

Article

Microstructure, Texture, and Mechanical Properties of 6N Ultra-High-Purity Copper Processed by Cryorolling for Advanced Sputtering Targets

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Abstract

The performance of ultra-high-purity copper sputtering targets is critical for nanoscale integrated circuit fabrication, yet challenges such as dynamic recovery and recrystallization hinder grain refinement and texture control. In the present work, cryogenic deformation was introduced to address these issues. Through electron backscatter diffraction (EBSD), X-ray diffraction (XRD), and mechanical testing, the microstructure, texture, and mechanical properties of 6N ultra-high-purity copper processed by room-temperature rolling (RTR) and cryorolling (CR) were comparatively investigated. Results reveal that RTR deformation is dominated by slip mechanisms; the RTR sample with 90% reduction exhibits obvious dynamic recrystallization (DRX) and forms a bimodal structure dominated by Copper ($\{112\}\langle 111 \rangle$) and S ($\{123\}\langle 634 \rangle$) textures. In contrast, CR suppresses thermal activation processes, enabling deformation mechanisms suggestive of twinning activity, leading to ultrafine fibrous structures, while shifting texture components toward Brass ($\{110\}\langle 112 \rangle$) and S. Compared to RTR-processed samples, CR-processed samples possess superior mechanical performance. The CR sample with 90% reduction exhibits: a microhardness of 164.60 HV, a yield strength of 385.61 MPa, and a tensile strength of 648.02 MPa, which are, respectively, 33.2%, 91.7%, and 84.6% higher than those of RTR counterparts. Williamson–Hall analysis confirms that the CR sample with 90% reduction achieves finer substructure sizes (~ 133 nm) and higher stored energy (~ 22 J·mol^{−1}) by suppressing dynamic recovery, providing a robust driving force for subsequent annealing. This work demonstrates that cryorolling optimizes microstructure and texture through twin-dislocation synergy, providing a fundamental basis for the development of advanced sputtering targets.



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Keywords: cryorolling; ultra-high-purity copper; dynamic recrystallization; texture evolution; stored energy; mechanical properties

1. Introduction

High-purity metallic sputtering targets serve as pivotal raw materials in integrated circuit manufacturing, and their performance metrics escalate exponentially with the miniaturization of process nodes. In sub-14 nm advanced technology nodes, copper sputtering targets must meet stringent criteria, including 6N-grade (99.9999 wt.%) ultra-high-purity, uniform fine grain size (≤ 50 μm), and weak crystallographic texture, to ensure critical thin-film properties such as thickness uniformity and step coverage for nanoscale IC fabrication [1,2].

The grain size, texture evolution, and mechanical properties of metallic materials are fundamentally governed by the synergistic interplay between plastic deformation processes and recrystallization annealing protocols [3,4]. Currently, rolling is the conventional fabrication method for sputtering targets due to its efficiency and versatility. Nevertheless, fabricating 6N ultra-high-purity copper targets presents unique challenges. During conventional rolling, workpiece temperature escalation elevates deformation temperatures above recrystallization thresholds, triggering dynamic recovery and dynamic recrystallization (DRX) [5]. Furthermore, the negligible impurity-induced grain boundary pinning in 6N copper accelerates boundary migration during annealing, potentially inducing abnormal grain growth and secondary recrystallization, which severely degrades microstructural homogeneity and complicates texture control [6]. Cryorolling (CR), an extreme-condition plastic deformation technique conducted in liquid nitrogen environments ($-197\text{ }^{\circ}\text{C}$), suppresses dynamic recovery by restricting dislocation annihilation, thereby elevating dislocation density and promoting nanoscale twin formation to achieve precise ultrafine-grained microstructure control [7,8]. Pioneering studies by Zherebtsov et al. demonstrated that CR significantly enhances twin density and refines grain size to submicron levels in pure titanium [9]. Similarly, Li et al. showed that the high-purity nickel obtained by room-temperature rolling (RTR) underwent static discontinuous recrystallization during annealing, whereas that obtained by CR underwent static and continuous recrystallization during annealing, which was caused by the seriously inhibited dislocation recovery in the rolling process under cryogenic conditions, leading to greater accumulated deformation energy storage in sheets [10]. Comparative investigations by Krishna et al. revealed that cryorolled Al-Mg-Si alloys exhibit superior Brass texture intensity, higher dislocation density, finer grains, and enhanced mechanical strength relative to conventionally rolled counterparts [11]. These findings collectively establish CR as a transformative approach for overcoming grain refinement limits of traditional methods through cryogenically constrained dislocation motion and twinning mechanisms, offering new pathways for grain refinement in high-performance sputtering targets.

To address the problems of DRX and secondary recrystallization occurring during RTR and annealing processes of 6N ultra-high-purity copper, this study systematically investigates the microstructure and texture evolution of 6N copper under RTR and CR using electron backscatter diffraction (EBSD) and X-ray diffraction (XRD). The mechanical performance under varying rolling conditions is also elucidated, providing critical guidelines for optimizing manufacturing protocols of next-generation sputtering targets.

2. Experimental Procedures

2.1. Material Preparation

A 6N ultra-high-purity copper ingot (99.9999 wt.%, supplied by Ningbo Jiangfeng Electronic Materials Co., Ltd., Ningbo, China) was homogenized via multi-directional forging to eliminate casting defects. The results of the elemental analysis of the experimental raw materials conducted using glow discharge mass spectrometry are presented in Table 1.

The metal ingots prepared by the casting method exhibit coarse grain structures and strong textures, necessitating multi-directional hot forging to eliminate the cast structure and achieve initial refinement of the grain size. The ingots are subjected to heat treatment in a furnace at $500\text{ }^{\circ}\text{C}$ for 2 h before undergoing hot forging, followed by three reductions and three draws in the X, Y, and Z directions, and then air cooling. Initial mechanical properties after hot forging are summarized in Table 2.

Table 1. Chemical composition of ultra-high-purity copper (wt-ppm).

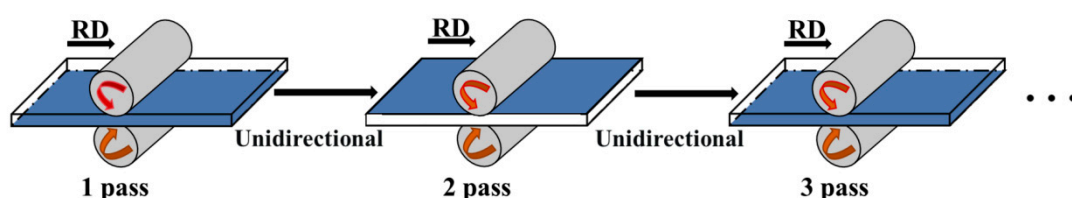
Ag	Al	As	Au	B	Ba	Be	Bi	Ca
0.05	<0.001	<0.005	<0.05	<0.001	<0.001	<0.001	<0.001	<0.005
Cd	Co	Cr	Fe	Ga	Hg	K	Li	Mg
<0.005	<0.005	<0.001	0.01	<0.001	<0.005	<0.005	<0.001	<0.005
Mn	Mo	Na	Nb	Ni	P	Pb	Sb	Si
<0.001	<0.005	<0.001	<0.005	<0.001	<0.001	<0.001	<0.001	0.04
Sn	Th	Ti	U	V	W	Zn	Zr	Cu
<0.005	<0.0001	<0.001	<0.0001	<0.001	<0.001	<0.01	<0.001	balanced

Table 2. Mechanical properties of hot-forged 6N copper.

Material	Microhardness (HV)	Yield Strength (MPa)	Tensile Strength (MPa)	Uniform Elongation (%)
6N Copper	54.22 ± 2.12	98.06 ± 4.34	244.48 ± 6.77	28.89 ± 1.58

2.2. Rolling Process

The above hot-forged Cu plates were used as the initial material for the subsequent rolling. Samples (40 mm × 20 mm × 10 mm) were deformed to reductions of 50%, 70%, and 90% by RTR and CR. To ensure direct comparability, identical multi-pass rolling schedules were employed for both RTR and CR at each reduction level. Rolling was performed on a two-high mill (rolling force: 42 t, roll diameter: 170 mm, speed: 0.2 m/s). The rolling of ultra-pure copper samples is conducted using a unidirectional rolling method, which involves alternating the upper and lower rolling surfaces along the rolling direction, as illustrated in Figure 1. To ensure uniform deformation of the plate during the rolling process, the deformation geometric parameters $\frac{l}{h}$ should be controlled between 1.00 and 3.60 [12,13]. Here, l represents the contact arc length between the roller and the sample, and h denotes the average thickness of the sample before and after rolling.

**Figure 1.** Schematic diagram of unidirectional rolling.

The rolling procedure is shown in Table 3. Based on the roll geometry and speed, the nominal strain rate during rolling is estimated to be approximately 2–3 s^{−1} for both RTR and CR; this ensures that the strain rate was not a variable between the two processes.

For CR, a strict thermal management protocol was followed. Samples were immersed in liquid nitrogen (LN₂, −196 °C) for 10 min prior to the first pass to achieve through-thickness thermal equilibrium. Between each subsequent pass, samples were re-immersed in LN₂ for 5 min to dissipate deformation heat and maintain low temperature. The actual surface temperature of the sample was monitored immediately before rolling using a calibrated infrared thermometer. The measured temperature ranged between −150 °C and −130 °C throughout the entire CR deformation process, confirming that deformation occurred under sustained cryogenic conditions. For RTR, samples were processed at ambient temperature (~25 °C). A comparable inter-pass time of 5 min was used to control for any potential time-dependent effects unrelated to temperature.

Table 3. Rolling schedule.

Rolling Pass	Pre-Rolling Thickness d_0/mm	Post-Rolling Thickness d/mm	$\frac{l}{h}$	Rolling Reduction/mm	Deformation/%
1	10	8.88	1.03	1.12	11.2
2	8.88	7.87	1.11	1.01	21.3
3	7.87	6.89	1.23	0.98	31.1
4	6.89	6.18	1.19	0.71	38.2
5	6.18	5.50	1.30	0.68	45.0
6	5.50	5.00	1.24	0.50	50.0
7	5.00	4.32	1.63	0.68	56.8
8	4.32	3.79	1.65	0.53	62.1
9	3.79	3.34	1.73	0.45	66.6
10	3.34	3.00	1.69	0.34	70.0
11	3.00	2.38	2.69	0.62	76.2
12	2.38	1.92	2.91	0.46	80.8
13	1.92	1.61	2.91	0.31	83.9
14	1.61	1.38	2.96	0.23	86.2
15	1.38	1.16	3.41	0.22	88.4
16	1.16	1.00	3.41	0.16	90.0

2.3. Characterization

To analyze the microstructural and textural evolution of metallic materials after rolling deformation, characterization is typically performed on multiple orthogonal planes. The coordinate system of the rolled sample comprises three mutually perpendicular axes: the Rolling Direction (RD), Normal Direction (ND), and Transverse Direction (TD). These axes correspond to three orthogonal planes: the RD plane, ND plane, and TD plane, which are perpendicular to RD, ND, and TD, respectively. The detailed characterizations of the copper samples are as follows:

- EBSD: A TESCAN MIRA3 SEM (supplied by Tescan Trading Co., Ltd., Shanghai, China) equipped with an EBSD detector (AZtecCrystal 2.1 software) was adopted to observe the microstructure on the TD plane. For subsequent characterization, the samples were first ground with water on 400#, 1000#, 2000#, 3000#, and 4000# sandpaper until they were flat and free of noticeable scratches. Due to the soft nature of pure copper, white silicon carbide sandpaper was selected for the grinding process. After grinding, the surface to be observed was subjected to electrolytic polishing. The electrolyte solution consisted of a mixture of phosphoric acid, ethanol, and distilled water in a volume ratio of 1:1:2. Polishing was carried out at a constant voltage of 8 V for a duration of 12–15 s. Upon completion of polishing, the sample was immediately rinsed with copious amounts of water to remove any residual electrolyte, followed by cleaning with ethanol and rapid drying using a cold air stream from a blower.
- XRD: A Rigaku D/MAX 2500 diffractometer (Cu-K α radiation, 40 kV/150 mA, supplied by Rigaku corporation, Tokyo, Japan) was used for macrotexture, substructure size, microstrain, and bulk stored energy analyses on the ND plane. Orientation distribution function (ODF) and texture volume fractions were calculated using Lab-Tex 3.0 software.
- Microhardness test: The equipment used in this study is a touch-screen automatic turret digital display Vickers hardness tester (YQ81C) manufactured by Chongqing

Libo Instrument Co., Ltd. (Chongqing, China). Vickers hardness measurements were conducted on the ND plane of rolled samples using a 300 g load, with 10 uniformly distributed points along the RD tested per specimen, and the average value recorded as the final hardness.

- Unidirectional static tensile test: The equipment used for the tensile test is an AG-X50KN universal mechanical testing machine (supplied by SHIMADZU corporation, Tokyo, Japan). Tensile specimens were machined along the RD via wire cutting and sequentially polished with 400#, 1000#, and 2000# grit sandpaper to minimize surface defects. Uniaxial tensile tests were performed at a strain rate of 1 mm/min to evaluate mechanical properties. Each condition tested 3 parallel samples to enhance data credibility.

3. Results and Discussion

3.1. The Structure and Texture of the Initial Material

Figure 2a,c presents the crystallographic texture and microstructure of copper subjected to multi-directional hot forging. Typical face-centered cubic (FCC) deformation textures—including Brass ($\{110\}\langle 112\rangle$), Copper ($\{112\}\langle 111\rangle$), Goss ($\{110\}\langle 001\rangle$), S ($\{123\}\langle 634\rangle$), Cube ($\{100\}\langle 001\rangle$), and P($\{110\}\langle 233\rangle$) components—were identified in orientation distribution function (ODF) sections at $\varphi_2 = 0^\circ, 45^\circ$, and 65° (Figure 2b). Although coarse grains were partially fragmented during forging, the microstructure remained inhomogeneous, dominated by irregularly distributed large grains (average size: 167.6 μm). Furthermore, high orientation density values (Brass texture: Max = 16.2) indicated pronounced texture sharpness in the hot-forged material, underscoring the inadequacy of conventional forging for achieving the stringent grain uniformity and weak texture required for sputtering targets.

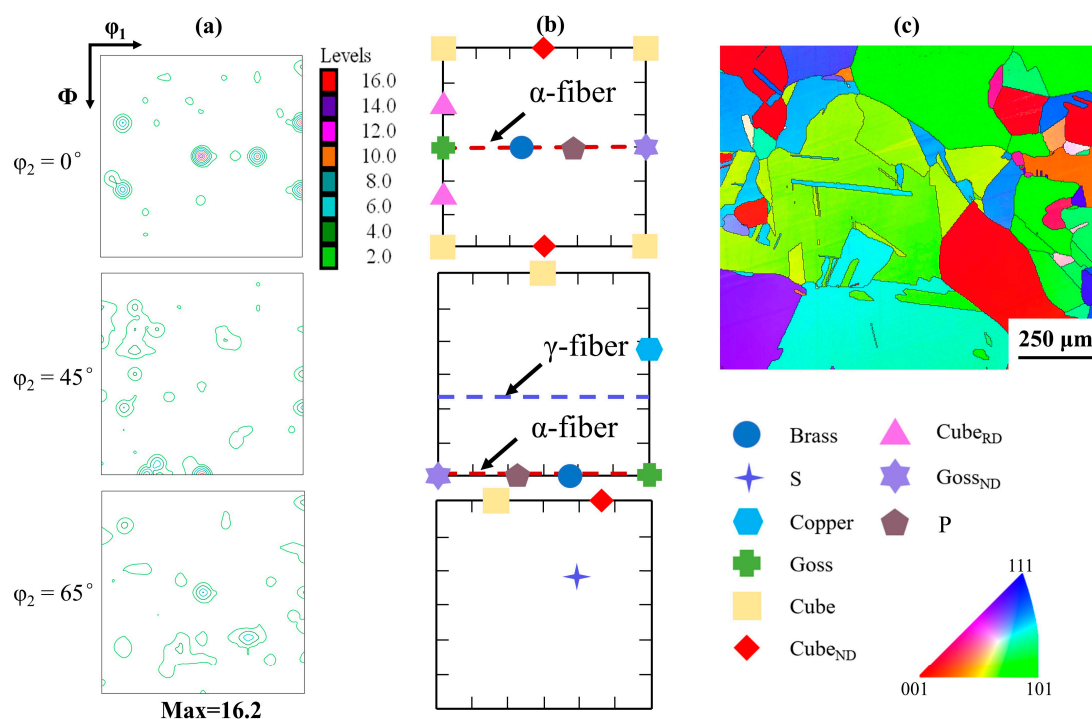


Figure 2. (a) ODF map, (b) typical textures in the three ODF sections, (c) Inverse pole Fig (IPF) map.

3.2. Microstructure Evolution

The boundary images, orientation reconstruction images, and pattern quality images of samples with different deformation amounts of the initially ultra-high-purity copper

after RTR are shown in Figure 3. At 50% reduction (Figure 3a–c), coarse grains in the as-received material are flattened and elongated along the RD, with high-angle grain boundaries (HAGBs, $>15^\circ$) remaining prominent. Grains oriented along “soft” slip systems preferentially undergo slip deformation, resulting in inhomogeneous strain distribution along the thickness direction. Cube-oriented grains experience preferential fragmentation, while the dominant texture components shift to Copper and Brass orientations.

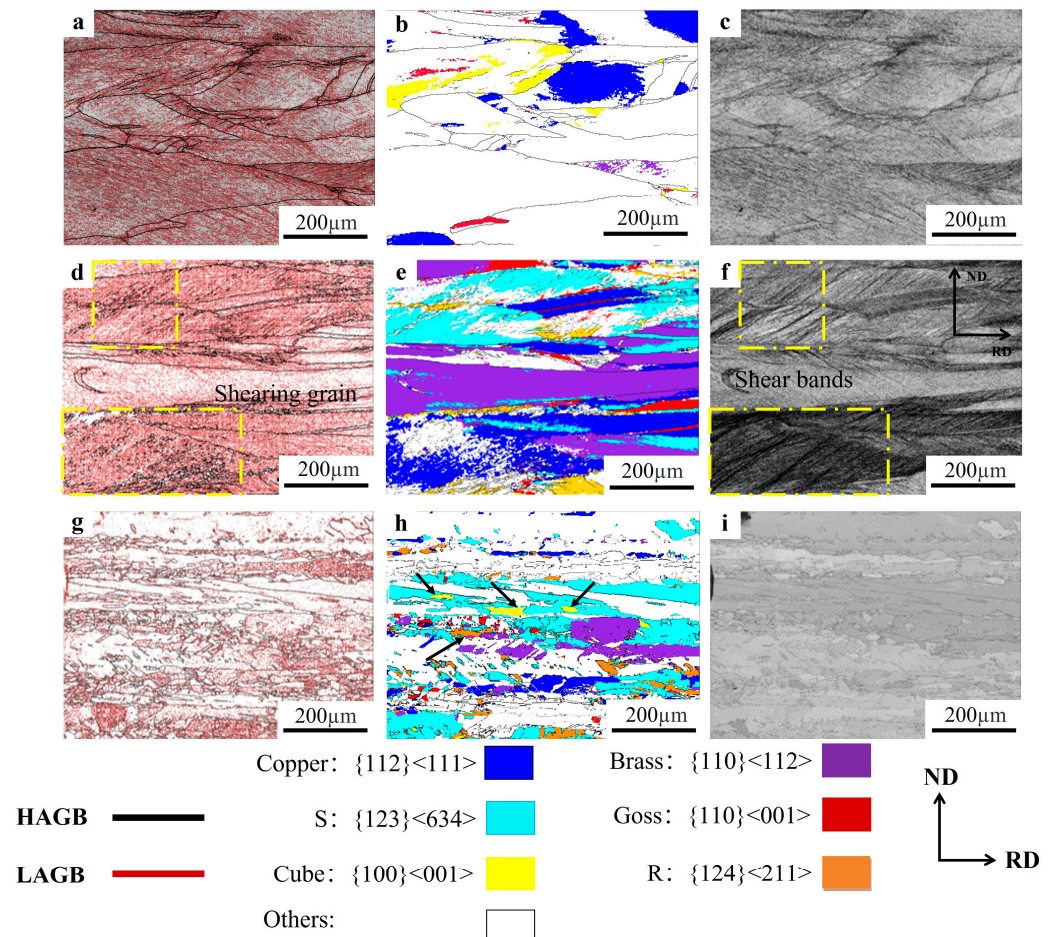


Figure 3. Grain boundary map, orientation reconstruction map, and pattern quality map of ultra-high-purity copper under RTR: (a–c) RTR-50%, (d–f) RTR-70%, (g–i) RTR-90%.

Upon increasing the reduction to 70% (Figure 3d–f), grains are further elongated into pronounced banded structures, accompanied by reduced interplanar spacing and partial dissolution of grain boundaries. A high density of low-angle grain boundaries (LAGBs, $2\text{--}15^\circ$) emerges within grains. Notably, shear bands inclined about 30° to RD (highlighted by dashed boxes in Figure 3d) exhibit localized high stored energy, as evidenced by dark contrast in image quality maps. These shear bands predominantly form in Copper- and S-oriented grains, which contain randomly oriented subdomains. The intensified deformation of Copper-oriented grains compared to Brass-oriented ones is reflected in their severe fragmentation and denser LAGB networks.

At 90% reduction (Figure 3g–i), the microstructure transitions to elongated fibrous structures with chain-like arrangements. LAGBs largely vanish due to DRX. DRX grains exhibit elongated morphologies with residual LAGBs, consistent with discontinuous DRX characteristics. As indicated by the arrows in the Figure 3h, Cube- and R-oriented DRX grains preferentially nucleate and grow along S-oriented deformation matrices, attributed to their $40^\circ\langle 111\rangle$ orientation relationship with the S-oriented parent grains, which accelerates

boundary migration during recrystallization. The final texture comprises dominant Copper, Brass, and S components, with minor Cube and R orientations.

In summary, RTR deformation in 6N copper is predominantly governed by slip mechanisms, with no mechanical twinning observed. Progressive strain accumulation triggers DRX at 90% reduction, facilitating grain boundary reorganization and recrystallized grain growth.

Figure 4 shows the boundary images, orientation reconstruction images, and pattern quality images of CR samples with varying deformation amounts. In the orientation reconstruction images and the pattern quality images, the green solid line is used to mark the deformation twin boundary characterized by a 60° rotation around $\langle 111 \rangle$. Figure 5 displays the plots of misorientation angle distribution between adjacent points along “L1” and “L2” within deformed grains of CR-50% and CR-70% samples.

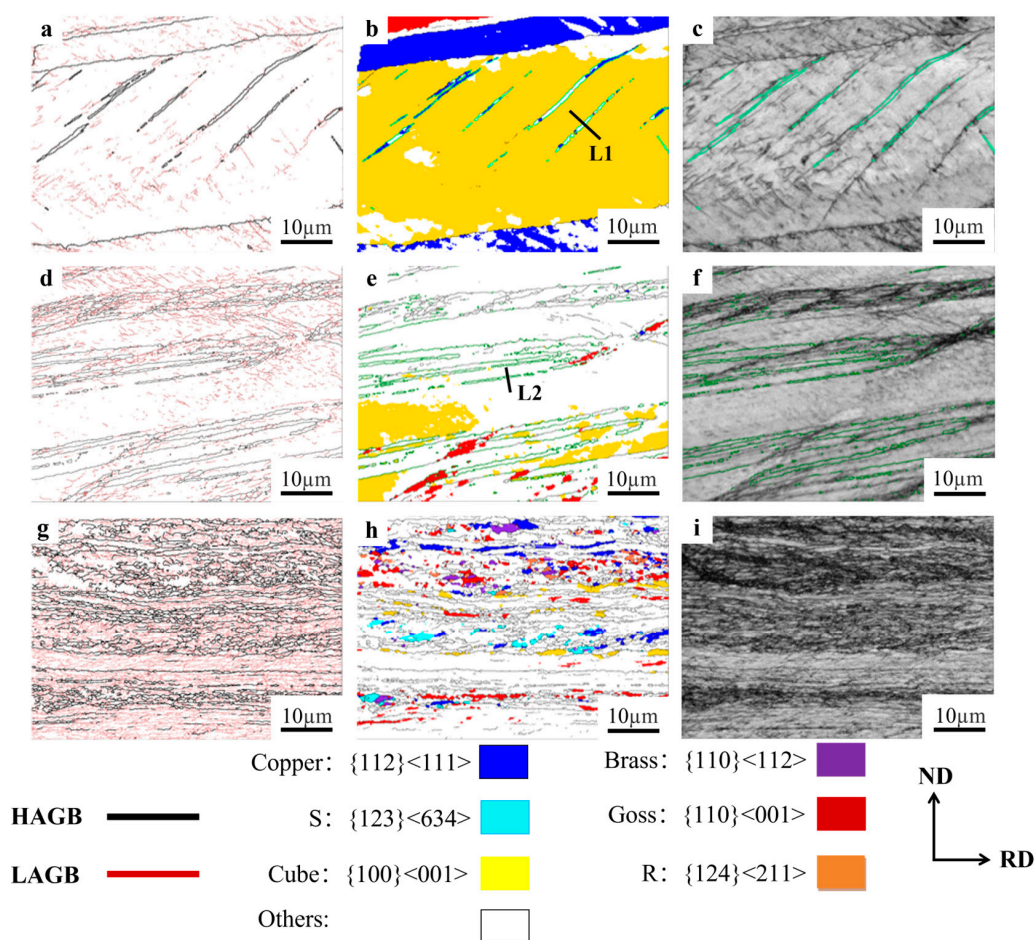


Figure 4. Grain boundary map, orientation reconstruction map, and pattern quality map of ultra-high-purity copper under CR: (a–c) CR-50%, (d–f) CR-70%, (g–i) CR-90%.

As depicted in Figure 4, CR induces progressive grain refinement in 6N ultra-high-purity copper with increasing reduction. At 50% reduction (Figure 4a–c), deformation twins with an average thickness of $0.6 \mu\text{m}$ form preferentially within Cube-oriented grains, aligned at an angle to the RD (Figure 5a). In contrast, deformation twins were not observed within the Goss and Copper grains. This can be attributed to the fact that compared with grains of other orientations, Cube grains have only two orthogonal Burgers vectors available for movement, resulting in negligible transverse deformation. Dislocations hardly play a role in Cube grains, making slip deformation difficult. As a result, the stored energy of Cube grains during deformation is the lowest. By 70% reduction (Figure 4d–f), twin density increases significantly, with reduced interlamellar spacing ($0.24 \mu\text{m}$) and alignment closer to

RD (Figure 5b). Twin formation expands to randomly oriented grains, reflecting intensified strain accommodation mechanisms. At 90% reduction (Figure 4g–i), the microstructure transitions to fully fragmented fibrous structures along RD, microstructural features refined beyond the resolution limit of EBSD ($\sim 0.1 \mu\text{m}$). The persistence of a discernible Brass texture component in the highly deformed CR-90% sample (Figure 4h), which is a potential indicator of twinning activity, alongside the extreme microstructural refinement, suggests that deformation mechanisms favoring twinning were prevalent under cryogenic conditions. In contrast to the RTR-90% sample, no significant dynamic recrystallization was observed in the CR-90% sample.

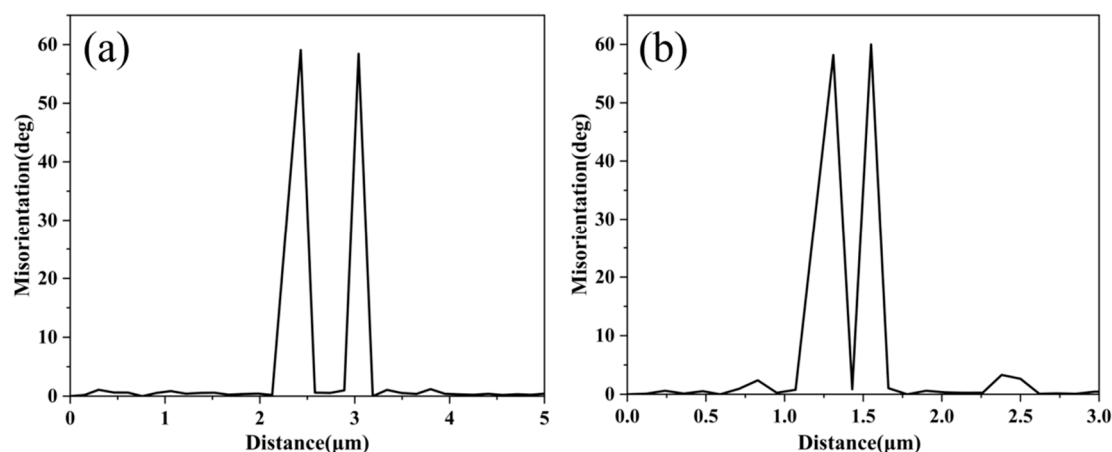


Figure 5. Misorientation angle distribution along the lines “L1” and “L2” in CR samples: (a) CR-50%, (b) CR-70%.

In summary, CR deformation in 6N copper proceeds via twin-assisted slip mechanisms. In addition, CR suppresses dynamic recovery and recrystallization, enabling twin-boundary-mediated dislocation accumulation. Thus, CR deformation is beneficial to elevate dislocation density and stored energy in the deformed 6N copper plates, which is critical for subsequent microstructural control during annealing.

3.3. Texture Evolution

Figure 6 presents the ODF maps of ultra-high-purity copper under RTR. At 50% reduction, the dominant deformation textures are Brass and Copper, with orientation densities of 8.0 and 6.8 multiples of random distribution (m.r.d.), respectively, accompanied by a weak S component. This indicates pronounced deformation texture formation at moderate strains. Increasing the reduction to 70% significantly weakens Brass and Copper textures (4.6 and 3.0 m.r.d.), attributed to grain fragmentation and reorientation during progressive strain accumulation.

At 90% reduction, texture intensities rebound sharply, with S texture emerging as the strongest component (7.2 m.r.d.), followed by Copper (7.0 m.r.d.) and Brass (5.8 m.r.d.), signifying a transition to Copper/S-dominated deformation textures. Notably, DRX occurs at this stage, evidenced by Cube-oriented grains in Figure 3h. However, the Cube texture has not become the dominant texture component for the sample with 90% reduction, as shown in Figure 6: The texture strength of the Cube is less than 3.0 m.r.d. in the RTR-90% sample. This is because the increase in Cube texture strength is not significant during the early stage of recrystallization. The strength of the Cube texture will only significantly increase when the recrystallization fraction reaches approximately 50% [14].

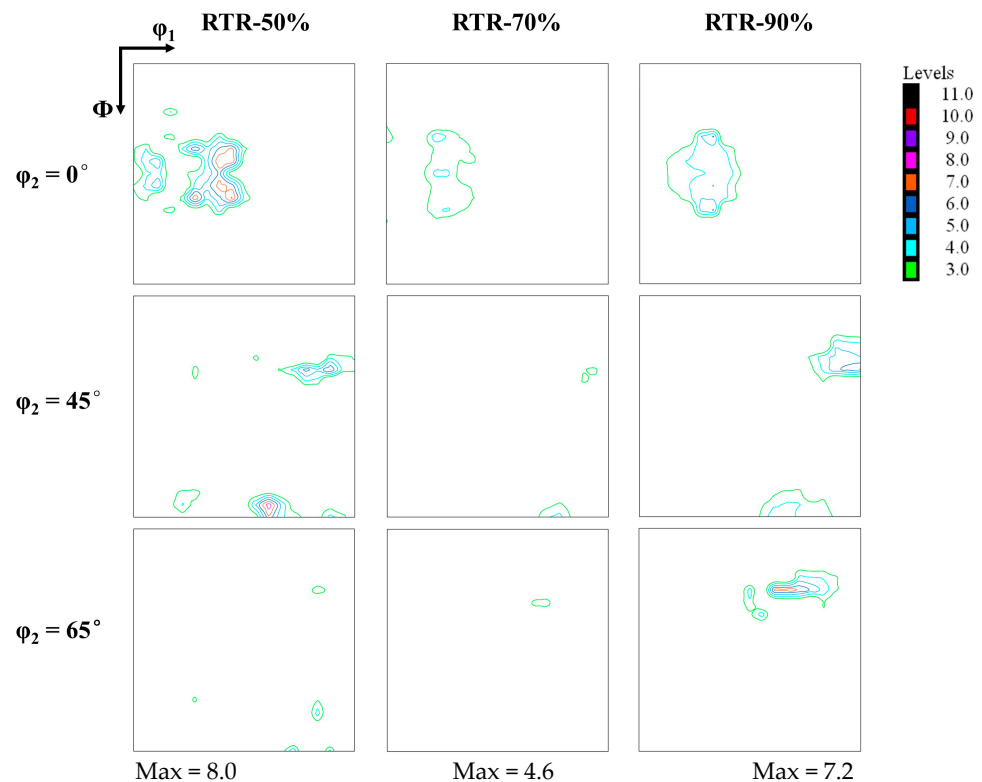


Figure 6. Sections of constant ϕ_2 ODF of ultra-high-purity copper under RTR.

In summary, RTR drives texture evolution along the β fiber, with Copper and S orientations dominating at high strains. This aligns with classical deformation behavior of high-purity FCC metals, where strain localization and DRX jointly govern texture transitions [15].

Figure 7 illustrates the ODF maps of ultra-high-purity copper under CR. At 50% reduction, the crystallographic orientations exhibit intensified clustering along the β fiber compared to RTR, with dominant Brass, Copper, and S textures displaying orientation densities of 11.0, 8.1, and 6.6 m.r.d., respectively. This signifies pronounced deformation texture formation under cryogenic conditions.

At 70% reduction, homogeneous grain fragmentation in the CR-70% sample leads to marked weakening of the Copper texture (3.8 m.r.d.), accompanied by reduced Brass (5.0 m.r.d.) and S (6.0 m.r.d.) components. By 90% reduction, Brass texture intensity rebounds to 6.1 m.r.d., while Copper further diminishes (3.4 m.r.d.), and S stabilizes at 5.0 m.r.d. This transition can be attributed to the reduced stacking fault energy (SFE) at cryogenic temperatures, which favors the formation of Brass/S-dominated deformation textures. The strengthening of Brass texture aligns with its role as a hallmark of deformation twinning, as evidenced in prior studies on cryorolled FCC alloys [16].

In summary, CR progressively shifts crystallographic orientations toward Brass and S components along the β fiber. The lower rolling temperatures drive a texture transition from Copper $\rightarrow$ S $\rightarrow$ Brass, consistent with deformation mechanisms governed by twin-mediated plasticity in low-SFE systems [17]. These findings underscore cryorolling's efficacy in tailoring texture evolution for advanced sputtering target applications.

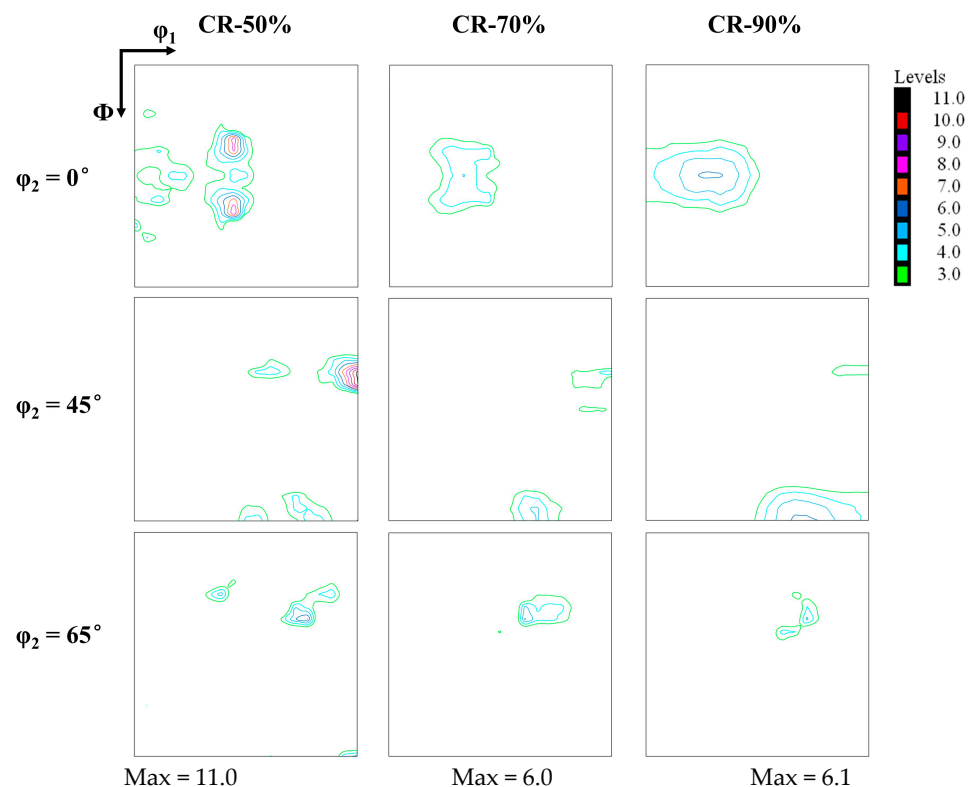


Figure 7. Sections of constant ϕ_2 ODF of ultra-high-purity copper under CR.

Figure 8 illustrates the evolution of texture component volume fractions in ultra-high-purity copper under RTR and CR. As discussed previously, deformation textures in FCC metals are distributed along the α and β fibers in Euler space, comprising stable orientations (e.g., Brass, Copper) and transient orientations (e.g., Goss, S). During cold deformation, randomly oriented grains progressively rotate along the β fiber, transitioning through transient orientations (Goss or S) before converging near stable orientations (Copper or Brass), thereby enhancing texture intensity along the β fiber.

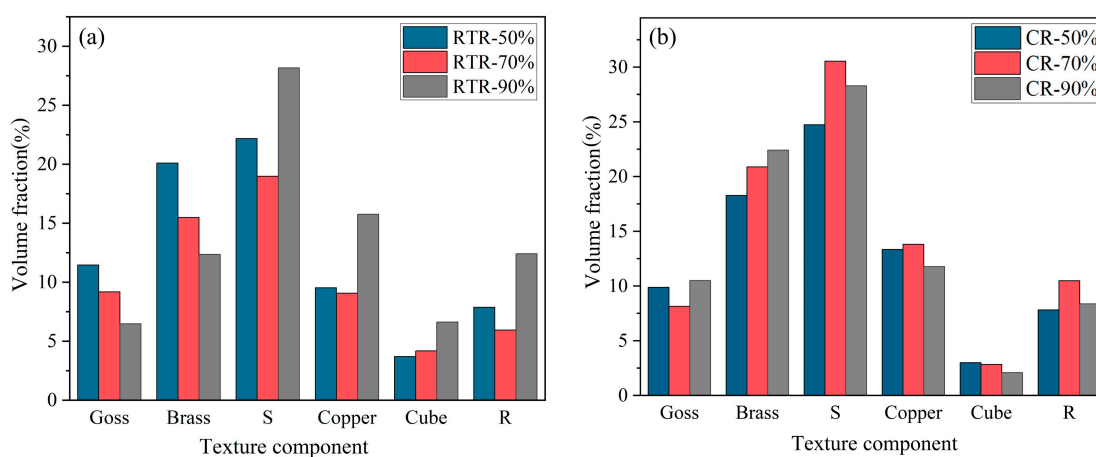


Figure 8. Relationship between volume fraction of different texture components and deformation of ultra-high-purity copper: (a) RTR, (b) CR.

Under RTR conditions, Goss and Brass components decrease with increasing strain, while Copper and S textures dominate at 90% reduction (Figure 8a). This aligns with the deformation behavior of medium-to-high SFE FCC metals, where dynamic recrystallization

(DRX) at 90% reduction promotes Cube and R texture formation through preferential nucleation at S-oriented matrices.

In contrast, CR suppresses dynamic recovery and DRX. Goss texture remains stable, while Brass intensity increases progressively with strain (Figure 8b). The fragmentation and reorientation of Cube grains under CR reduce their volume fraction, resulting in Brass/S-dominated textures characteristic of CR samples with high reduction. This transition is attributed to twin-mediated deformation mechanisms under cryogenic conditions, which enhance Brass texture stability by restricting dislocation cross-slip.

3.4. Mechanical Properties

3.4.1. Microhardness

The relationship between microhardness and rolling reduction for ultra-high-purity copper under different rolling temperatures is illustrated in Figure 9. The data points represent the mean values, and the error bars indicate the standard deviation from multiple measurements. CR samples exhibit significantly higher microhardness compared to RTR counterparts across all strain levels. This is attributed to the suppression of dynamic recovery and DRX during CR, enabling continuous accumulation of dislocations and strain hardening. At 90% reduction, CR achieves a peak microhardness of 164.60 HV, representing a 204% increase over the initial forged state. In contrast, RTR samples undergo competing mechanisms of work hardening and dynamic softening. The observed microhardness decline in RTR-90% samples (123.60 HV) directly evidences active DRX, which reduces dislocation density through boundary migration and subgrain coalescence.

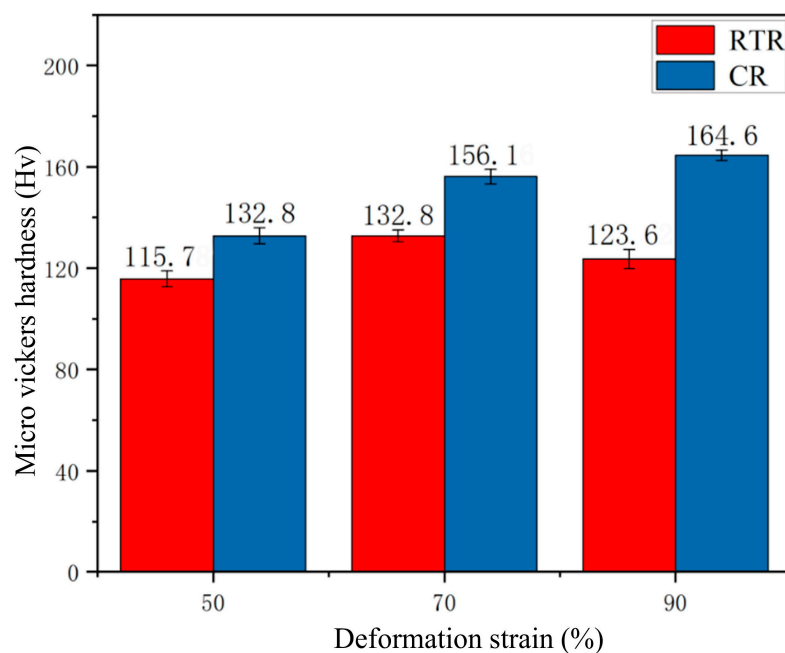


Figure 9. Relationship between microhardness and deformation in the ultra-high-purity copper plates processed by RTR and CR.

These results align with prior studies on cryogenic deformation, where suppressed thermal activation preserves dislocation structures and enhances mechanical strength [18]. The superior hardness retention in CR-processed copper highlights its potential for applications requiring high stored energy and microstructural stability.

3.4.2. Stress–Strain Behavior

Figure 10 displays the representative engineering stress–strain curves, and the corresponding average mechanical properties with standard deviations are summarized in Table 4. The data represent the mean $\pm$ standard deviation of three independent tests for each condition. Notably, CR samples exhibit significantly higher yield strength (385.61 MPa at 90% reduction) and tensile strength (648.02 MPa) compared to RTR counterparts at equivalent strain levels. This enhancement stems from intensified plastic deformation during CR, which simultaneously refines grain structures and elevates dislocation density, thereby strengthening the material through Hall–Petch hardening mechanisms [19].

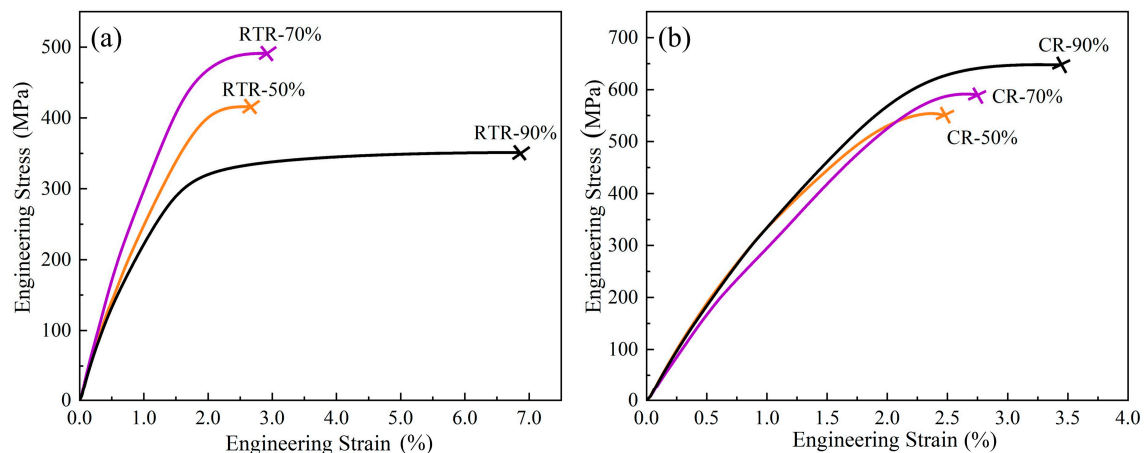


Figure 10. Stress–strain curve of ultra-high-purity copper under different rolling temperature conditions: (a) RTR, (b) CR.

Table 4. Mechanical properties of ultra-high-purity copper under different rolling temperatures.

Rolling Temperature Conditions	Thickness Reduction	Yield Strength (MPa)	Tensile Strength (MPa)	Uniform Elongation (%)
RTR	50%	257.26 $\pm$ 5.82	415.88 $\pm$ 8.91	2.51 $\pm$ 0.23
	70%	326.41 $\pm$ 7.15	491.09 $\pm$ 9.24	2.77 $\pm$ 0.19
	90%	201.17 $\pm$ 12.37	351.20 $\pm$ 10.55	6.66 $\pm$ 0.71
CR	50%	347.43 $\pm$ 6.23	544.06 $\pm$ 11.20	2.35 $\pm$ 0.18
	70%	359.51 $\pm$ 8.45	591.42 $\pm$ 12.33	2.63 $\pm$ 0.21
	90%	385.61 $\pm$ 9.12	648.02 $\pm$ 13.77	3.32 $\pm$ 0.25

For RTR samples, the interplay between work hardening and DRX governs mechanical behavior. At 90% reduction, a remarkable increase in uniform elongation (6.66%) correlates with DRX-induced microstructural homogenization. Cube- and R-oriented DRX grains nucleate preferentially along S-oriented deformation matrices, forming a bimodal structure comprising coarse and fine grains. During tensile testing, coarse grains accommodate strain to enhance ductility, while fine grains contribute to strength retention via boundary strengthening [20].

In CR-processed samples, uniform elongation progressively improves with increasing reduction (from 2.35% at 50% to 3.32% at 90%), attributed to twin-mediated plasticity. Deformation twins act as barriers to dislocation motion, promoting dislocation pile-ups at twin boundaries that enhance strain absorption. As strain escalates, twin density increases while interlamellar spacing decreases, synergistically improving both strength and ductility [21,22].

3.5. The Microstrain and Average Substructure Size

The XRD peak broadening is influenced by microstructural refinement (e.g., grain, subgrain, and cell size reduction) and lattice distortions (e.g., microstrain and local strain heterogeneity). To systematically investigate the effects of rolling temperature on these parameters in ultra-high-purity copper, {220} diffraction peaks from RTR and CR samples were analyzed using *JADE 6.0* software (Figure 11). The FWHM of the {220} peaks exhibits a progressive increase with rolling reduction for both RTR and CR conditions, indicating intensified grain fragmentation and microstrain accumulation. Notably, CR samples consistently display larger FWHM values compared to RTR counterparts at equivalent strains, signifying enhanced plastic deformation severity under cryogenic conditions.

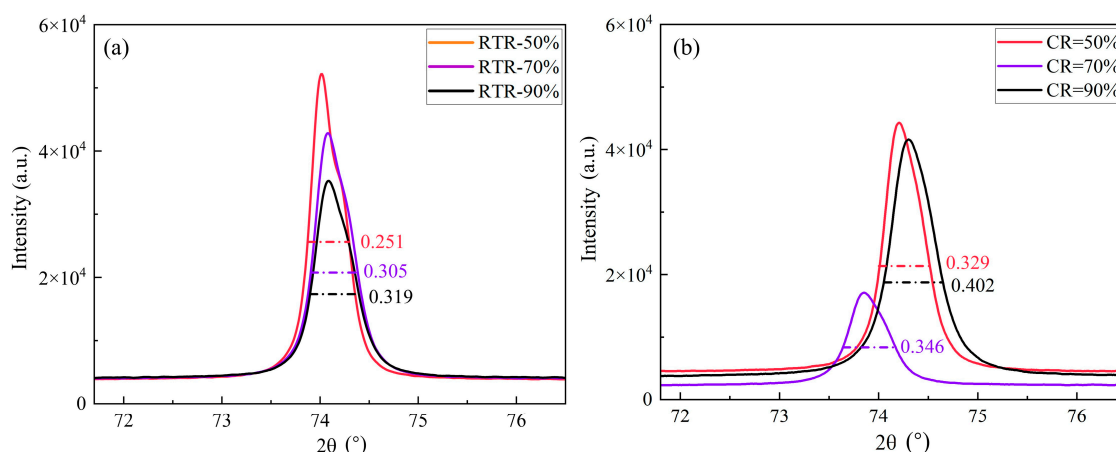


Figure 11. {220} peak diffraction pattern of ultra-high-purity copper: (a) RTR, (b) CR.

The Williamson–Hall method was employed to quantify microstructural refinement and microstrain evolution in ultra-high-purity copper under RTR and CR at 90% reduction. Diffraction peaks of {111}, {200}, {220}, and {311} planes were analyzed using *JADE 6.0* software, with results summarized in Table 5. The Williamson–Hall equation [23–25] is expressed as:

$$\beta \cdot \cos\theta = \frac{K\lambda}{d} + 4\epsilon \cdot \sin\theta \quad (1)$$

where

- β = the full width at half maximum (FWHM). Instrumental broadening was calibrated using a fully annealed, high-purity copper reference sample. This reference sample was prepared by annealing a piece of the same 6N-purity copper at 600 °C for 2 h, followed by furnace cooling to eliminate dislocations and ensure coarse grains, thereby minimizing any physical broadening contribution. The FWHM of its diffraction peaks was taken as the instrumental broadening (β_i). The physical broadening β is obtained by correcting the measured broadening β_m using the following relationship:

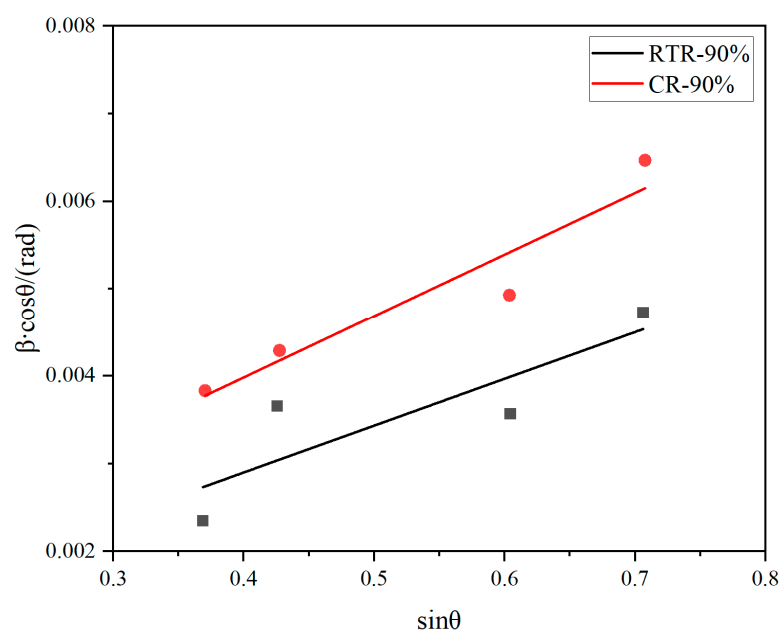
$$\beta = \sqrt{\beta_m^2 - \beta_i^2} \quad (2)$$

- θ = Bragg angle (degrees)
- k = Scherrer constant (dimensionless, ~1.0)
- λ = X-ray wavelength (1.54 Å for Cu-Kα)
- d = average substructure size (nm)
- ϵ = microstrain (%)

Table 5. XRD data of ultra-high-purity copper with 90% deformation under RTR and CR.

Sample	2θ	HKL	$\beta_m/^\circ$	$\beta_i/^\circ$	$\sin\theta$	$\beta \cdot \cos\theta/(\text{rad})$
RTR-90%	43.278	111	0.188	0.120	0.36876	0.00235
	50.394	200	0.283	0.163	0.42573	0.00365
	74.061	220	0.318	0.188	0.60442	0.00357
	89.858	311	0.457	0.250	0.70623	0.00473
CR-90%	43.483	111	0.265	0.120	0.37042	0.00383
	50.622	200	0.317	0.163	0.42753	0.00429
	74.265	220	0.401	0.188	0.60366	0.00493
	90.083	311	0.581	0.250	0.70762	0.00647

The microstrain (ϵ) and average substructure size (d) were determined by fitting the linear relationship between $\beta \cdot \cos\theta$ and $\sin\theta$ derived from the Williamson–Hall analysis (Equation (1)). Figure 12 illustrates the linear regression plots for RTR-90% and CR-90% samples (The red circles and gray squares represent the actual values calculated for the CR samples and RTR samples, respectively). The linear fits exhibited coefficients of determination (R^2) greater than 0.92, confirming the reliability of the derived microstrain and substructure size values used for subsequent stored energy calculations. Based on the fitted plots, the substructure size and microstrain of the RTR-90% and CR-90% samples were obtained and listed in Table 6. The CR-90% sample exhibits notably finer substructure size (~ 133 nm) and higher microstrain ($\sim 0.18\%$), indicating enhanced lattice distortion and localized strain under cryogenic conditions. These results confirm that CR introduces more severe plastic deformation compared to RTR, as reflected by the 23.5% reduction in substructure size and 37.5% rise in microstrain.

**Figure 12.** Fitting straight lines according to the Williamson–Hall equation.**Table 6.** Average microstructural size and microstrain of ultra-high-purity copper under RTR-90% and CR-90% conditions.

Sample	Substructure Size (nm)	Microstrain (%)
RTR-90%	173.64	0.128
CR-90%	132.76	0.176

3.6. The Stored Energy of Deformation

The stored energy of deformation (SE) refers to the energy retained within metallic materials during plastic deformation, primarily arising from dislocation accumulation, twin formation, and lattice distortion. Generally, SE increases with decreasing deformation temperatures and increasing strain levels due to suppressed dynamic recovery and enhanced defect density. The release of this stored energy acts as the driving force for recovery and recrystallization during annealing, critically influencing microstructural evolution (e.g., grain refinement) and texture modification (e.g., weakening of deformation textures). For cold-rolled metals, SE can be quantified using the Stibitz equation [26]:

$$SE_{(hkl)} = \frac{3}{2} Y_{(hkl)} \frac{\left(\frac{\Delta d}{d}\right)^2}{1 + 2V_{(hkl)}^2} \quad (3)$$

where

- $Y_{(hkl)}$ = Young's modulus (GPa) for the $\{hkl\}$ plane
- $\nu_{(hkl)}$ = Poisson's ratio for the $\{hkl\}$ plane
- $\Delta d/d$ = relative lattice spacing change, calculated as:

$$\frac{\Delta d}{d} = \frac{\sqrt{\beta_m^2 - \beta_i^2}}{2 \tan \theta} \quad (4)$$

The Stibitz equation provides a simplified, scalar estimate of stored energy by relating XRD-measured lattice strain to elastic strain energy. While this model involves assumptions (e.g., isotropic elasticity within a given crystallographic plane), it offers a self-consistent and comparative framework for evaluating the relative differences in stored energy between different processing conditions (CR vs. RTR) and crystallographic planes, which is the primary objective of this analysis. The absolute values should therefore be interpreted within this comparative context.

Young's modulus ($Y_{(hkl)}$) and Poisson's ratio ($\nu_{(hkl)}$) for the $\{111\}$, $\{200\}$, $\{220\}$, and $\{311\}$ orientations of pure copper were obtained from prior studies [27,28] to calculate the SE via Equation (3). Figure 13 compares the XRD profiles of $\{111\}$, $\{200\}$, $\{220\}$, and $\{311\}$ diffraction peaks for RTR and CR ultra-high-purity copper at 90% reduction. By combining Equations (1) and (3), SE values were computed and tabulated in Table 7. At 90% reduction, the CR-processed sample exhibits higher stored energy across all orientations compared to RTR counterparts. This enhancement correlates with CR-induced suppression of dynamic recovery, which preserves dislocations and twins while amplifying lattice distortions.

The SE for ultra-high-purity copper under 50% and 70% reductions was calculated across multiple crystallographic planes using the same methodology, with results summarized in Table 8. A pronounced orientation dependence is observed, where the $\{111\}$ plane exhibits the highest SE, consistent with its role as the primary slip system in FCC metals. This anisotropy arises because the $\{111\}$ planes accommodate higher dislocation densities due to their geometrically favorable slip geometry. In contrast, the $\{200\}$, $\{220\}$, and $\{311\}$ planes display progressively lower SE values, correlating with reduced slip activity and dislocation storage capacity.

CR samples consistently exhibit higher SE compared to RTR counterparts at equivalent strains. This enhancement stems from CR-induced suppression of dynamic recovery and recrystallization, which preserves dislocations and twins while minimizing defect annihilation. The elevated stored energy in CR-processed materials provides a greater driving force for nucleation during subsequent annealing, enabling finer grain structures and weaker residual textures—critical attributes for high-performance sputtering targets.

The orientation-specific energy hierarchy further underscores the importance of crystallographic texture control in optimizing thermo-mechanical processing routes.

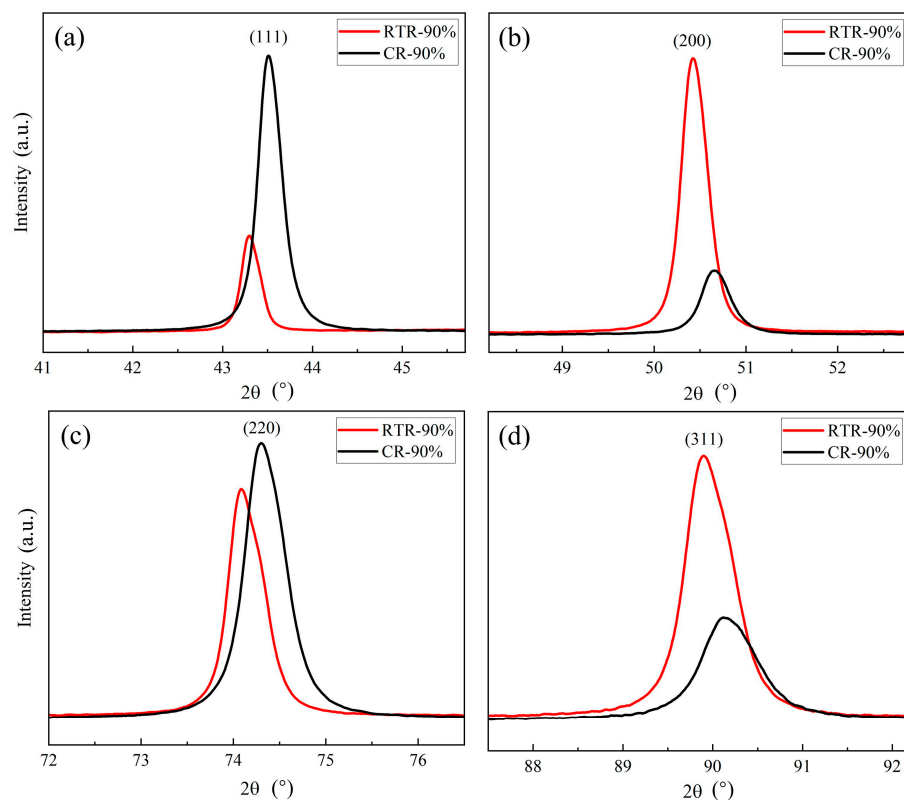


Figure 13. Comparison of diffraction peaks of ultra-high-purity copper with 90% deformation by RTR and CR: (a) {111}, (b) {200}, (c) {220}, (d) {311}.

Table 7. Calculation of diffraction plane storage energy of RTR-90% and CR-90% samples.

Sample	HKL	$\gamma_{(hkl)}/\text{Gpa}$	$\nu_{(hkl)}$	$\beta_m/^\circ$	$\beta_l/^\circ$	$SE_{(hkl)}/(\text{J}\cdot\text{mol}^{-1})$
RTR-90%	111	193.0	0.294	0.188	0.120	8.13
	200	67.1	0.419	0.283	0.163	4.46
	220	163.0	0.302	0.318	0.188	5.93
	311	117.0	0.340	0.457	0.250	5.20
CR-90%	111	193.0	0.294	0.265	0.120	21.66
	200	67.1	0.419	0.317	0.163	6.15
	220	163.0	0.302	0.401	0.188	11.31
	311	117.0	0.340	0.581	0.250	9.77

Table 8. Statistics of deformation storage energy of ultra-high-purity copper on different diffraction planes under different rolling conditions.

Rolling Temperature Conditions	Deformation	$SE_{(111)}/(\text{J}\cdot\text{mol}^{-1})$	$SE_{(200)}/(\text{J}\cdot\text{mol}^{-1})$	$SE_{(220)}/(\text{J}\cdot\text{mol}^{-1})$	$SE_{(311)}/(\text{J}\cdot\text{mol}^{-1})$
RTR	50%	5.44	2.41	4.92	2.70
	70%	9.42	4.03	5.24	4.95
	90%	8.13	4.46	5.92	5.20
CR	50%	9.99	5.77	6.59	7.52
	70%	13.37	5.00	7.73	6.98
	90%	21.66	6.15	11.31	9.77

4. Conclusions

This study systematically investigates the effects of rolling temperature and strain level on the microstructure, texture, and mechanical properties of ultra-high-purity copper (6N). Key findings are summarized as follows:

1. The dominant deformation mechanisms differ fundamentally between RTR and CR. RTR is governed by slip, leading to DRX at 90% reduction. In contrast, CR suppresses thermal activation, enabling a twin-mediated slip mechanism that generates ultrafine fibrous structures without DRX.
2. Texture evolution follows distinct pathways. At 90% reduction, RTR develops a texture dominated by Copper and S components, influenced by DRX. CR, however, promotes a progressive shift towards Brass and S textures, a signature of deformation twinning under cryogenic conditions.
3. CR specimens demonstrate significantly superior mechanical properties. Notably, the 90% cryorolled sample achieves a simultaneous enhancement of strength and ductility, exhibiting a yield strength of 385.61 MPa, a tensile strength of 648.02 MPa, and a uniform elongation of 3.32%. This represents an increase of 91.7%, 84.6%, and a relative improvement in ductility compared to the RTR-90% sample, attributable to intensified dislocation–twin interactions.
4. Quantitative microstructural analysis confirms that CR effectively suppresses dynamic recovery, leading to finer substructures (~ 133 nm vs. ~ 174 nm for RTR), higher microstrain (0.176% vs. 0.128%), and significantly greater deformation stored energy, particularly on the {111} plane (~ 22 J·mol^{−1} vs. ~ 8 J·mol^{−1}). This elevated stored energy provides a robust driving force for microstructural refinement during subsequent annealing, which provides a fundamental basis for the development of advanced sputtering targets.

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