furthermore, laser additive manufacturing has emerged as a promising method for fabricating components with complex geometries. By tailoring processing parameters, this technique enables the design of unique microstructures with enhanced performance. Advanced processing techniques not only address scalability challenges but also create new possibilities for creating tailored microstructures, thereby expanding the application potential of Cu-Ti alloys in power, electronics, aerospace, and other advanced fields.

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铜钛合金强度与导电率协同提升:成分设计、微观结构和加工工艺

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摘 要: Cu-Ti 合金因具有出色其优异的机械强度, 已在航空航天、电气工程、轨道交通等领域得到广泛应用。然而, 较低的导电率限制了其应用领域, Ti 元素的偏析、氧化和不连续析出等问题也限制了其综合性能的提升和工程领域的应用。本文综述了 Cu-Ti 合金微观组织演变及性能调控方面的研究进展, 阐述了连续析出相与不连续析出相形成机理及其演变对合金力学性能与导电性能的影响规律。此外, 还总结了成分设计策略、先进制备技术以及热机械处理。在此基础上, 提出了基于成分优化调控、热处理工艺优化和显微组织调控等综合手段, 构建多尺度多相协同强化的异质结构是进一步提高 Cu-Ti 合金拉伸强度、屈服强度和导电率的可行技术路径, 有望制备出具有良好加工性能、高强、高导铜合金, 满足电气、航空等高端制造领域的高速发展需求。

关键词: 铜钛合金; 成分设计; 显微组织; 加工工艺; 性能

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