ROLE OF MICROSTRUCTURE ON THE DEFORMATION BEHAVIOUR OF CoCrFeNi BASED HIGH ENTROPY ALLOYS WITH Ti AND Al ADDITIONS

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CERTIFICATE

This is to certify that the thesis entitled "**ROLE OF MICROSTRUCTURE ON THE DEFORMATION BEHAVIOUR OF CoCrFeNi BASED HIGH ENTROPY ALLOYS WITH Ti AND Al ADDITIONS**" is being submitted by **Ms. BUSHRA** to the Indian Institute of Technology Delhi for the award of the degree of **DOCTOR OF PHILOSOPHY**. This is a record of bonafide research work carried out by her under our supervision and guidance. The matter presented in this thesis has not been submitted, in part or in full to any other University or Institute for the award of any degree or diploma.

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Abstract

Metals and their alloys have long served as foundational materials across various industries due to their versatile properties. With advancing technology, the need to enhance and tailor the properties of metals and alloys, has become increasingly crucial to satisfy modern application requirements. High entropy alloys (HEAs) represent a new class of metallic materials characterized by their unique multi-element compositions, providing an expansive range of compositional possibilities and enabling unprecedented opportunities in materials science. HEAs have demonstrated remarkable properties across diverse fields, including outstanding strength, toughness, corrosion resistance, and thermal stability. Due to their superior mechanical and thermal characteristics, HEAs show significant potential as alternatives to conventional structural materials like steel, titanium and Ni super alloys. However, the underlying mechanisms responsible for these exceptional attributes are not yet fully understood in current literature, inspiring researchers to explore the mechanisms behind their unique behavior and to develop methods that would enhance their properties and, hence, broaden their applicability. Among the most promising are CoCrFeNi-based HEAs, which exhibit desirable mechanical properties, particularly when alloyed with Al and Ti. These elements have been shown to improve precipitation strengthening, further enhancing mechanical performance. However, the deformation mechanisms in non-equimolar CoCrFeNi HEAs with Al and Ti additions, particularly the effects of aging and compositional variations on deformation, remain largely unexplored. This thesis presents a systematic investigation into the deformation behavior of $Al_xCo_{1.5}CrFeNi_{1.5}Ti_y$ (where x + y = 0.5, in atomic ratio and x = 0, 0.2, 0.3, 0.5) HEAs, with a specific focus on understanding how alloy composition, aging, and microstructure affect their tensile, strain-hardening and hot deformation properties.

In the initial stages of this study, the four HEA compositions were subjected to solutionizing and peak aging treatments. Tensile tests on both solutionized and peak-aged samples were used to derive stress-strain and strain hardening curves. An increase in Ti content and aging notably enhanced the strength and elevated the strain hardening rate of each alloy. Fractographic analysis revealed that the alloy with highest Ti content has the highest tendency for brittle fractures, showing cleavage features, while the alloy with lowest Ti content retains the most ductile characteristics.

Further, high-resolution transmission electron microscopy was employed to examine the microstructure in deformed regions after tensile tests. The study found that Ti additions increased the work-hardening rate and affected deformation by inducing planar slip and forming Taylor lattices and stacking faults. TEM analysis further confirmed a shift in deformation mechanism from wavy to planar slip as Ti content increased. The precipitation hardening mechanisms varied in various age hardened alloys, with B2 precipitates enhancing hardening through Orowan looping, whereas $L1_2$ precipitates primarily caused hardening through shearing by partial dislocations and the interaction of stacking faults forming Lomer–Cottrell (LC) locks. The deformation substructure, specifically Taylor lattices, were observed exclusively in the solutionized condition, with their formation significantly reduced upon aging, thereby absent in peak-aged conditions. Deformation in all the alloys primarily occurred via planar slip on {111} planes.

The alloy $Al_{0.3}Co_{1.5}CrFeNi_{1.5}Ti_{0.2}$ (Al03Ti02), after aging, emerged as the only alloy among the four to exhibit two types of precipitates in peak-aged condition, achieving the highest yield strength increase while maintaining considerable ductility. Peak aging after 120 hours produced both B2 and $L1_2$ precipitates, resulting in a ~187% increase in yield strength, and a ~214% rise in hardness compared to the solutionized state. Hence, the thesis presents findings from a detailed analysis of the mechanical properties, aging behavior, and strain hardening mechanisms of Al03Ti02 alloy, and was selected as a primary focus for further studies on hot deformation due to its intermediate Ti content and balanced mechanical properties.

Henceforth, the thesis explores the hot deformation behavior of Al03Ti02 alloy at temperatures from 923 K (650 °C) to 1,373 K (1100 °C) and strain rates of 10^{-3} to 1 s^{-1} using a Gleeble® 3800 thermomechanical simulator. Constitutive modeling and processing maps, based on the Dynamic Materials Model, were developed to identify optimal processing conditions and safe work domains. At 923 K, the power-law breakdown was observed, and flow curves showed no softening. While the highest hot workability efficiency (~34%) was found in the 1,300 K (1027 °C) temperature range at strain rates between 0.03 s^{-1} and 1 s^{-1}, the unstable region predominantly occurred within the strain rate range of 0.01 s^{-1} to 1 s^{-1} and the temperature range of 923 K (650 °C) to 1,165 K (892 °C), characterized by the formation of voids and cracks. Dislocation climb and discontinuous dynamic recrystallization were identified as the primary deformation mechanisms.

Overall, this thesis provides a comprehensive understanding of how alloying, aging, and microstructure influence the mechanical and deformation behavior of $Al_xCo_{1.5}CrFeNi_{1.5}Ti_y$ HEAs, with detailed insights into strain hardening and hot deformation mechanisms. These findings underscore the critical role of precipitates, dislocation substructures, and microstructural evolution, and open pathways for optimizing the properties of HEAs through controlled alloying and heat treatment techniques. The outcomes contribute valuable knowledge for developing advanced high-performance materials suitable for demanding structural applications. Future research could focus on exploring the effects of additional alloying elements such as

Mo, Nb, and C in non-equiatomic CoCrFeNi systems, as well as refining grain size through thermomechanical processing, to enhance strength and provide deeper insight into microstructural evolution and deformation mechanisms.

सार

धातुएं और उनके मिश्रधातु लंबे समय से विभिन्न उद्योगों में बुनियादी सामग्री के रूप में प्रयुक्त होते आ रहे हैं, जो अपनी बहुमुखी गुणों के कारण लोकप्रिय रहे हैं। प्रौद्योगिकी के निरंतर विकास के साथ, इनकी विशेषताओं को सुधारना और अनुकूलित करना आवश्यक हो गया है ताकि आधुनिक अनुप्रयोगों की मांग को पूरा किया जा सके। हाई एंट्रॉपी मिश्रधातुएं (HEAs) धातुओं की एक नवीन श्रेणी हैं, जिनकी विशेषता उनकी बहु-तत्वीय संरचना है। यह संरचना व्यापक संयोजन संभावनाएं प्रदान करती है और सामग्री विज्ञान में अभूतपूर्व अवसर खोलती है।

HEAs ने विविध क्षेत्रों में असाधारण गुण प्रदर्शित किए हैं, जैसे उच्च ताकत, कठोरता, संक्षारण प्रतिरोध और तापीय स्थिरता। इनकी बेहतर यांत्रिक और तापीय विशेषताओं के कारण HEAs पारंपरिक संरचनात्मक सामग्रियों जैसे स्टील, टाइटेनियम और निकल आधारित सुपरएलॉय का विकल्प बनने की क्षमता रखते हैं। हालांकि, इन असाधारण गुणों के पीछे के यांत्रिक तंत्र अभी भी पूरी तरह से समझे नहीं गए हैं, जिससे शोधकर्ताओं को इनकी व्यवहारगत विशेषताओं को समझने और इनकी कार्यक्षमता को बढ़ाने के लिए प्रेरणा मिलती है।

CoCrFeNi आधारित HEAs को सबसे अधिक संभावनाशील माना जाता है, विशेषकर जब उन्हें एल्यूमिनियम (Al) और टाइटेनियम (Ti) जैसे तत्वों से मिश्रित किया जाता है। ये तत्व अवक्षेप कड़ीकरण (precipitation strengthening) को बढ़ाते हैं और इस प्रकार यांत्रिक प्रदर्शन को और बेहतर बनाते हैं। हालांकि, गैर-समानुपातिक CoCrFeNi HEAs में Al और Ti के साथ डाली गई संरचना, वृद्धावस्था और यांत्रिक गुणों पर प्रभाव का अध्ययन सीमित रहा है।

इस शोध में $Al_xCo_{1.5}CrFeNi_{1.5}Ti_y$ (जहाँ $x + y = 0.5$; $x = 0, 0.2, 0.3, 0.5$) HEAs की यांत्रिक व्यवहार पर एक प्रणालीबद्ध अध्ययन प्रस्तुत किया गया है, जिसमें मिश्रधातु संरचना, वृद्धावस्था और सूक्ष्मसंरचना के प्रभाव को समझने का प्रयास किया गया है।

शुरुआती चरणों में चारों मिश्रधातुओं को समाधान ताप उपचार (solutionizing) और चरम वृद्धावस्था (peak aging) प्रक्रियाओं से गुजारा गया। तन्यता परीक्षणों (tensile tests) से प्राप्त तनाव-विकृति व कड़ीकरण वक्रों के विश्लेषण से पाया गया कि Ti की मात्रा और वृद्धावस्था से ताकत में वृद्धि हुई और कड़ीकरण दर में उल्लेखनीय सुधार हुआ। फ्रैक्टोग्राफिक विश्लेषण ने दर्शाया कि उच्च Ti वाली मिश्रधातु में भंगुर विखंडन की प्रवृत्ति अधिक थी, जबकि सबसे कम Ti वाली मिश्रधातु अधिक नम्य (ductile) व्यवहार दर्शाती है।

तन्यता परीक्षण के बाद उच्च-रिज़ोल्यूशन ट्रांसमिशन इलेक्ट्रॉन माइक्रोस्कोपी (TEM) से विकृत क्षेत्रों का सूक्ष्म विश्लेषण किया गया। परिणामों से पता चला कि Ti की उपस्थिति से प्लास्टिक विकृति में प्लानर स्लिप, टेलर लैटीस तथा स्टैकिंग फॉल्ट्स जैसी विशेषताएं उत्पन्न होती हैं। L12 प्रकार के अवक्षेप आंशिक विवर्तन द्वारा तथा B2 अवक्षेप ओरवान लूपिंग द्वारा कड़ीकरण में योगदान देते हैं। टेलर लैटीस संरचना केवल सॉल्यूशनाइज्ड अवस्था में देखी गई और पीक एजिंग के बाद पूरी तरह अनुपस्थित थी। सभी मिश्रधातुओं में विकृति मुख्य रूप से {111} तल पर प्लानर स्लिप के माध्यम से हुई।

चारों में से $Al_{0.3}Co_{1.5}CrFeNi_{1.5}Ti_{0.2}$ (Al03Ti02) मिश्रधातु, पीक एजिंग के बाद, $L1_2$ और B2 दोनों प्रकार के अवक्षेप प्रदर्शित करने वाली एकमात्र मिश्रधातु थी। इसमें यील्ड स्ट्रेंथ में ~187% और कठोरता में ~214% की वृद्धि देखी गई। इस संतुलित यांत्रिक गुणों के कारण Al03Ti02 को आगे के हॉट डिफॉर्मेशन अध्ययनों के लिए चुना गया।

आगे शोध में Al03Ti02 मिश्रधातु का हॉट डिफॉर्मेशन व्यवहार 923 K से 1373 K तक की तापमान सीमा और 10^{-3} से 1 s^{-1} की स्ट्रेन रेट सीमा में Gleeble® 3800 थर्मोमैकेनिकल सिम्युलेटर द्वारा अध्ययन किया गया। डायनेमिक मटेरियल्स मॉडल (DMM) पर आधारित कॉन्स्टिट्यूटिव मॉडल और प्रोसेसिंग मैप्स विकसित किए गए, जिससे उपयुक्त प्रसंस्करण स्थितियां और सुरक्षित कार्यक्षेत्र पहचाने जा सके। 923 K पर पॉवर लॉ ब्रेकडाउन देखा गया और फ्लो कर्व्स में कोई सॉफ्टनिंग नहीं दिखी। सबसे उच्च कार्यकुशलता (~34%) 1300 K और 0.03–1 s^{-1} की स्ट्रेन रेट सीमा पर पाई गई, जबकि अस्थिरता क्षेत्र मुख्यतः 923 K–1165 K के बीच था, जिसमें क्रैक और वॉइड्स बनने की प्रवृत्ति देखी गई। प्रमुख विकृति तंत्र में डिस्लोकेशन क्लाइंब और असतत डायनामिक रिक्रिस्टलाइज़ेशन पाए गए।

इस प्रकार, यह शोध AlxCo1.5CrFeNi1.5Tiy HEAs में मिश्रधातु संरचना, वृद्धावस्था और सूक्ष्मसंरचना के प्रभाव को व्यापक रूप से समझाता है और इनके तनाव-कड़ीकरण तथा हॉट डिफॉर्मेशन व्यवहार के अंतर्निहित तंत्रों पर रोशनी डालता है। परिणाम दर्शाते हैं कि नियंत्रित मिश्रधातु संयोजन और हीट ट्रीटमेंट तकनीकों द्वारा HEAs की गुणधर्मों को अनुकूलित किया जा सकता है। भविष्य के शोध में Mo, Nb, तथा C जैसे तत्वों के प्रभाव और थर्मोमैकेनिकल प्रसंस्करण द्वारा ग्रेन आकार नियंत्रण की दिशा में काम किया जा सकता है।

Table of Contents

CERTIFICATE i

Acknowledgements ii

Abstract iv

Table of Contents xi

List of Figures xvi

List of Tables xxvi

List of abbreviations xxvii

List of symbols xxx

1 Introduction 1

2 Literature Review 9

- 2.1 Background 9
- 2.2 Defining HEAs 11
  - 2.2.1 Composition-based definition 11
  - 2.2.2 Entropy-based definition 11
- 2.3 Core effects of HEAs 13
  - 2.3.1 High entropy effect 14
  - 2.3.2 Lattice distortion effect 14
  - 2.3.3 Sluggish diffusion effect 15
  - 2.3.4 Cocktail effects 16

2.4 Composition notation of HEAs ... 17

2.5 Classification of HEAs ... 17

2.5.1 Solid Solutions with BCC Structure ... 20

2.5.2 Solid Solutions with FCC Structure ... 20

2.5.3 Mixture of FCC and BCC Solid Solution Phases ... 21

2.5.4 Solid Solutions with HCP Structure ... 21

2.6 CoCrFeNi based HEAs with Al/Ti additions ... 21

2.6.1 Solid solution strengthening ... 24

2.6.2 Precipitation behaviour and strengthening ... 27

2.6.3 Strain hardening behaviour and dislocation strengthening ... 43

2.6.4 Grain boundary strengthening ... 50

2.7 Hot deformation studies ... 51

2.7.1 Constitutive equations ... 52

2.7.2 Processing maps ... 53

2.8 Potential applications and challenges of HEAs ... 61

2.8.1 Applications ... 61

2.8.2 Challenges ... 63

2.9 Summary ... 64

3 Motivation and Objectives ... 66

4 Materials and Methodology ... 69

4.1 Initial Material ... 69

4.2 Heat treatments 71
  4.2.1 Solutionizing 71
  4.2.2 Aging 71
4.3 Metallography 72
4.4 Material characterization techniques 73
  4.4.1 Optical microscopy (OM) 74
  4.4.2 Scanning electron microscopy (SEM) 74
  4.4.3 Electron backscattered diffraction (EBSD) analysis 74
  4.4.4 X-ray Diffraction (XRD) 76
  4.4.5 Transmission electron microscopy (TEM) 77
4.5 Determination of mechanical properties 79
  4.5.1 Micro-hardness 79
  4.5.2 Tensile testing 79
  4.5.3 Hot compression 80
5 Aging and Tensile Behaviour of Non-Equiatomic CoCrFeNi High Entropy Alloys with Ti and Al Additions 83
5.1 Introduction 83
5.2 Preliminary microstructural characterization 84
5.3 Aging behaviour of Al03Ti02 alloy 91
5.4 Characterization of peak aged alloys 99
5.5 Influence of alloying on tensile behaviour 104
5.6 Influence of aging on tensile behaviour 105

5.7 Fractography 107

5.8 Summary 111

6 Influence of Alloying and Aging Treatment on the Strain Hardening Behavior of Non-Equiatomic CoCrFeNi High Entropy Alloy 113

6.1 Introduction 113

6.2 Influence of alloying on strain hardening behaviour 114

6.3 Influence of aging on strain hardening behaviour 120

6.4 Work hardening behaviour of Al03Ti02 alloy 127

6.4.1 Work hardening behaviour of solution treated Al03Ti02 alloy 128

6.4.2 Work hardening behaviour of peak aged Al03Ti02 alloy 131

6.5 Summary 138

7 Study of Hot Deformation Behaviour and Development of Processing Maps for $Al_{0.3}Co_{1.5}CrFeNi_{1.5}Ti_{0.2}$ HEA 140

7.1 Introduction 140

7.2 Initial microstructure before hot deformation testing 141

7.3 Flow stress behaviour 142

7.4 Constitutive Equation analysis 146

7.5 Processing Maps 152

7.6 Dynamic deformation mechanisms 155

7.7 Summary 166

8 Conclusions and Future work 168

8.1 Conclusions 168

8.2 Future work 172

References 174

Biodata.. 208

List of Figures

Figure 1.1: Historical development of Engineering materials showing the emergence of HEAs. This figure is adapted from reference [5]. 3

Figure 1.2: Year-wise number of publications on High entropy alloys determined from the Scopus database. 3

Figure 1.3: Strength versus ductility properties of common HEAs compared with other conventional alloys [6]. 4

Figure 2.1: (a) Schematic showing in a binary system configurational entropy reaches maximum at equiatomic composition [24], (b) Schematic showing that configurational entropy increases with the number of elements for equiatomic alloys [24]. 10

Figure 2.2: Classification of alloys based on configurational entropies [24]. 12

Figure 2.3: (a) Matrix of a random solid solution containing 10 elements [24] and (b) Schematic illustrating the cocktail effect by transformation of phase from FCC to BCC in $Al_xCoCrCuFeNi$ alloy [41]. 16

Figure 2.4: The classification of HEAs based on the phases present within the alloy [42]. 18

Figure 2.5: Room temperature property data of few HEAs based on the phases present [53]. 19

Figure 2.6: (a) XRD patterns of CoCrFeNi and $CoCrFeNiAl_{0.1}$ HEAs [19], and (b) SEM image of CoCrFeNi HEA showing the presence of single FCC phase [78]. 22

Figure 2.7: Stress – strain data of $CoCrFeNiTi_x$ alloys under compression [78]. 25

Figure 2.8: (a) TEM-EDS analysis of $CoCrFeNiTi_{0.3}$ and (b) SEM-EDS analysis of $CoCrFeNiTi_{0.5}$ HEA [78]. 26

Figure 2.9: Compressive stress strain curves for $Al_xCoCrFeNiTi$ HEA [98]. 26

Figure 2.10: Micro-tensile stress-strain curve of $FeCoNiAl_{0.4}Ti_{0.6}$ HEA [9]. 28

Figure 2.11: Aging behaviour of $Al_{0.5}Co_{1.5}CrFeNi_{1.5}$, $Al_{0.3}Co_{1.5}CrFeNi_{1.5}Ti_{0.2}$, and $Co_{1.5}CrFeNi_{1.5}Ti_{0.5}$ at 750 °C [92]. 29

Figure 2.12: Secondary electron (SE) SEM images showing the microstructure of peak aged (a) $Al_{0.5}Co_{1.5}CrFeNi_{1.5}$, (b) $Al_{0.3}Co_{1.5}CrFeNi_{1.5}Ti_{0.2}$, and (c) $Co_{1.5}CrFeNi_{1.5}Ti_{0.5}$ HEA showing the presence of needle shaped B2, spherical $L1_2$, and cuboidal $L1_2$ precipitates, respectively [92]. 30

Figure 2.13: BF-TEM image showing needle-shaped B2 precipitates in $Al_{0.3}CoCrFeNi$ HEA with inset revealing the dark field TEM image at higher magnification [110]. ..31

Figure 2.14: (a) BF-TEM image and (b) corresponding SADP in [111] zone axis, revealing the presence of B2 precipitates in $Al_{0.5}Co_{1.5}CrFeNi_{1.5}$ HEA [92]. 32

Figure 2.15: SEM microstructure showing formation of $L1_2$ phase in (a) $Co_{1.5}CrFeNi_{1.5}Ti_{0.5}$ and (b) $Al_{0.2}Co_{1.5}CrFeNi_{1.5}Ti_{0.3}$ HEAs [21]. 33

Figure 2.16: TEM images of $(FeCoNiCr)_{89}Ti_6Al_5$ HEA (a) HAADF image revealing an FCC + $L1_2$ + $L2_1$ microstructure; (b) and (c) are corresponding SADPs of different regions in (a), confirming presence of $L2_1$ and $L1_2$ precipitates, respectively [116]. ..34

Figure 2.17: SEM microstructures of $Al_{0.2}Co_{1.5}CrFeNi_{1.5}Ti_{0.3}$ showing (a) CPs/DPs and spherical precipitates at low magnification and (b) CPs formation at grain boundary at high magnification [119]. 35

Figure 2.18: SEM images of the σ phase in $Al_{0.6}CoCrFeNi$ HEA (a) at low magnification and (b) at high magnification [120] 36

Figure 2.19: Schematic diagram of a precipitate – dislocation interaction by: (a) shearing mechanism and (b) Orowan looping mechanism around the precipitates. This figure is drawn from the reference [125]. 37

Figure 2.20: Schematic illustration of the typical precipitate - dislocation interaction mechanism by shearing and/or bowing mechanism in materials as function of radius of precipitate (r) [126]. 38

Figure 2.21: Figure (a) gives the DF-TEM image under two beam condition with condition $g = [220]$, (b) and (d) give STEM image, and (c) and (e) HAADF image, all showing the precipitate shearing of $L1_2$ particles in $(NiCoCr)_{76}(Ni_6AlTi)_3$ alloy [131]. 39

Figure 2.22: BF-TEM image of Ni based super alloy showing Orowan looping of dislocation around $L1_2$ precipitates [132]. 40

Figure 2.23: Schematic illustrating shearing of γ' ordered precipitates by paired dislocations [136]. 41

Figure 2.24: BF-TEM showing coexistence of paired dislocations and partial dislocations in a Ni-based alloy, GH4037 turbine blade [137]. 42

Figure 2.25: (a) The strain hardening curve of a $FeMnCr_{0.25}Co_{0.25}$ HEA subjected to tensile testing along the [123] crystallographic orientation, (b) displays BF-TEM images taken at 18% strain, revealing the formation of deformation twins, (c) and (d) provide BF-TEM images at the failure strain, showing the presence of stacking faults and Taylor dislocation lattices, respectively [153]. 48

Figure 2.26: (a) Strain hardening curve of $Al_{0.3}CoCrFeNi$ HEA, (b) presents a BF-TEM image illustrating the occurrence of twinning, and (c) provides HRTEM image that reveals the presence of a deformation twin [154]. 49

Figure 2.27: (a) BF-TEM image displaying elongated grains with a (111) rolling texture, (b) SADP taken from the area marked as L1 in (a), revealing a single FCC phase, (c) HRTEM image demonstrating SFs and LC locks, and (d) presents the SAD pattern from area L2 in (c), showing streaking of spots [155]. 50

Figure 2.28: Processing map of $Al_{0.3}CoCrFeNi$ HEA at strain $\varepsilon = 0.6$. Instability region is marked in red [169]........58

Figure 2.29: Flow stress curves of Cantor alloy at various temperatures and strain rates [171]. 59

Figure 2.30: EBSD maps of the Cantor alloy showing recrystallized grains that are formed after deformation at various strain rates and temperatures [171]........60

Figure 4.1: Field emission scanning electron microscope machine (JSM 7800F, JEOL) integrated with energy-dispersive X-ray spectrometer and electron backscattered diffraction detector (Oxford Instruments). 76

Figure 4.2: Schematic illustration showing the extraction of TEM samples from regions near the fracture zone of tensile specimens, specifically chosen to study deformation behaviours post-tensile testing........79

Figure 4.3: (a) schematic diagram of the tensile specimen, and (b) Universal testing machine integrated with a video extensometer (Zwick/Roell, Germany). 80

Figure 4.4: (a) Experimental setup for hot compression testing, and (b) schematic of the sample configuration used in the hot compression tests........81

Figure 5.1: Pseudo binary phase diagram of $Al_xCo_{1.5}CrFeNi_{1.5}Ti_y$ (x, y values are in atomic ratio, $x + y = 0.5$). 85

Figure 5.2: As-cast microstructures of (a) Al05, showing absence of second phase particles, (b) Al03Ti02, (c) Al02Ti03 and (d) Ti05, showing the presence of second phase intermetallic, indicated by blue arrows. Black arrow in (b) points at the FCC (γ) phase. 87

Figure 5.3: EDS mapping of the as-cast (a) Ti05 and (b) Al03Ti02 alloy showing presence of (Ni, Ti)-rich and (Ti, Co)-rich regions. 88

Figure 5.4: Solutionized microstructures of (a) Al05, (b) Al03Ti02, (c) Al02Ti03, and (d) Ti05 consisting of single FCC phase. 90

Figure 5.5: (a) Phase map, and (b) IPF image from EBSD showing single phase γ grains; (c) XRD diffraction pattern of the Al03Ti02 solutionized alloy. 90

Figure 5.6: Aging curve of Al03Ti02 at 750 °C for various times from 0 h to 1500 h showing peak hardness at 120 h 91

Figure 5.7: SEM images of under-aged microstructure at 24 h of aging Al03Ti02 alloy at (a) lower magnification indicating B2 and $L1_2$ precipitates, and at (b) higher magnification indicating presence of $L1_2$ precipitates. 92

Figure 5.8: Peak aged microstructure of Al03Ti02 alloy showing presence of B2 (indicated by white arrows) and $L1_2$ precipitates (indicated by red arrow). Image (a) is taken at 3000x magnification while (b) and (c) are taken at 10,000x and 25,000x, respectively. 93

Figure 5.9: SEM images of the over-aged microstructure of the Al03Ti02 alloy after 400 hours of aging, displaying (a) and (b) cellular precipitates along grain boundaries, and (c) and (d) $L1_2$ and B2 precipitates within the matrix. 94

Figure 5.10: TEM analysis of peak aged condition sample showing: (a) SAD pattern taken in $Z = [112]_{FCC}$ confirming γ (FCC); (b) dark field image from the superlattice spot encircled in red in (a). The dashed circle in red in (b) indicates a γ′ ($L1_2$) precipitate; (c) TEM-EDS confirming the presence of [Ni_3(Al, Ti)] type $L1_2$ precipitates; (d) bright field image showing B2 precipitates present in the microstructure, (e) corresponding SAD pattern, $Z = [011]_{B2}$. 95

Figure 5.11: Aging behavior of different CoCrFeNi based HEAs containing varying additions of Al and Ti at 750 °C [92]. 98

Figure 5.12: (a) BF-TEM image of peak aged Al05 alloy showing B2 precipitates, (b) corresponding SAD pattern indicating Kurdjumov-Sachs (K-S) orientation relationship between B2 and FCC matrix. 100

Figure 5.13: (a) BF-STEM image of the peak-aged Al05 alloy, revealing the presence of B2 precipitates, (b-f) TEM-EDS elemental maps revealing precipitates are rich in Ni and Al........ 101

Figure 5.14: (a) and (b) BF-TEM images of peak aged Al03Ti02 alloy, indicating presence of $L1_2$ and B2 precipitates. (c) and (d) show the corresponding SAD patterns confirming them. SAD pattern given in (d) is taken from the blue encircled region in (b). 102

Figure 5.15: (a) and (b) show BF-TEM images of the peak-aged Al02Ti03 and Ti05 alloys, respectively, indicating the presence of $L1_2$ precipitates. The corresponding SAD patterns in (c) for Al02Ti03 and (d) for Ti05 confirm the formation of these $L1_2$ precipitates........ 103

Figure 5.16: True stress-strain plots for different alloys showing the effect of elemental addition on tensile behaviour in solutionized condition........ 104

Figure 5.17: (a), (b), (c), and (d) True stress-strain graphs of Al05, Al03Ti02, Al02Ti03, and Ti05, respectively in solutionized revealing the effect of aging on the tensile behaviour of these alloys. 106

Figure 5.18: SEM fractographic images of the solutionized alloys: (a) Al05, (b) Al03Ti02, (c) Al02Ti03, and (d) Ti05, illustrating the progressive reduction in dimples and the increasing presence of cleavage features as Ti content increases from Al05 to Ti05........ 108

Figure 5.19: SEM fractographic images of the peak aged alloys: (a) Al05, (b) Al03Ti02, (c) Al02Ti03, and (d) Ti05, showing reduction in dimples and increase in cleavage features as Ti content increases from Al05 to Ti05. 109

Figure 5.20: SEM micrographs showing tensile fracture surface of (a) solutionized and (b) peak aged Al03Ti02 HEA. 110

Figure 6.1: Strain hardening plots for different alloys in the solutionized condition, illustrating the effect of elemental additions on strain hardening behavior. The arrow indicates an increase in work hardening with increasing Ti concentration. 115

Figure 6.2: BF-TEM images after deformation by tensile loading of different alloys (a) Al05; (b) Al03Ti02; (c) Al02Ti03; (d) Ti05 in solutionized condition. All the images have been taken at the fracture strain except for (a1) which is taken at 1% strain. (a1) Dislocation cells and (a2) HDDWs are being formed in Al05. With the introduction of Ti in the system, SFs (b1), (c1), (d1) and Taylor lattices (b2), (c2), (d2) are formed. 118

Figure 6.3: (a), (b), (c), and (d) Strain hardening plots of Al05, Al03Ti02, Al02Ti03, and Ti05, respectively in solutionized and peak aged conditions revealing the effect of aging on the strain hardening behaviour of these alloys. 121

Figure 6.4: BF-TEM images after deformation by tensile loading of HEAs in peak-aged condition. All images are at fracture strain except (a1), taken at 1% strain. (a) Dislocation forests around B2 precipitates in Al05. Numerous intersecting SFs can be seen in (b), (c), and (d): (b2) STEM-BF image shows slip traces along {111} planes intersecting at ~70°. Insets in (b1) and (c2) show FFT images with spot streaking (green arrows), confirming SF presence. 124

Figure 6.5: HRTEM images of peak aged (a) Al05 and (b) Ti05 alloys showing the boundaries between FCC matrix and precipitate. Matrix and B2 precipitates in (a) Al05

alloy are separated by an incoherent boundary while as FCC matrix and $L1_2$ precipitates share a coherent boundary in (b) Ti05. The insets in (b) are the FFT images pertaining to FCC and $L1_2$ phase. 125

Figure 6.6: Strain hardening plots for solutionized and peak aged condition of Al03Ti02. 128

Figure 6.7: TEM images of solutionized Al03Ti02 HEA tensile tested to fracture: (a) BF image showing the presence of numerous stacking faults (marked with yellow arrows) and LC lock; (b) Magnified image taken from a region in (a) showing intersection of stacking faults. The inset shows FFT image with crossing diffraction fringes marked by arrows confirming the presence of SFs instead of twinning; (c) BF image showing dislocation substructures, i.e., Taylor lattice and SFs. 130

Figure 6.8: TEM images taken along z = [011] of the peak aged Al03Ti02 HEA: (a) and (b) STEM-BF images and their corresponding HAADF images in the insets. (a) shows a high density of dislocation pairs and $L1_2$ precipitates, (b) Orowan looping is seen around $L1_2$ precipitates which coexist with the dislocation pairs. Green arrows mark dislocation pairs, yellow arrows point out Orowan loops, and red arrows indicate $L1_2$ precipitates. 134

Figure 6.9: TEM images taken along z = [011] of the peak aged Al03Ti02 alloy tensile tested to fracture: (a) HRTEM image showing the absence of ordered $L1_2$ phase, which is confirmed by the (b) FFT given in the inset; (c) IFFT of marked region in (a) showing the presence of SFs and numerous dislocations; (d) BF image showing the presence of SFs marked with arrows, LC locks and high-density dislocation walls (HDDWs). SADP in the inset confirms the presence of SFs and no twinning; (e) STEM-BF image revealing the {111} slip traces intersecting at ~ 70°. 137

Figure 7.1: EBSD maps of the hot rolled Al03Ti02 HEA showing (a) inverse pole figure (IPF) map, (b) phase map, and (c) kernel average misorientation (KAM) map........ 142

Figure 7.2: (a) Cylindrical sample used for hot compression testing, and (b) sample after the hot compression testing up to 50% strain under specific temperature and strain rate... 143

Figure 7.3: True stress- strain compression flow curves for Al03Ti02 HEA at different temperatures and strain rates... 144

Figure 7.4: Variation of stress at ε = 0.5 with (a) strain rate at various temperatures and (b) temperature at various strain rates for Al03Ti02 HEA alloy. 144

Figure 7.5: Constitutive equation plots relating (a) $ln\varepsilon\ vs. ln\sigma$, (b) $ln\varepsilon\ vs. \sigma$, and (c) $ln\varepsilon\ vs. ln\ [sinh\alpha\sigma]$ at various temperatures; (d) plot between $ln\ sinh\ (\alpha\sigma) vs. 1/T$ at various strain rates. 148

Figure 7.6: Graph of $ln(Z)$ vs $ln\ [sinh\ (\alpha\sigma)]$ for Al03Ti02 alloy incorporating data points from all temperatures considered in this study. Data points encircled by the black dashed line correspond to 923 K (650 °C), showing significant deviation and disrupting the overall hypothetical linear trend of the dataset. 149

Figure 7.7: Fitting of (a) $ln\varepsilon\ vs\ ln\sigma$, (b) $ln\varepsilon\ vs\ \sigma$, (c) $ln\varepsilon\ vs\ ln\ [sinh\alpha\sigma]$ (d) $ln\ sinh\ (\alpha\sigma) vs\ 1/T$, and (e) $ln(Z)$ vs. $ln\ [sinh\ (\alpha\sigma)]$ plots, while only considering temperatures greater than 1,000 K (727 °C) to calculate the material parameters for the development of constitutive equation. 151

Figure 7.8: Processing map of Al03Ti02 at 0.5 strain, showing three regions with different efficiencies. 154

Figure 7.9: Micrographs showing (a) EBSD-IPF map and (b, c) optical micrographs of the alloy post-deformation at 923 K (650 °C)/1 s − 1, aligning with the domain III of the processing map.. 157

Figure 7.10: TEM images of the post-deformed alloy at 923 K (650 °C)/$0.1\,\mathrm{s}-1$, aligning with domain III in the processing map. (a) BF TEM image showing a stacking fault; (b) and (c) SAD patterns from regions marked by red and yellow circles in (a), respectively; (d) and (e) HRTEM images of the area highlighted by the yellow circle in (a); (f), (g), and (h) FFT patterns from regions 1, 2, and 3 respectively in (d) and (e), showing the existence of (f) FCC phase, (g) coexistence of FCC and B2 phases, and (h) tetragonal σ phase. 159

Figure 7.11: TEM micrographs of the alloy post-deformation at (a, b, and c) 1,223 K (950 °C)/0.01 s^{-1} and (d, e, and f) 1,373 K (1100 °C)/0.1 s^{-1}, corresponding to domain II and domain I of the processing map, respectively (a) BF TEM image; (b) and (c) SAD patterns from regions marked by circles in red in (a), revealing the presence of L1$_2$ and B2 phase respectively, along with the FCC phase. (d) BF TEM image showing presence of sub grain boundaries and DRX grain; (e) and (f) SAD patterns from regions marked by red circles in (d), revealing the presence of single FCC phase............................. 161

Figure 7.12: EBSD maps of Al03Ti02 HEA post hot deformation at different conditions corresponding to different domains in the processing map. (a) Domain II (1,223 K (950 °C), 0.01s^{-1}), (b) domain I (1,373 K (1100 °C), 0.1s^{-1}), and (c) domain I (1,373 K (1100 °C), 1s^{-1}). (a1), (b1), and (c1) are the IPF maps of the alloy showing complete microstructure at the respective conditions while (a2), (b2), and (c2) are the corresponding IPF maps highlighting only the recrystallized grains with GOS < 3°. (a3), (b3), and (c3) are the grain boundary maps revealing HAGBs (> 15°) in black, LAGBs (5° - 15°) in green, and $\Sigma3$ twin boundaries in red. Scale bar is same as (a) for all the other images of this figure. 164

Figure 7.13: SEM micrograph corresponding to domain II of the processing map at 1,223 K (950 °C), 0.01s^{-1} revealing the occurrence of grain boundary bulging. 165

List of Tables

Table 2.1: Configurational entropies of some traditional alloys [24]. 13

Table 4.1: Nominal chemical compositions of the as-cast HEAs used in this work... 71

Table 5.1: Mixing enthalpies of different elemental pairs [182]................................. 88

Table 5.2: Mechanical properties of solutionized and peak aged Al03Ti02 HEA samples upon tensile testing 106

Table 7.1: Hot deformation parameters for constitutive equation of Al03Ti02 HEA at ε = 0.5 152

List of abbreviations

HEA	High Entropy Alloy
Al02Ti03	$Al_{0.2}Co_{1.5}CrFeNi_{1.5}Ti_{0.3}$ (in atomic ratio)
Al03Ti02	$Al_{0.3}Co_{1.5}CrFeNi_{1.5}Ti_{0.2}$ (in atomic ratio)
Al05	$Al_{0.5}Co_{1.5}CrFeNi_{1.5}$ (in atomic ratio)
APB	Anti-Phase Boundaries
BCC	Body Centered Cubic
BF	Bright Field
CALPHAD	CALculation of PHAse Diagrams
CDRX	Continuous Dynamic Recrystallization
CRSS	Critical Resolve Shear Stress
DDRX	Discontinuous Dynamic Recrystallization
DF	Dark Field
DMM	Dynamic Materials Modeling
DRV	Dynamic Recovery
DRX	Dynamic Recrystallization
EBSD	Electron Backscatter Diffraction
EDM	Electrical Discharge Machining
EDS	Electron Dispersive Spectroscopy
FCC	Face Centered Cubic
FFT	Fast Fourier Transformation
GOS	Grain Orientation Spread
HAADF	High Annular Angular Dark Field
HAGB	High-Angle Grain Boundaries

HCP	Hexagonal Cubic Packed
HDDW	High-Density Dislocation Wall
HRTEM	High Resolution Transmission Electron Microscopy
IFFT	Inverse Fast Fourier Transformation
IPF	Inverse Pole Figure
KAM	Kernal Average Misorientation
K-S	Kurdjumov-Sachs
LAGB	Low-Angle Grain Boundaries
LC Locks	Lomer-Cottrell Locks
MEA	Medium Entropy Alloy
OES	Optical Emission Spectrometer
OM	Optical Microscopy
PLB	Power Law Breakdown
SAD	Selected Area Diffraction
SEM	Scanning Electron Microscopy
SF	Stacking Fault
SFE	Stacking Fault Energy
SRO	Short Range Ordering
STEM	Scanning Transmission Electron Microscopy
TDL	Taylor Dislocation Lattice
TEM	Transmission Electron Microscopy
Ti05	$Co_{1.5}CrFeNi_{1.5}$Ti0.5 (in atomic ratio)
TRIP	Transformation Induced Plasticity
TWIP	Twinning Induced Plasticity

UTS	Ultimate Tensile Strength
VEC	Valence Electron Configuration
WHR	Work Hardening Rate
XRD	X-Ray Diffraction

List of symbols

Δs_{conf}	Configurational entropy
R	Universal gas constant
k_B	Boltzmann constant
x_i	Mole fraction of i^{th} element
N	Number of elements
ΔG	Free energy change
ΔH	Enthalpy change
T	Temperature
σ_y	Yield stress
ε_f	Strain to fracture
σ_0	Frictional stress
k_s	Solid solution strengthening coefficient
c	Solute concentration
σ	Sigma phase
B2	Ordered BCC phase
$L1_2$ (γ′)	Ordered FCC phase
γ	Gamma (FCC)
r^*	Critical precipitate size
b	Burgers vector
G	Shear modulus
δ	Lattice misfit
a_{ppt}	Lattice parameter of precipitate

a_γ	Lattice parameter of gamma matrix
σ_{sh}	Shearing stress associated with full dislocation
σ_c	CRSS associated with paired dislocation
σ_{Or}	Orowan dislocation looping stress
M	Taylor Factor
γ_{APB}	Anti-phase boundary energy
f	Volume fraction of precipitates
l, λ_P	Average inter-particle distance
r_0	Dislocation core radius
ν	Poisson ratio
ρ	Dislocation density
k_y	Hall-Petch constant
Q	Activation energy of deformation
Z	Zener–Holloman parameter
A, n', β, α, b	Material constants
σ	Flow stress
n	Stress exponent
$\dot{\varepsilon}$	Strain rate
P	power dissipated during deformation
G	power lost as heat due to deformation processes
J	power associated with microstructural variations
m	strain rate sensitivity
η	power dissipation efficiency
$\xi(\dot{\varepsilon})$	Flow instability parameter