Study of Effect of Annealing on Micro-Hardness of Molybdenum Single Crystals

MS (Research) Thesis

By

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DEPARTMENT OF MECHANICAL ENGINEERING

INDIAN INSTITUTE OF TECHNOLOGY INDORE

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A THESIS

Submitted in fulfillment of the
requirements for the award of the degree
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by

Manik Bhowmik

DEPARTMENT OF MECHANICAL ENGINEERING
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CANDIDATE'S DECLARATION

I hereby certify that the work being presented in the thesis entitled **Study of Effect of Annealing on Micro-Hardness of Molybdenum Single Crystals** in the fulfilment of the requirements for the award of the degree of **MASTER OF SCIENCE (RESEARCH)** and submitted in the **DISCIPLINE OF MECHANICAL ENGINEERING, INDIAN INSTITUTE OF TECHNOLOGY INDORE**, is an authentic record of my work carried out during the period from July 2022 to July 2024 under the supervision of **Dr. Indrasen Singh**, Assistant Professor, Indian Institute of Technology Indore, India

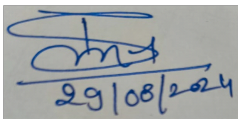
The matter presented in this thesis has not been submitted by me for the award of any other degree of this or any other institute.

Manik Bhowmik
26/08/24

Signature of the student with date

(Manik Bhowmik)

This is to certify that the above statement made by the candidate is correct to the best of my knowledge.



Signature of the Supervisor of

MS (Research) thesis

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Manik Bhowmik has successfully given his/her MS (Research) Oral Examination held on **16th August 2024**.

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29/08/2024
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Signature of Head of Discipline with date

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Manik Bhowmik

DEDICATION

My research is dedicated to my parents, especially my father Lt. Manish Bhowmik, whose profound influence has significantly contributed to shaping my character and providing unwavering support throughout my journey. While words may not suffice to express my gratitude for the pivotal role my parents have played in moulding both my professional career and personal growth, I am confident that their invaluable contributions will continue to enrich my life. This thesis serves as a testament to the enduring impact of their guidance, love, and steadfast belief in my abilities, for which I am deeply thankful.

Abstract

Molybdenum (Mo) crystals exhibit excellent mechanical properties such as high yield strength, high elastic modulus, very high melting point, and excellent corrosion resistance, making them a suitable choice for various industrial applications. The mechanical behaviour of these crystals has been investigated through tension, compression, and indentation experiments. The indentation experiments on annealed Mo single-crystal thin film show an increase in hardness with an increase in annealing temperature from 400-650˚C. However, it is not clear whether this behaviour is specific to the Mo thin films, or these are applicable to the bulk samples of single crystals also. In order to address these issues, the Vickers indentation experiments are performed on as-received and annealed samples of (100)-, (110)- and (111)-oriented Mo single crystals. The results show that the low-temperature annealing leads to an increase in micro-hardness by 9% for (100)-oriented crystals. The X-ray Diffraction (XRD), Electron Backscatter Diffraction (EBSD) and energy dispersive X-ray spectroscopy (EDS) studies have shown that there is a drop in the number of dislocation sources or dislocation density (ρ) with no high-angle grain boundary formation or any microstructural changes or any oxide formation. This necessitates to enhance the applied stress required for significant yielding (or yield strength) which results in an increase in the hardness. Based on experimental observations, a hardening mechanism governed by dislocation annihilation during annealing has been proposed in the present study.

LIST OF PUBLICATIONS

1) Bhowmik, M., Dadhich, R. and Singh, I., 2024. The effect of annealing on micro-hardness of molybdenum single crystals. Physica Scripta, 99(7), 075981. 10.1088/1402-4896/ad5796

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NOMENCLATURE

Chapter 1: Introduction and Literature Review

τ_R	Resolved Shear Stress
τ_{th}	Theoretical Critical Shear Stress
τ_C	Critical Resolved Shear Stress
G	Shear Modulus
σ	Tensile Stress
A	Cross-sectional Area
F	Tensile Force in Schmid Analysis
F_c	Tensile Force Necessary to Initiate Slip
ϕ	Angle between Tensile Force F and the normal to the slip plane
δ	Angle between tensile force F and the Slip Direction
T_m	Melting Temperature

Chapter 2: Effect of Annealing on Micro-hardness of Molybdenum Single Crystals

P	Indentation Load
P_{max}	Maximum Indentation Load
H	Hardness
ρ	Dislocation Density
ρ_0	Dislocation Density of As-received Crystal
ρ_T	Dislocation Density of Annealed Crystal
β	Peak Broadening (in radians)

β_0	Initial Peak Broadening of Machine (in radians)
θ	Bragg angle (in radians)
λ	wavelength of XRD source
K	Fitting Constant in Scherrer Equation

ACRONYMS

BCC	Body Centered Cubic
FCC	Face Centered Cubic
HCP	Hexagonal Close Packed
Mo	Molybdenum
Nb	Niobium
Ti	Titanium
W	Tungsten
Ta	Tantalum
ISE	Indentation Size Effect
CRSS	Critically Resolved Shear Stress
NC	Nanocrystalline
XRD	X-ray Diffraction
EBSD	Electron Backscatter Diffraction
EDS	Energy Dispersive X-ray Spectroscopy
EDM	Electron Discharge Machining
SEM	Scanning Electron Microscopy
IPF	Inverse Pole Figure
BF	Bright Field
DF	Dark Field
FE	Finite Element

Chapter 1

Introduction and Literature Review

1.1. Introduction

Molybdenum (Mo) is a BCC material which has the potential to be used in automotive, chip, solid-state devices, space, military and medical industries [1], owing to its outstanding mechanical properties including high tensile strength (about 324 MPa) and compressive yield strength (about 400 MPa) [2], large modulus of elasticity (325 GPa), high melting point (2890 K), and excellent corrosion resistance [3]. Nevertheless, molybdenum is normally used as an alloying element with steel, which may be due to a lack of comprehensive understanding of its deformation behaviour. However, several studies have investigated the orientation-dependent deformation behaviour of Mo single crystals by performing tension and compression [4] experiments at various temperatures [5,6] and strain rates [7].

Indentation has also been employed to investigate the direction dependent deformation behaviour of Mo single crystals [8,9]. However, the effect of low-temperature annealing on the hardness of Mo single crystals has not been investigated yet, though such studies have been performed on thin films of Mo single crystals (110) deposited on Si substrate (400) by Khojier et al [10]. They reported a gradual increase in hardness with an increase in annealing temperature from 375 - 650°C, which they correlated to annealing induced change in crystal structure. It is not clear from this study if these observations are specific to the Mo thin film or applicable to the bulk crystals of Mo also. Therefore, the effect of low-temperature annealing on the indentation response of Mo single crystals needs to be investigated, and hence it has been undertaken in this thesis. The Vickers indentation experiments are performed on as-received and annealed samples of (100)-, (110)-, and (111)-oriented Mo single crystals. SEM, XRD, EBSD and EDS are used to characterize the crystals. The relevant background to understand the deformation behaviour of Mo crystals is given below.

1.2. Crystallography

The atoms in a crystalline material are arranged periodically over a long atomic distance. Most of the metals possess either of the following structures: FCC, BCC and HCP crystals. In FCC, the atoms are arranged at the corners of a cube and the centers of each cube face (refer to figure 1.1 (a)), while in BCC, the atoms are positioned at the corners of a cube with an additional atom at the center of the cube (refer to figure 1.1 (b)). In contrast to FCC and BCC the atoms in HCP are arranged in tightly packed hexagonal layers (refer to figure 1.1 (c)). FCC crystal structure is widely present in metallic elements and alloys (such as aluminium, copper, gold and nickel) with a high ductility which gives them excellent electrical conductivity as well as thermal conduction properties along with low hardness. On the other hand, metals such as molybdenum (Mo), chromium (Cr) and tungsten exhibit BCC crystal structure, which makes them excellent candidates for the structural application that requires strength together with toughness. HCP is common in metals like magnesium and zinc and in some non-metallic substances.

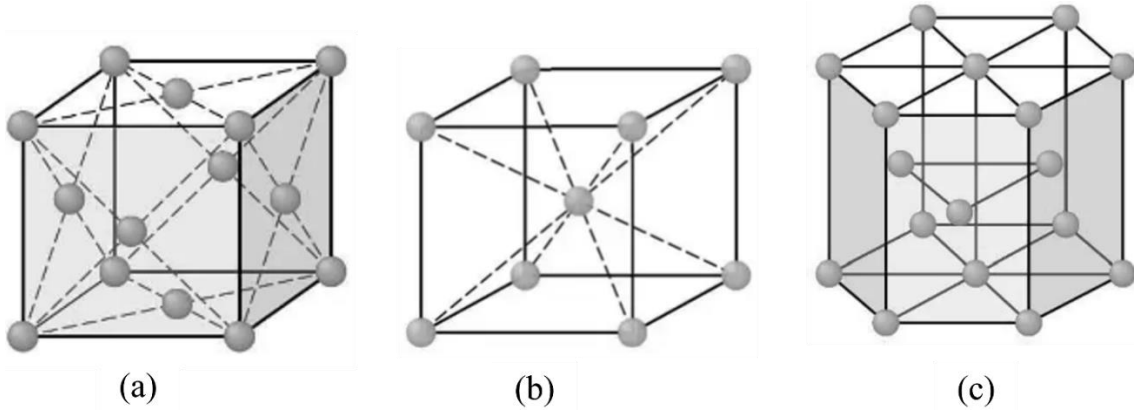


Figure 1.1: Atomic structure of (a) FCC, (b) BCC and (c) HCP unit crystals (reproduced from the article [11]).

1.3. Defects in Single Crystals

In reality, atomic arrangements in a lattice are not perfectly periodic. During crystal solidification, deviations occur due to thermal vibrations, non-equilibrium processes, impurities, etc., leading to crystal defects. The deviation of a few atoms is termed as a point defect, while widespread deviations is referred to as lattice imperfections. The most common point defects in a crystal are vacancies, interstitial atoms, and impurity atoms. Vacancies are created when an atom

goes missing from the lattice, whereas interstitial defects arise when an atom is trapped within the lattice, and impurities occur when a foreign atom distorts the lattice (see Figure 1.2). Point defects are also known as one-dimensional imperfections. Imperfections over two-dimensional areas are called line defects (dislocations), and those over three-dimensional regions are known as surface defects, such as stacking faults, grain boundaries, and twin boundaries.

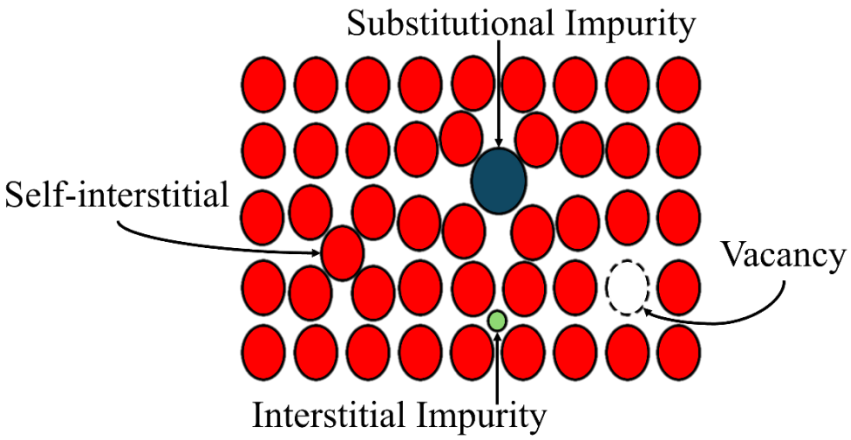


Figure 1.2: Schematic showing different types of point defects (reproduced from the article [12]).

1.3.1. Dislocations

Taylor [13] and Orowan [14] independently introduced the concept of "dislocation" to account for the discrepancy between theoretical and practical yield strength of metals. The shear stress necessary for atom movement from one position to another position is given by equation 1.1 [15] (also refer to figure 1.3):

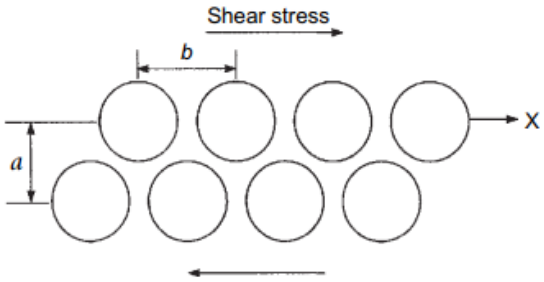


Figure 1.3: Schematic showing the action of shear stress in a crystal lattice (taken from Hull and Bacon [16]).

$$\tau = \frac{Gb}{2\pi a} \sin \frac{2\pi x}{b} \tag{1.1}$$

The maximum shear stress that can be sustained by an ideal defect-free crystal before plastic deformation represents the theoretical upper limit of shear stress. Beyond this threshold limit, the crystal experiences an irreversible change in structure. The theoretical critical shear stress for an atom movement is given by $\tau_{th} = G/2\pi$, where G is the shear modulus. The realistic value of τ_{th} is 10^{-4} to 10^{-8} G, which is many orders of magnitude lower than the observed values. This difference between the theoretical and practical values was first explained independently by Orowan, Polanyi and Taylor [13,14,17] by using the theory of dislocations. A dislocation is defined as the boundary that demarcates the slipped and un-slipped regions within a material, which can be divided into two categories, namely, edge and screw dislocations. An edge dislocation forms when an extra half plane is missing from the lattice system or an extra half plane is inserted into the lattice system (refer to figure 1.4 (a)). However, a screw dislocation is a defect in a crystal lattice where one part is displaced relative to another in a spiral or helical pattern along the dislocation line (refer to figure 1.4 (b)). The line which makes the distinction between the two regions is called the dislocation line. An edge dislocation moves perpendicular to the slip plane through the addition or removal of atoms along the dislocation line, a process known as dislocation climb (refer to figure 1.5), which is governed by the diffusion of vacancies. On the other hand, the movement of screw dislocations is primarily parallel to the dislocation line, contributing to the material's ability to deform plastically.

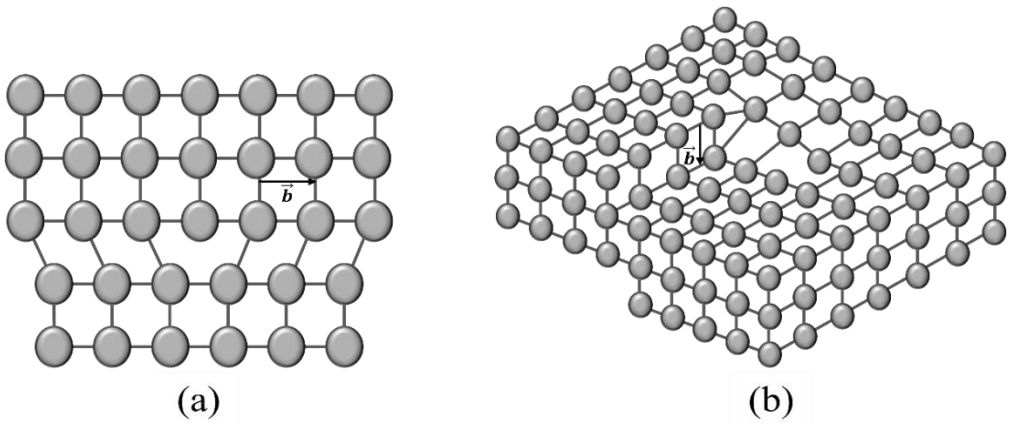


Figure 1.4: Schematic showing two types of dislocations, (a) edge and (b) screw dislocation (reproduced from Xijia Wu, 2019 [18]).

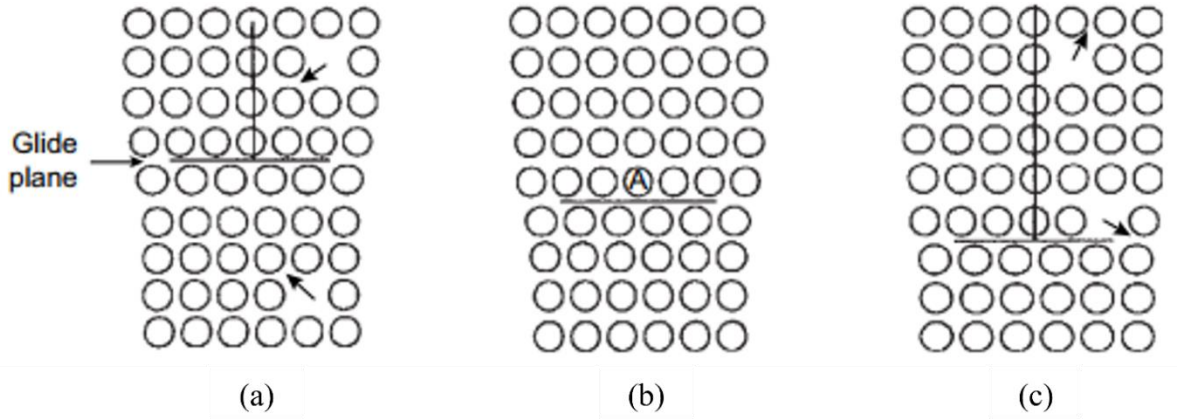


Figure 1.5: Schematic (a) represents the climb movement of an edge dislocation, positive sense of dislocation climb wherein the vacancies in the crystal diffuse to the dislocation (note, the sense of direction of vacancy motion is indicated by arrows), (b) represents a dislocation centered on the row of atoms A, and (c) illustrates the negative dislocation climb, where vacancies form at the dislocation line and subsequently diffuse away (taken from Hull and Bacon, 2011 [16]).

Practically, it is very rare to observe a pure screw or a pure edge dislocation in crystals. Instead, dislocations are typically present in crystals as loops comprising both edge and screw components, referred to as mixed dislocations, as illustrated in figure 1.6. The dislocation, being curved, exhibits characteristics of both edge and screw dislocations, which change at different points along the dislocation line.

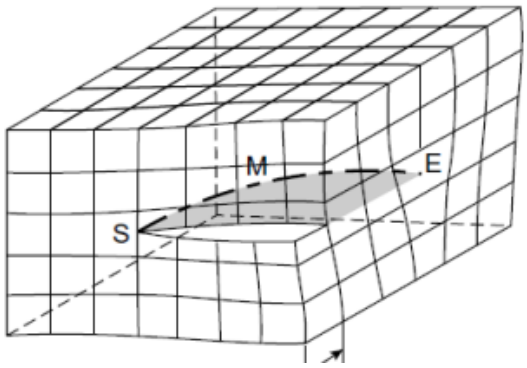


Figure 1.6: Schematic shows a mixed dislocation. Note, the dislocation at locations E, S and M exhibit the characteristics of edge, screw and mixed dislocation respectively (taken from Hull and Bacon, 2011 [16]).

1.4. Plastic Slip in Body Centered Cubic Metals

1.4.1. Slip Systems

Slip systems are defined by specific combinations of slip planes and slip directions within the crystal structure. Generally, slip directions and planes are the most densely packed directions and planes in the crystals and these slip systems facilitate easier movement of dislocations. This is because atomic displacement in these directions and planes is shorter resulting in lower energy requirements. Understanding slip systems is essential for comprehending the mechanical behaviour of materials. Unlike FCC and HCP metals, the slip planes are not well defined for BCC metals [16,19]. Nevertheless, the <111> direction is the most closely packed direction in BCC metals and slip always occurs along this closely packed direction [16]. There are three families of slip planes, {110}, {112}, and {123}, present in BCC metals, whereas there is only one <111> slip direction (refer to figure 1.7) [16]. Thus, it can be understood that there are 12 slip systems of {110}<111> type, 12 slip systems of {112}<111> type, and 24 slip systems of {123}<111> type, resulting in a total of 48 slip systems in a BCC crystal [16].

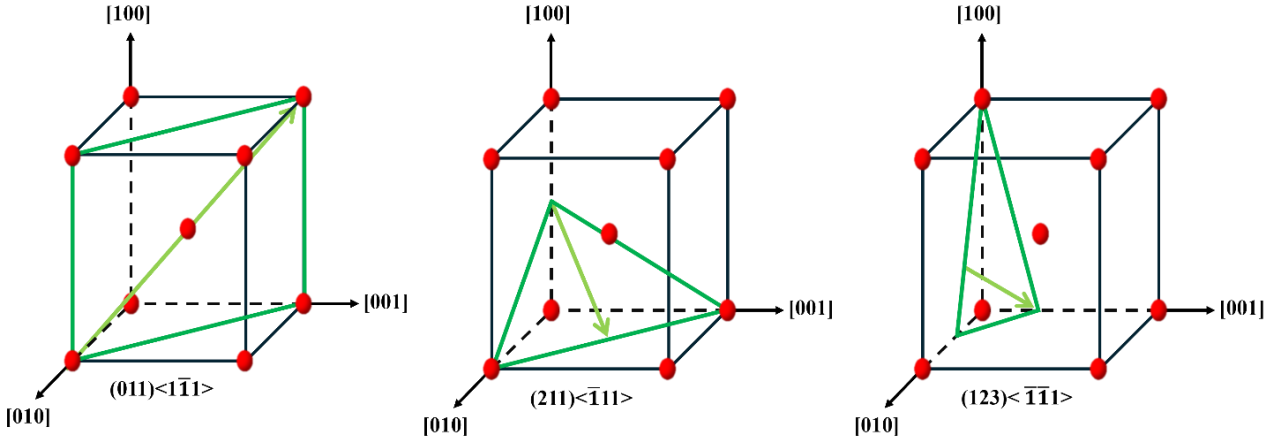


Figure 1.7: Three types of slip systems in a BCC crystal.

1.4.2. Mechanism of Plastic Slip in a Crystal

In metals, plastic deformation mainly occurs by the movement of dislocations on slip systems. This movement of dislocations can be classified into two fundamental types: glide movement and climb movement. The glide motion, occurs when the dislocation moves within a plane containing both dislocation line and Burgers vector. Dislocations that can move in this

manner are termed glissile, otherwise, they are referred to as sessile. On the other hand, the climb occurs when the dislocations move out of the glide planes, in a perpendicular direction to the Burgers vector. The glide motion of numerous dislocations leads to slip. The shortest lattice vectors in BCC, FCC, and HCP crystals are 1/2<111>, 1/2<110> and 1/3<11$\bar{2}$0>, respectively.

For any slip movement, characteristic shear stress is necessary, which is called as τ_R, Consider crystal depicted in figure 1.8 is being deformed under tension force *F*. The component of force along the slip direction is $F\ cos\delta$, where δ is the angle between *F* and the slip direction. Thus, the resolved shear stress along slip direction on a slip plane is given by:

$$\tau_R = \frac{F}{A/cos\phi}\ cos\delta = \frac{F}{A}\cos\phi\cos\delta, \tag{1.2}$$

Where ϕ is the angle between force and the slip plane normal. Note that the term, $\cos\phi\cos\delta$, in equation. (1.2) is referred to as the Schmid factor. For plastic deformation to take place, it is essential that the resolved shear stress must increase a certain threshold, referred to as the CRSS, τ_c for slip [20]. This principle is encapsulated in what is known as Schmid's law. Note that BCC metals do not follow Schmid's law.

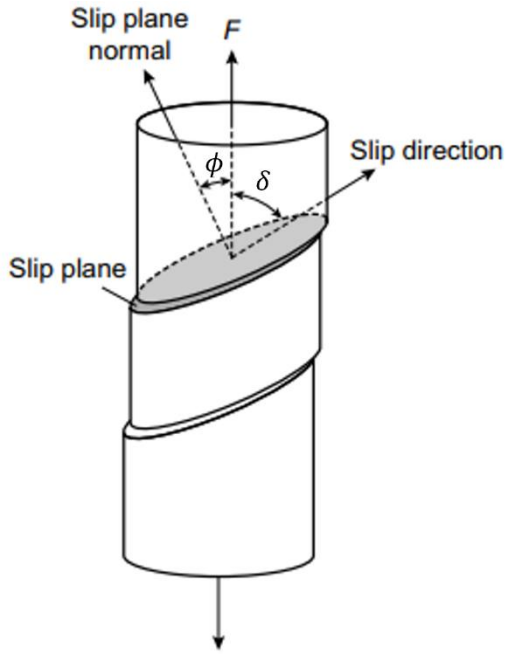


Figure 1.8: Schematic of slip analysis in a slip (reproduced from Hull and Bacon, 2011 [16]).

1.5. Indentation Response of Mo Single Crystals

Hardness experiments on various BCC metals have shown that hardness is orientation dependent [8,21]. The materials studied include Ta, Mo, and W single crystals. Moreover, hardness tends to decrease with increasing indentation load; a phenomenon known as ISE. Stelmashenko et al. [8] conducted microhardness experiments on different orientations of W and Mo single crystals using a Vickers indenter and they found a significant ISE in all cases. In the low load regime, the (111) orientation shows the lowest hardness, while the (100) orientation shows the highest and (110) orientation falls between the two. Conversely, in the high load regime, the trend reverses, with the (111) orientation exhibiting the highest hardness and the (100) orientation exhibiting the lowest (refer to figure 1.9). In addition, they also reported that the pile-up patterns on (100), (110), and (111) oriented molybdenum crystals exhibit four-, two-, and three-fold symmetry, respectively. Later, Cech et al. [22] showed that this pile-up morphology is related with the active slip systems out of plane directions.

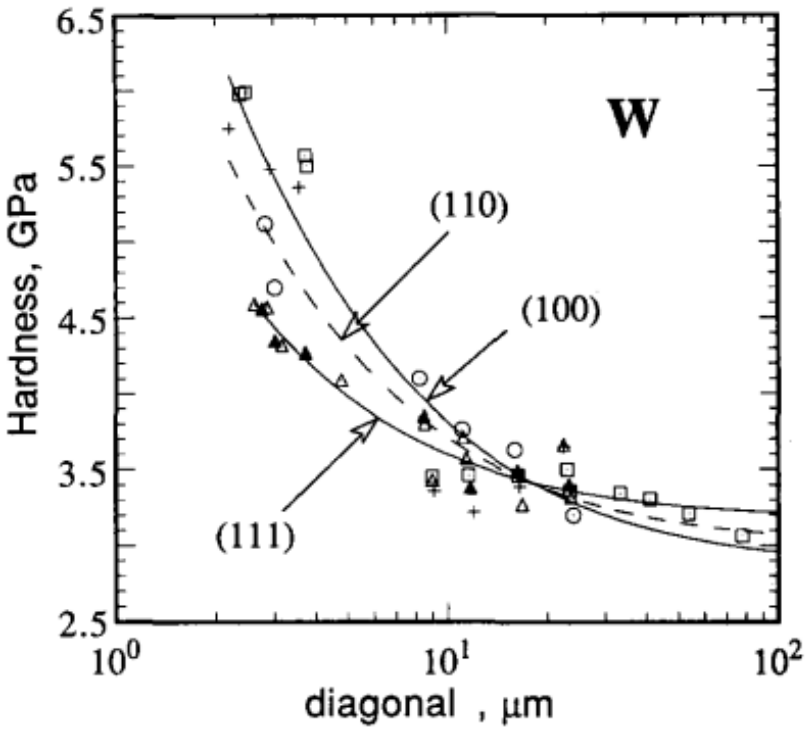


Figure 1.9: Dependence of the hardness on the diagonal length for W single crystals (taken from Stelmashenko et al., 1993 [8]).

1.6. Annealing

Annealing is a heat treatment method that involves controlled heating of the material to a specific temperature (below the melting point), holding for a specific duration at that temperature followed by controlled cooling to room temperature. It can be utilized to tune the mechanical properties by controlling the heating rate, holding time, and cooling rate of annealing. Annealing can be classified as high-temperature annealing and low-temperature annealing based on the maximum temperature up to which the sample was heated. These are discussed briefly in the following subsections.

1.6.1. High Temperature Annealing

The annealing process is known as high temperature annealing if the samples are heated above their recrystallisation temperature which is a temperature at which full recrystallization occurs within one hour. Typically, for metals and their alloys, this temperature ranges from one-third to one-half of the T_m of material. Since the holding temperature is above recrystallisation temperature in high-temperature annealing, the resulting structure is highly dependent on the rate of cooling. When the cooling rate is high the atoms start to get organized from multiple nucleation sites, resulting in the formation of smaller grains, while a slow cooling rate allows the formation of larger grains within the crystals.

1.6.2. Low Temperature Annealing

The annealing is termed as low-temperature annealing if the holding temperature is lower than the recrystallisation temperature. It is also known as stress relieving annealing. In this process, the lattice structure maintains its crystallinity during annealing but since the samples are heated and held at a higher temperature than room temperature the properties in the crystals might alter. This process is mainly performed to reduce the residual stresses in materials, particularly metals and alloys.

1.7. The Effect of Annealing

The material's dislocation structure is altered during the heating step of annealing, which facilitates the rearrangement of these dislocations and the elimination of defects. The holding step allows for the completion of recrystallization or the growth of new, strain-free grains (refer to

figure 1.10). Controlled cooling at a slow rate ensures the development of desired mechanical properties which minimizes the risk of introducing new stresses. The resulting properties can differ based on various factors such as cooling rate, duration of holding, and the number of iterations [23–25]. Annealing has a variety of effects on the properties and structure of materials. One of the key results of annealing is the densification of materials, where the atoms rearrange themselves into a more stable atomic structure [26]. In addition, annealing typically decreases the hardness of metals, referred to as annealing induced softening, a useful treatment for the following manufacturing processes, such as shaping and forming. Additionally, due to annealing internal stresses are released that may have built up in the material due to cold working or welding during previous stages of the manufacturing. This stress relief can improve dimensional stability and reduce the risk of mechanical failure. Another consequence of the annealing process is that when the sample is held for an extended period the grain size of the material increases [27]. This change in grain size can significantly impact the mechanical properties of the material. Furthermore, annealing may also lead to phase transformation of a material [10]. In conclusion, annealing has various types of applications, and it is useful for the alteration of properties of materials to match the required specifications for different industrial and technological applications.

1.7.1. Effect of Annealing on Polycrystalline Metals

Annealing has significant effects on the properties of polycrystalline metals. In general, high-temperature annealing causes a decrease in the strength of polycrystalline metals such as aluminium [28], copper [29,30] and iron [31]. Similarly, the hardness is also found to be decreasing after annealing [29,32,33]. For example, the microhardness of copper has been reported to decreases due to increase in grain size after annealing [29,34]. In polycrystals, high-temperature annealing causes grain growth in the crystals which reduces the obstacle in dislocation movement, leading to a reduction in strength or hardness. Conversely, it is also observed that the hardness/strength of NC Ni [35] and Al [36] increases after annealing. This enhancement in strength/hardness is attributed to the grain boundary relaxation in NC metals. Unlike conventional metals, intra-grain dislocations are not present in NC materials so when annealing is conducted in the NC materials, the dislocations present in grain boundaries are relaxed by dislocation annihilation. Due to this, the grains reach a more stable state where the activation energy of grain boundary diffusion is more than that of the grain boundary relaxation. Due to the more stable state

of grain boundaries, the movement of remaining dislocations is much more difficult, which further increases the strength/hardness of the materials. In addition, there might be various reasons behind the hardening in the NC materials after annealing, such as the densification of materials [37], and redistribution of impurities [35]. Due to high-temperature annealing recrystallization occurs in the materials which causes rearrangements of atoms, forming a denser structure. Similarly, annealing might also enhance the mechanical properties by redistribution of impurities in the crystals. Furthermore, the effect of annealing on the polycrystalline Mo is discussed below.

1.7.1.1. The Effect of Annealing on the Deformation Behavior of Mo Polycrystals

Several studies show that annealing can result in a significant change in the ductility, strength, and hardness of crystals [38–40]. For instance, Wang et al. [38] performed three-point bend experiments on pure Mo bars annealed at 1073 K, 1173 K, 1253 K, 1323 K, 1423 K and 1523 K respectively for 1 hr followed by furnace cooling. They found that the ductility increases with an increase in annealing temperature, and it attains a peak at around 1253 K and begins to drop thereafter. By contrast, Suzuki et al. [41] reported insignificant changes in the ductility of Mo rods after annealing at 1773K.

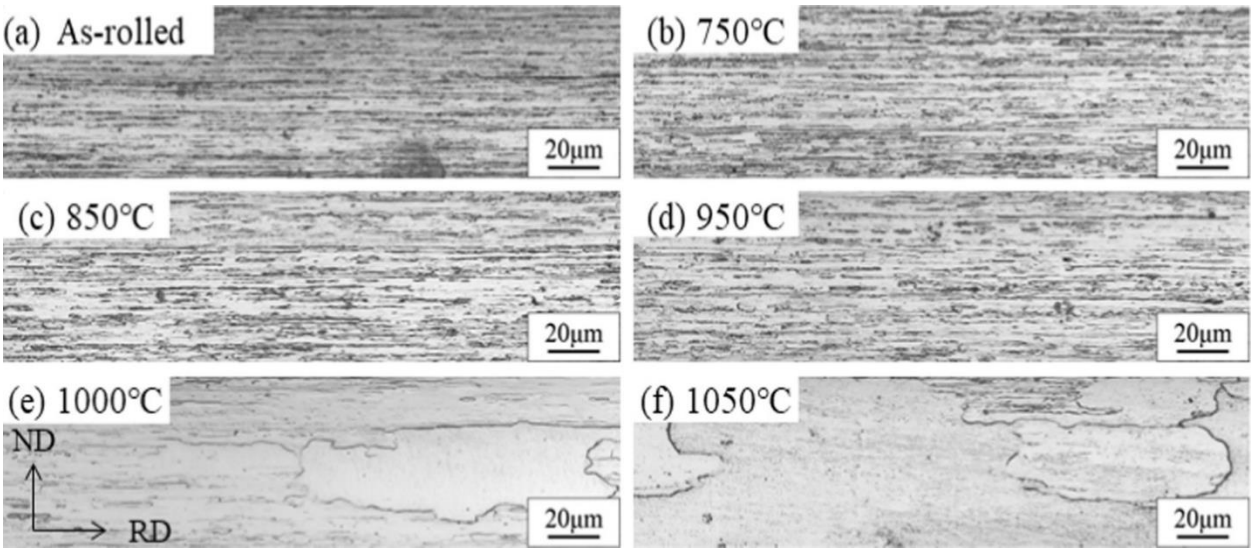


Figure 1.10: The microstructure of Mo foil (a) as-rolled, and annealed at (b) 750°C, (c) 850°C, (d) 950°C, (e)1000°C, (f)1050°C (reproduced from Fu et al., 2020 [39]).

Fu et al. [39] performed tension experiments on polycrystalline Mo foils made by hot-rolling and unidirectional cold-rolling. These foils were annealed in a vacuum furnace to achieve the desired thermal conditions. The mechanical properties, such as yield strength and tensile strength of these molybdenum foils showed a gradual reduction, after annealing at different temperatures [39]. On the other hand, the hardness of polycrystalline Mo sheets was reported to remain almost unchanged after low-temperature annealing [40], whereas it was observed to drop after high-temperature annealing (annealing temperature>900°C) (refer to figure 1.11). A similar effect of annealing on the Vickers hardness of Mo polycrystalline foils has also been reported by Marden and Wroughton [42]. Thus, the microhardness of polycrystalline Mo sheets/foils can be altered through high-temperature annealing, but it may remain unchanged after low-temperature annealing.

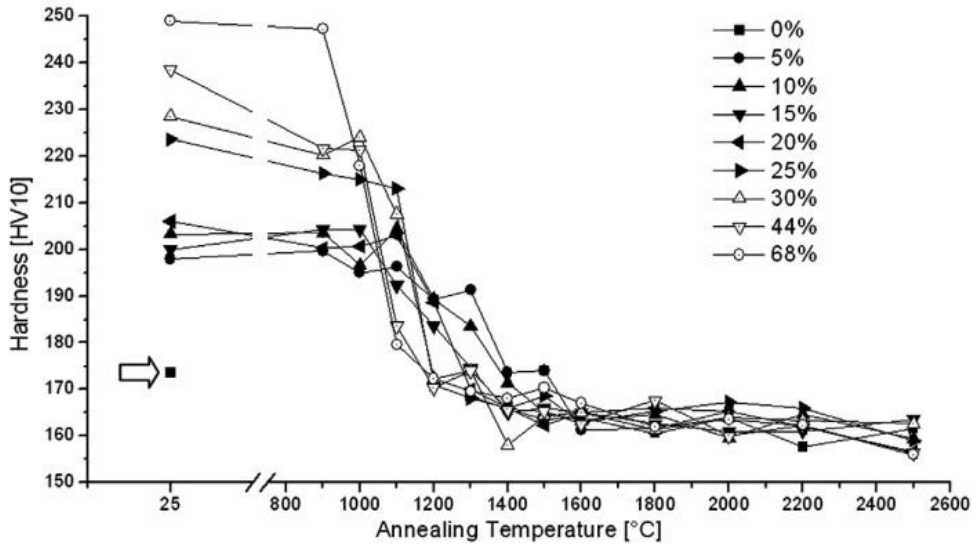


Figure 1.11: The variation of hardness with annealing temperature for different rolling deformation (taken from Primig et al., 2010 [40]).

1.7.2. Effect of Annealing on Single Crystalline Metals

Unlike polycrystals, there are no grains or grain boundaries in the single crystals so the effect of annealing in single crystals is quite different. One of the primary effects of annealing in single crystals is the reduction in dislocation density [43,44]. When the dislocation density is reduced by a large amount, fewer dislocations remain in the crystals to facilitate deformation, a phenomenon known as dislocation starvation. This results in increase in the strength of the material

as higher stress is required to create new dislocations for the deformation. But in the case of deformed or irradiated single crystals, the dislocation density is high so annealing in these crystals leads to a decrease in the strength of the crystals [45]. Further, low-temperature annealing increases the possibility of precipitation in the crystals [46]. Moreover, annealing can also induce structural changes in the crystals [47], which might lead to a change in the strength/hardness of the crystals [48]. Furthermore, the effect of annealing on the Mo single crystals is discussed below.

1.7.2.1. The Effect of Annealing on the Deformation Behavior of Mo Single Crystals

The effect of high-temperature annealing on the compressive, tensile, and micro-indentation response is studied for both pure Mo single crystals [49], Mo - Nb single crystals [50] and Mo bi-crystals [51]. Lowry et al. [49] performed nano-compression experiments on nano-pillars of Mo single crystals subjected to two-step high-temperature annealing. In the first step, they annealed samples at 1845°C for 790 hours and subsequently, in the secondary treatment, they performed annealing at 2330°C for 24 hours. They reported much higher shear strength (almost near to ideal strength) in annealed samples than that of as-prepared nano-pillars. The enhancement in strength was correlated with the drastic drop in the dislocation density during annealing (refer to figure 1.12) which resulted in strength almost close to the theoretical shear strength of Mo. Note that in the experiments of Lowry et al. [49], annealing was performed at a temperature above critical temperature. Thus, they investigated the effect of high-temperature annealing and have not studied the effect of low-temperature annealing on the compressive strength of Mo crystals. Huang et al. [50] also investigated the effect of high-temperature annealing (1100-1700°C for 2 hours) on the tensile response of Mo - Nb single crystals. They observed a notable decrease in strength following annealing, while the ductility of Mo-Nb single crystals was substantially enhanced. It is important to note that the study of Huang et al. [50] pertained to Mo - Nb single crystals and was not related to the high-purity Mo single crystals.

Hiraoka [51] performed Knoop indentation experiments across the interface of two Mo single crystals with identical orientations joined through brazing. He reported that the hardness at the interface of the crystals was increased after annealing performed at 1500°C. However, the hardness away from the interface was almost identical to that of as-fabricated crystals. It must be

noted that the primary objective of the experiments of Hiraoka [51] was to investigate the effect of the high-temperature annealing on the hardness of the brazed interface, and not on the hardness of Mo single crystals. Also, Hiraoka [51] has not studied the effect of low-temperature annealing on the indentation response of Mo single crystals. In fact, to the best of our knowledge, the effect of low-temperature annealing on the indentation response of Mo single crystals has not been investigated yet. However, the effect of low-temperature annealing on the indentation response of thin films of Mo single crystals (110) deposited on Si substrate (400) has been investigated by Khojier et al. [10]. They reported that the hardness of the annealed crystal increases gradually with an increase in annealing temperature from 400-650°C and drops thereafter (refer to figure 1.13). They correlated the increase in hardness with a rise in annealing temperature up to 650°C with the change in crystal structure from BCC to FCC due to the diffusion of Nitrogen in the Mo thin film.

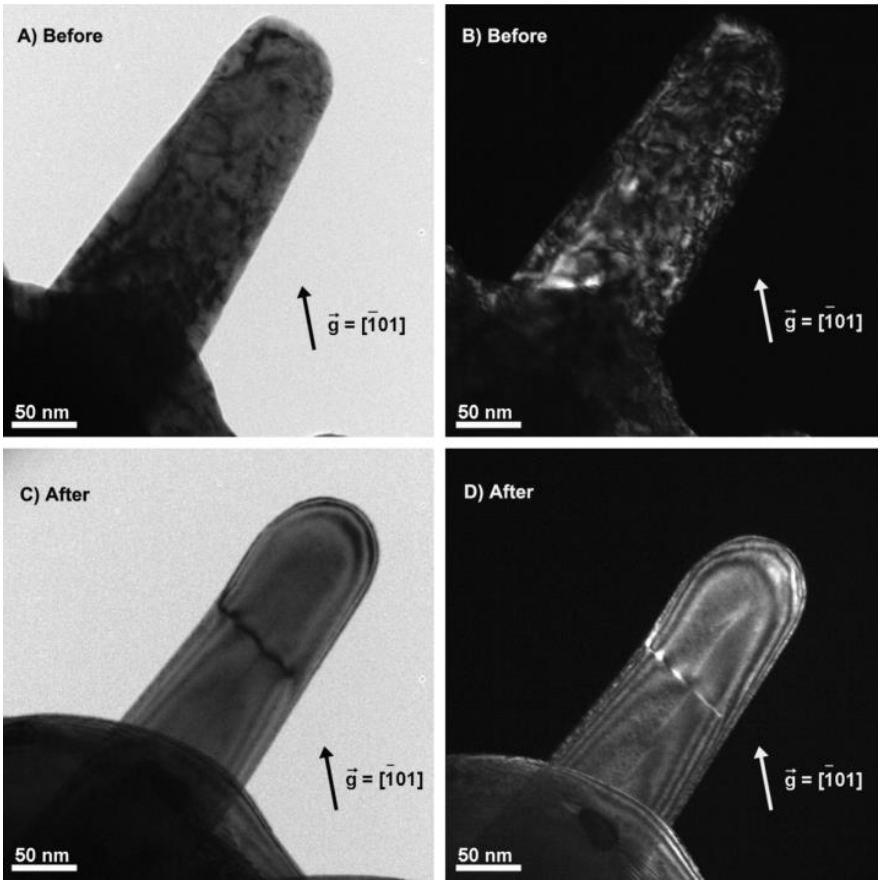


Figure 1.12: Schematic showing a molybdenum nanopillar before and after annealing. (A) & (C): bright field (BF) images and (B) & (D) dark field (DF) images (reproduced from Lowry et al., 2020 [49]).

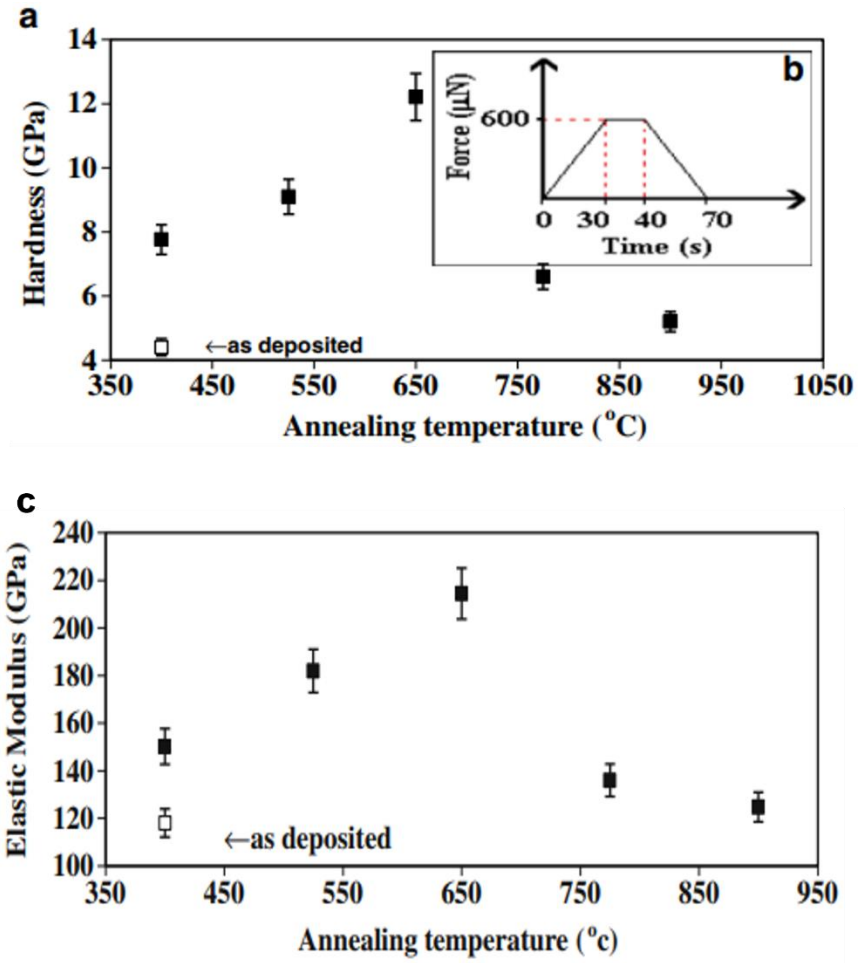


Figure 1.13: Schematics shows the variation of (a) hardness with annealing temperature, (b) loading force as a function of time and (c) elastic modulus with annealing temperature for the sample of molybdenum nitride thin films (reproduced from Khojier et al., 2020 [10]).

1.8. Issues for Investigation

It can be deduced from the above-discussed literature that many researchers tried to study the effect of high-temperature annealing on the deformation behaviour of Mo single crystals but there has been less focus on investigating the influence of the low-temperature annealing. Moreover, the effect of annealing on the ISE and indentation response has also not been studied properly. The following issues pertaining to the indentation response of Mo single crystals need to be addressed:

1. It is not clear from the study of Khojier et al. [10] that whether the observed trend in hardness with an increase in annealing temperature is specific to the Mo thin films or these are also applicable to the bulk samples of Mo single crystals.

2. Further, the hardness enhancement in the experiments of Khojier et al. [10] was caused by the formation of Mo_2N during annealing, therefore, a fundamental question pertaining to the effect of annealing on the hardness of Mo single crystals "Would the conventional annealing performed in the presence of atmospheric air also lead to enhancement in the hardness?" arises.

1.9. Objectives of the Thesis

In order to address the issues listed in previous section, the following objectives are identified:

1. To perform micro-indentation experiments at different loads on the as-received Mo single crystals oriented along (100), (110), and (111) directions.

2. To perform annealing at temperatures of 250^{o}C and 500^{o}C on (100)-, (110)-, and (111)-oriented Mo single crystals.

3. To perform micro-indentation experiments at different loads on the annealed Mo crystals.

4. To investigate the Pile-up and sink-in behaviour on the indented surfaces.

5. To investigate the effect of low-temperature annealing on the micro hardness of Mo single crystals and to investigate the rational behind the observed behavior.

1.10. Organization of the Thesis

The remaining chapters of this thesis are organized as follows:

In Chapter 2, micro-indentation experiments were conducted on both as-received and annealed Mo single crystals. This study utilized three Mo single crystals oriented along (100), (110), and (111) planes, with annealing carried out at two temperatures, 250°C and 500°C. Additionally, in this chapter a microhardness enhancement mechanism attributed to dislocation annihilation during the annealing process is also proposed.

In Chapter 3, the important conclusions are summarized and the possible further works are also discussed.

Chapter 2

Effect of Annealing on Micro-hardness of Molybdenum Single Crystals

2.1. Introduction

Molybdenum (Mo) has emerged as a potential candidate for diverse applications in the semiconductor, defense, and medical industries [52] owing to its high strength, superior fracture strength, extremely high melting point, excellent thermal conductivity, and exceptional corrosion resistance [3,53]. Most of the studies pertaining to annealing on Mo single crystals aimed to understand the effect of high-temperature annealing on their compressive, tensile, and micro-indentation response, though Khojier et al. [10] studied the effect of low-temperature annealing on the indentation response of thin films of Mo single crystals. They reported an increase in hardness with an increase in annealing temperature, but it is not clear from their study if these observations are specific to the Mo thin films only or applicable to the bulk crystals of Mo also.

Therefore, the effect of low-temperature annealing on the indentation response of Mo single crystals is analyzed in this chapter. For this purpose, Vickers indentation experiments are performed on annealed and as received Mo single crystals oriented along the (100), (110), and (111) directions. The structure of this chapter is as follows: section 2.2 details the experimental methodology, section 2.3 presents and discusses the key results, and section 2.4 summarizes the findings of this chapter.

2.2. Experimental Methodology of Micro-indentation

The (100)-, (110)-, and (111)-oriented molybdenum (Mo) single crystals (4N purity), manufactured by the floating zone melting method [54] are obtained from MaTeck, Germany. The dimensions of these crystals are Φ12mm×1.5mm, Φ10mm×1mm, and Φ10mm×1mm, respectively. Further, the crystals are diced into four equal parts using wire-cut electron discharge machining (EDM), at a speed of 300 Hz with molybdenum wire. For all three orientations, micro-

indentation experiments are performed on as-received samples (un-annealed) as well as on the samples annealed at 250 °C and 500 °C. For annealing, the samples are heated in a Nabertherm GmbH muffle furnace (LHTCT 01/16) at a rate of 5 °C /min and kept for 1 hour at the maximum temperature, followed by furnace cooling. To understand the effect of annealing on crystal structure, all the samples are analyzed by X-ray diffraction (XRD) (Marvalene PANalytical X-ray diffractometer) after mirror polishing. The XRD analysis is performed using Cu/K_{α} radiation with the wavelength of 1.5406 Å in the diffraction angle range of 20°-125° with a step width of 0.026°.

Before indentation, the sample surfaces are mirror-polished using 0.25 μm diamond paste and cleaned ultrasonically. The Vickers micro-indentation (Micro Mach Technologies, India) experiments are performed using Vickers diamond indenter under load control mode at maximum load, $P_{max} = 0.49, 0.98, 1.96, 2.94, 4.9$ N. The loading and unloading are performed at a constant velocity of 60 μm/s with a dwell time of 12 seconds. To obtain statistically reproducible data, ten indentations are performed at each P_{max} and the distance between two consecutive indents is taken at least 10 times the indentation depth to avoid strain field interaction. The mean values of Vickers hardness (H) are reported along with standard deviation with the help of error bars. To visualize the indentation region, the optical microscope (AXI0 Zeiss) with magnifications ranging from 10x to 100x is used. Furthermore, energy dispersive X-ray spectroscopy (EDS) is used to investigate the oxide formation on the polished surface, Electron Backscatter Diffraction (EBSD) is employed to investigate the structural change after annealing, and XRD is used to determine the dislocation density in the crystals.

2.3. Results and Discussion

2.3.1. X-Ray Diffraction Analysis

The XRD patterns of (100)-, (110)-, and (111)-oriented Mo single crystals (Reference Code, COD: 96-400-1309) are shown in figure 2.1 (a)-(c), respectively. In these figures, the XRD patterns for the samples of as-received, annealed at 250 °C, and annealed at 500 °C Mo single crystals are displayed.

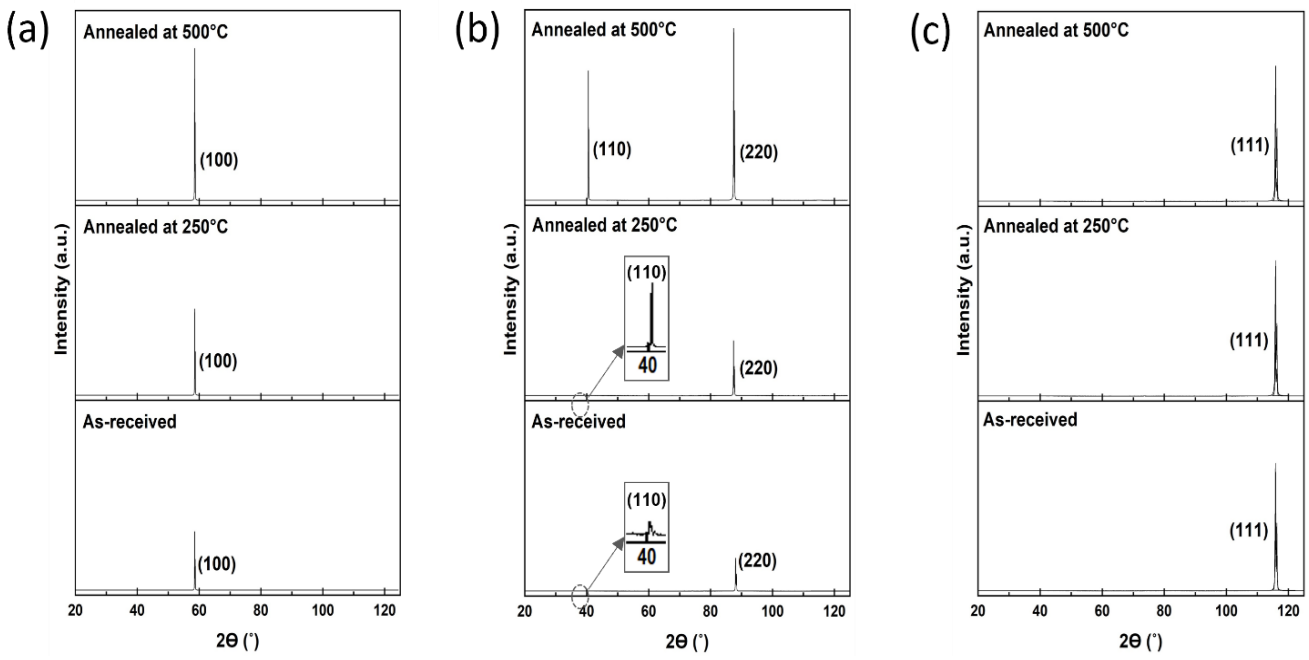


Figure 2.1 The X-ray diffraction (XRD) patterns for (a) (100)-, (b) (110)-, and (c) (111)-oriented Mo single crystals.

It can be seen from figure 2.1 that all the samples maintained their crystallinity after annealing since the annealing temperatures are far below the recrystallization temperature (900 ℃-1200 ℃) [39,40,55].

2.3.2. Optical images of Residual Indent Imprint

Figure 2.2 shows the optical images of the residual imprints corresponding to an indentation load of 4.9 N for all the samples. It can be noticed from these images that for a fixed orientation the shape of the imprint is almost identical, irrespective of the annealing conditions. For example, the edges of the imprint on the samples of (100) -oriented crystals are slightly curved near the corners which makes them appear like a four-sided star (refer to figure 2.2 (a)-(c)).

By contrast, two opposite edges seem to be pulled towards the center, while the remaining two are pushed away from the center in all images displayed in figure 2.2 (d)-(f). This resulted in the imprint on (110)-oriented samples to look like a power drum. On the other hand, all the edges in figure 2.2 (g)-(i) are almost straight, with two adjacent edges being shorter than the other two, consequently the imprint on (111)-oriented samples to look like a kite. Thus, it can be deduced

from the above observations that the shape of the indent imprint in Mo single crystals is mainly governed by the orientation of the crystal, and it is poorly influenced by annealing conditions.

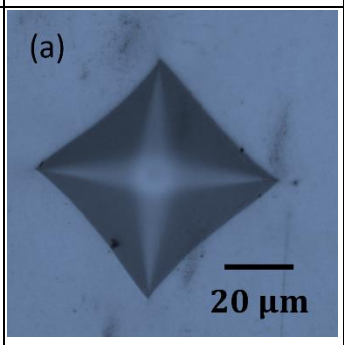
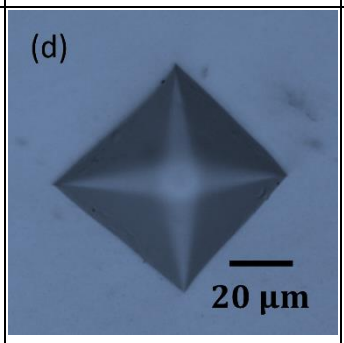
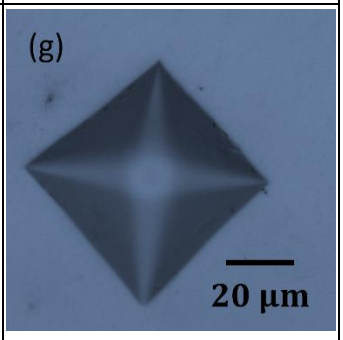
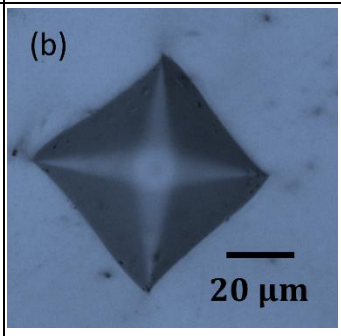
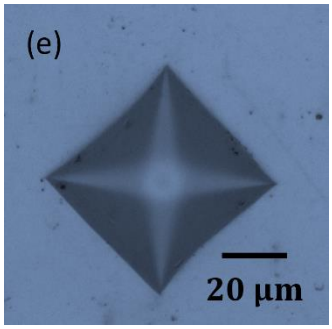
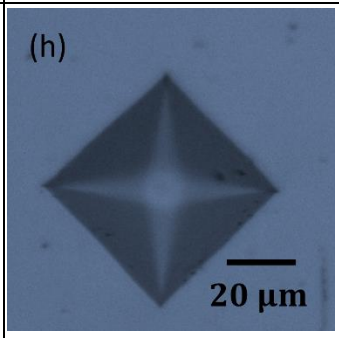
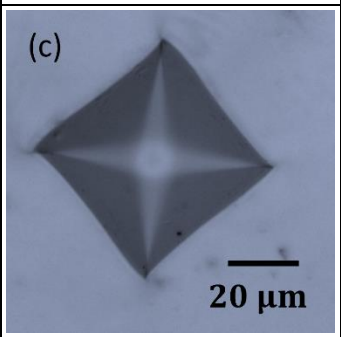
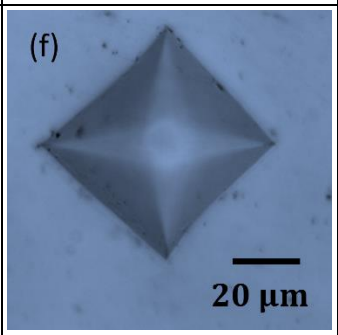
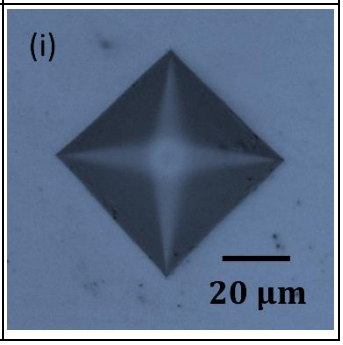
P_{max}=4.9 N	(100)	(110)	(111)
As received			
Annealed at 250 ˚C			
Annealed at 500 ˚C			

Figure 2.2 The optical microscope images of the residual imprints on (a)-(c) (100)-, (d)-(f) (110)-, and (g)-(i) (111) oriented plane of as-received and annealed Mo single crystals.

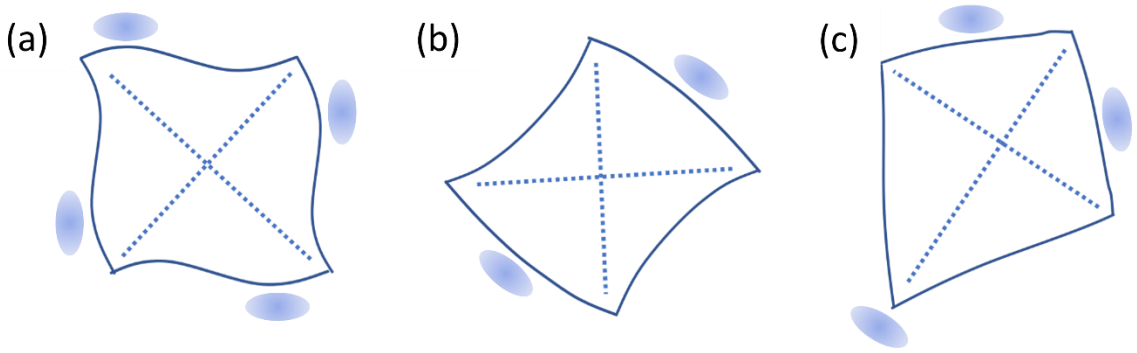


Figure 2.3 Schematics showing four-, two-, and three-fold symmetry in pile-ups causing the different shapes of imprint for (a) (100)-, (b) (110)-, and (c) (111)-orientation.

Single crystals exhibit either pile-up or sink-in effect during indentation depending on their mechanical properties and orientation [8]. Indeed, Han et al. [56] showed from crystal plasticity finite element simulations that pile-up and sink-in behaviour in Ni-based single crystal superalloy depends on the active slip systems out of the plane of the indentations. Thus, the pile-up or sink-in morphology on an indented surface has been linked with the number of slip systems triggered due to the indentation load [8,22,57]. For the indentation of Mo single crystals, the position of pile-ups can be correlated with the orientation of $\{110\} < 111 >$ slip systems with respect to loading directions [8]. Since the pile-up is predominantly found along the out-of-plane $< 111 >$ slip directions [22], the pile-up pattern near the indent imprint follows four-, two-, and three-fold symmetry for (100), (110), and (111) orientation, respectively. Due to the four pile-ups in the (100) orientation, the shape of the indent imprint for this case looks like a four-sided star (refer to figure 2.3 (a)), whereas the shape of the imprint for (110) and (111) orientation appears like a power drum and a kite owing to two and three pile-ups, respectively (refer to figure 2.3 (b), and 3 (c)).

2.3.3. The Variation of Micro-hardness with Indentation Load

Figures 2.4 (a), (b) and (c) display the variation of H with P_{max} for as-received, annealed at 250 °C and 500 °C samples, respectively. Note that H decreases with an increase in load and eventually attains a saturation level which signifies that Mo single crystals show indentation size effect (ISE), irrespective of the annealing conditions and their orientation. Further, (111)-oriented crystal shows the highest hardness for all the annealing conditions (refer to figures 2.4 (a)-(c)).

The highest hardness along (111) orientation has also been reported for other BCC crystals such as Tantalum [21] and Tungsten [8].

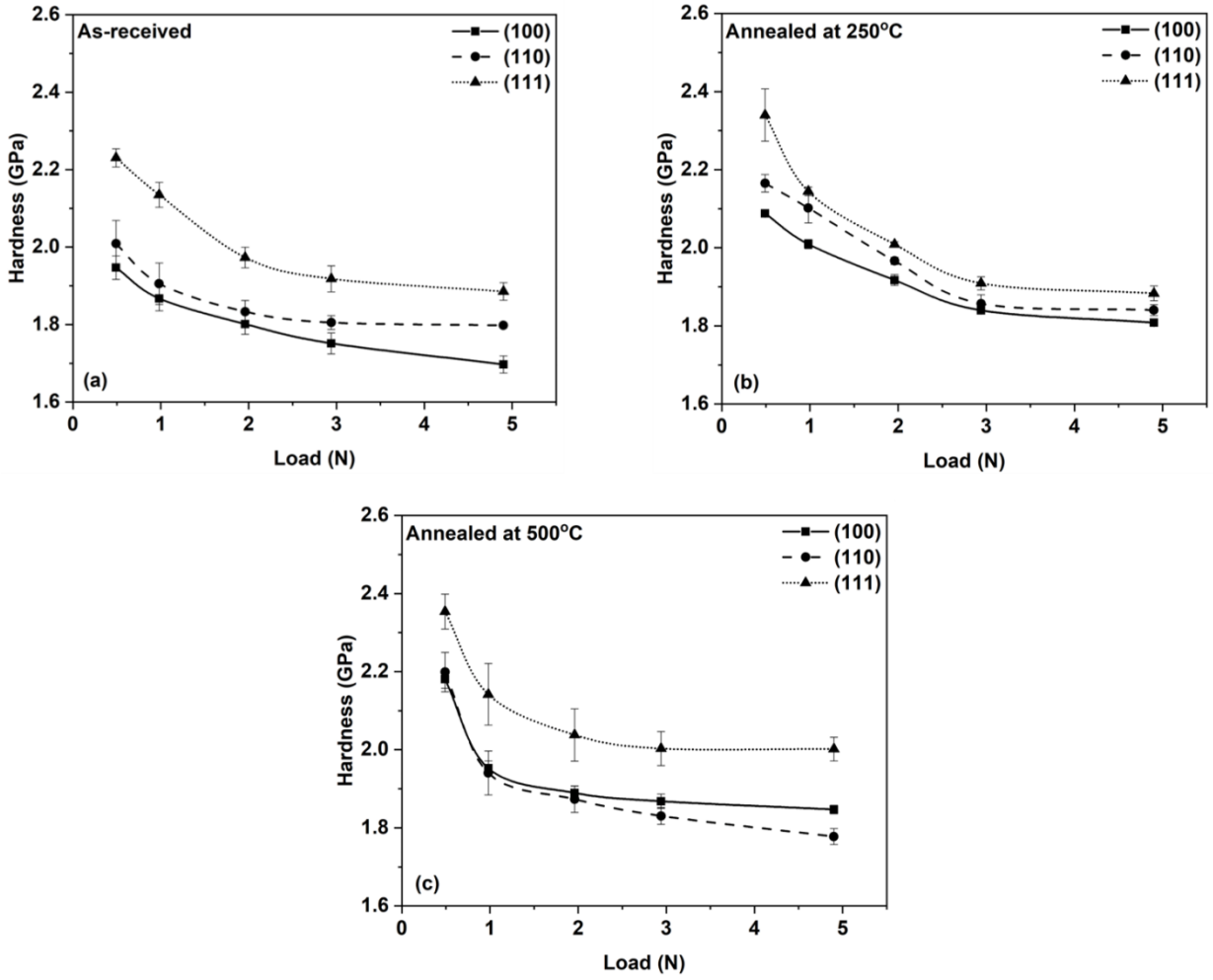


Figure 2.4 The variation of Vickers hardness (H) with indentation load (P) for (a) as-received, (b) annealed at 250 °C , and (c) annealed at 500 °C , Mo single crystals.

2.3.4. The Effect of Annealing Temperature on Micro-hardness

Figure 2.5 (a)-(c) show the effect of annealing temperature on the relationship of H and P for (100)-, (110)-, and (111)-oriented Mo single crystals, respectively. It is interesting to note from figure 2.5 (a) that for (100) orientation, annealing results in enhancement in H for all values of P. In particular, the saturation hardness of (100) orientation increases by around 9% after annealing performed at 500 °C. A similar trend can be observed in figure 2.5 (c) for (111)

orientation. By contrast, annealing has an almost negligible effect on the (saturation) hardness for (110) orientation (figure 2.5 (b)).

The increase in hardness after annealing has also been reported in nanocrystalline materials, which has been attributed to the grain boundary interaction [58], grain refinement [36], and reduction in dislocation sources [36,59,60]. In the context of the present study on the Mo single crystals, the enhancement in hardness after annealing might be due to the oxidation and reduction in dislocation sources during annealing**.** In general, MoO_2 and MoO_3 are the two most common oxides of Mo which are believed to form on the surface and interior of the crystal, respectively [61,62]. It should also be noted that Mo is a refractory metal and less reactive in comparison to other metals and hence difficult to oxidize [61,63]. Indeed, Simnad and Spilners [63] reported insignificant formation of MoO_3 even after the annealing performed at 500 °C for 15 hours. It has also been reported that the formation of Mo oxides were negligible even after sintering at $1700°C$ for 18 hours in the presence of oxygen[64]. Since annealing is performed only for one hour in the present study, the formation of MoO_3 can be considered to be negligible. Thus, MoO_2 is the only oxide that would have formed on the surface during annealing. It is commonly accepted that the thickness of the oxide layer formed during annealing is much less in weight [63] or in depth, around 100 nm [65]. It must be noted that all the samples (annealed as well as as-received) are diamond-polished before indentation, therefore, around 25 μm thick surface layer has been removed from all the samples. Thus, it can be deduced that the chances of the presence of MoO_2 in the samples employed in the present experiments are minimal. Still, to ensure the absence of MoO_2 and MoO_3 in samples, the energy dispersive X-ray spectroscopy (EDS) analysis is performed, and the results are presented in figure 2.5 (i)-(iii), which confirms the absence of oxides of Mo in the crystal. Therefore, it can be concluded that the oxide formation is not the reason for the enhancement in hardness after annealing.

Further, the XRD pattern displayed in figure 2.1 shows that all the samples remain single crystals and their orientation also remains unchanged after annealing. Thus, figure 2.1 suggests that the chances of structural changes leading to enhancement in the hardness are minimal. In order to confirm, the EBSD analysis is performed on as-received and annealed samples, and the corresponding two-dimensional maps are displayed in figure 2.6 (a)-(c) for (100)-oriented samples. The EBSD maps also show that the annealing could not lead to any structural changes in

the crystals. Similar behaviour has been observed for the other two orientations also. Therefore, it can be concluded that the enhancement in hardness of annealed crystals observed in the present experiments is not associated with the structural changes.

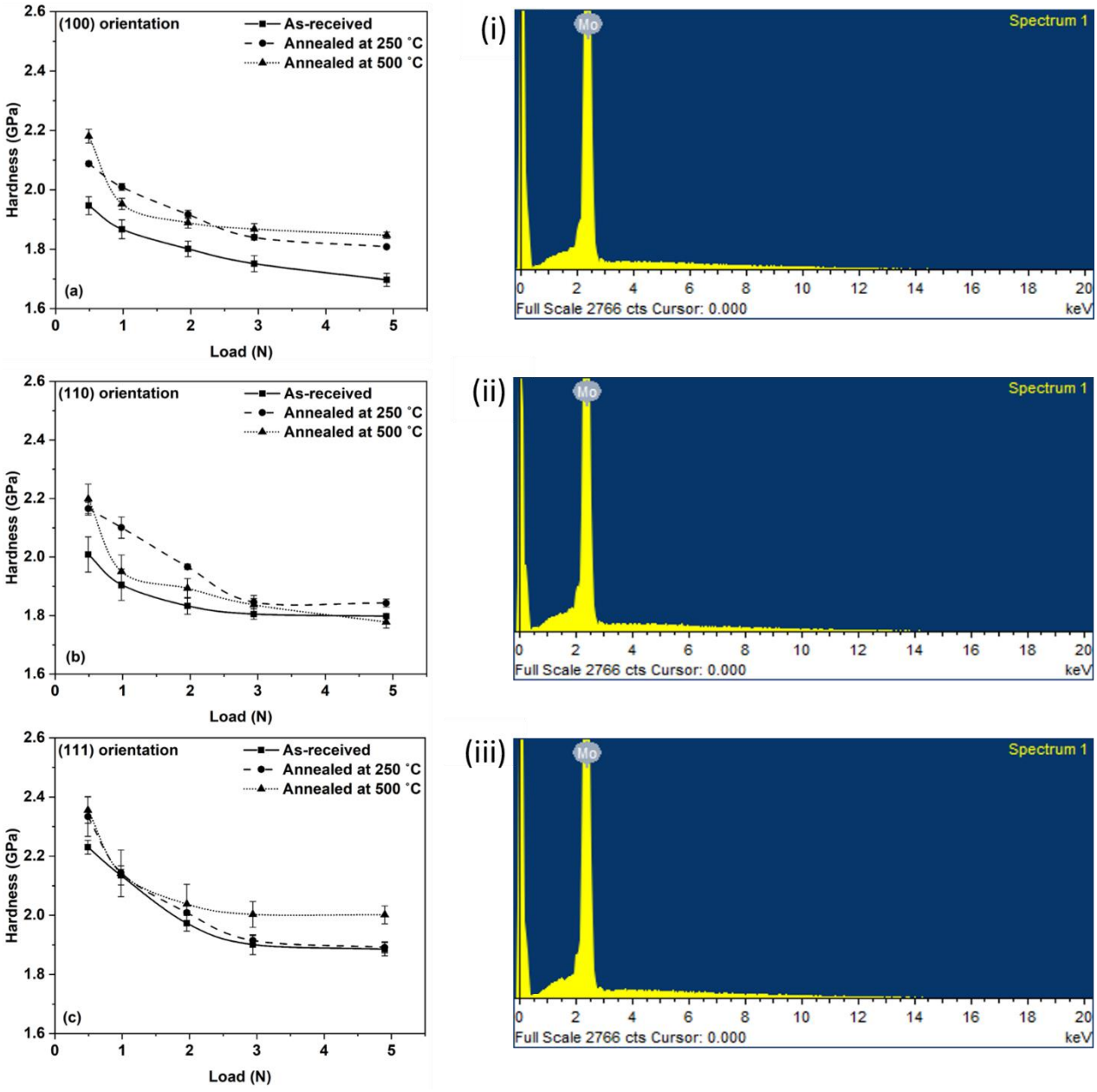


Figure 2.5 The effect of annealing on the relationship of Vickers hardness (H) and indentation load (P) for (a) (100)-, (b) (110)-, and (c) (111)-oriented Mo single crystals (Left). The energy

dispersive X-ray spectroscopy (EDS) analysis of (i) (100)-, (ii) (110)-, and (iii) (111)-oriented Mo single crystals after annealing at 500 °C for one hour (Right).

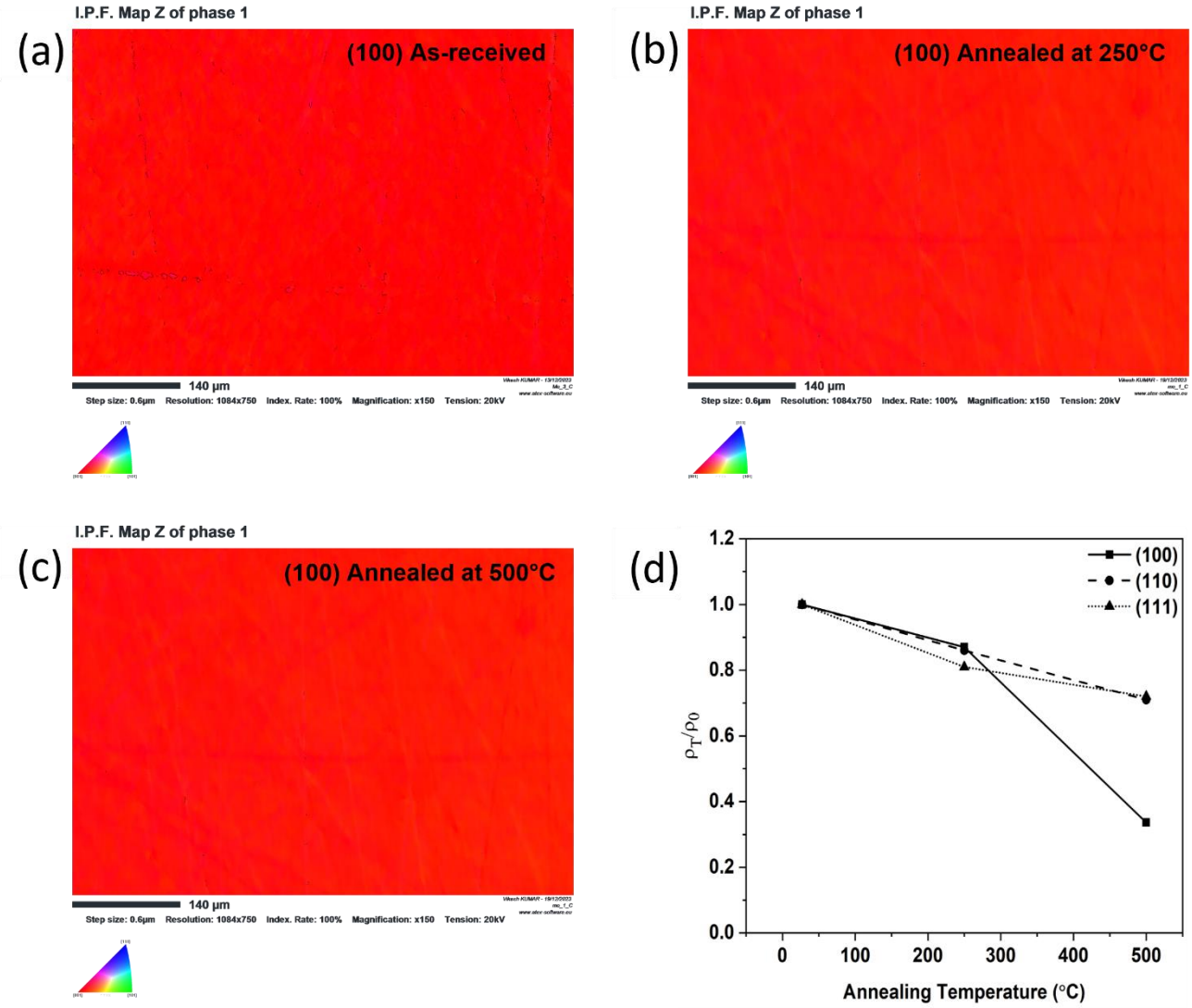


Figure 2.6 Inverse pole figure (IPF) mapping from EBSD analysis of, (a) as-received, (b) annealed at 250 °C, and (c) annealed at 500 °C, (100)-oriented Mo single crystal and (d) shows the variation of normalized dislocation density, $\frac{\rho_T}{\rho_o}$ in Mo single crystals with annealing temperature.

The observed increase in hardness after annealing of Mo single crystals can be correlated with the drop in dislocation sources due to annihilation of dislocation (or dislocation starvation). In this connection, it should be noted that the (Peierls [66]) barriers for dislocation movement are

comprised of both thermal and athermal components [16]. The former depends upon the mechanical energy given to the system during plastic deformation [67], while the latter is associated with the thermal energy supplied to the material [16]. For dislocation to move, the available energy must be sufficient enough to overcome the Peierls barriers. This energy can be either provided by mechanical deformation, thermal energy, or a combination of both. Annealing may offer enough energy for some of the dislocations to move [68]. In BCC crystals, the movement of kinks in screw dislocations (especially in long dislocations) is restricted by point defects [16]. The thermal energy supplied during annealing might overcome these barriers resulting in the depinning of the kinks from point defects, eventually, the dislocations tend to move towards the free surfaces. Thus, the dislocation gets annihilated to the free surfaces, consequently, the number of dislocation sources (or dislocation density) in the annealed samples might decrease. The annihilation of dislocation further increases causing a reduction in dislocation sources with an increase in annealing temperature. The above hypothesis can be verified by determining the dislocation density, ρ in crystals by using XRD patterns shown in figure 2.1 and invoking the Scherrer equation, given as [69]:

$$\rho = \left(\frac{(\beta^2 - \beta_o^2)^{0.5} \cos\theta}{K\lambda} \right)^2 \tag{2.1}$$

Here, the parameters β, β_o, θ and λ represent peak broadening (in radians), initial peak broadening of machine (in radians) Bragg angle (in radians) and wavelength of XRD source, respectively, while K is a fitting constant. The value of λ pertaining to α source is 1.5406 Å and for cubic crystals, K is taken as 0.94. Thus, by employing equation 2.1 and using data displayed in figure 2.1, the dislocation densities ρ_o and ρ_T in an as-received and annealed crystals, respectively, are determined. The variation of normalized dislocation density ρ_T/ρ_o with annealing temperature is shown in figure 2.6 (d) which clearly shows drop in dislocation density after annealing. Thus, it can be concluded from figure 2.6 (d) that thermal energy supplied during annealing caused dislocation annihilation leading to reduction in number of dislocation source or dislocation density in Mo single crystals. This, in turn, results in an enhancement in the yield stress of an annealed crystal in comparison to that of corresponding as-received crystals, because a higher level of stress needs to be applied to activate new dislocation sources for significant macroscopic yielding in an annealed crystal. The increase in the yield strength is reflected as an increase in the

hardness of annealed crystals in the present study (refer to figure 2.5). It must be noted that the enhancement in yield strength and hardness caused by a drop in the number of dislocation sources during low-temperature annealing has also been reported from experiments [36,49] as well as atomistic simulations [70] in nanocrystalline materials. It must be noted that the mechanism discussed above for the increase in yield strength and hardness in Mo single crystal is different from the mechanism responsible for the reduction in strain hardening after annealing in conventional poly-crystalline metals. When a deformed conventional poly-crystalline metal is annealed at a temperature below recrystallization temperature, the dislocation density decreases inside the grains, at grain boundaries and triple junction. All these effects cause a reduction in dislocation-motion induced strain hardening. Moreover, in the XRD plots (refer to figure 2.1) it is observed that after annealing the intensity of the peaks increased. The reduction in dislocation density after annealing makes the crystals more organized and due to this, the planes are more synchronized in the crystal, so the peak intensity increases due to more synchronized parallel planes.

Furthermore, in the crystal, it is interesting to notice that though there is a noticeable reduction in dislocation density with annealing temperature for (110)-oriented crystal too, in figure 2.6 (d), the enhancement in hardness after annealing is insignificant in figure 2.5 (b). This suggests that there are additional factors influencing the post-annealing hardness in Mo single crystals which need to be investigated by employing complementary advanced simulations.

2.4. Summary

In conclusion, the micro-indentation experiments are conducted on annealed as well as as-received (unannealed) Mo single crystals with (100), (110), and (111) orientations using a Vickers indenter. The shapes of indentation imprint are analyzed for all the crystals. Moreover, an increase in hardness with annealing temperature is observed. The route causes for annealing induced hardening are investigated by employing several characterization techniques, including Electron Backscatter Diffraction (EBSD), Energy Dispersive X-ray Spectroscopy (EDS), and X-ray Diffraction (XRD).

Chapter 3

Conclusion and Future Work

3.1 Conclusion

The important observations from the work, reported in Chapter 2, are summarized here. The important conclusions from the present work are as follows:

1) The low-temperature annealing does not alter the crystal structure of the crystals. Thus, single crystallinity remains after annealing for all the crystals.

2) The shape of the indent imprint for (100) orientation looks like a four-sided star due to four-fold symmetry in pile-ups. However, it appears like a power drum and a kite owing to two and three-fold symmetry in pile-ups for (110) and (111) orientation, respectively. The annealing doesn't have any significant effect on the shape and size of the indentation imprint.

3) The hardness decreases with an increase in load and eventually attains a saturation level which signifies that Mo single crystals show indentation size effect (ISE), irrespective of the annealing conditions and their orientation.

4) The (111)-oriented crystal shows the highest hardness for all the annealing conditions which is in corroboration with the trend observed for other BCC crystals such as Tantalum and Tungsten.

5) Annealing results in enhancement in H for (100) orientation, irrespective of the indentation load. In particular, the saturation hardness of (100) orientation increases by around 9% after annealing performed at 500^{o}C. A similar trend is observed for (111) orientation also. By contrast, annealing has an almost negligible effect on the (saturation) hardness for (110) orientation.

6) The marginal enhancement of hardness in Mo single crystals can be correlated with a drop in number of dislocation sources which results in an increase in applied stress for

significant yielding and hence hardness.

3.2 Future Work

Based on the insights obtained from this research, the following studies can be pursued in future:

1) Bonded indentation experiments can be on different orientations of Mo single crystal to understand the slip activation behaviour.

2) Indentation with different strain rates can be performed to understand the effect of strain rate on the hardness of Mo single crystals.

3) FE simulations of indentation can be performed on different Mo single crystals to investigate the active slip systems underneath the indenter.

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