Chapter 2 Literature Review

The development of titanium alloys has been extensively studied over the past several decades due to their unique combination of low density, high specific strength, and exceptional corrosion resistance, which makes them essential in aerospace, biomedical, and energy applications [1-3]. Among these alloys, Ti-6Al-4V, a dual-phase $\alpha+\beta$ alloy, and CP-Ti Grade 2, a single-phase α alloy, serve as benchmark systems for studying the relationship between alloy chemistry, microstructure, and mechanical performance [4-7]. Several studies have addressed their phase equilibrium, thermomechanical processing, and property optimization, yet key questions remain regarding their response to severe plastic deformation (SPD) at cryogenic temperatures.

Early research established the fundamental allotropic transformation of titanium from the HCP (α) phase to the BCC (β) phase above approximately 883 °C [8, 9]. Further research indicates that β-stabilising elements, such as vanadium and molybdenum, can balance the α/β phases, resulting in finer grain sizes, increased strength, and improved formability. [10, 11]. Recently, SPD techniques such as high-pressure torsion (HPT), equal-channel angular pressing (ECAP), and cryogenic deformation demonstrated substantial grain refinement to the sub-micron or nanometre scale, leading to significant strengthening while maintaining ductility [12-18].

Despite these advances, systematic comparisons of dual-phase Ti-6Al-4V and single-phase CP-Ti under identical cryo-rolling processes are still limited. Furthermore, the influence of initial microstructure (as-received versus heat-treated) on dislocation density and grain-boundary characteristic distribution has not been systematically clarified [19-22]. Addressing these gaps is essential for optimizing processing routes aimed at simultaneously enhancing strength and ductility while maintaining phase stability. This chapter reviews the current advancements in titanium alloy metallurgy, cryogenic deformation, grain refinement mechanisms, and the relationship between microstructure and properties, providing a foundation for the experimental program described in subsequent chapters.

2.1 Importance of Ti-6Al-4V and CP-Ti Grade 2

Titanium alloys play a crucial role among high-performance structural materials. Within this family, Ti-6Al-4V and CP-Ti Grade 2 are the most commonly studied alloys used for both fundamental research and engineering applications [4, 6].

2.1.1 Ti-6Al-4V (*α+β* Alloy)

Ti-6Al-4V consists of almost 6 wt.% aluminium (α-stabiliser) and 4 wt.% vanadium (β-stabiliser), with the rest being titanium. Its dual-phase microstructure provides a unique combination of high strength, moderate density, and good fracture toughness [23-25]. Key features include:

- **Aerospace application:** Ti-6Al-4V accounts for more than half of all titanium used in aerospace structures, including compressor blades, airframe components, and fasteners [10].
- **Mechanical performance:** Wrought products typically exhibit yield strengths of 800-950 MPa and ultimate tensile strengths exceeding 900 MPa while retaining useful ductility (percentage elongation around 10-14 %) [26].
- **Processing flexibility:** The presence of both *α* and *β* phases enables significant microstructural enhancement via thermomechanical processing (TMP) and heat treatment, helping to attain desired combinations of strength, toughness, and fatigue resistance [5, 8].
- **Model for dual-phase deformation:** Ti-6Al-4V is extensively used to investigate strain partitioning, slip transfer at *α/β* interfaces, and the effect of retained *β* on recovery and recrystallization during SPD [27, 28].

2.1.2 CP-Ti Grade 2 (Single-Phase *α* Alloy)

Commercially pure titanium (CP-Ti) Grade 2 consists of 99.5 wt.% titanium along with small amounts of oxygen, nitrogen, carbon, and iron. Its importance comes from its properties that complement those of the Ti-6Al-4V alloy:

- **Excellent corrosion resistance:** A stable, self-healing TiO_2 film provides outstanding resistance to seawater, various acids, and environments containing chlorides [29, 30].
- **Biocompatibility:** Low alloying content and inert oxide surface make it widely used in medical implants and surgical devices [31, 32].
- **High ductility and formability:** While its yield strengths (275-450 MPa) are lower than Ti-6Al-4V, it exhibits elongations over 25%, enabling the fabrication of complex shapes [33].
- **Model for single-phase *α* deformation:** The absence of *β* phase simplifies the interpretation of dislocation storage, twinning, and grain-boundary evolution, making CP-Ti an ideal baseline for studying cryogenic SPD [34].

2.1.3 Basis for Comparative Study

Studying Ti-6Al-4V and CP-Ti Grade 2 together provides a systematic approach to understanding how phase composition and alloying elements influence cryogenic rolling behaviour. Ti-6Al-4V demonstrates the response of a dual-phase, precipitation-hardenable alloy, while CP-Ti serves as a near-pure α reference. Their different chemistries and microstructures allow for a comprehensive evaluation of:

- The influence of retained β phase compared to single α phase on dislocation accumulation and the suppression of recovery,
- The effect of initial grain morphology on texture evolution and grain-boundary characteristics, and
- Differences in achievable grain refinement and the strength-ductility relationship under the same cryogenic rolling conditions.

In summary, Ti-6Al-4V and CP-Ti Grade 2 are the primary types of structural titanium alloys. Their extensive industrial applications, well-defined baseline properties, and notably different phase structures make them ideal model systems for exploring the microstructural and mechanical impacts of cryogenic SPD, their comparative roles during cryogenic applications are shown in Table 2.1.

Table 2.1: Comparative roles of Ti-6Al-4V and CP-Ti during cryogenic applications.

Parameters	Ti-6Al-4V	CP-Ti
Phase composition	Dual phase (α+β)	Single phase (α)
Primary applications	Aerospace components	Corrosion-resistant parts
Strengthening mechanisms	Phase interactions, β retention	Dislocation storage, twinning
SPD research focus	Strain partitioning, texture	Grain refinement, FCC phase

Table 2.1 highlights the complementary roles of Ti-6Al-4V and CP-Ti in cryogenic studies, emphasizing their distinct phase-driven deformation behaviours.

2.2 HCP Crystal Structure and Deformation Mechanisms

The hexagonal close-packed (HCP) crystal structure of titanium imposes fundamental constraints on its plastic deformation behaviour. Unlike cubic structures, HCP titanium consists of limited independent slip systems at room temperature, which often results in anisotropy and poor formability. The crystallographic c/a ratio (1.587 for Ti) deviates from the ideal close-packed value (1.633), resulting in distinct slip and twinning behaviours [35]. Table 2.1 shows some common deformation slip and twin systems observed in titanium [36-47].

In titanium, the activity of slip generally takes place along the prismatic plane having $\{10\bar{1}0\}$ $<11\bar{2}0>$ slip systems, which are easily activated at room temperature due to their relatively low critical resolved shear stress (CRSS). Reed-Hill et al. [48] were among the first to identify prismatic slip as the dominant deformation mechanism in HCP crystal-structured materials under ambient conditions in 1957. With increasing temperature, activation of basal $\{0001\}$ $<11\bar{2}0>$ slip is enhanced, while pyramidal $<c+a>$ slip systems $\{10\bar{1}1\}$ $<11\bar{2}3>$ are required to accommodate deformation along the c-axis [49]. These $<c+a>$ slip systems are required to satisfy the von Mises criterion of five independent slip systems essential for general plasticity. However, their activation demands significantly higher stresses, restricting their influence at lower temperatures [50].

Table 2.2: Common deformation slip and twin systems observed in HCP titanium [36-47].

Mode	Type	System
Slip Systems	Basal $<a>$	$\{0001\} <11\bar{2}0>$
	Prismatic $<a>$	$\{10\bar{1}0\} <11\bar{2}0>$
	Pyramidal $<a>$	$\{10\bar{1}1\} <11\bar{2}0>$
	1st order Pyramidal $<c+a>$	$\{10\bar{1}1\} <11\bar{2}\bar{3}>$
	2nd order Pyramidal $<c+a>$	$\{11\bar{2}2\} <11\bar{2}\bar{3}>$
Twin Systems	Tensile	$\{11\bar{2}1\} <11\bar{2}\bar{6}>$
		$\{11\bar{2}3\} <11\bar{2}\bar{2}>$
		$\{10\bar{1}2\} <10\bar{1}\bar{1}>$
	Compressive	$\{10\bar{1}1\} <10\bar{1}\bar{2}>$
		$\{11\bar{2}2\} <11\bar{2}\bar{3}>$
		$\{11\bar{2}4\} <22\bar{4}\bar{3}>$

Critical slip and twinning system in HCP titanium, governing plasticity under cryogenic deformation.

Deformation twinning serves as a supplementary mechanism for accommodating strain in HCP titanium. Stanford et al. [51] reported that $\{10\bar{1}2\} <10\bar{1}1>$ tensile twins are the most common at low to moderate strains, particularly in CP-Ti as shown in Figure 2.1. However, $\{11\bar{2}1\} <11\bar{2}\bar{6}>$ compression twins are activated when subjected to high-strain or compressive loading conditions [52]. Salem et al. [53] demonstrated that twinning enhances strain hardening in CP-Ti through grain reorientation and activation of additional slip systems, although this mechanism also intensifies texture and anisotropy. Table 2.2 represents the common deformation slip and twin systems observed in titanium [36-47].

Recent research has highlighted the combined contribution of slip and twinning in polycrystalline titanium. Gurao et al. [54] examined EBSD and TEM-based observations and concluded that the relative contributions of slip and twinning strongly depend on alloy composition, grain size, and deformation temperature. Hailiang et al.

[55] further demonstrated that in ultrafine-grained (UFG) titanium, twinning is significantly suppressed with the reduction in grain size when subjected to high-strained conditions. Thus, the slip-induced deformation, along with the enhancement of strength, takes place.

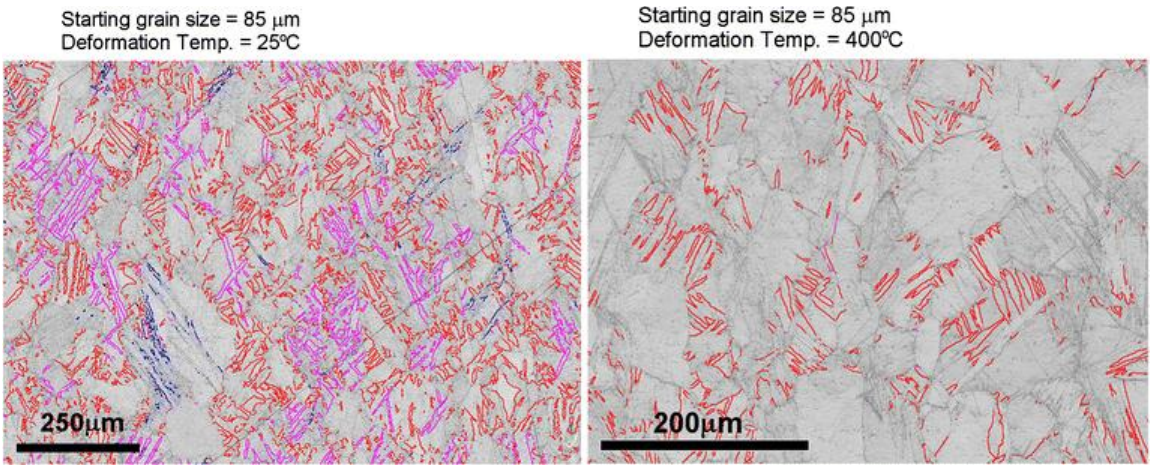

Figure 2.1: EBSD orientation maps of samples after deformation to a strain of 0.2 at the temperatures shown. The EBSD maps are displayed with $\{10\bar{1}2\}$ twin boundaries shown in red, $\{11\bar{2}2\}$ twin boundaries shown in pink, and $\{11\bar{2}1\}$ boundaries shown in blue [51].

In α+β alloys such as Ti-6Al-4V, deformation mechanisms become more complex due to the presence of the β phase. Semiatin et al. [56] observed that the distribution of strain between α and β phases affects deformation mechanisms. The β phase mainly allows dislocation glide across multiple cubic slip systems, while the α phase deforms primarily due to prismatic slip and limited twinning. This interaction between the two phases decreases anisotropy compared to single-phase α alloys, but the evolution of texture remains a concern.

Furthermore, recent research has documented structural transformations caused by deformation. Wu et al. [57] provided evidence of an HCP to FCC transformation in titanium during rolling as shown in Figure 2.2, suggesting that under extreme conditions, non-classical mechanisms can contribute to deformation. Such findings expand the conventional understanding of HCP deformation and suggest that metastable pathways could be involved in titanium alloys during cryogenic or SPD conditions.

The transformation from HCP to FCC structure in titanium is primarily associated with the accumulation of stacking faults within the close-packed planes. In the HCP structure, the atomic stacking sequence follows an ABAB arrangement, whereas the FCC structure follows an ABCABC sequence. The introduction of intrinsic stacking faults alters the local stacking sequence, and successive faulting can progressively convert HCP regions into an FCC-like arrangement. This process is energetically feasible under conditions of high local stress and reduced temperature, where dislocation mobility is restricted and planar slip is favoured.

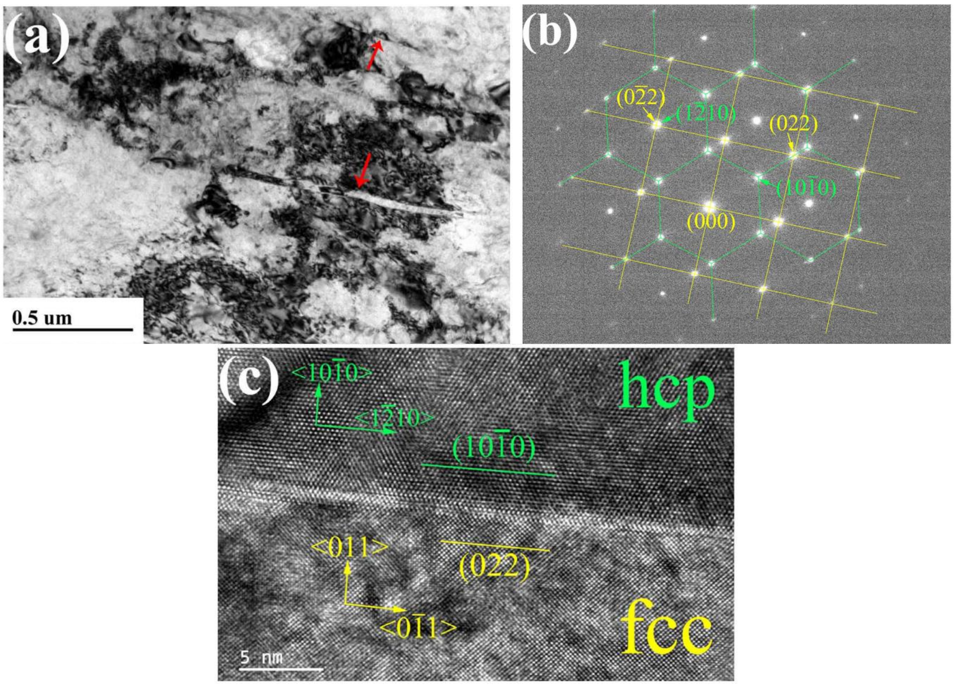

Figure 2.2: Orientation relationship between hcp matrix and fcc band. (a) Platelet bands in cold-rolled titanium indicated by red arrows. (b) SAED patterns of the interface between hcp and fcc, where patterns outlined by green lines corresponding to hcp and by yellow lines corresponding to fcc. (c) HRTEM image of the interface showing the orientation relationship to be $\langle 0001 \rangle_{hcp} || \langle 001 \rangle_{fcc}$ and $\{1010\}_{hcp} || \{011\}_{fcc}$ [57].

Overall, these studies show that the deformation mechanisms in hcp titanium involve a complex interaction of prismatic slip, limited <*c*+*a*> slip, and deformation twinning. This interplay is influenced by factors such as alloy composition, grain size, and processing temperature. Gaining a clear understanding of these mechanisms is essential for improving TMP methods and advanced techniques like cryo-rolling and SPD.

2.3 Thermomechanical Processing of Titanium Alloys

Thermomechanical processing (TMP) plays a crucial role in controlling the microstructure and enhancing the mechanical properties of titanium and its alloys. Early systematic research conducted by Lütjering et al. [1] established the foundation for understanding the relationship between the microstructure and properties of titanium and its alloys. It emphasizes the conditions and parameters for controlling phase transformations and deformation conditions in tailoring equiaxed, lamellar, and bimodal microstructures. Similarly, Leyens et al. [3] highlighted the industrial importance of TMP, particularly in near-*α* and *α*+*β* alloys, where the microstructure directly influences the balance among strength, ductility, fatigue resistance, and creep behaviour.

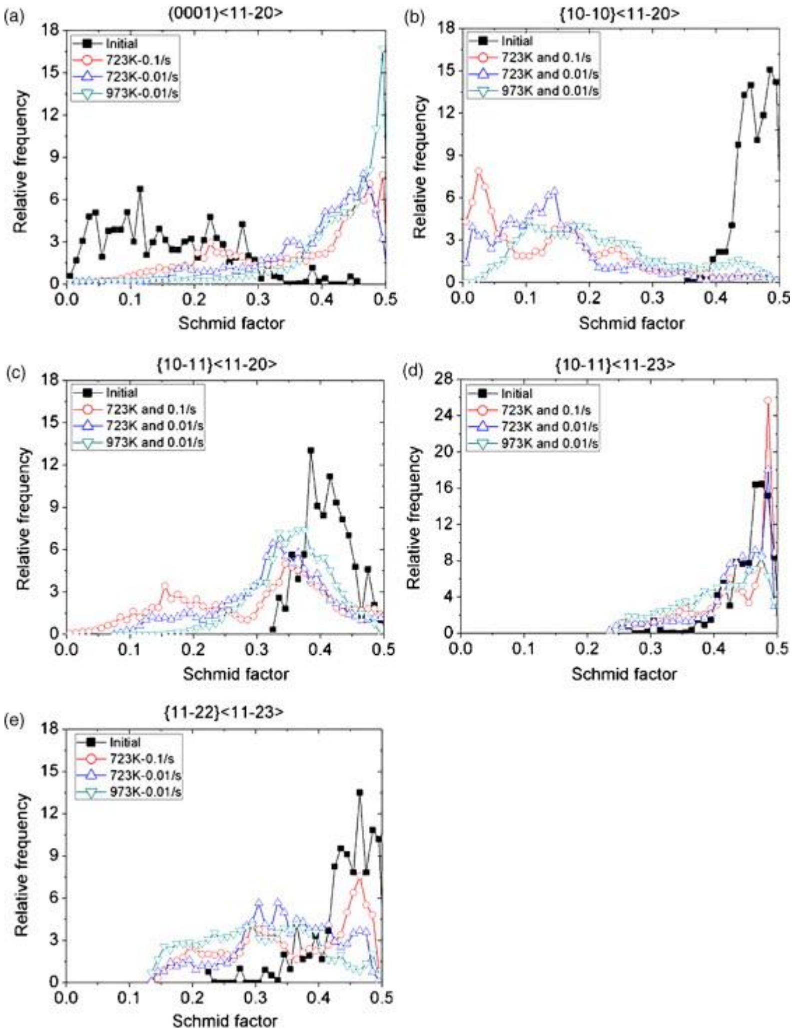

Figure 2.3: Relative frequency of Schmid factor values before and after deformation for (a) basal slip, (b) prismatic slip, (c) pyramidal slip, (d) 1st order pyramidal slip and (e) 2nd order pyramidal slip [58].

Initial studies showed that TMP greatly promotes texture development in CP-Ti due to its limited active slip systems in the HCP structure. Salem et al. [53] showed that deformation at room temperature produces strong basal textures, leading to significant anisotropy in the mechanical behaviour. Zhipeng et al. [58] and Sahoo et al. [59] further revealed that hot deformation of CP-Ti causes grain elongation and the development of strong basal textures as shown in Figure 2.3. Gurao et al. [54] further investigated the changes in microstructure and texture evolution in titanium alloys, emphasizing that the inherent crystallographic constraints of the HCP phase restrict the ability of TMP to achieve isotropic properties.

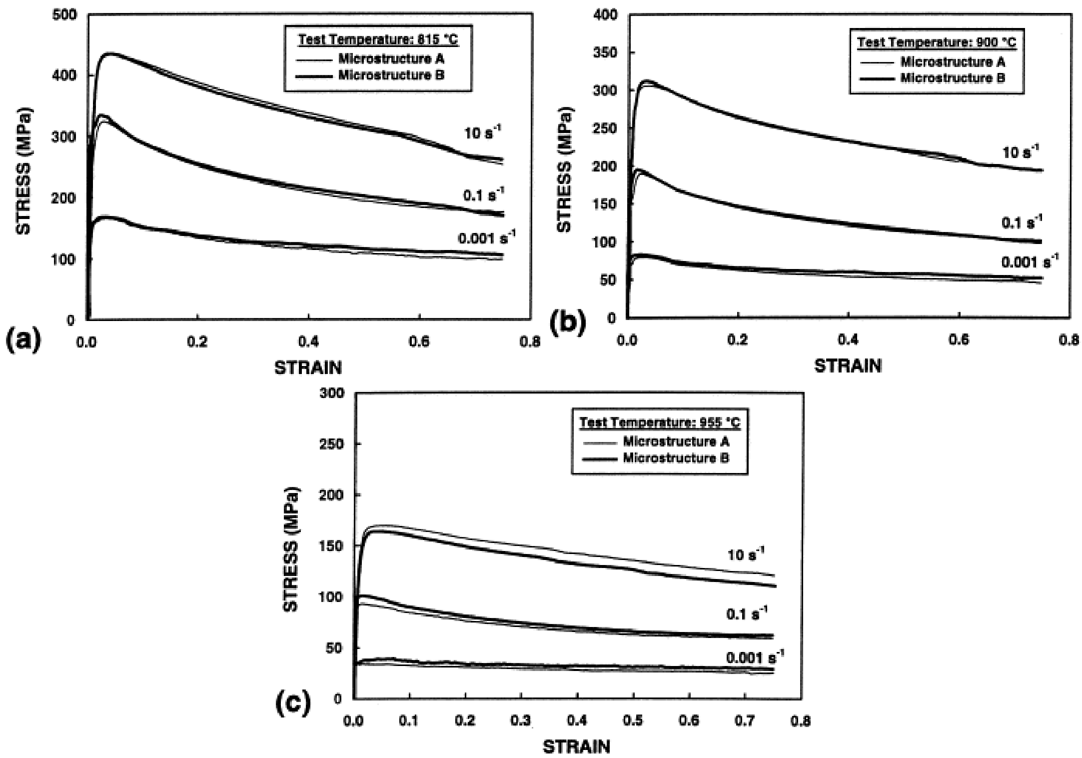

Figure 2.4: Measured true stress-true strain (flow) curves for Ti–6Al–4V tested at (a) 815°C; (b) 900°C; or (c) 955°C [56].

In Ti-6Al-4V, the most commonly used $\alpha+\beta$ alloy, TMP has been thoroughly researched due to its broad applications in aerospace and biomedical industries. Semiatin et al. [56, 60] systematically examined the sub-transus hot working of Ti-6Al-4V, demonstrating that the globularization of α lamellae occurs under specific strain and temperature conditions, leading to enhanced ductility while retaining strength as shown in Figure 2.4. Weiss et al. [61] also highlighted that deformation within the $\alpha+\beta$ field promotes bimodal microstructures, which provide a favourable compromise between tensile strength and fracture toughness.

Bhattacharjee et al. [62] examined near-α titanium alloys and found that TMP in the α+β region promotes the formation of fine, equiaxed α grains that enhance both strength and fracture toughness. This result supports the broader conclusion that TMP conditions influence the shape and spatial arrangement of α and β phases, ultimately shaping the alloy’s final mechanical properties.

Microstructural refinement via TMP has also been associated with improved fatigue and creep performance. Pilchak et al. [63] demonstrated that equiaxed and bimodal Ti-6Al-4V microstructures offered superior resistance to fatigue crack initiation compared to lamellar structures, although the latter displayed enhanced creep strength. Lutjering

[25], made similar observations, indicating that the microstructures developed during TMP significantly affect fatigue life and crack growth rates.

The evolution of texture continues to be a consistent theme in the TMP of titanium alloys. Gurao et al. [54] highlighted the presence of strong basal or prism textures, commonly observed in CP-Ti and Ti-6Al-4V as shown in Figure 2.5, resulting in anisotropic tensile properties. Recent EBSD-based studies, such as those by Shi et al. [64] and Zhu et al. [65], demonstrated that TMP-induced textures can be modified through controlled deformation schedules, providing new routes for reducing anisotropy as shown in Figure 2.6.

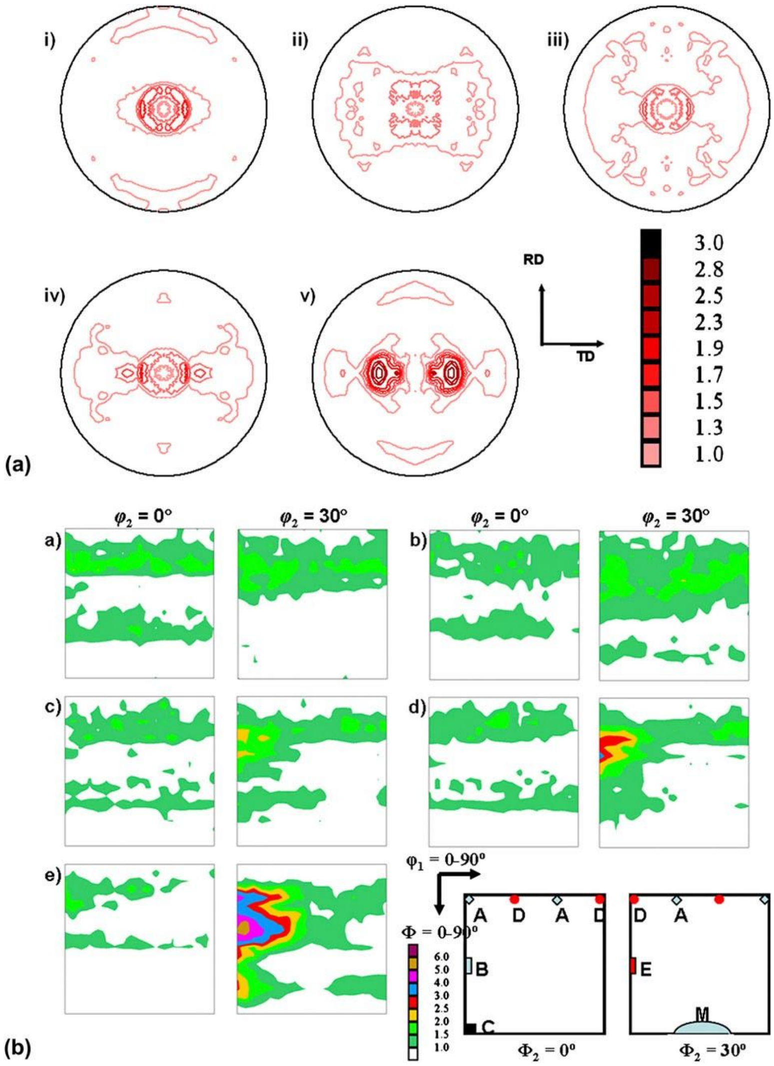

Figure 2.5: (a) (0002) pole figures and (b) $\varphi_2 = 0°$ and 30° sections of the ODF for SMG Ti samples rolled to a strain of (i) 0.10, (ii) 0.29, (iii) 0.69, (iv) 1.2, and (v) 2.3 [54].

The development of SPD and cryogenic processing has led to a new understanding of the effect of TMP in titanium refinement. Wang et al. [66] observed the development of UFG structures and improved ductility in nanocrystalline titanium processed through low-temperature deformation. Wu et al. [57] observed an unusual HCP to FCC phase transformation during the rolling of titanium at room temperature, indicating that TMP can explore metastable deformation pathways, which are not considered in earlier studies.

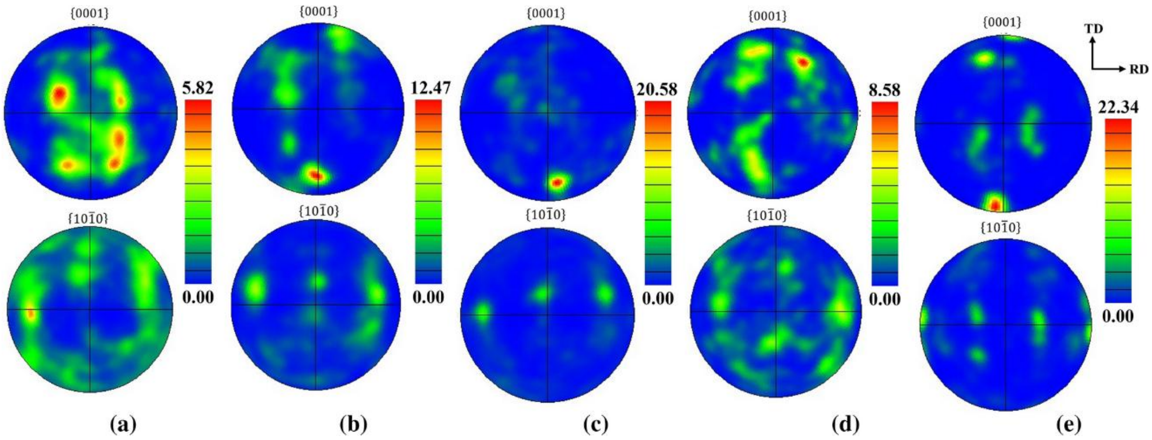

Figure 2.6: Texture evolution of (a) as cross rolled (b) 680 °C annealed (c) 720 °C annealed (d) 760 °C annealed and (e) 840 °C annealed [64].

Taken together, these studies demonstrate that TMP is an effective process for tailoring microstructures in titanium alloys. Nevertheless, there are ongoing challenges in decreasing texture-induced anisotropy, achieving a balance between strength and ductility in dual-phase alloys, and understanding the role of metastable phase transformations influence advanced TMP processes.

2.4 Severe Plastic Deformation

Severe plastic deformation (SPD) is extensively researched as a technique to create UFG and nanostructured titanium with significantly enhanced strength. Valiev and co-workers established the modern SPD pattern. They were among the first to provide a systematic understanding, demonstrating that extensive imposed strains can produce severe grain refinement and enhance the mechanical properties in a wide range of metals, including titanium. They systematically investigated the evolution of the microstructure, including intense dislocation generation, the formation of dislocation cells and sub-grains, gradual boundary rotation, and the eventual stabilization into UFGs. These features are linked to the increased strength observed in SPD-treated materials [12]. Later, they developed expectations for ECAP processing, emphasizing repeated pass techniques and texture development that impact future work on titanium [67]. Zhilyaev et al. [13] extended these concepts to HPT, observing that HPT achieves some of the most significant equivalent strains and smallest steady-state grain sizes in bulk form. This fact has been incorporated in multiple studies on titanium.

Initial experiments applying SPD to titanium demonstrated its feasibility and revealed trade-offs. Multiple researchers found that techniques like ECAP and HPT can refine CP-Ti and Ti alloys to sub-micron and nanometer grain sizes, significantly enhancing YS. However, tensile ductility often decreases unless post-processing annealing or carefully designed processing schedules are employed [68, 69]. These studies showed that the strength-ductility relationship is mainly influenced by the boundary structures and dislocation networks retained during SPD.

Work specifically on Ti-6Al-4V highlighted that the phase constitution influences the refinement pathways. Floriano et al. [70] reported that α+β interactions modify strain distribution during ECAP/HPT, resulting in different steady-state grain sizes and textures compared to single-phase CP-Ti. The β phase can either help accommodate strain or hinder α-phase dislocation movement, depending on its morphology and scale, thus necessitating alloy-specific process design. Follow-up studies confirmed that the same SPD schedules do not yield identical microstructures in α and α+β systems, which justifies the direct alloy-to-alloy comparisons employed in this thesis.

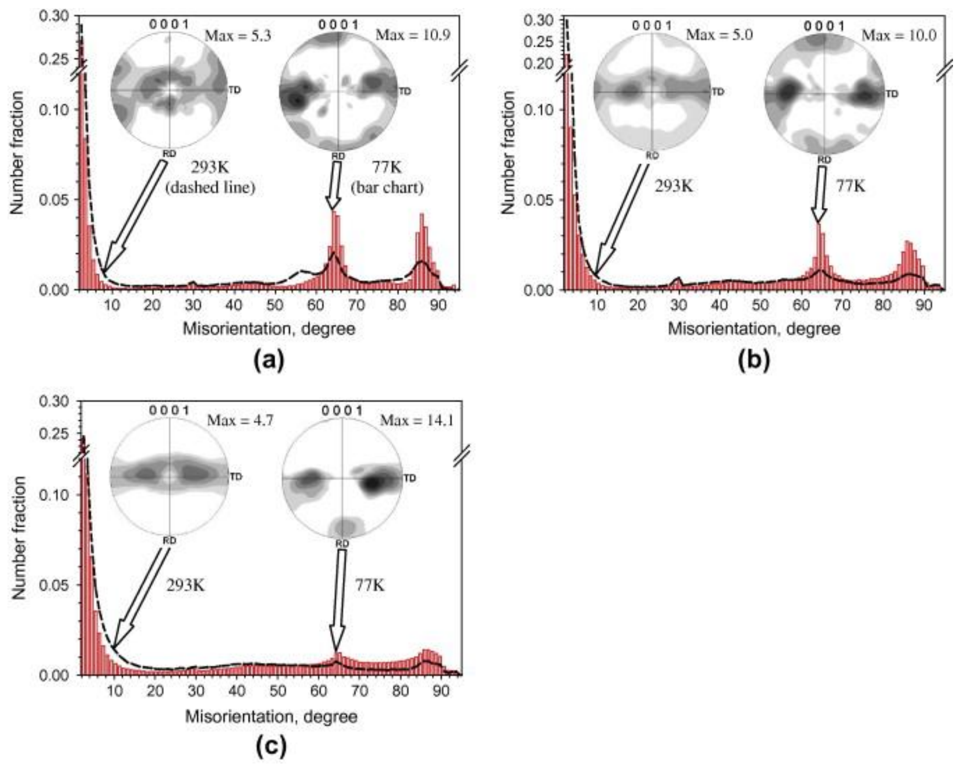

Figure 2.7: Misorientation distributions and corresponding (0 0 0 2) pole figures for CP Ti samples rolled at 293 or 77 K to a true thickness strain ε_{th} of (a) 0.16, (b) 0.36 or (c) 0.92 [17].

Rolling-based SPD and cryogenic variants have gained interest because they are naturally compatible with sheet materials. Zherebtsov et al. [17] demonstrated that the cryogenic rolling of CP-Ti resulted in the formation of very fine sub-grain structures and nanoscale equiaxed regions as shown in Figure 2.7, which can be attributed to suppressed recovery at approximately -196 °C and high retained dislocation densities. Liang et al. [71] confirmed these findings by analysing EBSD and TEM results, and correlated them with increased hardness and YS, followed by cryo-rolling. Recent studies showed that cryo-rolling of Ti-6Al-4V, when combined with optimized short annealing, can achieve higher strength and ductility in sheet products, compared to that of conventional cold rolling. [18, 72].

Mechanistic understanding has progressed through detailed microscopic research. Humphreys et al. [73] proposed pathways for continuous dynamic recrystallization (CDRX), which involves dislocation accumulation leading to the formation of sub-grains, increasing misorientation, and ultimately resulting in the formation of high-angle grain boundaries (HAGBs). This framework is commonly used to explain the formation of UFGs induced by SPD in titanium. Christian et al. [49] subsequent HCP-focused studies clarified how deformation twinning interacts with dislocation activity to accelerate subdivision and reorientation, an effect particularly relevant in CP-Ti and under low-temperature or high-strain conditions. Pantleon [74] investigated an EBSD-based geometrically necessary dislocations (GND) estimation methodology, cautioned about step-size effects, and emphasised the importance of TEM cross-validation.

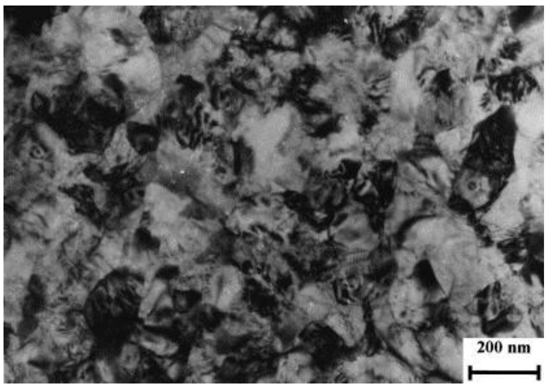

Figure 2.8: TEM micrograph of titanium subjected to severe torsion straining [12].

Several studies provided careful investigation of EBSD-TEM cross-validation in SPD titanium. TEM analysis conducted by Valiev's group showed that the presence of dislocation cells remains during SPD, and that low-angle grain boundaries (LAGBs) gradually transform into high-angle grain boundaries (HAGBs) in materials deformed by ECAP or HPT [12, 13, 67, 68] as shown in Figure 2.8. Zherebtsov et al. [17] combined EBSD-generated kernel average misorientation (KAM) maps along with TEM to demonstrate that cryo-rolling produces abundant LAGBs and very high local misorientations, which correlate with an increase in hardness. These studies emphasize that using a combination of advanced characterization techniques is required to obtain a reliable estimation of dislocation density and grain size, which are essential for mechanistic understanding models.

Practical and conceptual limitations have also been documented. Valiev et al. [67] and Zhilyaev et al. [13] highlighted challenges associated with scaling up the process. ECAP and HPT create excellent microstructures in lab settings but are difficult to apply to large sheets or structural components. Common processing issues include surface cracking, strain inhomogeneity in specific geometries, and sensitivity to temperature fluctuations [12, 17, 71]. Methodologically, Pantleon [74] notified that EBSD-derived GNDs can underestimate the total dislocation content unless the step size and processing parameters are carefully examined. This adds complexity to cross-study comparisons and the validation of quantitative dislocation densities.

In summary, the SPD research on titanium confirms that:

- SPD consistently produces UFGs and nanostructured titanium with significantly enhanced strength [12, 13, 67].
- The $\alpha+\beta$ composition in Ti-6Al-4V alters strain distribution and steady-state microstructures compared to CP-Ti, necessitating alloy-specific approaches [70].
- Rolling-based SPD and cryo-rolling provide effective, sheet-compatible methods for achieving high dislocation densities and fine sub-grain structures, provided thermal management is maintained [17, 18, 71, 72].
- Mechanistic pathways are primarily characterized by coupled dislocation accumulation, sub-grain rotation, CDRX, and twin-assisted subdivision. However, a quantitative evaluation of dislocation metrics still requires validation through EBSD and TEM [49, 73, 74].

These findings highlight key gaps, including the need for matched, directly comparable SPD or cryo-rolling datasets under identical thermal and strain conditions, thorough cross-validation of EBSD-derived dislocation data with TEM, and practical guidance for consistent sheet-scale cryo-rolling processes.

2.5 Impact of Cryo-Rolling on Microstructural Evolution and Deformation Mechanisms

Cryo-rolling has emerged as one of the most important SPD techniques for achieving significant grain refinement, involving deformation carried out at an extreme negative temperature, such as approximately -196 °C for liquid nitrogen. Cryo-rolling, compared to traditional cold rolling, inhibits dynamic recovery and preserves dislocations, leading to faster grain subdivision and refinement. Over the past two decades, several researchers have studied the mechanisms of cryo-rolling in titanium and its alloys. Their research highlights both the benefits and the remaining challenges of this technique.

One of the earliest systematic contributions was made by Zherebtsov et al. [17], who demonstrated that cryo-rolling of CP-Ti produced finer sub-grains and higher dislocation densities compared with rolling at ambient temperature. Their research highlighted that inhibiting thermally activated recovery encouraged the development of submicron-sized grains surrounded by HAGB, which led to notable strengthening. Following this, D'yakonov et al. [75] extended these findings by conducting a detailed microstructural analysis. They found that $\{10\bar{1}2\}$ tensile twins nucleated easily under cryogenic conditions and helped refine the grain structure by serving as obstacles to dislocation movement and as points where misorientation accumulates. This research emphasized twinning as a key process for rapid grain refinement in cryo-rolled titanium.

Further studies by Liang et al. [71] confirmed these findings as shown in Figure 2.9 and highlighted the significance of precise measurement of dislocation density and misorientation distributions. Their work emphasized that quantifying GNDs derived from KAM maps generated by EBSD requires validation with TEM to ensure reliable estimation. Nonetheless, they consistently observed that cryo-rolling produces higher GND densities and greater work hardening compared to cold rolling.

Research has also examined the response of dual-phase titanium alloys like Ti-6Al-4V, in addition to CP-Ti. Floriano et al. [70] noted that during SPD, the distribution of strain was affected by the presence of β-phase regions. While the β phase can accommodate deformation and delay crack initiation, it might also serve as a site of stress concentration, affecting the refinement process differently than single-phase α alloys. Recently, Yu et al. [76] demonstrated that Cryo-rolling combined with short-period annealing in Ti-6Al-4V resulted in a good balance of strength and ductility, as shown in Figure 2.10. This shows that heat treatments after deformation can restore ductility while maintaining the benefits of cryogenic strengthening.

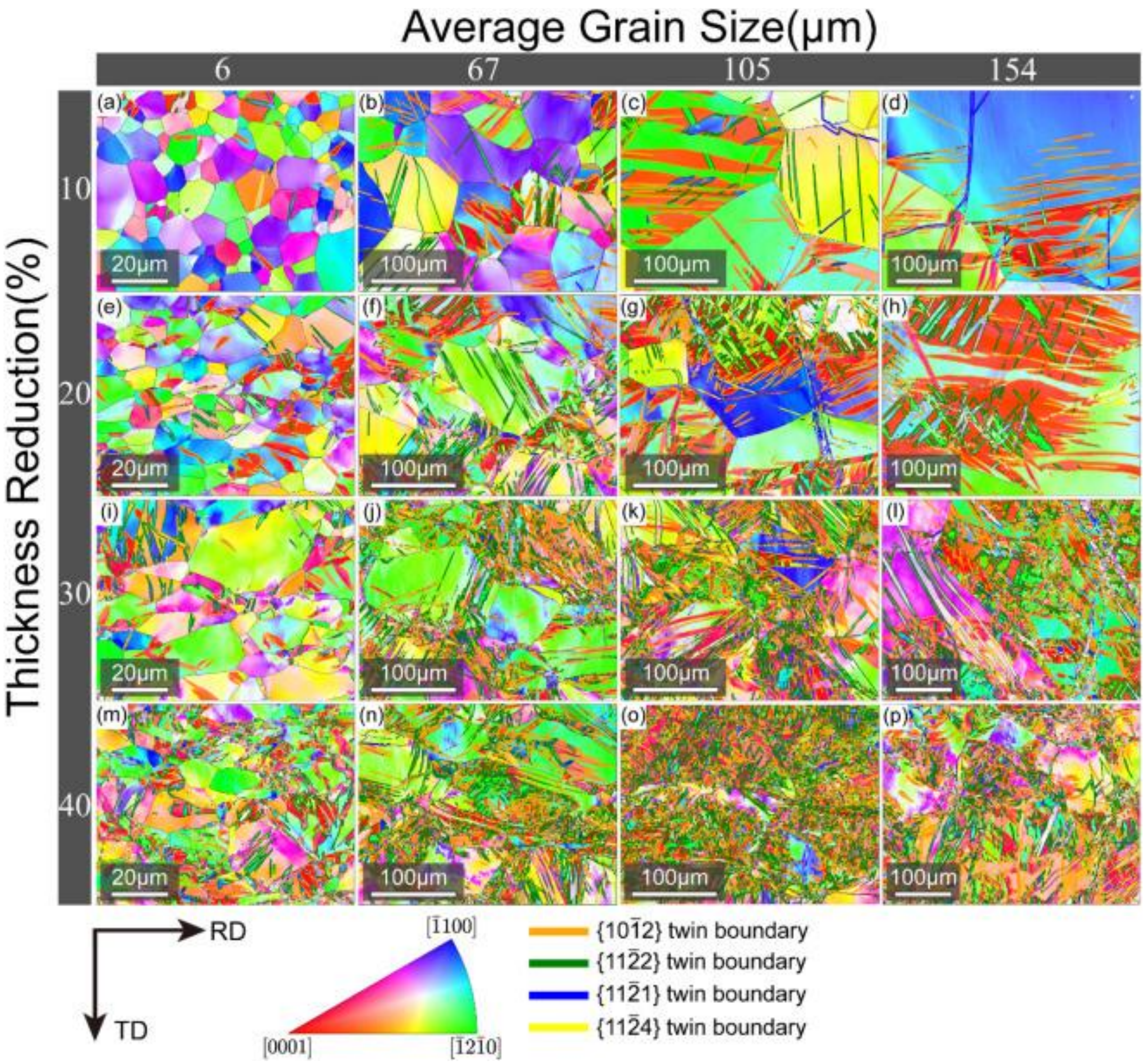

Figure 2.9: EBSD inverse pole figures of titanium subjected to cryogenic rolling. (a-d) IPF maps of titanium samples with grain sizes of 6 μm, 67 μm, 105 μm, and 154 μm subjected to 10% cryogenic rolling. (e-h) IPF maps of samples subjected to 20% cryogenic rolling. (i-l) IPF maps of samples subjected to 30% cryogenic rolling. (m-p) IPF maps of samples subjected to 40% cryogenic rolling [71].

In summary, these studies offer several insights into the underlying mechanisms:

- Cryo-rolling promotes dislocation buildup by restricting climb and cross-slip.
- The dislocation networks formed initially transform into LAGBs, then into HAGBs via CDRX, leading to the formation of UFGs.

- Cryogenic conditions substantially promote deformation twinning, facilitating intense grain refinement.

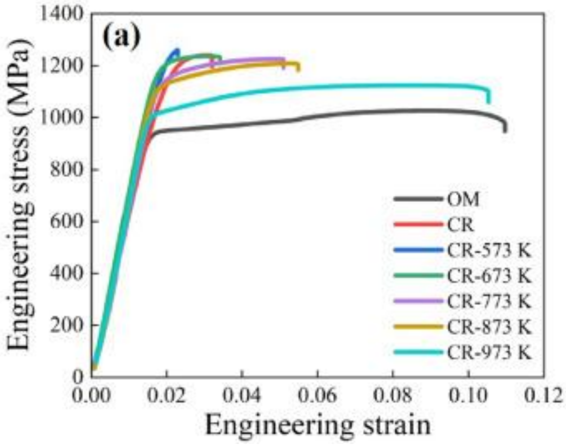

Figure 2.10: Engineering stress-strain curves of As-Received (OM), Cryo-Rolled (CR), and cryo-rolled Ti–6Al–4V sample with post-annealing at temperatures of 573–973 K [76].

2.6 HCP to FCC Phase Transformation in Titanium

The presence of a metastable FCC phase in titanium has gained significant interest recently, as it provides new understanding of plastic deformation processes and the possibility of improved ductility in HCP systems. Initial studies conducted by Ahmed et al. [9] reported that deformation-induced transformations could locally modify lattice structures in Ti alloys, particularly under extreme plastic strain. Following this, Lütjering et al. [1] pointed out that the stability of the α-HCP structure in titanium is not absolute. Under specific non-equilibrium conditions, like high strain or SPD, it may transform into metastable structures.

Yang et al. [77] are among the initial researchers who conducted significant research on these non-classical structural transformations. They proposed a mechanistic model for HCP to FCC transformation in titanium based on partial dislocation glide and supported by first-principles calculations as shown in Figure 2.11. This was further studied by Wu et al. [57], who observed that nanoscale FCC domains of titanium are embedded within the HCP matrix of rolled samples, suggesting that high strain suppresses recovery and promotes stacking rearrangements. Although these FCC domains are still nanoscale and their reproducibility is debated, their consistent observation indicates that rolling at ambient temperature might enable deformation pathways that are usually not activated at higher temperatures.

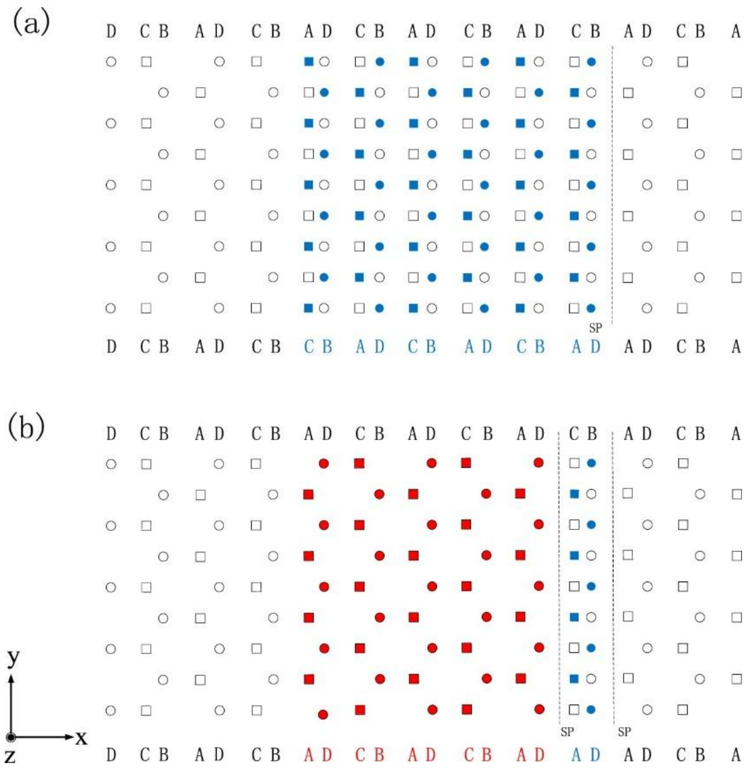

Figure 2.11: Atomic positions of HCP Ti after (**a**) the first and (**b**) the second slips of Shockley partial dislocation of 1/6 $\langle 1\bar{2}10\rangle$ on $\{10\bar{1}0\}$ planes. The *x* axis is along $\langle 10\bar{1}0\rangle_{hcp}$ and $\langle 1\bar{1}0\rangle_{fcc}$, the *y* axis is along $\langle 1\bar{2}10\rangle_{hcp}$ and $\langle 110\rangle_{fcc}$, and the *z* axis is along $\langle 0001\rangle_{hcp}$ and $\langle 001\rangle_{fcc}$. The hollow square and circular symbols represent atoms on {0001} and {0002} planes, respectively. The filled blue and red symbols are atoms after the first and second slips of Shockley partial dislocation, respectively, and SP stands for the slip plane [77].

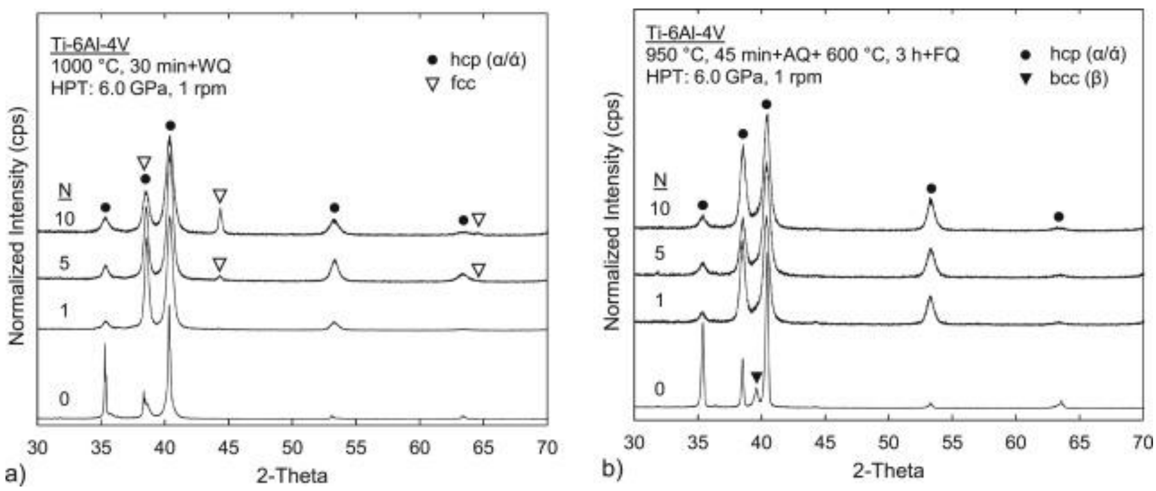

Figure 2.12: X-ray patterns of (a) the α' and (b) the α + β alloys near the edges of the disks before (*N* = 0) and after HPT processing through 1–10 turns [78].

Shahmir et al. [78] directly demonstrated the transition from HCP to FCC in titanium through HPT processing. They performed X-ray diffraction (XRD) as shown in Figure 2.12 and TEM analysis to detect nanoscale FCC domains within deformed titanium, indicating that the presence of stacking faults facilitates this transformation by producing local structures aligned with FCC stacking sequences. Subsequent studies by

Zhao et al. [79] and Hong et al. [80] confirmed this observation, showing that dislocation activity during cryogenic deformation facilitates stacking rearrangements, which help stabilize FCC titanium within the HCP matrix.

The influence of deformation temperature on the stability of FCC phase has been thoroughly studied. In particular, Shahmir et al. [78] and Wu et al. [57] observed that HPT and cold rolling can both initiate the transformation of FCC titanium. Similarly, Bai et al. [81] reported that with the increase in strain, the FCC structure becomes more frequently observed, emphasizing the importance of suppressed recovery and recrystallization in stabilizing non-equilibrium structures.

The formation of stacking faults and subsequent phase transformation is strongly influenced by the stacking fault energy (SFE) of the material. Lower SFE promotes dissociation of perfect dislocations into partial dislocations, which facilitates the formation of extended stacking faults. Under high strain conditions, such as cryogenic deformation, the increased dislocation density and restricted cross-slip enhance planar slip behaviour, leading to the accumulation of faults on specific crystallographic planes. These faulted regions can act as nucleation sites for metastable FCC domains.

Cryo-rolling plays a critical role in promoting such transformations by suppressing dynamic recovery mechanisms. At low temperatures, dislocation annihilation and rearrangement are limited, resulting in higher stored strain energy and dense dislocation structures. This condition enhances strain localization and increases the probability of stacking fault formation. Consequently, the combined effect of high stress, limited recovery, and planar slip activity facilitates the stabilization of metastable phases such as FCC in HCP titanium.

Computational research has provided additional insights into the source of this transformation. First-principals calculations by Aguayo [82] and Yang et al. [77] predicted that FCC Ti is energetically closer to the HCP structure but stays metastable under ambient conditions, indicating that stress-induced processing routes or lattice defects might stabilize FCC locally. Recently, density functional theory (DFT) simulations by Tao et al. [83], Wu et al. [57] and Yang et al. [84] validated these findings. They proposed that shear stresses and dislocation pileups can lower the energy barrier for the HCP to FCC transformation, aligning with experimental findings.

Overall, the stability of the FCC phase is therefore not intrinsic but strain-induced, and its retention depends on the balance between stored strain energy and the thermodynamic driving force for reversion to the HCP structure.

Although some progress has been made, a detailed understanding of the stability and reversibility of FCC titanium remains incomplete. While some authors suggest that FCC domains act as transitional structures, supporting plasticity through their ability to allow partial dislocation movement [85, 86], other researchers propose that these domains could remain as metastable states, considerably affecting strain hardening and ductility. [79, 81]. Although the HCP to FCC transformation in Ti and Ti alloys under non-equilibrium conditions has often been observed, its thermodynamic stability, kinetic behaviour, and overall property effects remain uncertain, marking a significant area for future investigation.

2.7 Mechanical Properties

Mechanical properties of titanium alloys are strongly influenced by their phase constitution, microstructural features, and processing history. Among these, grain size, phase distribution, crystallographic texture, and dislocation density play a dominant role in determining strength, ductility, and strain hardening behaviour. In particular, thermomechanical processing routes such as rolling, severe plastic deformation (SPD), and cryogenic deformation significantly alter these attributes, thereby modifying the mechanical response.

Grain refinement is one of the most effective approaches for enhancing strength, as described by the Hall–Petch relationship. Ultrafine-grained (UFG) and nanostructured titanium alloys produced through SPD techniques such as equal channel angular pressing (ECAP) and high-pressure torsion (HPT) have demonstrated substantial improvements in yield strength and ultimate tensile strength compared to their coarse-grained counterparts as shown in Figure 2.13. However, this increase in strength is often accompanied by a reduction in ductility due to limited strain hardening capacity and early plastic instability [12, 13].

Cryogenic deformation, including cryo-rolling, has been reported to suppress dynamic recovery and promote higher dislocation density, thereby enhancing strength. The reduced temperature limits dislocation annihilation, thereby increasing stored strain energy and contributing to grain subdivision. Studies on titanium alloys have shown that cryo-rolling can significantly improve strength while retaining reasonable ductility, depending on the degree of deformation and subsequent heat treatment [17, 18] as shown in Figure 2.14.

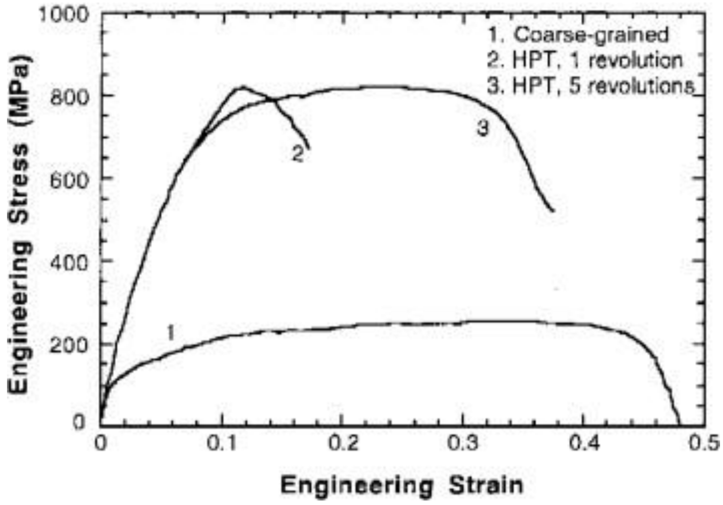

Figure 2.13: Engineering stress–engineering strain curves for commercial purity titanium tested at 523 K using a strain rate of 10−3 s−1 [13].

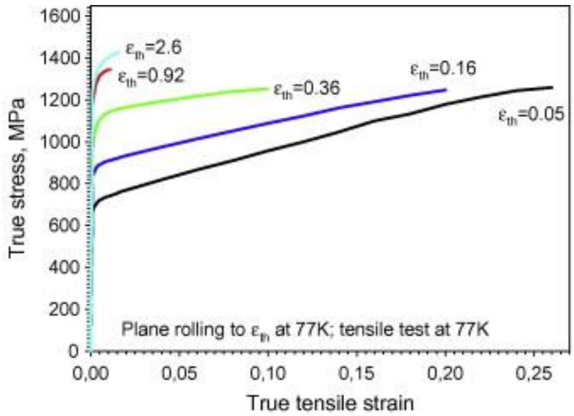

Figure 2.14: True stress–true strain curves for the CP Ti rolled at 77 K [17].

The balance between strength and ductility is also influenced by phase stability and morphology. In α+β titanium alloys, the distribution and morphology of α and β phases play a critical role. A fine and homogeneous distribution of phases enhances strength, while a coarser microstructure generally favours ductility. Additionally, metastable β titanium alloys can exhibit transformation-induced plasticity (TRIP) or twinning-induced plasticity (TWIP) effects, which contribute to improved work hardening and ductility [8].

Texture evolution during deformation also affects anisotropy in mechanical properties. Rolling processes often lead to the development of strong crystallographic textures, which can influence yield strength, elongation, and deformation mechanisms. The control of texture is therefore essential for optimizing mechanical performance in titanium alloys [1].

Furthermore, the mechanical response is highly sensitive to strain rate and temperature. At lower temperatures, increased strength and reduced ductility are commonly observed due to restricted dislocation mobility. Conversely, elevated temperatures promote dynamic recovery and recrystallization, enhancing ductility but reducing strength. The interplay between these mechanisms governs the overall deformation behaviour of titanium alloys under different processing and service conditions.

In summary, the mechanical properties of titanium alloys are governed by a complex interaction of microstructural features and processing parameters. Techniques such as cryo-rolling provide an effective pathway for tailoring strength and ductility through microstructural refinement and dislocation engineering. However, achieving an optimal balance between these properties requires careful control of deformation conditions and post-processing treatments.

2.8 Research Gaps

Even though there has been substantial progress in understanding TMP, deformation mechanisms, SPD, and cryogenic treatments of titanium and its alloys, several important knowledge gaps remain unexplored.

Most research on titanium thermomechanical processing has concentrated on traditional hot and warm deformation methods, with well-understood microstructure-property relationships are relatively well established [1, 2]. Nevertheless, the impact of cryogenic deformation conditions has not been thoroughly examined. For instance, while Zhang et al. [87] and Won et al. [88] reported promising evidence of enhanced grain refinement and ductility in cryo-rolled titanium. These works were limited to a single alloy system and did not thoroughly explore their comparison with the other alloy systems or the role of the starting microstructure. Therefore, a comprehensive understanding of various alloy systems and their initial microstructures, which influence deformation behaviour at cryogenic temperatures, is still lacking.

Research on HCP titanium crystal deformation has primarily focused on dislocation slip and twinning mechanisms [50, 53, 89]. Although these methods are well documented, the relationship between twinning, sub-grain rotation, and CDRX during cryogenic rolling remains not fully understood. These specific nanoscale defective structures, which are formed during the cryogenic temperature deformation process, have been characterized through limited TEM-based studies [90, 91], and their influence on overall ductility remains largely uncertain.

In the wider SPD research field, the majority of studies have focused on processing techniques like ECAP, HPT, and accumulative roll bonding (ARB), which have effectively produced ultrafine grain structures. [92-100]. However, cryo-rolling is a straightforward and scalable method that has not been thoroughly researched for titanium alloys, particularly for Ti-6Al-4V, which is essential for many advanced applications. Existing reports are scattered and lack a cohesive framework that provides the relationship between microstructure evolution, defect formation, and mechanical properties across different cryogenic strains.

The analysis of the metastable FCC phase in titanium under cryogenic or severe deformation conditions offers a new perspective on understanding [80, 101, 102]. However, challenges remain regarding stability, volume fraction, and reproducibility across different deformation conditions, as these areas are not yet thoroughly explored. Furthermore, the significance of this FCC phase in accommodating strain and enhancing ductility remains debated. Some studies consider it a transitional structure, while others view it as a metastable phase that influences mechanical behaviour [57].

While progress has been made, significant gaps still exist. Most of the research has concentrated on CP-Ti, whereas there is comparatively less research on dual-phase alloys like Ti-6Al-4V, especially under the same cryogenic conditions. Additionally, the influence of initial microstructure, such as equiaxed versus elongated grains, on cryogenic deformation mechanisms is still not well understood. Addressing these challenges is essential for developing strong processing-structure-property relationships, which can enhance the performance of titanium alloys processed through cryo-rolling.

Overall, the existing literature highlights several essential research gaps:

- **Inadequate cryo-rolling research on titanium alloys:** Most studies focus on individual strain levels, but the impact of increasing cryo-rolling strains on microstructure and tensile properties has not been studied in detail.
- **Uncertain influence of prior microstructure:** The influence of initial microstructure on grain refinement kinetics, dislocation accumulation, and mechanical properties during cryo-rolling is not clearly understood.
- **Limited understanding of the mechanisms related to low-temperature deformation:** The roles of twinning, dislocation slip, and sub-grain rotation/CDRX under cryogenic conditions remain not fully understood, especially regarding their impact on retaining ductility.

- **Lack of understanding related to metastable FCC phase stability:** Although FCC titanium has been often observed, its stability, reproducibility, and influence on bulk properties during cryo-rolling remain unclear.
- **Scarcity of systematic datasets for CP-Ti and Ti-6Al-4V:** Unavailability of data comparing CP-Ti with Ti-6Al-4V under the same cryo-rolling conditions limits understanding of their distinct deformation mechanisms.

These gaps in existing literature justify the current research, which systematically explores the effects of cryo-rolling strain, initial microstructure, and deformation mechanisms on the evolution of microstructure and mechanical properties in CP-Ti and Ti-6Al-4V.

2.9 Summary of Knowledge Gaps and Foundation for the Current Work

The literature review in the previous sections shows that, although titanium and its alloys have been widely researched under conventional TMP and SPD methods, cryo-rolling is still relatively underexplored. Research on cryogenic deformation of titanium has shown promising enhancements in grain refinement, dislocation accumulation, and the relationship between strength and ductility. However, these studies typically focus on specific strain levels or individual alloy systems, which limits their ability to provide widely applicable mechanistic insights.

Section 2.2 emphasizes that deformation in HCP titanium alloys is governed by crystallographic constraints, which involve a complex interplay between slip and twinning. Nevertheless, the specific roles of these mechanisms, along with sub-grain rotation and CDRX, remain unclear under cryo-rolling conditions. Section 2.4 shows that SPD methods like ECAP, HPT, and ARB are extensively used for titanium alloys, but their scalability is still restricted. Cryo-rolling, on the other hand, is a straightforward and scalable industrial process, but its basic deformation mechanisms in titanium alloys are still not fully understood.

Additionally, as outlined in Section 2.6, the identification of the metastable FCC phase in titanium subjected to SPD or cryogenic conditions prompts essential questions regarding its stability, reproducibility, and role in the bulk mechanical properties of the material. Currently, there is no comprehensive research available that relates cryo-rolling strain, initial microstructure, and the possible formation of FCC phases to the resulting macroscopic tensile properties.

The lack of systematic datasets comparing CP-Ti and Ti-6Al-4V under the same cryo-rolling conditions limits the ability to draw alloy-specific mechanistic conclusions. Specifically, previous studies have not thoroughly examined the influence of the initial microstructure on deformation uniformity, dislocation accumulation, and ductility preservation.

Addressing these gaps is crucial for developing a detailed, measurable understanding of cryo-rolling processes in titanium alloys. This research systematically investigates the effect of cryo-rolling at different strain levels, uses different initial microstructures, and analyzes deformation features across various scales to establish consistent microstructure-property relationships for CP-Ti and Ti-6Al-4V. The findings will clarify the effect of low-temperature deformation mechanisms and metastable phases on the material. They will offer practical processing guidelines to enhance the combination of strength and ductility in titanium alloys.

Reference

[1] G. Lütjering, J.C. Williams, Fundamental aspects, Titanium, Springer2007, pp. 13-50.

[2] G. Welsch, R. Boyer, E. Collings, Materials properties handbook: titanium alloys, ASM international1993.

[3] C. Leyens, M. Peters, Titanium and titanium alloys: fundamentals and applications, Wiley Online Library2006.

[4] M.J. Donachie, Titanium: a technical guide, ASM international2000.

[5] S. Semiatin, T. Bieler, The effect of alpha platelet thickness on plastic flow during hot working of TI–6Al–4V with a transformed microstructure, Acta materialia 49(17) (2001) 3565-3573.

[6] F. Froes, Titanium: physical metallurgy, processing, and applications, ASM international2015.

[7] V. Gaur, R. Gupta, V.A. Kumar, Electron Beam Welding and Gas Tungsten Arc Welding Studies on Commercially Pure Titanium Sheets, International Conference on Advances in Materials Processing: Challenges and Opportunities, Springer, 2022, pp. 89-94.

[8] D. Banerjee, J. Williams, Perspectives on titanium science and technology, Acta Materialia 61(3) (2013) 844-879.

[9] T. Ahmed, H. Rack, Phase transformations during cooling in α+ β titanium alloys, Materials Science and Engineering: A 243(1-2) (1998) 206-211.

[10] M. Peters, J. Kumpfert, C.H. Ward, C. Leyens, Titanium alloys for aerospace applications, Advanced Engineering Materials 5(6) (2003) 419-427.

[11] D. Banerjee, A.L. Pilchak, J.C. Williams, Processing, structure, texture and microtexture in titanium alloys, Materials Science Forum, Trans Tech Publ, 2012, pp. 66-84.

[12] R.Z. Valiev, R.K. Islamgaliev, I.V. Alexandrov, Bulk nanostructured materials from severe plastic deformation, Progress in Materials Science 45(2) (2000) 103-189.

[13] A.P. Zhilyaev, T.G. Langdon, Using high-pressure torsion for metal processing: Fundamentals and applications, Progress in Materials science 53(6) (2008) 893-979.

[14] Y. Iwahashi, Z. Horita, M. Nemoto, T.G. Langdon, The process of grain refinement in equal-channel angular pressing, Acta Materialia 46(9) (1998) 3317-3331.

[15] V.V. Stolyarov, Y.T. Zhu, T.C. Lowe, R.Z. Valiev, Microstructures and properties of ultrafine-grained pure titanium processed by equal-channel angular pressing and cold deformation, Journal of nanoscience and nanotechnology 1(2) (2001) 237-242.

[16] I.P. Semenova, G.I. Raab, L.R. Saitova, R.Z. Valiev, The effect of equal-channel angular pressing on the structure and mechanical behavior of Ti–6Al–4V alloy, Materials Science and Engineering: A 387-389 (2004) 805-808.

[17] S. Zherebtsov, G. Dyakonov, A. Salem, V. Sokolenko, G. Salishchev, S. Semiatin, Formation of nanostructures in commercial-purity titanium via cryorolling, Acta materialia 61(4) (2013) 1167-1178.

[18] F. Yu, Y. Zhang, C. Kong, H. Yu, Microstructure and mechanical properties of Ti–6Al–4V alloy sheets via room-temperature rolling and cryorolling, Materials Science and Engineering: A 834 (2022) 142600.

[19] A. Pilchak, C. Szczepanski, J. Shaffer, A. Salem, S. Semiatin, Characterization of microstructure, texture, and microtexture in near-alpha titanium mill products, Metallurgical and Materials Transactions A 44(11) (2013) 4881-4890.

[20] A. Pilchak, G. Sargent, S.L. Semiatin, Early stages of microstructure and texture evolution during beta annealing of Ti-6Al-4V, Metallurgical and Materials Transactions A 49(3) (2018) 908-919.

[21] R. Ding, Z. Guo, A. Wilson, Microstructural evolution of a Ti–6Al–4V alloy during thermomechanical processing, Materials Science and Engineering: A 327(2) (2002) 233-245.

[22] X.-n. Peng, H.-z. Guo, Z.-f. Shi, C. Qin, Z.-l. Zhao, Microstructure characterization and mechanical properties of TC4-DT titanium alloy after thermomechanical treatment, Transactions of Nonferrous Metals Society of China 24(3) (2014) 682-689.

[23] R.R. Boyer, An overview on the use of titanium in the aerospace industry, Materials Science and Engineering: A 213(1-2) (1996) 103-114.

[24] S. Semiatin, S. Knisley, P. Fagin, D. Barker, F. Zhang, Microstructure evolution during alpha-beta heat treatment of Ti-6Al-4V, Metallurgical and Materials Transactions A 34(10) (2003) 2377-2386.

[25] G. Lütjering, Influence of processing on microstructure and mechanical properties of (α+ β) titanium alloys, Materials Science and Engineering: A 243(1-2) (1998) 32-45.

[26] F. Froes, D. Eylon, Titanium, Elsevier, Oxford, UK, 2000.

[27] M. Bache, A review of dwell sensitive fatigue in titanium alloys: the role of microstructure, texture and operating conditions, International journal of fatigue 25(9-11) (2003) 1079-1087.

[28] M. Qian, F.H. Froes, Titanium powder metallurgy: science, technology and applications, (2015).

[29] D. Blackwood, K. Seah, S. Teoh, Corrosion of metallic implants, Engineering materials for biomedical applications, World Scientific2004, pp. 3-1-3-56.

[30] G. Manivasagam, D. Dhinasekaran, A. Rajamanickam, Biomedical implants: corrosion and its prevention-a review, Recent patents on corrosion science (2010).

[31] M. Long, H. Rack, Titanium alloys in total joint replacement—a materials science perspective, Biomaterials 19(18) (1998) 1621-1639.

[32] M. Geetha, A.K. Singh, R. Asokamani, A.K. Gogia, Ti based biomaterials, the ultimate choice for orthopaedic implants–A review, Progress in materials science 54(3) (2009) 397-425.

[33] Y. Hou, D. Myung, J. Park, J. Min, H. Lee, A. El-Aty, M. Lee, A Review of Characterization and Modelling Approaches for Sheet Metal Forming of Lightweight Metallic Materials. Materials 2023, 16, 836, 2023.

[34] J.W. Won, J.H. Lee, J.S. Jeong, S.-W. Choi, D.J. Lee, J.K. Hong, Y.-T. Hyun, High strength and ductility of pure titanium via twin-structure control using cryogenic deformation, Scripta Materialia 178 (2020) 94-98.

[35] G. Lütjering, J. Williams, A. Gysler, Microstructure and mechanical properties of titanium alloys, Microstructure And Properties Of Materials: (Volume 2)2000, pp. 1-77.

[36] A. Akhtar, Basal slip and twinning in α-titanium single crystals, Metallurgical Transactions A 6(5) (1975) 1105-1113.

[37] S. Cai, Z. Li, Y. Xia, Evolution equations of deformation twins in metals—Evolution of deformation twins in pure titanium, Physica B: Condensed Matter 403(10-11) (2008) 1660-1665.

[38] A. Akhtar, E. Teghtsoonian, Prismatic slip in α-titanium single crystals, Metallurgical and Materials Transactions A 6(12) (1975) 2201.

[39] A. Wilkinson, E. Clarke, T. Britton, P. Littlewood, P. Karamched, High-resolution electron backscatter diffraction: an emerging tool for studying local deformation, The Journal of Strain Analysis for Engineering Design 45(5) (2010) 365-376.

[40] Y.B. Chun, S.-H. Yu, S. Semiatin, S.-K. Hwang, Effect of deformation twinning on microstructure and texture evolution during cold rolling of CP-titanium, Materials Science and Engineering: A 398(1-2) (2005) 209-219.

[41] S. Zaefferer, A study of active deformation systems in titanium alloys: dependence on alloy composition and correlation with deformation texture, Materials Science and Engineering: A 344(1-2) (2003) 20-30.

[42] M. Glavicic, A. Salem, S. Semiatin, X-ray line-broadening analysis of deformation mechanisms during rolling of commercial-purity titanium, Acta materialia 52(3) (2004) 647-655.

[43] X. Li, Y. Duan, G. Xu, X. Peng, C. Dai, L. Zhang, Z. Li, EBSD characterization of twinning in cold-rolled CP-Ti, Materials characterization 84 (2013) 41-47.

[44] F. Xu, X. Zhang, H. Ni, Y. Cheng, Y. Zhu, Q. Liu, Effect of twinning on microstructure and texture evolutions of pure Ti during dynamic plastic deformation, Materials Science and Engineering: A 564 (2013) 22-33.

[45] S. Huang, J. Li, H. Liang, H. Tan, K. Liu, J. Yu, H. Xiao, Mechanistic Role of Dislocation-Grain Boundary Interaction in the Strength-Ductility Trade-Off of High-Oxygen Grade 4 Titanium During Cold Rolling, Available at SSRN 5339706.

[46] S.Y. Mironov, M. Myshlyaev, Evolution of dislocation boundaries during cold deformation of microcrystalline titanium, Physics of the Solid State 49(5) (2007) 858-864.

[47] C. Schuman, L. Bao, J. Sébastien Lecomte, Y. Zhang, J. Marc Raulot, M. Jeanne Philippe, C. Esling, A new variant selection criterion for twin variants in titanium alloys (Part 1), Advanced Engineering Materials 13(12) (2011) 1114-1121.

[48] R.E. Reed-Hill, W.D. Robertson, Deformation of magnesium single crystals by nonbasal slip, Jom 9(4) (1957) 496-502.

[49] J.W. Christian, S. Mahajan, Deformation twinning, Progress in materials science 39(1-2) (1995) 1-157.

[50] M. Yoo, Slip, twinning, and fracture in hexagonal close-packed metals, Metallurgical transactions A 12(3) (1981) 409-418.

[51] N. Stanford, U. Carlson, M. Barnett, Deformation twinning and the Hall–Petch relation in commercial purity Ti, Metallurgical and Materials Transactions A 39(4) (2008) 934-944.

[52] P. Partridge, The crystallography and deformation modes of hexagonal close-packed metals, Metallurgical reviews 12(1) (1967) 169-194.

[53] A.A. Salem, S.R. Kalidindi, R.D. Doherty, Strain hardening of titanium: role of deformation twinning, Acta Materialia 51(14) (2003) 4225-4237.

[54] N. Gurao, S. Suwas, Evolution of crystallographic texture during deformation of submicron grain size titanium, Journal of Materials Research 26(4) (2011) 523-532.

[55] H. Yu, L. Wang, M. Yan, H. Gu, X. Zhao, C. Kong, Y. Wang, A. Pesin, A.P. Zhilyaev, T.G. Langdon, Microstructural evolution and mechanical properties of ultrafine-grained Ti fabricated by cryorolling and subsequent annealing, Advanced Engineering Materials 22(10) (2020) 1901463.

[56] S. Semiatin, V. Seetharaman, I. Weiss, Flow behavior and globularization kinetics during hot working of Ti–6Al–4V with a colony alpha microstructure, Materials Science and Engineering: A 263(2) (1999) 257-271.

[57] H. Wu, A. Kumar, J. Wang, X. Bi, C. Tomé, Z. Zhang, S. Mao, Rolling-induced face centered cubic titanium in hexagonal close packed titanium at room temperature, Scientific reports 6(1) (2016) 24370.

[58] Z. Zeng, Y. Zhang, S. Jonsson, Microstructure and texture evolution of commercial pure titanium deformed at elevated temperatures, Materials Science and Engineering: A 513-514 (2009) 83-90.

[59] S.K. Sahoo, R.K. Sabat, S. Sahni, S. Suwas, Texture and microstructure evolution of commercially pure titanium during hot rolling: Role of strain-paths, Materials & Design 91 (2016) 58-71.

[60] S. Semiatin, V. Seetharaman, I. Weiss, Hot workability of titanium and titanium aluminide alloys—an overview, Materials Science and Engineering: A 243(1-2) (1998) 1-24.

[61] I. Weiss, S. Semiatin, Thermomechanical processing of beta titanium alloys—an overview, Materials Science and Engineering: A 243(1-2) (1998) 46-65.

[62] A. Bhattacharjee, B. Saha, J. Williams, Titanium alloys: part 2—alloy development, properties and applications, Aerospace Materials and Material Technologies: Volume 1: Aerospace Materials, Springer2016, pp. 117-148.

[63] A. Pilchak, J. Williams, The effect of friction stir processing on the mechanical properties of investment cast and hot isostatically pressed Ti-6Al-4V, Metallurgical and Materials Transactions A 42(6) (2011) 1630-1645.

[64] X. Shi, Z. Cao, Z. Fan, J. Qiao, Texture Evolution Behavior and Its Triggered Mechanical Anisotropy of CP Ti During Severe Cold Rolling and Subsequent Annealing, Acta Metallurgica Sinica (English Letters) 33(9) (2020) 1271-1282.

[65] W.-G. Zhu, J. Pu, C.-H. Zhang, Q.-B. Wang, Y.-L. Wang, T.-C. Shu, X.-X. Wang, J. Wang, Microstructure evolution and anisotropy effect during low temperature cross rolling and annealing of Ti6Al4V, Metallurgical and Materials Transactions A 54(9) (2023) 3550-3562.

[66] Y. Wang, M. Chen, F. Zhou, E. Ma, High tensile ductility in a nanostructured metal, nature 419(6910) (2002) 912-915.

[67] R.Z. Valiev, T.G. Langdon, Principles of equal-channel angular pressing as a processing tool for grain refinement, Progress in materials science 51(7) (2006) 881-981.

[68] I. Semenova, G. Salimgareeva, G. Da Costa, W. Lefebvre, R. Valiev, Enhanced strength and ductility of ultrafine-grained Ti processed by severe plastic deformation, Advanced engineering materials 12(8) (2010) 803-807.

[69] R.Z. Valiev, A.P. Zhilyaev, T.G. Langdon, Bulk nanostructured materials: Fundamentals and applications, John Wiley & Sons2013.

[70] R. Floriano, K. Edalati, Effects of severe plastic deformation on advanced biomaterials for biomedical applications: a brief overview, Materials Transactions 64(8) (2023) 1673-1682.

[71] X. Liang, H. Wang, X. Zhou, Q. Zhu, C. Zhang, W. Xiao, Y. Guo, Z. Li, Y. Liu, P. Kang, Revealing Cryo-loading Induced Twinning and its Impact on Titanium via Correlative Data-driven Mechanomicroscopy, Available at SSRN 5457659.

[72] H. Yu, M. Yan, J. Li, A. Godbole, C. Lu, K. Tieu, H. Li, C. Kong, Mechanical properties and microstructure of a Ti-6Al-4V alloy subjected to cold rolling, asymmetric rolling and asymmetric cryorolling, Materials Science and Engineering: A 710 (2018) 10-16.

[73] F.J. Humphreys, M. Hatherly, Recrystallization and related annealing phenomena, elsevier2012.

[74] W. Pantleon, Resolving the geometrically necessary dislocation content by conventional EBSD, Symposium on Advanced Methods in Electron Backscattered Diffraction, Ecole Nationale Superieure des Mines, 2010.

[75] G. D’yakonov, S. Zherebtsov, M. Klimova, G. Salishchev, Microstructure evolution of commercial-purity titanium during cryorolling, The Physics of Metals and Metallography 116(2) (2015) 182-188.

[76] F. Yu, Y. Zhang, C. Kong, H. Yu, High strength and toughness of Ti–6Al–4V sheets via cryorolling and short-period annealing, Materials Science and Engineering: A 854 (2022) 143766.

[77] J.X. Yang, H.L. Zhao, H.R. Gong, M. Song, Q.Q. Ren, Proposed mechanism of HCP→ FCC phase transition in titianium through first principles calculation and experiments, Scientific reports 8(1) (2018) 1992.

[78] H. Shahmir, T.G. Langdon, An evaluation of the hexagonal close-packed to face-centered cubic phase transformation in a Ti-6Al-4V alloy during high-pressure torsion, Materials Science and Engineering: A 704 (2017) 212-217.

[79] H. Zhao, N. Ding, Y. Ren, H. Xie, B. Yang, G. Qin, Shear-induced hexagonal close-packed to face-centered cubic phase transition in pure titanium processed by equal channel angular drawing, Journal of Materials Science 54(10) (2019) 7953-7960.

[80] D. Hong, T. Lee, S. Lim, W. Kim, S. Hwang, Stress-induced hexagonal close-packed to face-centered cubic phase transformation in commercial-purity titanium under cryogenic plane-strain compression, Scripta Materialia 69(5) (2013) 405-408.

[81] F. Bai, L. Yin, W. Zhao, H. Zhou, M. Song, Y. Liu, X. Liu, Deformational behavior of face-centered cubic (FCC) phase in high-pure titanium, Materials Science and Engineering: A 800 (2021) 140287.

[82] A. Aguayo, G. Murrieta, R. De Coss, Elastic stability and electronic structure of fcc Ti, Zr, and Hf: A first-principles study, Physical Review B 65(9) (2002) 092106.

[83] S. Tao, P. Notten, R. Van Santen, A. Jansen, Density functional theory studies of the hydrogenation properties of Mg and Ti, Physical Review B—Condensed Matter and Materials Physics 79(14) (2009) 144121.

[84] M. Yang, J. Hu, S. Cao, G. Feng, Y. Yang, R. Liu, S. Li, F. Zhao, A. Feng, Q. Hu, Influence of nonmetallic interstitials on the phase transformation between FCC and HCP titanium: a density functional theory study, Metals 12(10) (2022) 1607.

[85] H. Shahmir, T.G. Langdon, Using heat treatments, high-pressure torsion and post-deformation annealing to optimize the properties of Ti-6Al-4V alloys, Acta Materialia 141 (2017) 419-426.

[86] M. Wang, Y. Wang, Q. He, W. Wei, F. Guo, W. Su, C. Huang, A strong and ductile pure titanium, Materials Science and Engineering: A 833 (2022) 142534.

[87] Z. Zhang, H. Pan, L. Meng, J. Zhang, X. Yang, H. Gao, Y. Gong, B. Shu, X. Zhu, Mechanical properties of pure titanium processed by cryogenic rolling and annealing, Materials Transactions 60(4) (2019) 513-518.

[88] J.W. Won, S.-W. Choi, J.-K. Hong, B.-C. Suh, J.H. Lee, B.J. Kwak, Microstructure and strength–ductility balance of pure titanium processed by cryogenic rolling at various rolling reductions, Materials Science and Engineering: A 798 (2020) 140328.

[89] D. Ryu, Y. Kim, S. Nahm, L. Kang, Recent developments in plastic deformation behavior of titanium and its alloys during the rolling process: a review, Materials 17(24) (2024) 6060.

[90] V. Moskalenko, A. Smirnov, R. Smolyanets, Low-temperature plastic deformation and strain-hardening of nanocrystalline titanium, Low temperature physics 40(9) (2014) 837-845.

[91] E. Tabachnikova, T. Hryhorova, S. Shumilin, Y. Semerenko, Y. Huang, T.G. Langdon, Cryo-Severe Plastic deformation, microstructures and properties of metallic nanomaterials at low temperatures, Materials Transactions 64(8) (2023) 1806-1819.

[92] D. Terada, S. Inoue, N. Tsuji, Microstructure and mechanical properties of commercial purity titanium severely deformed by ARB process, Journal of Materials Science 42(5) (2007) 1673-1681.

[93] D. Terada, M. Inoue, H. Kitahara, N. Tsuji, Change in mechanical properties and microstructure of ARB processed Ti during annealing, Materials transactions 49(1) (2008) 41-46.

[94] J. Gubicza, Z. Fogarassy, G. Krállics, J.L. Lábár, T. Törköly, Microstructure and mechanical behavior of ultrafine-grained titanium, Materials Science Forum, Trans Tech Publ, 2008, pp. 99-104.

[95] I. Semenova, A. Polyakov, G. Raab, T. Lowe, R. Valiev, Enhanced fatigue properties of ultrafine-grained Ti rods processed by ECAP-Conform, Journal of Materials Science 47(22) (2012) 7777-7781.

[96] C.T. Wang, A.G. Fox, T.G. Langdon, Microstructural evolution in ultrafine-grained titanium processed by high-pressure torsion under different pressures, Journal of Materials Science 49(19) (2014) 6558-6564.

[97] K. Hajizadeh, B. Eghbali, K. Topolski, K. Kurzydlowski, Ultra-fine grained bulk CP-Ti processed by multi-pass ECAP at warm deformation region, Materials Chemistry and Physics 143(3) (2014) 1032-1038.

[98] A. Derakhshandeh, H. Shahmir, M. Nili-Ahmadabadi, Microstructure and mechanical properties of ultrafine-grained titanium processed by multi-pass ECAP at room temperature using core–sheath method, Journal of Materials Research 33(22) (2018) 3809-3817.

[99] W.J. Chen, J. Xu, D.T. Liu, D.B. Shan, B. Guo, T.G. Langdon, Thermal stability of ultrafine-grained pure titanium processed by high-pressure torsion, Materials Science Forum, Trans Tech Publ, 2021, pp. 338-344.

[100] X.-r. Yang, Z.-l. Wang, Y. Dai, B.-w. Li, Z. Jin, L. Luo, X.-y. Liu, J.-z. Wang, Evolution of microstructure, macrotexture and mechanical properties of high strength biomedical TA4 pure titanium during multi-pass ECAP, Journal of Materials Research and Technology 28 (2024) 3976-3987.

[101] Z. Zhang, M. Li, D. Guo, Y. Shi, X. Zhang, H.-E. Schaefer, Enhancement of TiZr ductility by hcp–fcc martensitic transformation after severe plastic deformation, Materials Science and Engineering: A 594 (2014) 321-323.

[102] Y.G. Liu, M.Q. Li, H.J. Liu, Deformation induced face-centered cubic titanium and its twinning behavior in Ti–6Al–4V, Scripta Materialia 119 (2016) 5-8.