



Effect of trace rare earth La on the thermal stability of oxygen-free copper

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Orange peel, texture, La, thermal stability, grain boundary segregation

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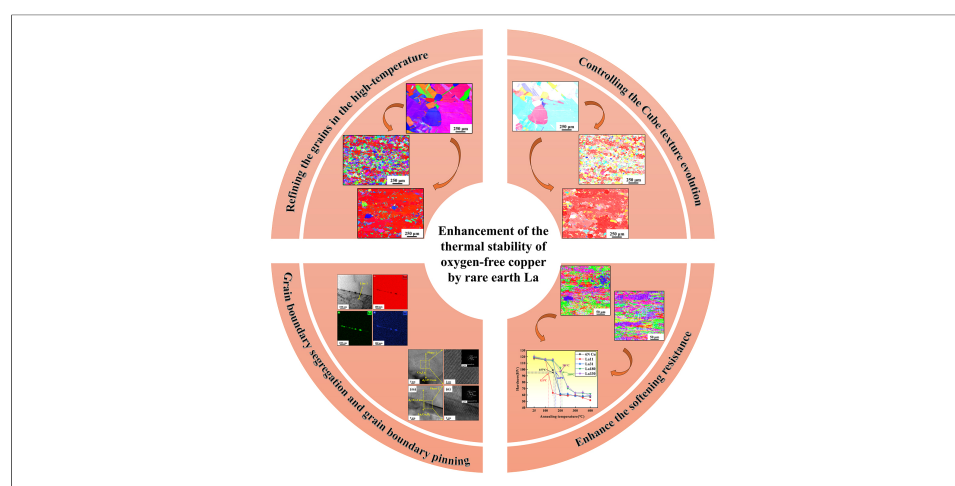
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Abstract

This study elucidates how rare-earth lanthanum (La) content regulates the thermal stability of oxygen-free copper (OFC). The stability was systematically assessed by investigating the influence of La on grain size, texture evolution, electrical conductivity, hardness, and softening temperature following high-temperature annealing. The results demonstrate that higher La contents (La180 and La330) significantly enhance the thermal stability of OFC. This is achieved by triggering multi-scale La-rich secondary phase precipitation and grain boundary segregation, which synergistically refine the grain structure through dual mechanisms of "promoting nucleation" and "inhibiting grain growth". Consequently, high electrical conductivity is maintained alongside a remarkable increase in hardness. Among them, La180 exhibits the most significant increase in softening temperature, reaching 210 °C, and also achieves the finest grain size of 38.64 μm after high-temperature annealing, suppressing grain coarsening and abnormal grain growth, markedly improving the "orange-peel" defect, and promoting the transition from Brass-Rec texture to Cube texture. Meanwhile, La180 maintains a high electrical conductivity of 101.3 %IACS after high-temperature annealing, providing a critical theoretical basis and a compositional design window for developing OFC materials that combine ultra-high electrical conductivity with excellent high-temperature softening



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resistance, suitable for high-reliability direct bonded copper devices.

INTRODUCTION

The insulated gate bipolar transistor (IGBT) serves as a critical power device in modern power electronic systems^[1,2], whose performance and reliability heavily depend on the quality of the direct bonded copper (DBC) substrate within the package module. Oxygen-free copper (OFC), owing to its superior electrical and thermal conductivity, excellent ductility, and compatibility with ceramic substrates, has been established as the material of choice for the copper layer in DBC substrates. It finds extensive application in high-end power electronic equipment such as new energy vehicles, rail transit, smart grids, marine vessels, and aerospace systems^[3-6]. A robust bond with the ceramic substrate is formed via a high-temperature bonding process, ensuring efficient heat dissipation and structural integrity of the module to meet the demanding service requirements of high-power density and high reliability in power electronic devices. However, the DBC bonding process requires the copper and ceramic layers to be joined and held at 800–1,000 °C^[7-10]. At these temperatures, processes such as dislocation annihilation, recrystallization, and grain growth^[11-13] readily induce abnormal grain coarsening and anomalous orientation in OFC. This leads to the formation of a characteristic "orange peel" defect^[14,15], which increases surface roughness^[16,17], degrades the mechanical properties of the copper layer, and reduces its thermal cycling stability^[18], thereby severely compromising the long-term service safety and reliability of the IGBT module. Wang *et al.*^[19] found that grain coarsening and the change of texture type are the key microstructural factors inducing the "orange peel" defect. When the grain size increases to a magnitude comparable to the material thickness, the influence of the deformation behavior of individual grains on the surface morphology is significantly amplified. Meanwhile, the presence of different crystallographic orientations in the matrix (e.g., Copper-oriented twins penetrating the Goss-textured matrix) further exacerbates the deformation incompatibility between grains and impedes the continuity of dislocation slip, thereby promoting the formation of the orange-peel defect. Therefore, achieving a single crystallographic orientation (e.g., Cube texture) through texture control can mitigate this defect. Hence, suppressing abnormal grain coarsening during high-temperature processing, optimizing the uniformity of texture components, ameliorating the orange-peel defect, and enhancing the thermal stability of OFC under DBC process conditions constitute a critical materials bottleneck that must be overcome for the advancement of high-end power electronics technology.

Currently, microalloying stands as one of the primary and most effective strategies for enhancing the thermal stability of copper and its alloys^[20]. The primary functions of microalloying elements in copper alloys encompass grain refinement strengthening, substructure strengthening, and dispersion strengthening via precipitate formation. By forming second-phase particles that pin grain boundaries, these added elements inhibit grain growth, thereby improving resistance to grain coarsening at elevated temperatures. In industrial production and technical applications, there is a difference in thermal stability between commercially pure copper (e.g., 3N, 4N, or even lower purity copper) and high-purity copper. Sakai *et al.*^[21] found that compared with 3N and 4N copper of relatively lower purity, 6N ultra-high-purity copper exhibits more pronounced grain growth due to the lack of impurity-atom pinning at grain boundaries, and its dynamically recrystallized grains undergo faster static softening at high temperatures, resulting in relatively weaker resistance to high-temperature softening. This implies that during the annealing of pure copper, second-phase elements play a critical role in pinning grain boundaries and suppressing grain growth. Sun *et al.*^[22] reported that Zr and Mn microalloying improved the high-temperature resistance to coarsening and mechanical properties of a high-temperature Al-Cu alloy. Their results indicated that microalloying with Zr and Mn plays a crucial role in stabilizing the primary strengthening metastable θ' phase under high-temperature conditions. Jiang *et al.*^[23] found that adding 0.1 at.% Zr to Cu followed by high-temperature heat treatment prevented catastrophic microstructural and property degradation. This was attributed to low grain

boundary mobility and the relaxation of non-equilibrium grain boundaries, maintaining a yield strength comparable to that of ultrafine-grained copper. Hornbuckle *et al.*^[24] discovered that adding 0.5 at. % Li to a Cu-3Ta alloy led to the formation of coherent, ordered Cu₃Li precipitates enveloped by a Ta-rich bilayer interphase boundary. This modified the interphase boundary and transformed the nanoprecipitate morphology from spherical to cubic, resulting in nanostructured precipitates with exceptional resistance to thermal coarsening, strength, and creep resistance. Although such microalloyed copper alloys exhibit high thermal stability and maintain excellent mechanical properties under high-temperature service conditions, their electrical conductivity often falls short of the stringent requirements for high-end electronic components like DBC substrates. Consequently, the key technological challenge in the field of copper-based electronic materials lies in further enhancing thermal stability while preserving the excellent electrical conductivity intrinsic to OFC. Tailoring the microstructure of copper alloys by doping with rare earth elements, which have a minimal impact on electrical conductivity, offers a promising route to significantly improve thermal stability while largely retaining conductive properties.

Rare earth elements such as Sc, Ce, and lanthanum (La) have been extensively investigated in copper and copper alloys^[25,26]. The influence of rare earth elements on the thermal stability of OFC is mainly reflected in increasing the recrystallization temperature, inhibiting high-temperature grain growth, and optimizing microstructural evolution. By doping with rare earth elements that have a minor impact on electrical conductivity to regulate the microstructure of OFC, it is expected to improve the thermal stability of OFC while ensuring that its electrical conductivity is essentially not compromised. These elements can enhance thermal stability by mechanisms including solute drag, solute segregation at grain boundaries, and pinning by second-phase particles, all of which reduce grain boundary migration rates at elevated temperatures. Chen *et al.*^[20] found that adding a trace amount of Ce (0.0017 wt.%) to OFC improved its resistance to high-temperature grain coarsening by suppressing high-temperature grain boundary migration through reduced grain boundary energy and solute pinning effects. Hao *et al.*^[27] reported that introducing Sc into 4N Cu produced minute, uniformly dispersed precipitates that hindered dislocation motion along with grain boundary movement, inhibiting recrystallization and improving resistance to thermal coarsening. Zeng *et al.*^[28] found that OFC processed material with a mass fraction of 0.006% rare earth Y can simultaneously improve high-temperature softening resistance, electrical conductivity, and corrosion resistance. As the Y content increases, the reduction rate of Vickers hardness before and after annealing gradually decreases, indicating an enhancement in softening resistance.

Among various rare earth elements, La has garnered significant attention and application due to its abundant natural reserves and relatively low production cost^[29]. The solid solubility of La in OFC is extremely low. Trace amounts of La do not exist as solute atoms within the copper lattice; instead, they form second-phase compounds with copper or impurity elements (e.g., O, P, S), which purify the matrix and help maintain high electrical conductivity^[30]. Furthermore, La can form second-phase particles that strongly impede grain boundary migration via dual mechanisms involving solute drag and Zener pinning, thereby enhancing thermal stability.

In the present work, five OFC specimens containing varying trace levels of rare-earth La were prepared based on 6N (> 99.9999%) OFC. The thermal stability of the materials was systematically evaluated by determining the softening temperature and conducting a comprehensive analysis of the microstructure, texture evolution, and mechanical and electrical properties after annealing at 900 °C. The microstructure and morphology of the materials were analyzed using electron backscatter diffraction (EBSD) and transmission electron microscopy (TEM). This revealed the influence mechanism of trace La on the evolution of microstructural morphology and texture in OFC after high-temperature annealing, clarified the mechanism by which La affects the softening temperature of OFC, and focused on analyzing the mechanism by which multi-scale La

Table 1. Mass fraction of rare earth element La in various OFC (wt.%)

Specimen	La addition/%	La content by measurement/%
6N Cu	-	-
La11	0.01	0.0011
La31	0.03	0.0031
La180	0.05	0.0180
La330	0.15	0.0330

OFC: Oxygen-free copper.

precipitation and grain boundary segregation enhance thermal stability. This work provides a foundational theoretical basis and an effective compositional design approach for engineering OFC materials which simultaneously exhibit high electrical conductivity and excellent thermal stability. The relevant findings are particularly applicable to power electronic devices (e.g., DBC substrates) and high-power functional electronic devices that undergo high-temperature processing or long-term service, demonstrating broad application prospects. This research also holds significant importance for promoting the entry of copper sheet and strip products into the high-end international market.

MATERIALS AND METHODS

Melting was conducted using a H20-04-type model induction vacuum furnace, with a charge mass of roughly 3 kg per batch. The raw materials used in the smelting process comprised electrolytic copper plates of 99.9999% (6N) purity together with high-purity La metal. The impurity contents in the initial 6N Cu master batch were determined by glow discharge mass spectrometry (GDMS) and a N/O gas analyzer, with the following results: $P < 0.001$ ppm wt%, $S < 0.005$ ppm wt% (measured by GDMS), and $O < 5$ ppm wt% (measured by the nitrogen/oxygen gas analyzer). After melting, the ingots were extruded at elevated temperature into 10-mm-thick plates, and specimens were then taken for compositional analysis via a 5110SVDV ICP-OES instrument, with the resulting compositions listed in Table 1. The samples were then subjected to cold rolling: first, an initial cold rolling with a reduction of 85% was performed using a two-roll mill to obtain OFC sheets with a thickness of 1.5 mm, subsequently, recrystallization annealing was carried out at 400 °C for 1 h to obtain a fine and uniform equiaxed grain structure. Afterward, a second cold rolling was applied to the samples, reducing them to a final thickness of 0.3 mm. The rolled samples were then used for softening temperature testing and high-temperature annealing treatments, respectively.

Electrical conductivity testing: Electrical conductivity measurements were performed using a Sigma 2008 series portable digital eddy current conductivity meter, with a measurement range of 0.51–112 %IACS. After the instrument is turned on, the probe is preheated for approximately 10 min to ensure measurement accuracy. For each sample, the conductivity is measured 5 times, and the average value is taken as the conductivity of the specimen measured.

Hardness testing: Hardness testing was performed using an HV-10MPTA Vickers hardness tester. Vickers hardness was measured at room temperature, with a test force of 0.3 kgf (i.e., 2.942 N) and a dwell time of 15 s. For each composition, five measurements were performed.

Softening temperature testing: According to the Chinese standard GB/T 33370-2016 for determining the softening temperature of copper and copper alloys, the softening temperature is defined as the holding temperature at which the hardness of the material decreases to 80% of its original value after being held for 1 h, followed by natural cooling to room temperature. In this test, the softening temperature range was from 100 to 400 °C with an interval of 50 °C. After natural cooling to room temperature, the Vickers hardness was

measured. At each temperature, five measurements were performed. The original hardness for reference was the Vickers hardness measured at 25 °C. The softening temperature behavior curve is a plot with the annealing temperature on the x -axis and the corresponding specimen hardness on the y -axis, used to characterize the resistance to high-temperature softening of copper and copper alloy materials.

High-temperature annealing: The samples after the second cold rolling were subjected to high-temperature annealing at 900 °C for 30 min. After holding, the samples were taken out and air-cooled. During annealing, a mixed gas of N_2 (93%) and O_2 (7%) was introduced to simulate the typical mild oxidation environment during high-temperature bonding of DBC substrates. Under this oxygen partial pressure, a dense Cu_2O layer preferentially forms on the copper surface during annealing at 900 °C; this oxide layer serves as an active layer for the subsequent eutectic reaction with the ceramic interface, promoting metallurgical bonding. If the oxygen content is too low (e.g., below 1%), insufficient Cu_2O is generated, which may lead to poor interfacial bonding; conversely, if the oxygen content is too high (e.g., 21% in air atmosphere), a loose, non-conductive CuO layer forms on the copper surface, accompanied by possible spallation, severely degrading the interfacial performance.

EBSD analysis was performed using two field-emission scanning electron microscopes (FESEMs): a Carl Zeiss SIGMA 500 equipped with an OXFORD C-Nano EBSD detector, and a Thermo Fisher Scientific Apreo 2C equipped with an OXFORD Symmetry S3 EBSD detector. For the Carl Zeiss SIGMA 500 FESEM, the operating conditions were: an accelerating voltage of 20 kV, a sample tilt angle of 70°, and a scan step size of 5 μm . A step size of 5 μm is used for the statistics of macro-texture and large area grain size distribution, with a relatively large scanning area. Samples subjected to high-temperature annealing treatment at 900 °C for 30 min will be tested using this FESEM. For the Thermo Fisher Scientific Apreo 2C FESEM, the conditions were: an accelerating voltage of 20 kV, a sample tilt angle of 70°, and a scan step size of 0.2 μm . A step size of 0.2 μm was used for the detailed analysis of local geometrically necessary dislocation (GND) and low-angle grain boundaries, with a relatively small scanning area. Samples subjected to softening treatment at 150 °C for 1 h will be tested using this FESEM. The EBSD technique was employed to obtain microstructural and textural information, including grain size distribution, grain boundary features, and crystal orientation mapping. The EBSD datasets were processed and evaluated using AZtecCrystal 2.1 software. Analyses comprised grain orientation spread (GOS), orientation distribution function (ODF), GND, kernel average misorientation (KAM), inverse pole figure (IPF), and coincident site lattice (CSL) boundary distributions. To further investigate the morphology and distribution of trace La-rich phases, microstructural observations were carried out with an FEI Talos F200X field-emission TEM running at an acceleration voltage of 200 kV. TEM specimens were prepared using a two-step process: initial thinning by electrolytic double-jet polishing (TJ100-SE system) followed by final precision ion milling (Gatan 695 system).

A detailed flowchart summarizing the experimental procedures and parameters is provided in [Figure 1](#).

RESULTS AND DISCUSSION

Effect of trace La on the microstructure and properties of OFC after high-temperature annealing

Microstructure morphology

[Figure 2A₁-E₁](#), [A₂-E₂](#), [A₃-E₃](#) displays EBSD IPF maps, grain boundary maps, and grain size distribution histograms, respectively, for OFC with varying La content upon annealing at 900 °C for a duration of 30 min. Rolling direction (RD) is defined as the direction along which the sheet was rolled (i.e., the direction of metal elongation). Transverse direction (TD) refers to the direction perpendicular to the RD within the rolling plane. As seen in [Figure 2A₁-E₁](#) and [A₃-E₃](#), the 6N Cu exhibits a large average grain size of 336.52 μm . The La11 and La31 samples have grain sizes of 332.32 and 323.45 μm , respectively, indicating negligible grain

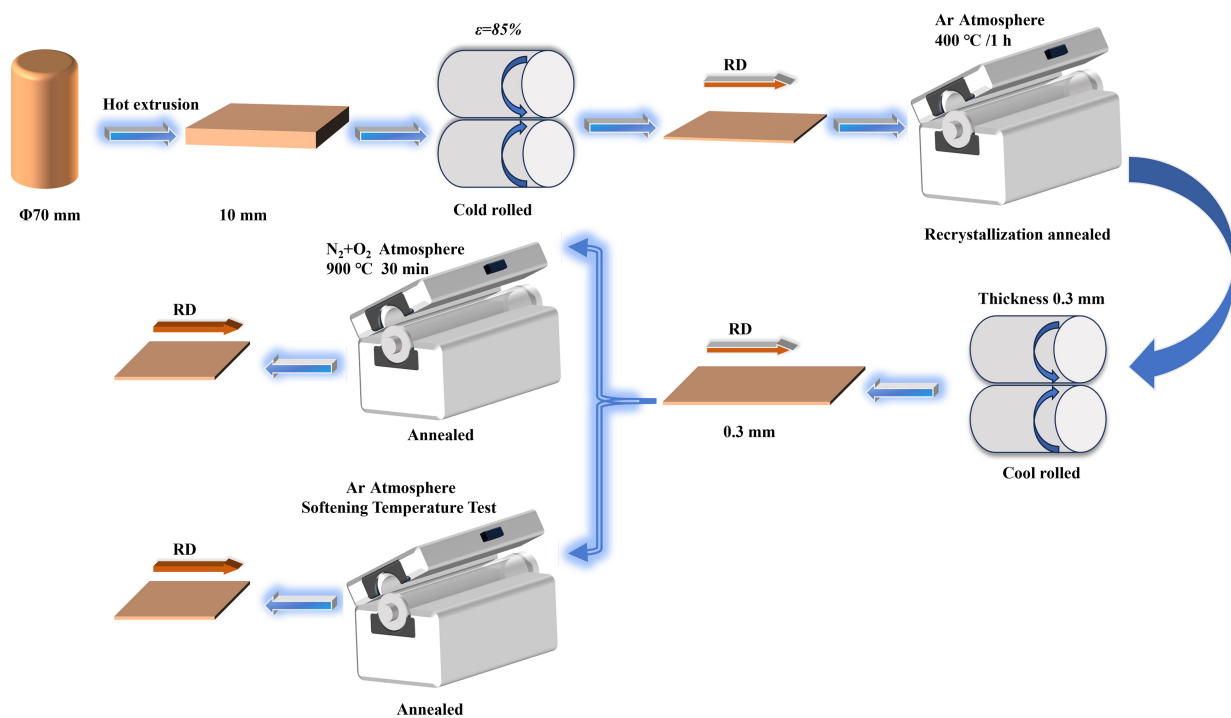


Figure 1. Schematic illustration of the experimental procedure.

refinement. This suggests that trace amounts of La are insufficient to inhibit grain coarsening in OFC. In contrast, the La180 and La330 samples show significantly refined grains with sizes of only 38.64 and 43.10 μm , respectively. This pronounced refinement confirms that these higher La contents suppress grain coarsening in OFC. From Figure 2A₂-E₂ and Figure 3, it can be seen that the La-containing OFC after 900 °C/30 min annealing is dominated by high-angle grain boundaries (HAGBs) and twin boundaries. Despite a slight local reversal at La11, the overall trend with increasing La content exhibits a general increase in the fraction of low-angle grain boundaries (LAGBs) and a general decrease in that of HAGBs. During the plastic processing of copper alloys, deformation tends to concentrate in the surface layer. Subsequent high-temperature annealing can lead to abnormal grain coarsening, transforming what should be a mirror-smooth surface into a rough, dull, and pitted appearance. The surface develops irregular polyhedral protrusions and depressions corresponding to individual grains, resembling orange peel—a phenomenon known as the "orange peel" defect^[14,17]. As marked by yellow circles in Figure 2A₁-C₁, grains with anomalous orientations are clearly observed. These grains appear as blocks or bands, with sizes significantly different from the matrix grains, and are mostly annealing twins formed during high-temperature annealing. This surface undulation, resulting from inhomogeneous strain distribution, creates the orange peel morphology^[19].

Figure 4 shows that as the content of the rare earth element La increases, the combined proportion of grains with {111}, {101}, and {001} orientations gradually increases. For La330, the majority of grains are oriented along {001}, accounting for 85.4%. The grain size distribution in 6N Cu, La11, and La31 is inhomogeneous, with numerous grains having anomalous orientations, resulting in high orientation anisotropy. This strong anisotropy is closely related to the "orange peel" defect formed after high-temperature annealing. From a micro-morphological perspective, for an individual grain, when the external force direction is favorably oriented relative to its slip systems (i.e., has a high Schmid factor), the grain is in a "soft orientation" and requires only a small, resolved shear stress to initiate slip, making it prone to deformation^[31]. Conversely, grains in "hard orientations" are difficult to deform. During surface finishing or service, regions of soft-oriented grains experience more deformation and tend to recess, while regions of hard-oriented grains

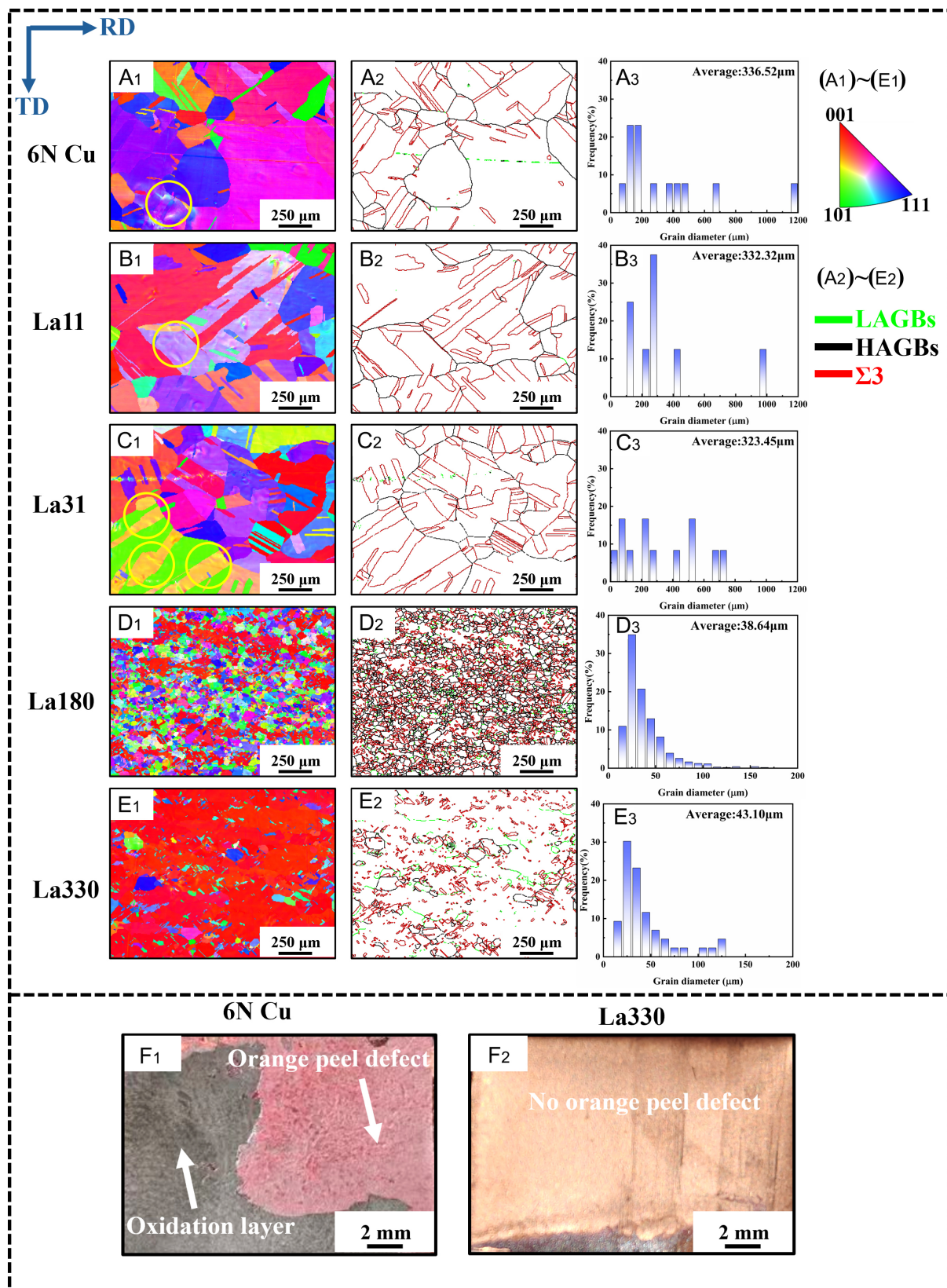


Figure 2. IPF map, grain boundary distribution, grain size statistics and macroscopic morphology of orange peel defect after annealing at 900 °C for 30 min: (A₁–A₃) 6N Cu, (B₁–B₃) La11, (C₁–C₃) La31, (D₁–D₃) La180, (E₁–E₃) La330, (F₁) 6N Cu, (F₂) La330.

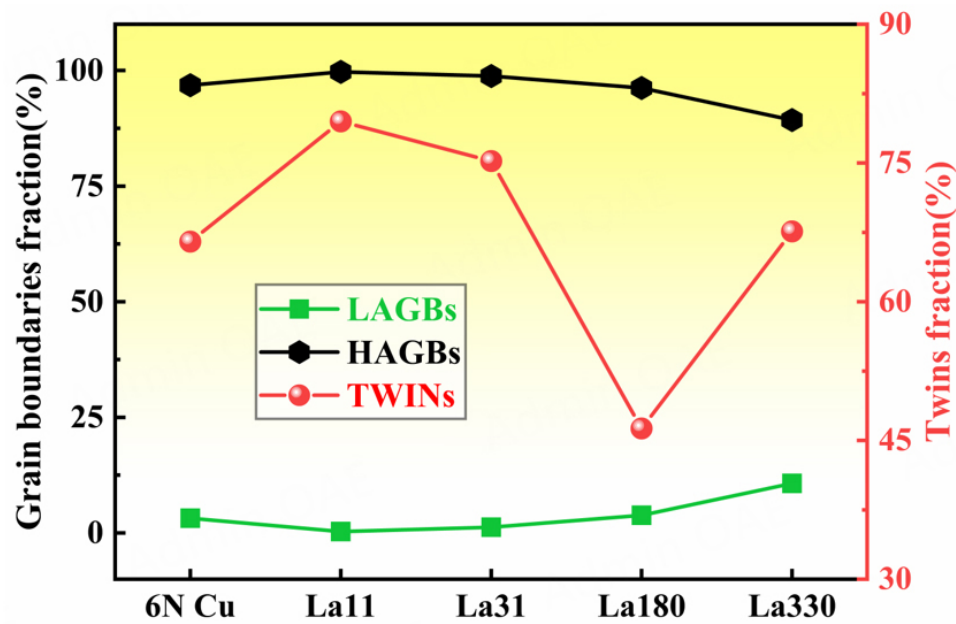


Figure 3. Fraction of various grain boundary types in OFC as a function of La content following annealing at 900 °C for 30 min.

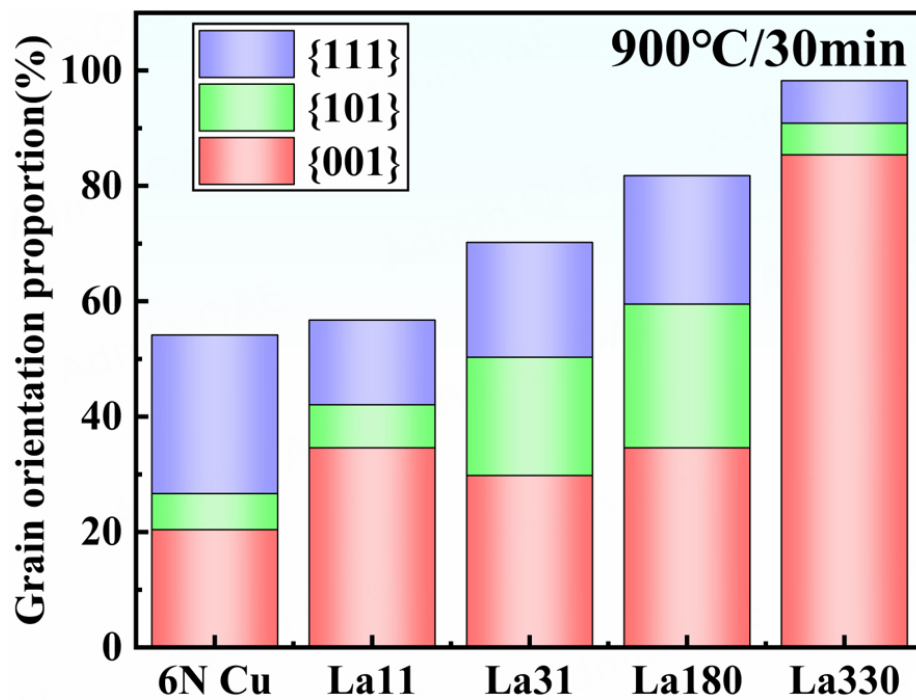


Figure 4. Fractional distribution of various grain orientations in OFC as a function of La content, following annealing at 900 °C for 30 min.

deform less and remain relatively protrusive. Due to the coarse grain size, each grain occupies a large area on the surface, causing this undulation to manifest on a per-grain scale and form the "orange peel" appearance. In La180 and La330, the grain orientations are more similar, and the grain distribution is more uniform, resulting in no significant "orange peel" defect. Macroscopic morphology is depicted in Figure 2F₁ and F₂. For the 6N Cu sample, the "orange peel" defect is distinctly observed beneath the oxide layer formed after high-temperature annealing, manifesting macroscopically as uneven, scaly textures. In contrast, the La330 sample exhibits a smooth surface with a mirror-like metallic luster. This observation suggests that the addition of a relatively high content of rare earth La mitigates the "orange peel" defect induced by abnormal grain coarsening.

Texture evolution

Figure 5A–E presents the texture distribution maps and the corresponding statistical charts of texture component fractions for OFC with different La contents after 900 °C/30 min annealing. Figure 6A–E shows the ODF maps for OFC with different La contents, at φ 2 sections of 0°, 25°, 45°, and 65°. Six common texture components in copper metals were statistically analyzed: Cube {001}<100>, Goss {011}<100>, Brass {011}<211>, Copper {112}<111>, S {123}<634>, and Brass Recrystallization {236}<385> (Brass Rec). As seen in Figure 5, the texture of 6N Cu and La11 is predominantly composed of Brass Rec. For La31, the texture components are roughly comparable, with Brass texture being more dominant and Goss texture less so. La180 is mainly characterized by S and Cube textures, while La330 exhibits a widespread Cube texture, with its fraction reaching as high as 85.1%. With increasing La content, the fraction of Brass Rec texture decreases significantly, while that of Cube texture increases markedly. Specifically, the Brass Rec fraction drops from 50.5% to 1.46%, and the Cube fraction increases from 2.83% to 85.1%. The ODF maps in Figure 6 also show a transition in the maximum texture intensity. The maximum intensity first weakens and then strengthens significantly, decreasing from 27.99 for 6N Cu to 8.47 for La31, and then increasing to 41.26 for La330. The texture evolves from a relatively strong Brass Rec in 6N Cu to an extremely strong Cube texture in La330. This indicates that the addition of rare earth La significantly promotes the transformation from Brass Rec to Cube texture in samples after 900 °C/30 min high-temperature annealing.

To further elucidate the influence of La on texture evolution in OFC, the major texture subsets and corresponding pole figures for OFC with variable La contents upon 900 °C/30 min annealing are presented in a correlated manner in Figure 7. It can be seen that the dominant texture in both 6N Cu and La11 is primarily the Brass Rec orientation, with very high intensities of 57.52 and 44.00, respectively. It is evident that the Brass Rec texture intensity in La11 shows a weakening trend compared to that in 6N Cu. For La31, the dominant texture type shifts, with Brass texture becoming predominant at an intensity of 39.12. For OFC with higher La content, namely La180 and La330, the dominant texture is primarily Cube. Their texture intensities are relatively close, at 51.91 and 49.44, respectively. Moreover, the Cube texture in La330 is more widespread. As also seen from the texture statistical chart in Figure 5F, the Cube texture fraction in La330 is 85.1%, representing a relative increase of 1.7 times (i.e., 170%) compared with the 31.2% in La180. Therefore, the addition of different amounts of La induces a transformation in the dominant texture of OFC after 900 °C/30 min high-temperature annealing. As the La content increases, the transformation path of the dominant texture follows the sequence: Brass Rec → Brass → Cube.

In the La180 and La330 specimens, the high-volume fraction of Cube texture {001}<100> imparts a highly consistent crystallographic orientation to the grains, significantly reduces the strain anisotropy between adjacent grains, and suppresses the nucleation and growth of abnormally oriented grains, thereby improving the "orange-peel" defect (characterized by surface unevenness and roughness) caused by incompatible grain deformation. It should be noted that this improvement is not solely attributable to the texture orientation alone but is instead built upon the significant grain refinement induced by rare-earth La: the fine-grained structure ensures the cooperative deformation capability of the polycrystal under external stress, while the orientation uniformity further optimizes the homogeneity of surface strain distribution. Only through the synergistic action of these two factors can the orange-peel defect be completely eliminated during plastic deformation, resulting in excellent surface quality.

The synergistic effect of texture control and grain refinement described above has deeper engineering significance for the actual service performance of DBC substrates. First, with respect to thermal cycling reliability, DBC substrates endure repeated temperature changes during service. Owing to the significant coefficient of thermal expansion mismatch between the copper layer and the ceramic substrate (Al_2O_3 or Aluminum nitride (AlN)), thermal cycling generates repeated thermomechanical stress^[8], leading to the

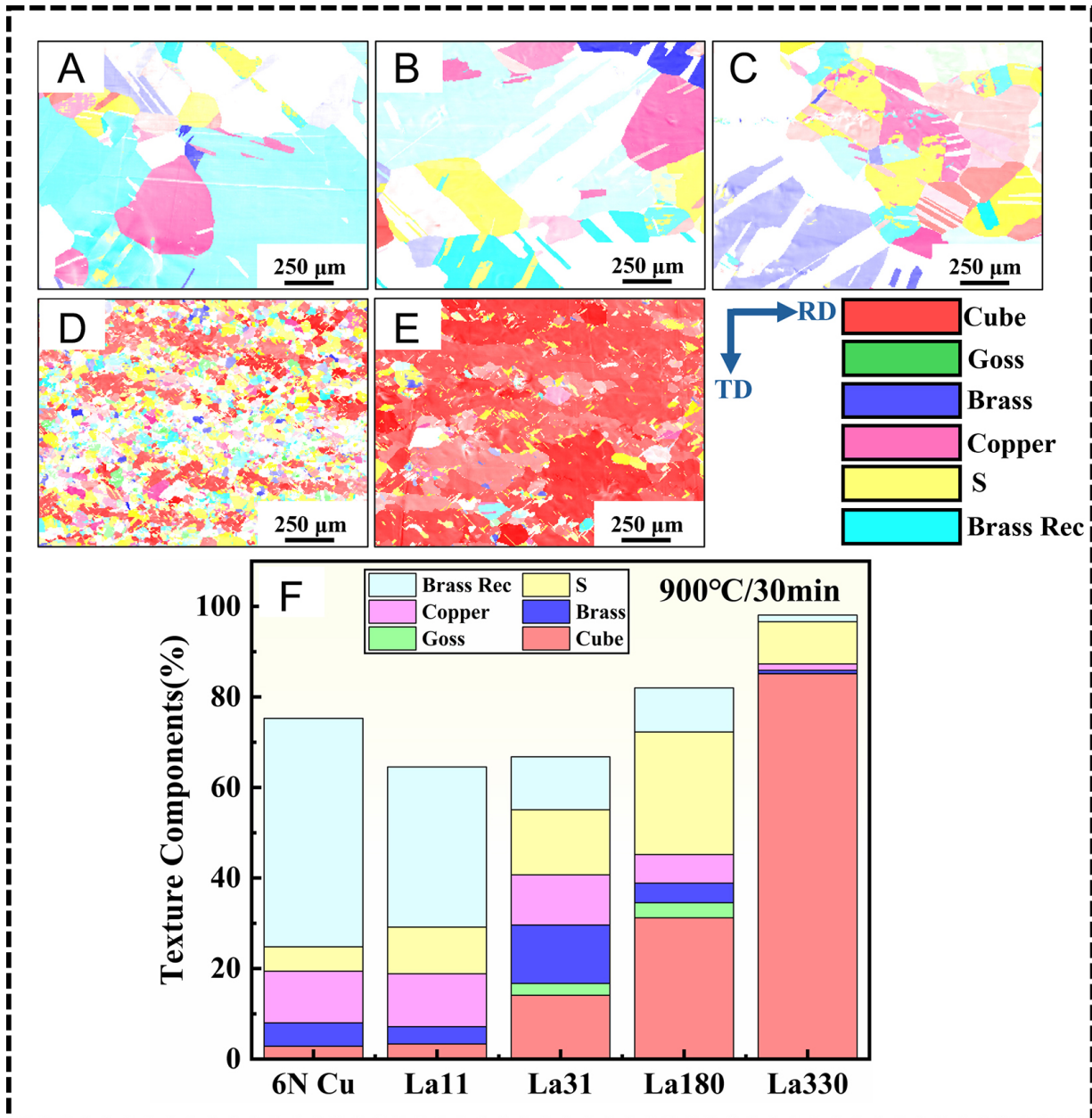


Figure 5. Texture distribution map and constituent texture components in OFC as a function of La content after annealing at 900 °C for 30 min: (A) 6N Cu, (B) La11, (C) La31, (D) La180, (E) La330, (F) Texture components diagram of the different samples.

initiation and propagation of fatigue cracks in the copper layer, and eventually causing delamination of the copper layer from the ceramic substrate^[10]. La180 and La330, by promoting the formation of Cube texture, reduce the local stress concentration caused by grain boundary reconstruction during thermal cycling, thereby delaying the initiation of fatigue cracks. Second, regarding surface coating adhesion, the surface of the copper layer on DBC substrates typically requires metallization treatments such as nickel plating or gold plating, or connection to power chips via silver sintering technology^[7]. The elimination of the orange-peel defect directly implies an improvement in the surface flatness of the copper layer^[19], which is crucial for the uniform coverage and interface bonding quality of subsequent coatings. In addition, La180 and La330, by promoting the formation of Cube texture, endow the copper surface with a highly consistent crystallographic orientation, altering the crystallographic preferred orientation distribution as well as the associated surface energy and surface oxidation behavior, thereby providing a new material design approach for optimizing the

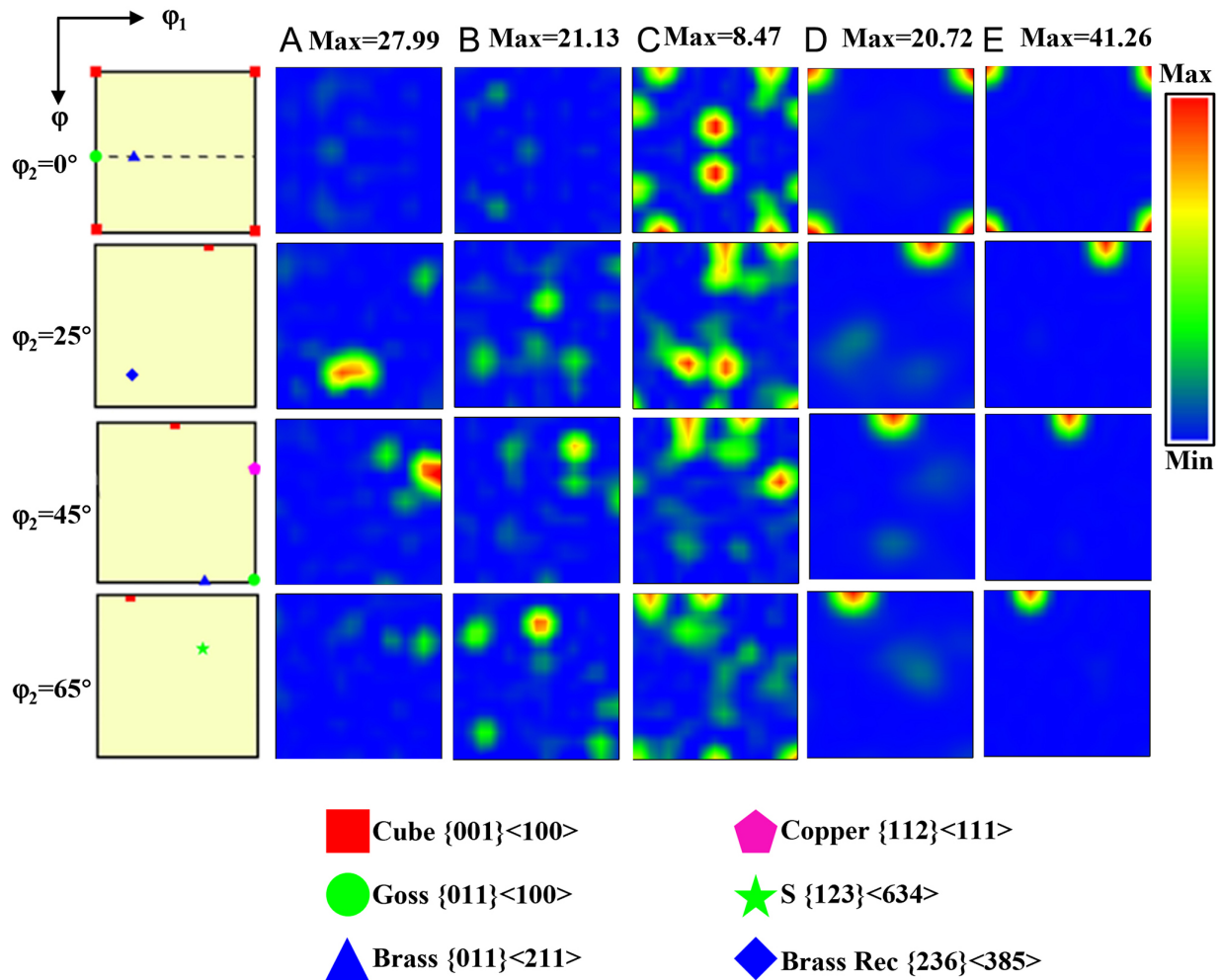


Figure 6. ODF sections of $\phi_2 = 0^\circ$, $\phi_2 = 25^\circ$, $\phi_2 = 45^\circ$ and $\phi_2 = 65^\circ$ of OFC with different La contents after annealing at 900 °C for 30 min: (A) 6N Cu, (B) La11, (C) La31, (D) La180, (E) La330.

metallization process on the copper surface of DBC substrates. Third, with regard to interfacial fracture resistance, interface failure in DBC substrates typically manifests as delamination or peeling between the copper layer and the ceramic substrate^[9]. La180, by promoting the formation of Cube texture, imparts a highly consistent crystallographic orientation to the copper layer, significantly reducing the strain anisotropy between adjacent grains and improving the orange-peel defect, thereby lowering the stress peaks at the interface.

In summary, La180, through the synergistic mechanism of "Cube texture orientation consistency and fine-grained structure cooperative deformation", not only eliminates the "orange peel" defect and improves the surface quality of the copper layer, but also significantly enhances the overall service performance of DBC substrates from three dimensions—thermal cycling reliability, surface coating adhesion, and interfacial fracture resistance. This provides a new theoretical basis and engineering pathway for improving the long-term reliability of DBC substrates from the source of copper foil materials through rare-earth microalloying.

Electrical conductivity and hardness

Figure 8 shows the electrical conductivity and hardness of OFC with different La contents after annealing at 900 °C for 30 min. Error bars denote the standard deviation (SD) of the measurements. As the La content increases, the hardness increases gradually, rising from 55.6 to 67.9 HV. With increasing La addition, the

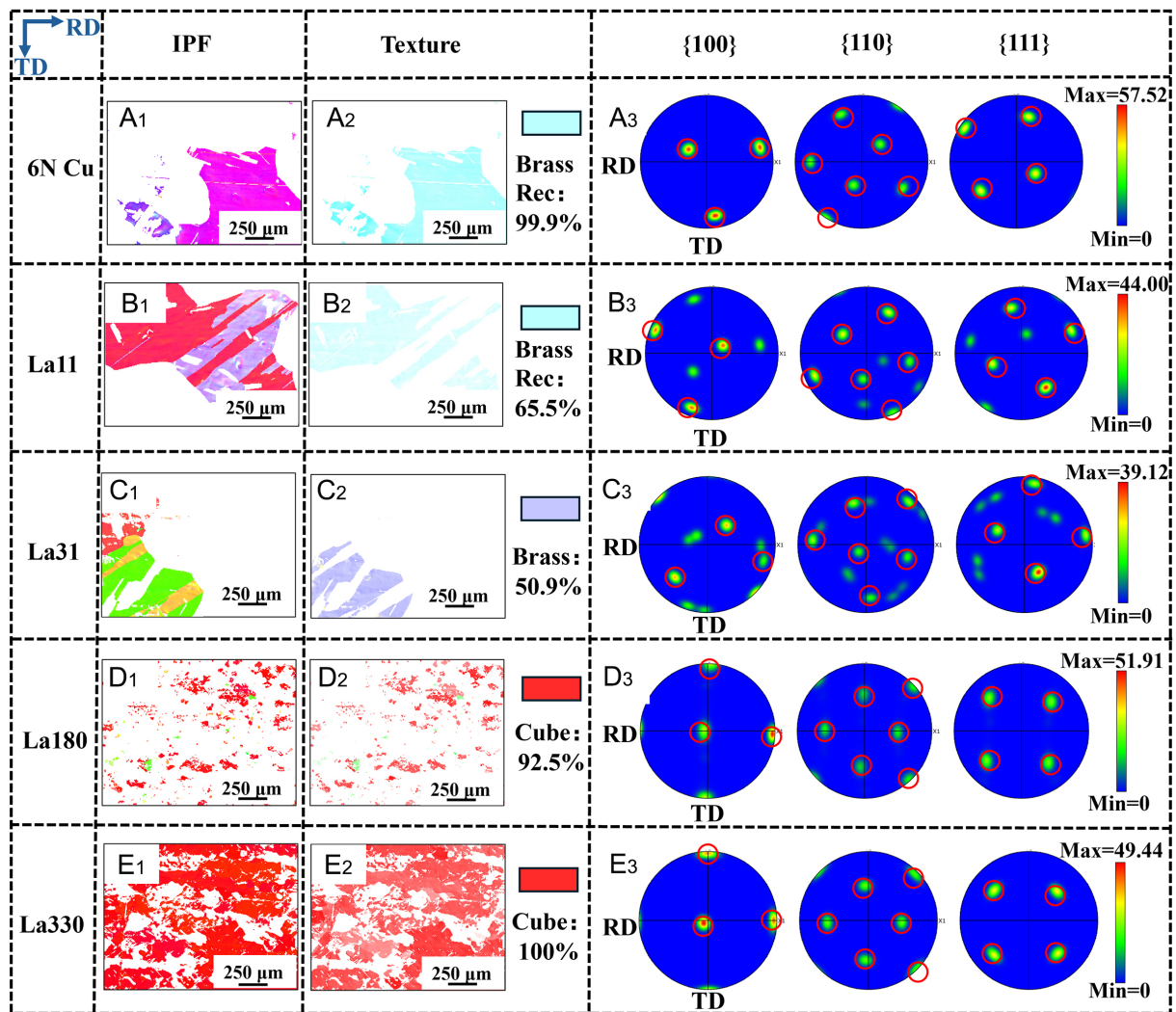


Figure 7. The IPF and texture maps of the pole figure and the corresponding regions of OFC with different La contents after annealing at 900 °C for 30 min: (A₁–A₃) 6N Cu, (B₁–B₃) La11, (C₁–C₃) La31, (D₁–D₃) La180, (E₁–E₃) La330.

electrical conductivity of OFC shows a trend of first decreasing rapidly and then gradually stabilizing. Conductivity decreases significantly from 104.2 %IACS for 6N Cu to 101.0 %IACS for La31. While, the La180 and La330 samples both maintain conductivity above 101.0 %IACS, at 101.3 %IACS, indicating that even with higher La additions, OFC can retain excellent high conductivity.

These variations in hardness and conductivity are closely related to the solid solubility of La in OFC, the characteristics of second-phase precipitation, and their influence on grain size and dislocation motion^[32]. The solid solubility of rare earth La in OFC is extremely limited, with virtually no solid solution. Except at very low concentrations where La atoms dissolve into the copper lattice via substitution or interstitial mechanisms, the large atomic radius mismatch between La and Cu causes severe lattice distortion^[30,33]. This has minimal influence on grain size, as shown in Figure 2B₁ and C₁. Under this condition, electrical conductivity decreases substantially, while hardness increases slightly due to solid solution strengthening, albeit to a limited extent. This corresponds to the conductivity and hardness trends observed for La11 and La31 in Figure 8. As La content increases, La exists as second-phase particles at grain boundaries and within grains. These La-rich particles are hard, incoherent with the matrix, and relatively large in size^[29].

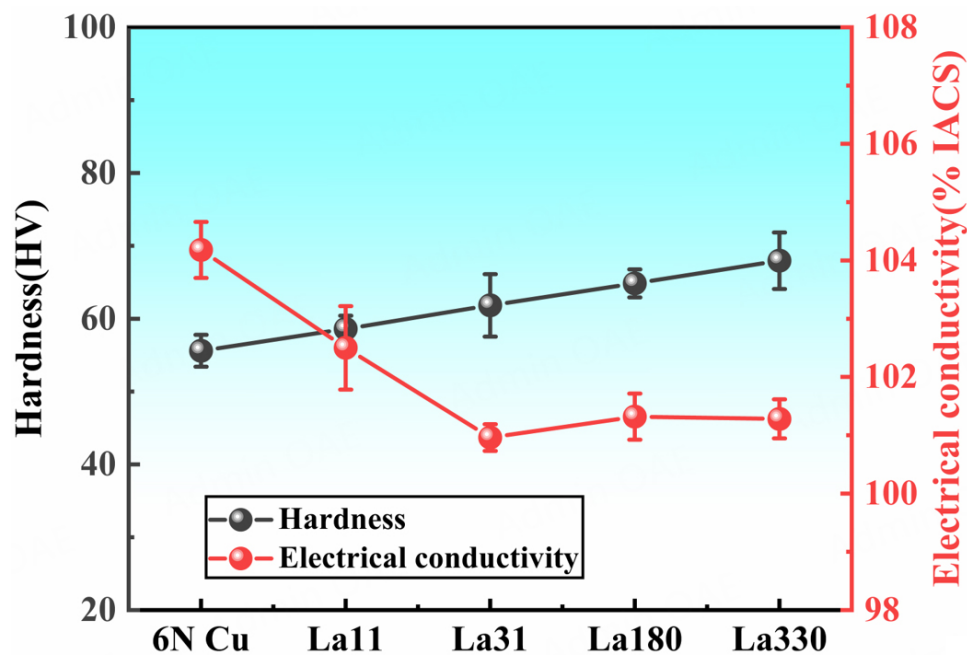


Figure 8. Results of electrical conductivity and hardness of OFC with different La contents after annealing at 900 °C for 30 min. Error bars denote the standard deviation (SD) of the measurements. For each sample, the conductivity is measured 5 times, and the average value is taken as the conductivity of the specimen measured.

Dislocations moving through the matrix are "pinned" upon encountering these particles, forced to bend and bypass them—a classic dislocation bypass mechanism (Orowan mechanism)^[34–36]. Furthermore, grain refinement becomes highly pronounced, as shown in Figure 2D₁ and E₁. This regime increases hardness but further degrades conductivity. However, because solute atoms precipitate from the copper matrix, thereby generating second-phase particles, scattering of electrons by solute atoms is greatly reduced. Additionally, La forms compounds with impurity elements such as O, P, and S, purifying the copper matrix. This allows conductivity to recover significantly, resulting in the noticeably slowed decline in conductivity from La31 to La330. The influence of La on the hardness and conductivity of OFC is highly dependent on its specific existing form within the copper. Different forms contribute to strengthening mechanisms with markedly varying effectiveness. To investigate and analyze this more deeply, we will employ TEM in the following Section "TEM analysis" to specifically analyze the form of La in OFC after high-temperature annealing, aiming to provide an experimental basis for subsequent optimization of composition design and conductivity regulation in rare-earth-modified OFC.

Effect of trace La on the softening temperature of OFC

Variation in softening temperature

The softening temperature is a fundamental concept in materials science. It describes the temperature range or characteristic temperature point at which a material undergoes a significant and permanent decline in its macroscopic mechanical properties (particularly hardness) during heating^[37]. In simple terms, the softening temperature signifies the temperature threshold at which a material permanently transitions from a "hard and strong" worked or high-strength state back to a "soft and ductile" annealed state. Figure 9 presents the annealing softening characteristic curves of OFC with different La contents. Error bars denote the SD of the measurements. The softening temperature is operationally defined here as the annealing temperature at which the hardness of a copper or copper alloy material drops to 80% of its original value after isothermal holding for 1 h, followed by natural cooling to room temperature. The temperatures at which the hardness of each sample dropped to 80% of its original value have been marked in Figure 9. In this test, the annealing

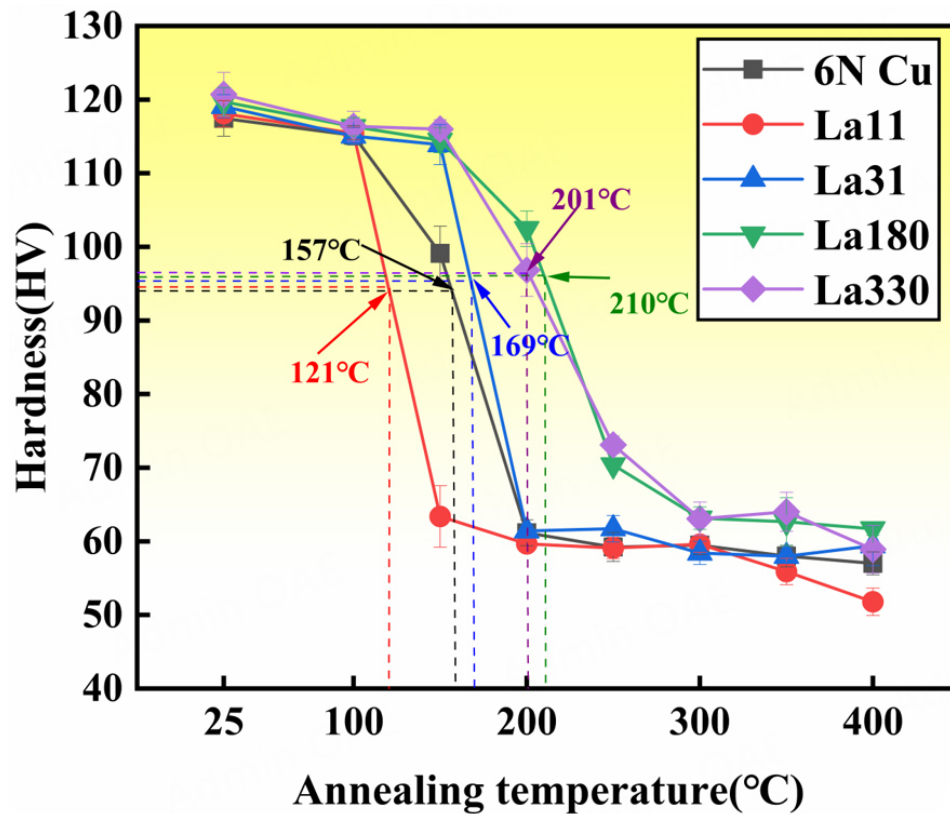


Figure 9. Annealing softening characteristic curves of OFC with different La contents. Error bars denote the SD of the measurements.

temperatures ranged from 100 to 400 °C in 50 °C intervals. After natural cooling to room temperature, the Vickers hardness was measured. The initial reference hardness was the Vickers hardness measured at 25 °C. The 6N Cu has a softening temperature of 157 °C. La11 lowers the softening temperature to 121 °C, while La31, La180, and La330 increase it. Among these, La180 shows the greatest increase, raising the softening temperature by 53 °C. This indicates that a higher La content raises the softening temperature of OFC, thereby enhancing its resistance to softening at elevated temperatures. To delve deeper into the intrinsic mechanisms underlying the decrease in softening temperature for La11 and the increase for La31, La180 and La330, this study selected samples subjected to a softening treatment at 150 °C for 1 h for EBSD characterization and analysis.

Microstructure after softening treatment at 150 °C for 1 h

The relationship between the softening temperature and recrystallization is direct and intimate: recrystallization is the core microscopic mechanism responsible for macroscopic softening, while the softening temperature typically serves as the macroscopic manifestation of the onset of recrystallization. For the vast majority of metals that have undergone cold deformation (e.g., rolling, drawing), the softening temperature is predominantly governed by the recrystallization process^[38,39].

Figure 10 presents the EBSD characterization data of different samples after the 150 °C × 1 h softening treatment. Figure 11 shows (A) the recrystallized fraction statistics chart and (B) the misorientation distributions map derived from the data in Figure 10. Boundaries with misorientation angles between 2° and 15° are defined as LAGBs and are depicted by green lines in the maps. Boundaries with angles greater than 15° are defined as HAGBs, shown by black lines. Σ3 twin boundaries are indicated by red lines.

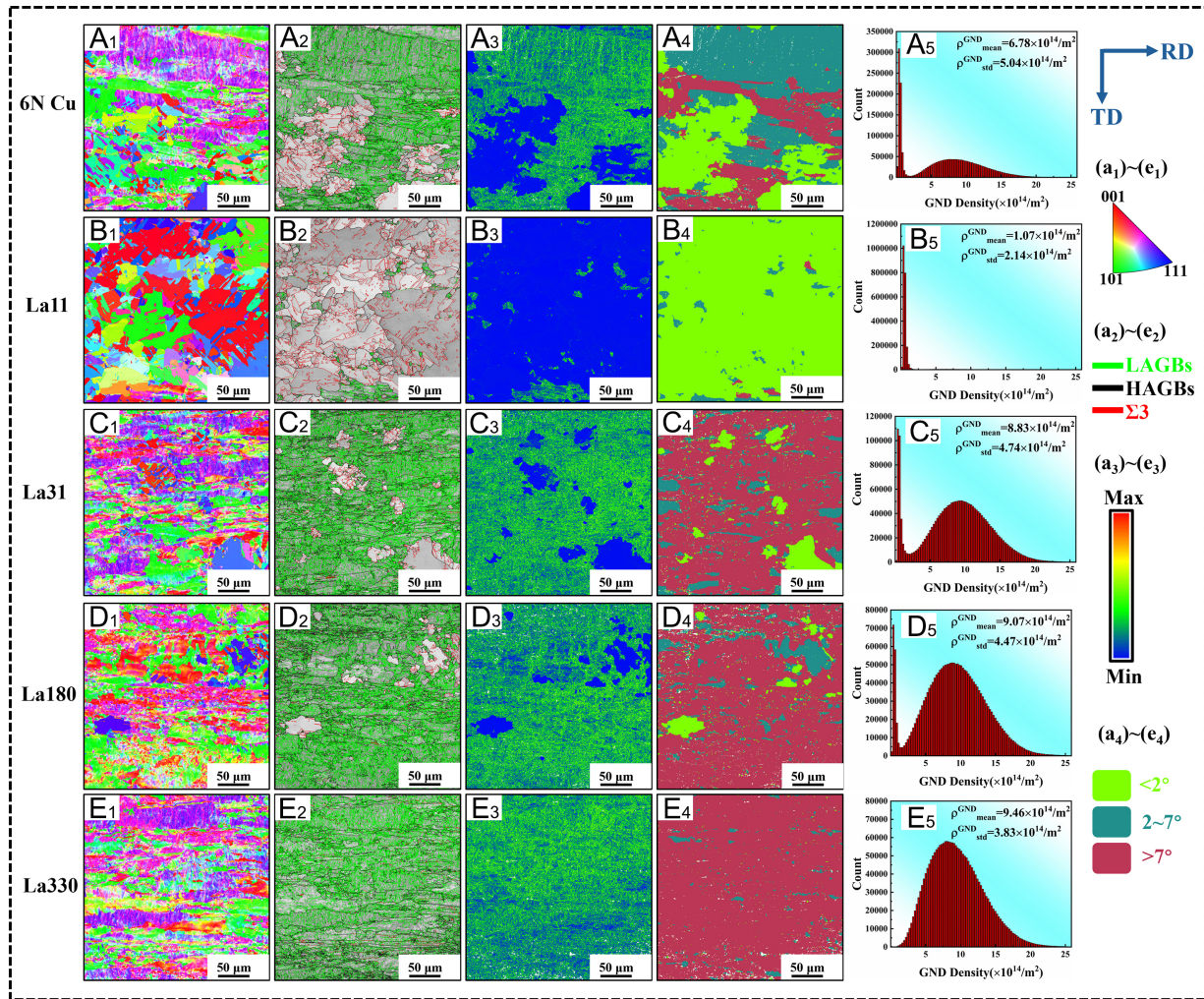


Figure 10. 6N Cu, La11, La31, La180, La330 after softening annealing at 150 °C for 1 h: (A₁–E₁) IPF map, (A₂–E₂) GB map, (A₃–E₃) KAM map, (A₄–E₄) GOS map (A₅–E₅) GND density.

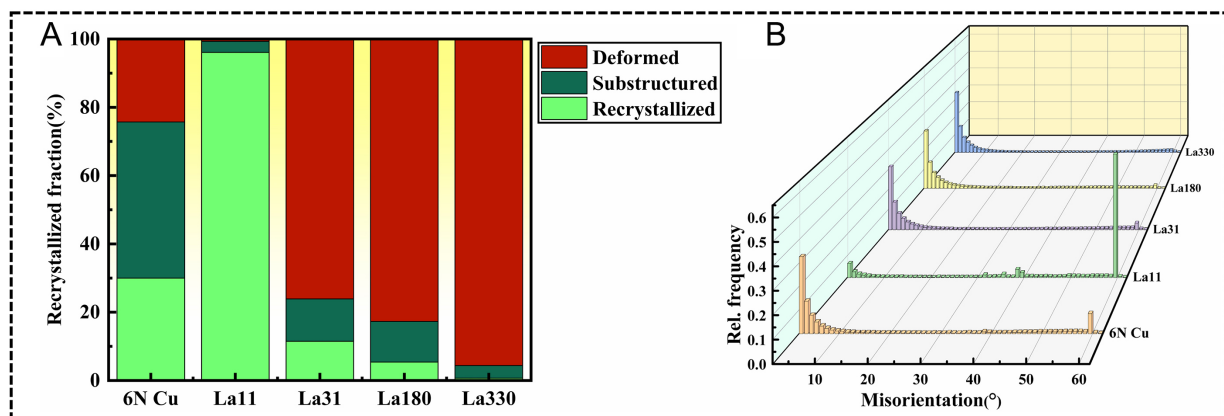


Figure 11. Recrystallized fraction statistics chart (A) and misorientation distributions map (B) from Figure 10.

KAM map, by quantitatively characterizing local misorientations, can directly reflect the distribution of microscopic strain and the characteristics of dislocation configurations within a material. As a key characterization technique linking bulk mechanical behavior to micro-scale deformation modes, KAM

technology holds significant application value in dynamically tracking the recrystallization progress. The magnitude of the local misorientation is positively correlated with the degree of microscopic strain in that region, and the strain state directly determines the distribution characteristics of internal stresses. When collecting and calculating KAM map data, the maximum angle is set to 5° , and the kernel size is 3×3 pixels. The misorientation between any given point and its neighboring points can be quantitatively calculated according to^[40,41]:

$$\theta_0 = \sum_{i=1}^{24} \theta_i \cdot I_{(\theta_i < \alpha)} / \sum_{i=1}^{24} I_{(\theta_i < \alpha)} \quad (1)$$

In this equation, $\alpha = 5^\circ$ indicates that misorientations exceeding 5° are excluded, θ_0 represents the local misorientation at the point, θ_i denotes the misorientation between this point and its neighboring points, and I is an indicator function. Subsequently, the formula for GND density can be simply derived based on the theoretical method of strain gradient^[42,43]:

$$\rho^{GND} = 2\theta_0 / \mu b \quad (2)$$

Here, ρ^{GND} is the GND density at the corresponding point, μ is the EBSD scan step size ($0.2 \mu\text{m}$), and b is the Burgers vector $= 0.5 \langle 110 \rangle$. ρ^{GND}_{mean} is the average GND density, and ρ^{GND}_{std} is the SD of the GND density. The calculation results are shown in Figure 10A₅-E₅.

GOS map achieves precise characterization of the degree of material recrystallization by quantitatively analyzing the orientation heterogeneity within individual grains^[44]. Essentially, the GOS value quantifies the average misorientation angle between the local crystallographic orientations of points within a grain and the grain's mean orientation. Based on the experimental system and characterization requirements of this study, the microstructural states corresponding to different GOS ranges are defined as follows: a GOS value in the range of 0° - 2° corresponds to a recrystallized grain, a GOS value between 2° - 7° corresponds to a subgrain, and a GOS value greater than 7° corresponds to deformed microstructure.

From Figure 10A₁-E₁ and A₂-E₂, and Figure 11B, it can be seen that after the 150°C for 1 h softening treatment, the microstructure of various specimens mainly exhibits a fibrous structure aligned along the RD from cold rolling, primarily composed of LAGBs, with a majority of grain orientations being $\{101\}$. In contrast, La11 displays a coarse equiaxed grain structure formed after annealing, consisting largely of HAGBs and $\Sigma 3$ twins, with a low content of deformed microstructure. The grain orientations in La11 are mainly $\{001\}$ and $\{101\}$. In the KAM maps of Figure 10A₃-E₃, the green regions indicate the presence of significant local strain concentration and a high crystallographic orientation gradient. The blue regions correspond to areas with smaller local strain, relatively intact crystal structure, and insignificant orientation variation. From Figure 10A₃-E₃ and A₅-E₅, it can be observed that due to the higher content of deformed microstructure, stress concentration is pronounced in 6N Cu, La31, La180, and La330, with a more widespread dislocation distribution. Their mean GND density (ρ^{GND}_{mean}) is far greater than that of La11. This indicates that the recrystallization degree of La11 is substantially different from that of the other four samples. From Figure 10A₄-E₄ and Figure 11A, the recrystallized area fraction in La11 is 96.1%, indicating complete recrystallization. In contrast, the recrystallization degree in 6N Cu, La31, La180, and La330 slows with increasing La content, with recrystallized area fractions of 30%, 11.5%, 5.4%, and 0.7%, respectively. The fundamental reason for this variation in recrystallization degree is closely related to the La addition amount and its solid solubility. After the $150^\circ\text{C} \times 1 \text{ h}$ softening treatment, the La content in the La11 sample is extremely low (only 11 ppm). At this ultralow concentration, La atoms primarily exist in the copper lattice in

the form of substitutional solid solution^[45]. Due to the difference in atomic radius between La and Cu, its solid solution leads to local elastic distortion of the host lattice, thereby introducing micro-strain. This lattice distortion stores a relatively high strain energy within the material. From a thermodynamic perspective, this stored energy constitutes additional free energy in the system^[46]. During subsequent annealing, this distortion energy can serve as an extra driving force for the recrystallization process. Specifically, it can lower the energy barrier for recrystallization nucleation and provide additional impetus for grain boundary migration^[47], thereby accelerating the overall nucleation and growth processes of recrystallization. The accelerated recrystallization process rapidly eliminates crystal defects such as high-density dislocations generated by prior processing within the OFC. The hardness contributed by dislocation strengthening in La11 decreases significantly, macroscopically manifesting as an accelerated softening process, which leads to a notable reduction in the softening temperature of La11. In contrast, 6N Cu, La31, La180, and La330 have a lower degree of recrystallization, allowing them to retain higher hardness after the $150\text{ }^{\circ}\text{C} \times 1\text{ h}$ softening treatment, thereby delaying the softening process. The above-mentioned phenomenon of abnormal decrease in softening temperature caused by trace rare-earth La is not an isolated case. In magnesium alloy systems, the addition of trace rare earth elements such as Ce, Nd, and Pr can induce texture softening, the addition of rare earths alters the evolution path of the deformation texture, leading to an increase in the Schmid factor and a decrease in the Taylor factor at elevated temperatures, thereby producing a softening effect^[48,49].

The reason why a higher content of rare earth La can increase the softening temperature of OFC is that when the La content exceeds its extremely low solid solubility in copper, La reacts with copper to form fine nanoscale intermetallic particles (e.g., Cu_6La). These particles exert a powerful "pinning effect": they act like "anchors," firmly gripping grain boundaries and dislocations. During annealing, for grain boundaries to migrate and dislocations to rearrange (i.e., for recrystallization to occur), they must overcome the constraints imposed by these pinning particles, which require higher thermal energy. Consequently, recrystallization is significantly delayed, leading to a substantial increase in the softening temperature. However, in La330, severe enlargement of the Cu_6La secondary phase leads to a reduction in pinning force, making dislocation elimination and grain boundary movement more readily take place. This results in reduced efficiency in restraining the recrystallization evolution^[33,50], ultimately causing its softening temperature to be lower than that of La180.

Texture evolution

Due to the varying degrees of recrystallization in the five OFC alloys with different La contents after the $150\text{ }^{\circ}\text{C} \times 1\text{ h}$ softening treatment, the texture components change significantly. As can be seen from Figure 12, the fully recrystallized La11 is dominated by the recrystallization texture Cube, accounting for 30.2%, while rolling textures such as S, Brass, and Copper are less distributed. In the partially recrystallized 6N Cu, both the recrystallization texture Brass Rec and the rolling textures S, Brass, and Copper are present in different proportions, with the Brass Rec texture accounting for 28.0%. The texture composition of La31, La180, and La330, which are almost entirely deformed microstructures, is mainly dominated by various rolling textures: S, Brass, and Copper. La330 has the highest fraction of rolling texture components, primarily S and Copper textures, with proportions of 34.4% and 28.4%, respectively. This indicates that after the $150\text{ }^{\circ}\text{C} \times 1\text{ h}$ softening treatment, compared with 6N Cu, higher La additions favor the suppression of the transformation from rolling textures (generated during rolling deformation) to recrystallization textures in OFC, thereby inhibiting the recrystallization process. In contrast, lower La additions can promote the formation of recrystallization textures, accelerating the recrystallization process, which consequently affects the softening process and the softening temperature.

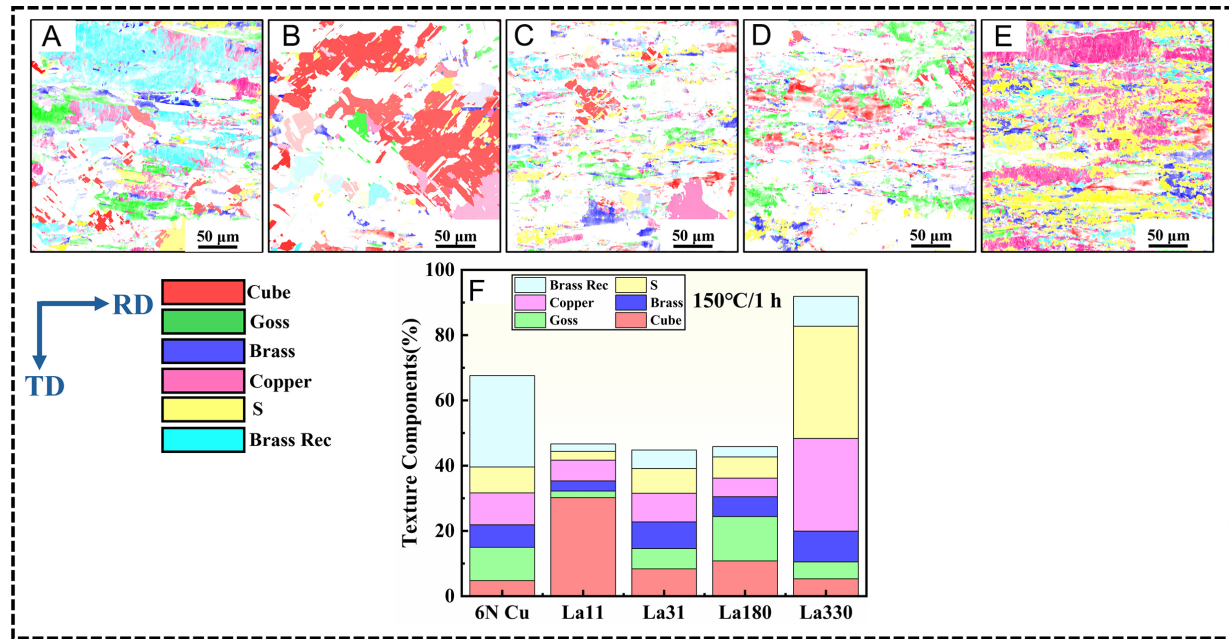


Figure 12. Texture distribution map and texture components after softening annealing at 150 °C for 1 h: (A) 6N Cu, (B) La11, (C) La31, (D) La180, (E) La330, (F) Texture components diagram of the different samples.

TEM analysis

To investigate the mechanisms by which rare earth La affects grain size, microstructure, and properties of OFC, and to clarify the existing forms of trace La in OFC, TEM was used to characterize La180 and La330 samples after annealing at 900 °C for 30 min. Figure 13 shows TEM micrographs of La180 after annealing at 900 °C for 30 min. As seen in Figure 13A and B, D-F, coarse annealing twins formed after high-temperature annealing, with twin widths reaching the micrometer scale. The formation of twins helps reduce intragranular dislocation density and minimizes electron scattering, thereby enhancing the electrical conductivity of OFC^[51]. Figure 14 presents TEM images of intragranular second phases in La180 after 900 °C annealing for 30 min. From Figure 14A-D, it can be seen that the grain interiors are enriched with micrometer-sized La-rich oxide compounds. The EDS mapping results are shown in Figure 14B-D. Selected area electron diffraction (SAED) pattern from Area 1 was indexed, confirming the phase as La_2O_3 ; La_2O_3 has lattice parameters of $a = 3.94 \text{ \AA}$, $b = 3.94 \text{ \AA}$, $c = 6.13 \text{ \AA}$, belonging to the hexagonal crystal system with a simple lattice. Figure 14G shows that the La_2O_3 within Area 2 has a definite orientation relationship with the copper matrix, specifically $[1\ 1\ 1]_{\text{Cu}} \parallel [0\ 0\ 1]_{\text{La}_2\text{O}_3}$. From the high-resolution transmission electron microscopy (HRTEM) characterizations in Figure 14H and I, the interplanar spacing of Cu was measured as $d_\alpha = 1.294 \text{ \AA}$, and that of La_2O_3 as $d_\beta = 1.980 \text{ \AA}$. The diffraction spots from FFT 1 (La_2O_3) and FFT 2 (Cu) in Figure 14H are indexed in Figure 14J and K, respectively. The lattice mismatch δ can be calculated according to^[52-54]

$$\delta = \frac{2/d_\alpha - d_\beta}{d_\alpha + d_\beta} \quad (3)$$

thus establishing the correlation between the secondary phase and the matrix. When $\delta < 0.05$, the interfacial relationship between the second phase and the matrix is coherent, when $0.05 < \delta < 0.25$, it is semi-coherent, and when $\delta > 0.25$, it is incoherent.

Figure 15 presents the TEM characterization of grain boundary segregation in La180 after annealing at 900 °C for 30 min. Figure 15A and E shows the grain boundary segregation region along the same grain boundary at two different magnifications. Figure 15B-D and F-H shows the EDS elemental maps

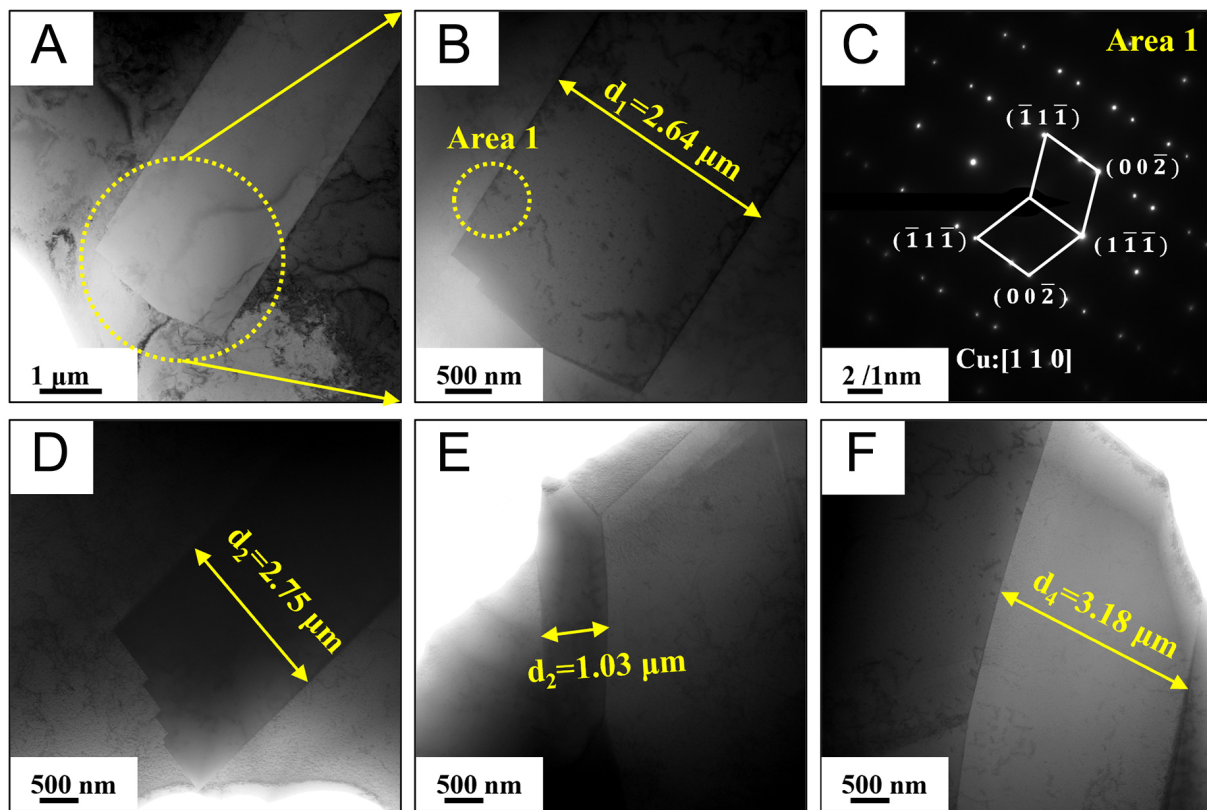


Figure 13. The TEM characterization results of La180 after annealing at 900 °C for 30 min: (A and B) and (D–F)Twins, (C) electron diffraction pattern of (B).

corresponding to the TEM bright-field images in (A) and (E), respectively. Line 1 is a line scan across a precipitate, with the result shown in Figure 15I. Line 2 is a line scan across the grain boundary but avoiding precipitates, with the result shown in Figure 15J. From Figure 15A–J, it can be observed that distinct grain boundary segregation occurs, and the precipitates may be composed of two or three elements among Cu, La, and O, forming stable precipitate phases. To clarify the phase composition and crystal structure of the precipitates at the grain boundary, targeted TEM structural characterization was performed on several precipitates in this region. HRTEM and FFT analysis and indexing were carried out separately on three precipitates in Area 1 and one precipitate in Area 2 of Figure 15K. As shown in Figure 15M and N, Phase 1 is nanoscale Cu_6La , with a precipitate size of 37.3 nm. Cu_6La crystallizes in the monoclinic crystal system with a primitive lattice, exhibiting lattice parameters $a = 5.143 \text{ \AA}$, $b = 10.204 \text{ \AA}$, $c = 8.144 \text{ \AA}$, and belongs to the monoclinic crystal system with a simple lattice. As shown in Figure 15O and P, Phase 2 is nanoscale $\text{La}_2\text{Cu}_2\text{O}_5$, with a precipitate size of 31.2 nm. $\text{La}_2\text{Cu}_2\text{O}_5$ has lattice parameters of $a = 13.864 \text{ \AA}$, $b = 3.7472 \text{ \AA}$, and $c = 27.943 \text{ \AA}$, and belongs to the monoclinic crystal system with a C-centered lattice. As shown in Figure 15Q and R, Phase 3 is nanoscale La_2CuO_4 , with a precipitate size of 7.5 nm. La_2CuO_4 has lattice parameters of $a = 5.3556 \text{ \AA}$, $b = 5.4011 \text{ \AA}$, $c = 13.149 \text{ \AA}$, and belongs to the orthorhombic crystal system with a face-centered lattice. As shown in Figure 15T and U, Phase 4 is nanoscale La_2O_3 , with a precipitate size of 29.3 nm.

Figure 16 presents the TEM characterization results of intragranular second phases in La330 after annealing at 900 °C for 30 min. As shown in Figure 16A–D, several micrometer-sized La-rich oxide particles are dispersed within the grain interior. The EDS mapping results are presented in Figure 16B. SAED pattern from Area 1 was indexed, confirming the phase as La_2O_3 . In Area 2, enrichment of S element is observed at

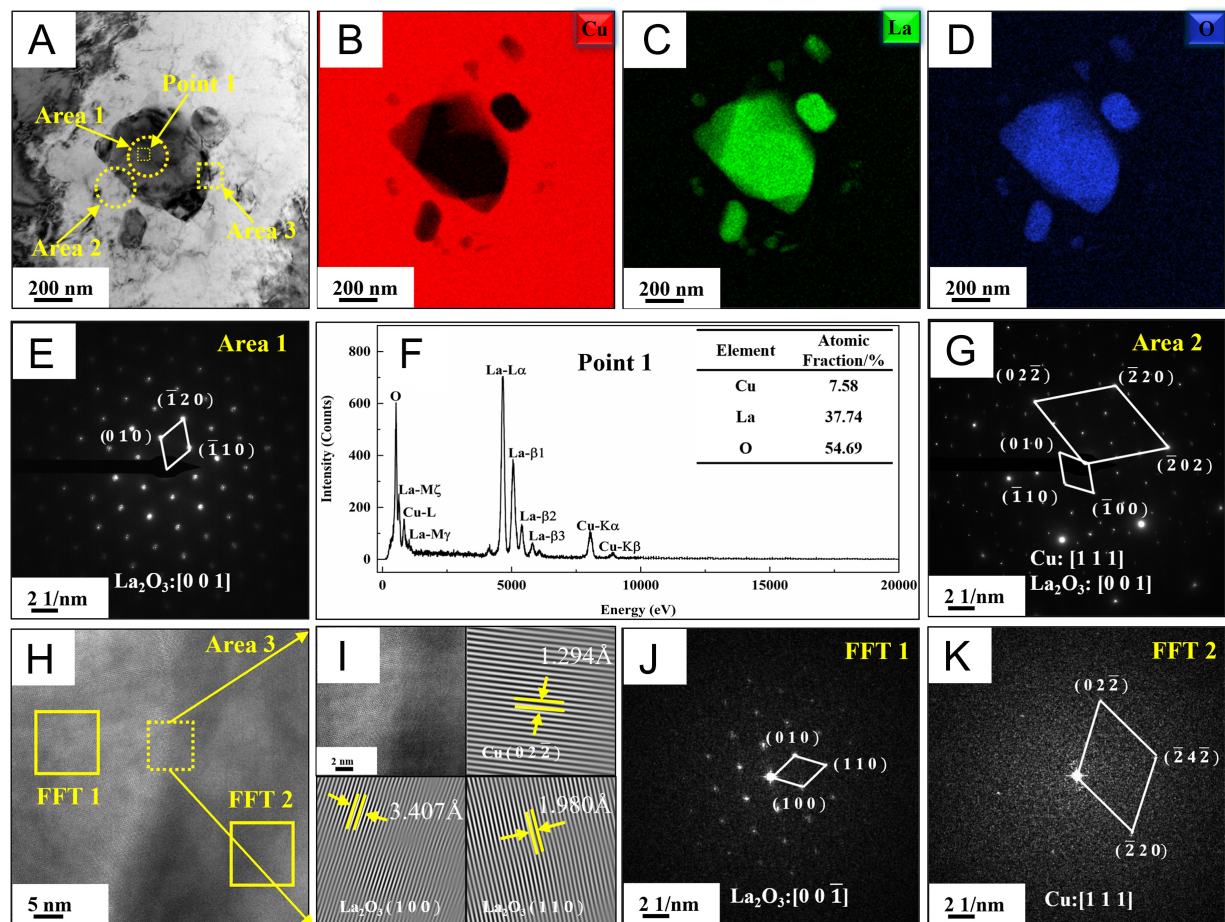


Figure 14. The TEM characterization of second phase in La180 after annealing at 900 °C for 30 min: (A) TEM bright-field images of second phase in La180, (B–D) EDS elemental map in (A), (E) electron diffraction pattern of La₂O₃ of Area 1, (F) Spectra from Point 1, (G) electron diffraction pattern of Area 2, (H) HRTEM images of Area 3, (I) enlarged image of the HRTEM image of (H) and the inverse Fast Fourier Transform (IFFT) lattice stripes, (J) FFT 1 in (H), (K) FFT 2 in (H).

the edges of the La-rich oxide particles. HRTEM and FFT analysis and indexing were performed on the S-rich phase in Area 3 [Figure 16E–G]. Combined with the point scan EDS result at Point 1 [Figure 16M], this S-rich phase is determined to be Cu₃₁S₁₆. It has a monoclinic crystal structure with a simple lattice, and lattice parameters of $a = 26.897$ Å, $b = 15.745$ Å, $c = 13.465$ Å. Furthermore, Figure 16H presents an individual micrometer-sized La-rich oxide particle. The corresponding EDS elemental maps are shown in Figure 16I–K. The point scan spectrum at Point 2 [Figure 16N] and the selected area diffraction pattern [Figure 16L] further confirm that this particle is also the La₂O₃ phase.

Figure 17 presents the TEM characterization of grain boundary segregation in La330 after annealing at 900 °C for 30 min. Figure 17A, E, and O shows three types of precipitates at the grain boundary. The corresponding EDS elemental maps for each precipitate are shown in Figure 17B–D, J–L, and P–R, respectively. Combined with HRTEM analysis and FFT indexing, the results indicate that the three precipitate types are essentially consistent with those in La180. They are: (1) nanoscale La₂Cu₂O₅ with a size of 37.4 nm (Phase 1, Figure 17E and F), (2) nanoscale Cu₆La with a size of 39.3 nm (Phase 2, Figure 17G and H), and (3) nanoscale La₂O₃ with a size of 18.2 nm (Phase 3, Figure 17S and T). Line 1 is a line scan across a precipitate, with the result shown in Figure 17M. Line 2 is a line scan across the grain boundary region avoiding precipitates, with the result shown in Figure 17N. Similar to La180, this indicates

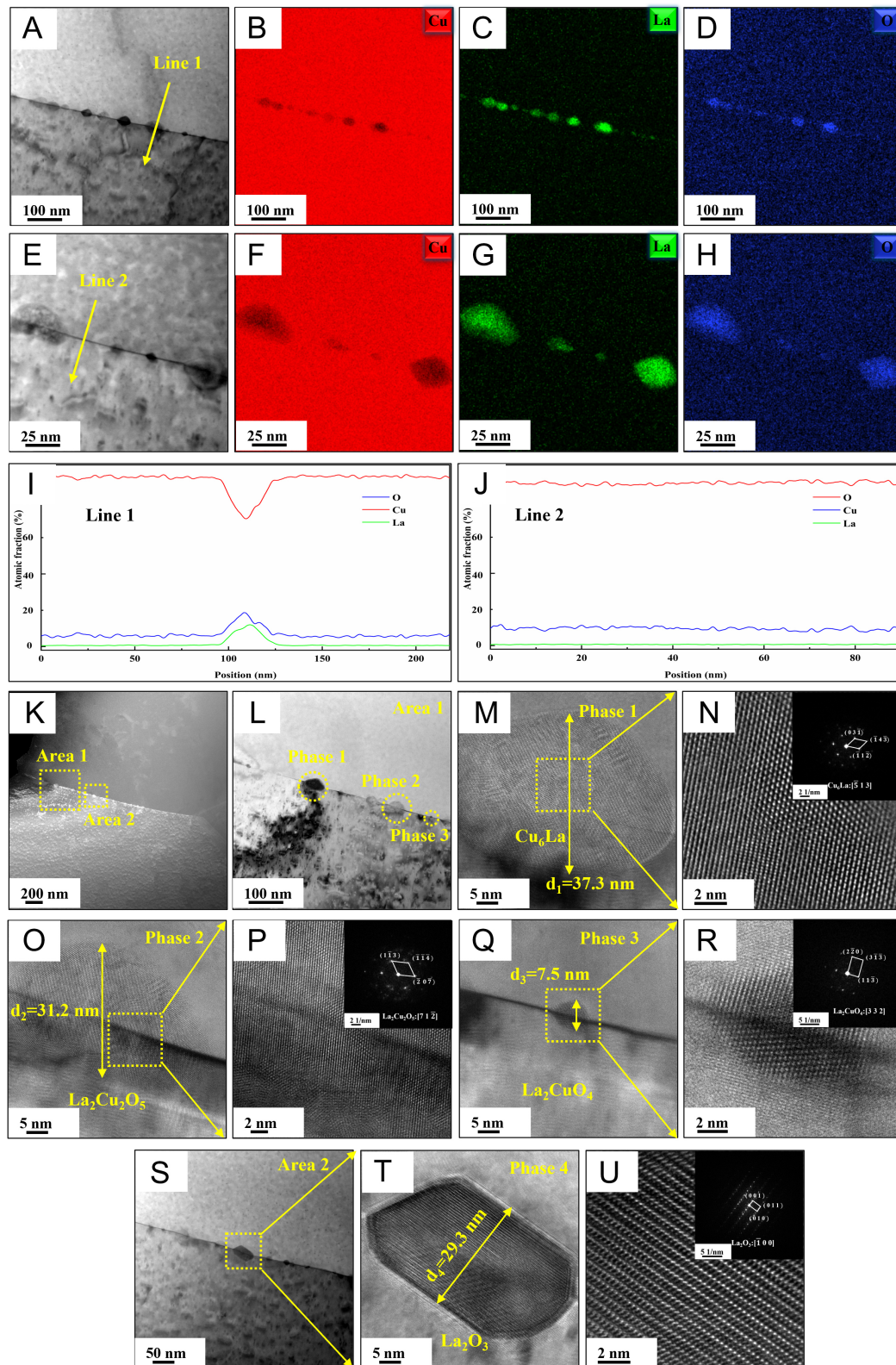


Figure 15. The TEM characterization of grain boundary segregation in La180 after annealing at 900 °C for 30 min: (A) and (E) TEM bright-field images of grain boundary segregation in La180, (B–D) EDS elemental map in (A), (F–H) EDS elemental map in (E), (I and J) EDS line scan, (K) TEM dark-field images of grain boundary segregation in La180, (L) TEM bright-field images of grain boundary segregation in Area 1, (M and N) HRTEM images and FFT of Phase 1, (O and P) HRTEM images and FFT of Phase 2, (Q and R) HRTEM images and FFT of Phase 3, (S) TEM bright-field images of grain boundary segregation in Area 2, (T and U) HRTEM images and FFT of Phase 4.

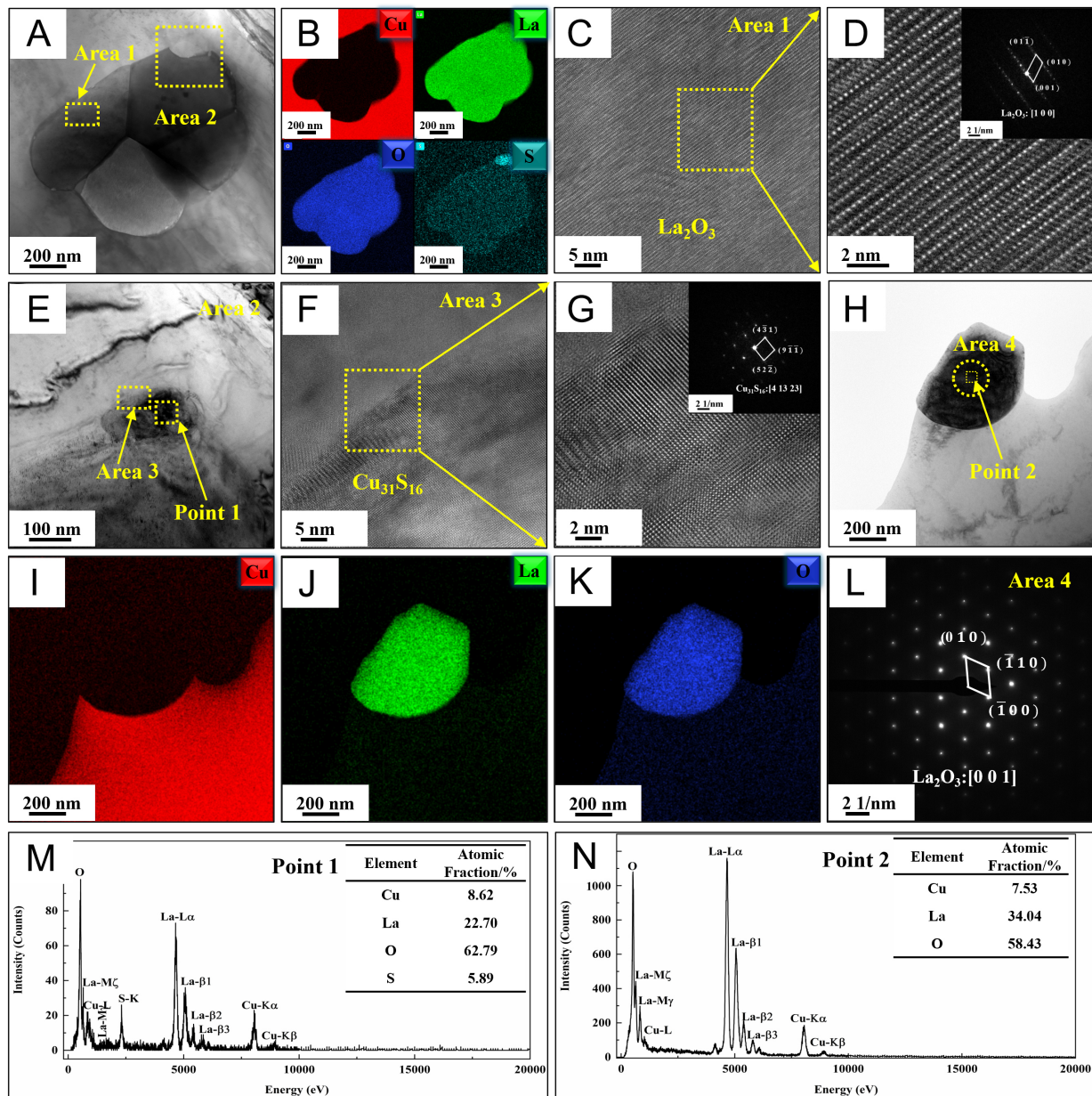


Figure 16. TEM characterization of second phase in La330 after annealing at 900 °C for 30 min: (A) TEM bright-field images of second phase in La330, (B) EDS elemental map in (A), (C and D) HRTEM images and FFT of Area 1, (E) TEM bright-field images in Area 2, (F and G) HRTEM images and FFT of Area 3, (H) TEM bright-field images of second phase in La330, (I-K) EDS elemental map in (H), (L) electron diffraction pattern of La₂O₃ of Area 4, (M) Spectra from Point 1, (N) Spectra from Point 2.

that after 900 °C high-temperature annealing for 30 min, stable precipitates formed at the grain boundaries in the La330 sample.

To quantitatively evaluate the Zener pinning effect of nanoscale La-rich precipitates on grain boundaries at high temperatures, theoretical estimations were carried out. The volume fraction f_v of La-rich precipitates is given in^[52]

$$f_v = \frac{1.4\pi}{6} \times \frac{4Nd^2}{A} \quad (4)$$

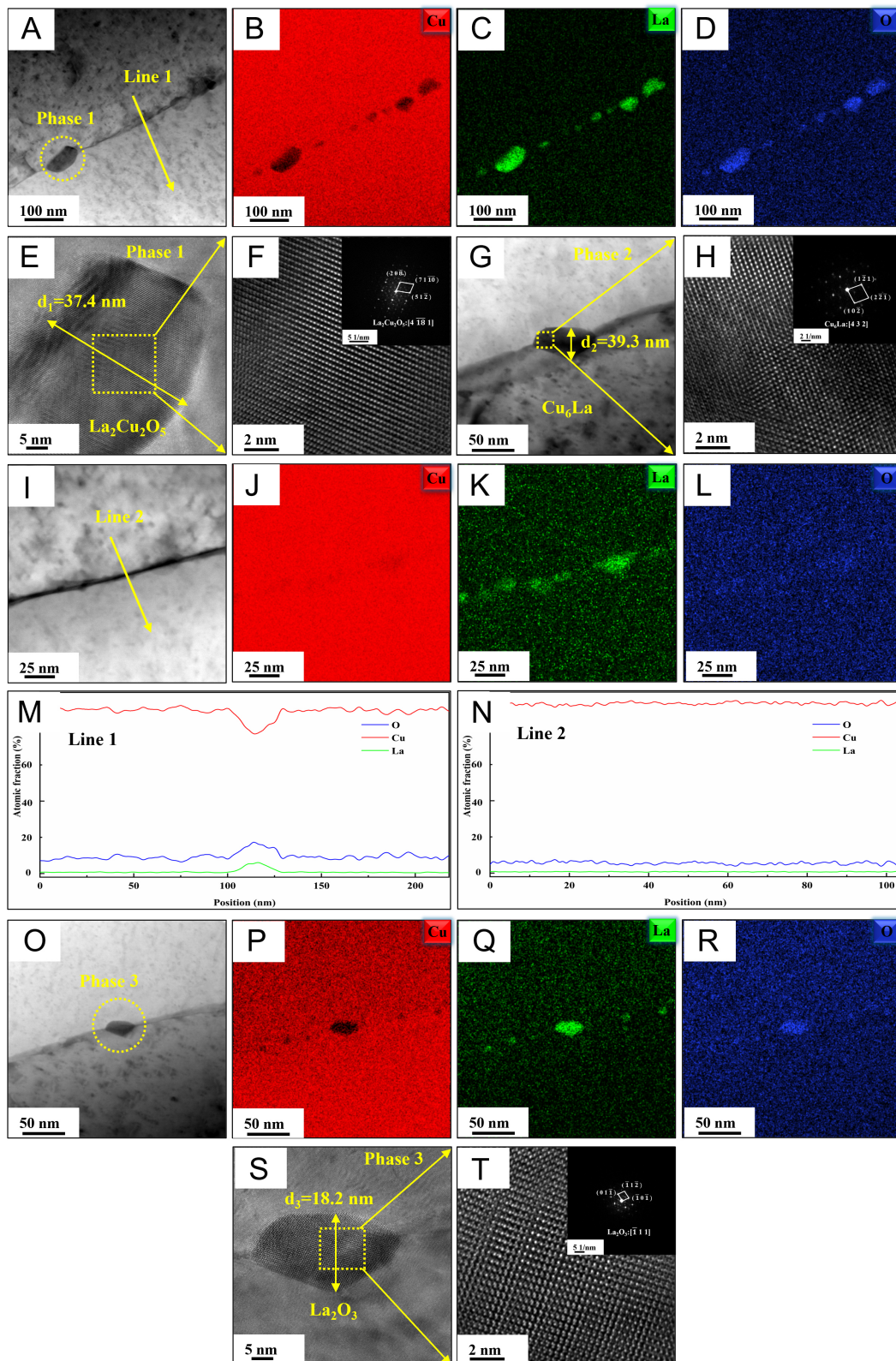


Figure 17. The TEM characterization of grain boundary segregation in La330 after annealing at 900 °C for 30 min: (A), (I and O) TEM bright-field images, (B–D) EDS elemental map in (A), (J–L) EDS elemental map in (I), (P–R) EDS elemental map in (O), (M and N) EDS line scan, (E and F) HRTEM images and FFT of Phase 1, (G and H) HRTEM images and FFT of Phase 2, (S and T) HRTEM images and FFT of Phase 3.

Table 2. Vol fraction (f_v), average diameter (d), average radius (r) and the pinning force (P_z) of La-rich precipitates in La180 after high-temperature annealing at 900 °C for 30 min

	Cu_6La	$\text{La}_2\text{Cu}_2\text{O}_5$	La_2CuO_4	La_2O_3
f (%)	1.04	0.73	0.04	1.01
d (nm)	37.30	31.20	7.50	29.30
r (nm)	18.65	15.60	3.75	14.65
P_z (MPa)	0.50	0.42	0.10	0.62

where N is the total number of precipitates obtained from image statistics, A is the sum of the measured areas in the TEM micrographs, and d is the average diameter of the precipitates. The pinning force P_z of different nanoscale La-rich second phases can be calculated based on their volume fraction. The Zener pinning is calculated using^[55]

$$P_z = \frac{3}{2} f_v \frac{\gamma}{r} \quad (5)$$

where r and γ denote the average radius of the particles, and the grain boundary energy, respectively.

The detailed calculation results of the pinning force of nanoscale La-rich second phases are presented in Table 2. As shown in Table 2, the nanoscale La_2O_3 , Cu_6La and $\text{La}_2\text{Cu}_2\text{O}_5$ segregated at grain boundaries in La180 are the main pinning phases, demonstrating that the intermetallic compound and the oxy-complex oxide are the core phases governing grain boundary pinning and contributing to grain refinement strengthening. These phases all preferentially segregate and precipitate at grain boundaries, forming a dense composite pinning that impedes grain boundary migration, refines the grains, and improves the thermal stability of oxygen-free copper. However, the pinning force of La_2CuO_4 is only 0.10 MPa, much lower than that of the other three phases. Even though this phase also segregates at grain boundaries, its anchoring role at the boundaries is very limited. To further elucidate the physical origin of the above differences, an in-depth analysis is required that considers the existing form of trace La in OFC after high-temperature annealing, the types of precipitates, and their thermodynamic and kinetic behavior.

Combining microstructural observations in Figures 14–17 with thermodynamic and kinetic analyses, it is evident that the existing forms and precipitate types of trace La in OFC after high-temperature annealing are not monolithic. On the one hand, large-sized micron-scale La_2O_3 oxide phases can form within the grain interiors; on the other hand, multiple nanoscale precipitates, including Cu_6La , $\text{La}_2\text{Cu}_2\text{O}_5$, and La_2O_3 , segregate at grain boundaries. Through different mechanisms of action, these phases exert a significant grain-refining effect on OFC grains after high-temperature annealing, while simultaneously improving hardness without compromising high electrical conductivity. Specifically, from a thermodynamic perspective, the rare-earth La acts as a potent deoxidizer^[56] and preferentially combines with residual oxygen in OFC. La reacts with oxygen atoms either dissolved in the copper matrix or located at lattice defects, forming La_2O_3 , which possesses extremely high thermodynamic stability. This reaction tends to occur within grain interiors, forming relatively large precipitates^[30], its thermodynamic driving force originates from the extremely low formation enthalpy of La_2O_3 , which causes oxygen atoms to diffuse toward La-rich regions inside the grains and then nucleate and grow. This process purifies the copper matrix and reduces the weakening or migration-promoting effects of low-melting-point impurities or other coarse, harmful phases on grain boundaries. The intragranularly distributed micron-scale La_2O_3 particles can serve as effective heterogeneous nucleation sites, significantly increasing the recrystallization nucleation rate and thereby refining the grains^[57]. From a kinetic

Table 3. Comparison of key thermodynamic parameters of La, Y, Sc, Zr, and Cr in copper^[65–70]

Element	Atomic radius (pm)	Standard enthalpy of solution at infinite dilution (kJ/mol) ^[65]	Grain boundary segregation energy (eV) ^[70]	Solid solubility in Cu ^[66–69]
La	187	-103	-3.00	Virtually insoluble in solid
Y	180	-105	-2.45	Extremely limited
Sc	162	-102	-1.50	Extremely limited
Zr	160	-44	-1.65	0.24 wt.%
Cr	128	+112	0.15	< 0.07 wt.%

perspective, grain boundaries, with their loose structure and irregular atomic arrangement, serve as fast diffusion paths for atoms. The segregation of solute atoms (La and its compounds) to grain boundaries reduces the lattice distortion energy, thereby lowering the total energy of the system, which is the thermodynamic driving force for segregation. Under high-temperature annealing conditions, the atomic diffusion coefficient increases exponentially with temperature, significantly enhancing the diffusion rates of La, Cu, O and other elements, making it easier for solute atoms to migrate to grain boundaries and allowing the segregation process to proceed rapidly^[58–60]. At the same time, grain boundaries themselves possess a driving force for migration at high temperatures. The nanoscale La-rich second phases (Cu_6La , $\text{La}_2\text{Cu}_2\text{O}_5$, La_2O_3 , etc.) segregated at grain boundaries exert a strong Zener pinning effect and solute drag effect^[61]. When a grain boundary migrates and attempts to break away from these particles, additional energy (i.e., the pinning force) must be consumed, thereby significantly reducing the effective driving force for grain boundary migration and decreasing the grain boundary mobility^[62]. Kinetically, the pinning effect of second-phase particles on grain boundaries can be quantitatively described by particle size, volume fraction, and distribution: nanoscale particles possess a higher pinning force per unit volume, hindering the migration and coalescence of grain boundaries during high-temperature annealing, suppressing grain growth^[63,64], while also impeding dislocation motion and increasing hardness. Further correlating the quantitative pinning force data from Tables 2 and 3 with the above thermodynamic and kinetic mechanisms provides a clearer explanation of why La_2O_3 , Cu_6La and $\text{La}_2\text{Cu}_2\text{O}_5$ are the most effective pinning phases.

In summary, the multi-scale precipitation and grain boundary segregation of La-rich second phases synergistically refine the grain structure through dual mechanisms of "promoting nucleation" and "inhibiting grain growth". Consequently, this significantly enhances hardness while maintaining high electrical conductivity, ultimately effectively improving the thermal stability of OFC.

Compared with conventional rare-earth elements (e.g., Y) and other typical microalloying elements (e.g., Sc, Zr, Cr), La possesses the largest atomic radius (187 pm), resulting in the greatest lattice misfit with the Cu matrix (128 pm). Table 3 summarizes the quantitative comparison data for atomic radius, limiting enthalpy of solution, grain-boundary segregation energy, and solid solubility of each element. In terms of atomic size effect, the atomic radius of La (187 pm) is larger than that of Y (180 pm), Sc (162 pm), Zr (160 pm), and Cr (128 pm), resulting in the maximum misfit with the Cu matrix, which provides a structural basis for strong grain boundary segregation of La. In terms of thermodynamic driving force for precipitation, the standard enthalpies of solution at infinite dilution^[65] for Y (-105 kJ/mol), La (-103 kJ/mol), and Sc (-102 kJ/mol) are substantially more negative than those for Zr (-44 kJ/mol) and Cr (+112 kJ/mol), indicating that rare earth elements possess an exceptionally strong thermodynamic tendency to precipitate from the Cu matrix and form stable second-phase particles. The enthalpy for Y is slightly more negative than that for La, but the difference is within experimental error and can be considered comparable. In terms of solid solubility^[66–69], La, Y, and Sc all exhibit extremely low solid solubility in Cu; The solubility limit of Cr in copper is below 0.07 wt%^[68]; Zr has a maximum solid solubility of 0.24 wt.%^[69]. The extremely low solid solubility of La means

that nearly all of the added La precipitates as second-phase particles, maximizing its contributions to second phase strengthening and grain boundary pinning. More critically, the differences in grain boundary segregation energy are decisive. Relevant calculation results show that^[70] when these elements occupy identical substitutional sites at Cu grain boundaries, the segregation energy of La (approximately -3.00 eV) is significantly lower than that of Y (approximately -2.45 eV), Sc (approximately -1.50 eV), Zr (approximately -1.65 eV), and Cr (approximately +0.15 eV). Although Y exhibits a comparable enthalpy of solution to La, the segregation energy of La is substantially more negative than that of Y (-3.00 eV vs. -2.45 eV), demonstrating that La possesses a unique and superior advantage in grain boundary segregation over Y. The positive segregation energy of Cr (approximately +0.15 eV) indicates repulsion rather than segregation at Cu grain boundaries, which is consistent with the thermodynamic characteristics of the immiscible Cu-Cr system. Combining the four sets of quantitative thermodynamic parameters—atomic radius, standard enthalpy of solution at infinite dilution, grain boundary segregation energy, and solid solubility—it can be concluded that even with an addition level as low as below 500 ppm, La, by virtue of its largest atomic size misfit, strong precipitation driving force comparable to Y and Sc (-103 kJ/mol), extremely low solid solubility (virtually insoluble in solid Cu), and the most negative grain boundary segregation energy (approximately -3.00 eV), can spontaneously and stably form an enrichment layer at grain boundaries. This strong grain boundary segregation behavior enables La to effectively inhibit grain growth via the solute drag effect and maintain the stability of nanoscale precipitates at elevated temperatures—a unique advantage that is difficult to achieve with other microalloying elements (Y, Sc, Zr, Cr). These thermodynamic results directly demonstrate the irreplaceable role of La in regulating the thermal stability and texture of ultra-high-purity copper.

In summary, La synergistically refines grains through the dual mechanisms of "promoting nucleation" and "inhibiting grain growth". At an extremely low addition level (180 ppm), it enables OFC to maintain a high electrical conductivity of 101.3% IACS while simultaneously significantly increasing hardness and enhancing thermal stability. The strong grain boundary segregation of La not only lowers the nucleation barrier for precipitates and provides a large number of fine heterogeneous nucleation sites, but also effectively retards grain boundary migration through solute drag and Zener pinning, thereby substantially suppressing grain growth at high temperatures. Y, Sc, Zr, and Cr, owing to their insufficiently negative segregation energies or excessively high solid solubility, are unable to achieve this synergistic effect. This work, for the first time, reveals the dual synergistic mechanism of La in grain refinement and its integrated optimization of electrical conductivity, hardness, and thermal stability, offering a new design strategy for high-strength, high-conductivity, and heat-resistant copper alloys.

Comparison of the effects of trace rare-earth elements on the thermal stability of pure copper

To quantitatively substantiate the superior comprehensive performance of the La180, Table 4 compares the key thermal-stability parameters of Cu-RE alloys with different rare-earth elements (La, Ce, Sc, Yb) reported in the literature, alongside our La330 specimen for reference. Under comparable annealing conditions (900 °C for 0.5 h), the La180 exhibits a grain size of only 38.64 µm, which is significantly finer than that of La330 (43.10 µm) under identical heat-treatment parameters. This indicates that increasing the La content beyond 180 ppm does not further refine the grain structure; instead, the optimal pinning effect of Cu₆La nanoparticles is achieved at the La180 level. In contrast, the Ce- and Yb-modified copper alloys, despite being subjected to a higher annealing temperature (1,070 °C for 0.3 h), display substantially coarser grains of 150.00 and 148.00 µm^[20], respectively—approximately four times larger than that of La180. The Sc-containing alloy^[71], annealed at 850 °C for 0.8 h, shows a grain size of 60.43 µm, which is still considerably larger than that of La180, although Sc exhibits a moderate grain-refining efficacy among the compared elements.

Table 4. Comparison of key thermal-stability parameters for copper with different trace rare-earth elements^[20,71]

Element	Rare-earth content (wt.%)	Grain size stability (μm)	Annealing process	Electrical conductivities (%IACS)
La (La180)	0.0180	38.64 μm	900 °C/0.5 h	101.3
La (La330)	0.0330	43.10 μm	900 °C/0.5 h	101.3
Ce ^[20]	0.0017	150.00 μm	1,070 °C/0.3 h	100.5
Sc ^[71]	0.012	60.43 μm	850 °C/0.8 h	98.5
Yb ^[20]	0.0014	148.00 μm	1,070 °C/0.3 h	101.5

In terms of electrical conductivity after the corresponding annealing treatments, La180 achieves 101.3% IACS, which is comparable to La330 (101.3% IACS) and Yb (101.5% IACS)^[20], and superior to Sc (98.5% IACS)^[71] and Ce (100.5% IACS)^[20]. This demonstrates that the exceptional grain refinement achieved by La180 is not accompanied by any degradation in electrical conductivity, thereby maintaining an optimal balance between thermal stability and electrical performance.

The superior performance of La180 can be attributed to the following factors: (i) the extremely low solid solubility of La in Cu ensures that nearly all added La precipitates as nanoscale Cu₃La particles, which exert a strong Zener pinning effect on grain boundaries; (ii) the large atomic radius misfit between La (187 pm) and Cu (128 pm) promotes strong solute drag and grain boundary segregation; and (iii) the combination of these mechanisms effectively suppresses grain growth and retards recrystallization even at elevated temperatures.

In summary, through systematic experiments, the unique nanoprecipitation strengthening mechanism of La in OFC has been revealed, which enables La180 to simultaneously achieve an extremely fine grain size (38.64 μm) and excellent electrical conductivity (101.3% IACS) after high-temperature annealing—a combination of overall properties that has never been attained in any previously reported Cu-RE system. The key lies in the fact that La synergistically refines grains through the dual mechanisms of "promoting nucleation" and "inhibiting grain growth". At an extremely low addition level (180 ppm), it enables oxygen-free copper to maintain a high electrical conductivity of 101.3% IACS while simultaneously significantly increasing hardness and enhancing thermal stability. In contrast, for the Ce-, Sc-, and Yb-modified alloys reported in the literature, even after annealing at higher temperatures or for longer durations, their grain sizes remain far larger than that of La180. The fundamental reason is that the precipitates in these elements undergo rapid coarsening or partial dissolution at high temperatures, rendering them unable to maintain effective grain boundary pinning. Therefore, this work proposes an OFC microalloying design criterion centered on "low solid solubility and high thermal stability" providing a new theoretical framework for the design of high-performance OFC.

CONCLUSION

(1) The addition of a higher content of rare-earth La effectively suppresses grain coarsening and abnormal grain growth after high-temperature annealing at 900 °C and significantly improves the "orange-peel" defect. Among them, La180 exhibits the finest grain size of 38.64 μm . Meanwhile, La180 maintains a high electrical conductivity of 101.3 %IACS after high-temperature annealing. This study provides a key theoretical basis and a feasible composition design strategy for OFC materials with high electrical conductivity and high thermal stability, applicable to high-temperature-resistant power electronics and high-power devices such as DBC and shows broad application prospects.

(2) The addition of rare-earth La significantly promotes the transition from Brass Rec texture to Cube texture, with the transformation sequence of strong textures being Brass Rec → Brass → Cube. In La330, a widely distributed Cube texture with high intensity is formed, accounting for as much as 85.1% of the texture

components, with a maximum texture intensity of 41.26.

(3) A higher content of rare earth La can form second phases that pin grain boundaries and suppress the transformation of rolling textures into recrystallization textures, thereby delaying the recrystallization process, increasing the softening temperature of OFC. La180 exhibits the highest softening temperature of 210 °C, representing an increase of 53 °C.

(4) The mechanism by which La significantly enhances the high-temperature thermal stability of OFC is primarily attributed to the synergistic effect between the multi-scale precipitation of La-rich second phases and their segregation behavior at grain boundaries. Through the dual mechanisms of "promoting nucleation" and "inhibiting grain growth" working in concert, the grain structure is refined. This leads to a significant increase in hardness while maintaining high electrical conductivity, ultimately effectively enhancing the thermal stability of OFC.

DECLARATIONS

Authors' contributions

Resources, project administration, methodology, funding acquisition, writing - review & editing, software: Peng, X.

Writing - review & editing, writing - original draft, visualization, validation, software, methodology, investigation, formal analysis, data curation, conceptualization: Xu, C.

Resources, funding acquisition: Yang, B.

Funding acquisition: Song, K.

Supervision: Hua, Y.; Huang, T.

Supervision, project administration, funding acquisition: Liu, H.

Availability of data and materials

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

AI and AI-assisted tools statement

Not applicable.

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Conflicts of interest

All authors declared that there are no conflicts of interest.

Ethical approval and consent to participate

Not applicable.

Consent for publication

Not applicable.

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