

**ALLOYING AND PRE-DEFORMATION  
EFFECTS ON THE AGING RESPONSE OF  
FCC BASED  $\text{Co}_{1.5}\text{CrFeNi}_{1.5}$  HIGH ENTROPY  
ALLOYS WITH VARYING Ti AND Al  
CONTENTS**

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**DEPARTMENT OF MATERIALS SCIENCE AND  
ENGINEERING**

**INDIAN INSTITUTE OF TECHNOLOGY DELHI**

**AUGUST 2021**

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**By**

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**Submitted**

**In fulfillment of requirements of the degree of Doctor of Philosophy**

**to the**



**INDIAN INSTITUTE OF TECHNOLOGY DELHI**

**AUGUST 2021**

# CERTIFICATE

This is to certify that the thesis entitled “**ALLOYING AND PRE-DEFORMATION EFFECTS ON THE AGING RESPONSE OF FCC BASED  $\text{Co}_{1.5}\text{CrFeNi}_{1.5}$  HIGH ENTROPY ALLOYS WITH VARYING Ti AND Al CONTENTS**” being submitted by **Mr. VICKEY NANDAL** 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 him 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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## Acknowledgments

First and foremost, I would like to express my profound and sincere gratitude to my supervisors **Dr. Jayant Jain** and **Dr. Suresh Neelakantan**, for their encouragement and excellent guidance throughout my research work as a Research scholar. Without their timely and untiring guidance, this thesis would not have been possible. Their vast pool of ideas and tremendous energy for research and teaching has been a constant source of inspiration for me. The confidence and experience I gained from research work, teaching assistantship and various projects assigned to me will go a long way in my entire life.

I would also like to thank SRC members Prof. Rajesh Prasad, Prof. D. Ravi Kumar and Dr. Nitya Nand Gosvami for their constant motivation. Their invaluable suggestions and comments have helped me tackle and overcome different aspects during my research work. I also express my profound gratitude to Prof. An-Chou Yeh at NTHU Taiwan for providing me HEA samples for this research.

I would also like to thank Prof. Sudhanshu Shekhar Singh for helping me out with SEM and TEM characterization. I am genuinely grateful for his help and support in using the ACMS facility at IIT Kanpur. Special thanks to Mr. R. Sarvesha for helping me diligently with these experiments. I will miss my heated discussions and the tireless nights in laboratories. My thanks to Mr. B. Prasad, for allowing me to access and learn various scientific equipment here at IIT Delhi.

Life is better with friends. Special thanks to my beloved colleagues - Anuz Zindal, Aditya Gokhale, Gaurav Singh, Shanta Mohapatra, Aravi Muzaffar, Prashant Mittal, Deepak Chauhan, Shrikanth S, Noorudin Ansari, Ranjeet Kumar, Amit Prasad, Kasi Maniyan, Chetan Singh, Abhishek Rastogi and Himanshu Rai for making the lab a lively place to work and learn. I am fortunate to have friends like Dharmendra Jangra,

Nimish Joseph, Sajan Wahi, Ajay Lodhi, Hardeep Singh, Sandeep Yadav, Sayandev, Ved Prakash, Vinay Saini, Anil Malik, Deepak Singh, Anoop Panduria, Saurabh Chandrakar, Manendra Singh, Abhinav Chatterjee, Girish Verma, Deverashi Maurya, Akhil Garg, Ritik Pugla, Manish Kashyap, Lakshay Kathuria, Sachin, Rahul, Sachin Khurana, Chirag Chandna, Sahib Saluja, Minal Yadav, Sahil Pasricha, Varun Tripathi, Nikita Khatri, Karishma Yadav and Arpita Singh for always being there whenever I needed you.

I would like to thank the Department of Applied Mechanics and Department of Materials Science and Engineering for allowing me to use various instruments. I am also thankful for the opportunities I got a chance to contribute, including international conferences and departmental activities. Special thanks to Prof. Kiran Seth and the whole SPICMACAY team for allowing me to lead during the 5<sup>th</sup> international convention at IIT Delhi. I would like to thank Dean Student Affairs, Dean Academics, CAIC, and SAC teams for your support during my tenure as the institute's Ph.D. representative. The confidence and leadership experience I gained will go a long way and help in my entire life. A big thanks to the staff and management of the Jwalamukhi hostel for making my stay more comfortable. Needless to say, hostel life will always be missed.

Lastly, but most importantly, I am immensely glad to value the unconditional love and encouragement provided by my family. My father, Kuldeep Singh; mother, Raj Bala Devi; brother, Ravinder Nandal; sister-in-law, Pooja Dagar Nandal and my whole Nandals' family - words cannot describe it, but I am sure you know it. This work is for you, my late grandfather Bharat Singh Patwari and my late grandmother Dhanpati Devi.

**VICKEY NANDAL**

## Abstract

High entropy alloys (HEAs) are a new class of materials formed with five or more elements in equiatomic or non-equiatomic proportions. They are also known as multi-principal element (MPEs) alloys or complex concentrated alloys (CCAs). HEAs have attracted much attention from materials scientists in recent years because of their unique compositions, excellent thermal stability, microstructures and adjustable properties. This Ph.D. dissertation presents the research work conducted to develop precipitation-hardenable high entropy alloys using face-centered cubic (FCC) non-equiatomic  $\text{Co}_{1.5}\text{CrFeNi}_{1.5}$  quaternary base system. The additions of aluminium (Al) and titanium (Ti) contents in the base system make the alloy amenable for precipitation hardening (through aging) by formation of the second phases in the FCC matrix. The addition of Ti specifically alters the grain size and precipitation hardening kinetics. Further the precipitation due to these elemental additions play a vital role in modifying the alloys mechanical properties.

A combinational approach has been used to assess the compositional, microstructural and property relationships. Vacuum arc melted  $\text{Al}_x\text{Co}_{1.5}\text{CrFeNi}_{1.5}\text{Ti}_y$  (where x, y values in atomic ratio, such that  $x + y = 0.5$ ) HEAs were selected for this study. Based on composition variation, three promising FCC-based precipitation-hardenable alloys have been identified-  $\text{Al}_{0.5}\text{Co}_{1.5}\text{CrFeNi}_{1.5}$  (labelled as  $\text{Al}_{05}$ ),  $\text{Al}_{0.2}\text{Co}_{1.5}\text{CrFeNi}_{1.5}\text{Ti}_{0.3}$  (labelled as  $\text{Al}_{02}\text{Ti}_{03}$ ) and  $\text{Co}_{1.5}\text{CrFeNi}_{1.5}\text{Ti}_{0.5}$  (labelled as  $\text{Ti}_{05}$ ). With the addition of Al content, elongated grains have been observed after solutionization treatment. Whereas, with an increase in Ti content, there was a gradual change from coarse columnar shaped grains to near equiaxed grains. Additionally, an increase in hardness value was observed due to the

significant lattice distortion in HEAs, revealing the contribution of solid solution hardening, primarily in solutionized condition.

The aged  $\text{Al}_{05}$ ,  $\text{Al}_{02}\text{Ti}_{03}$  and  $\text{Ti}_{05}$  alloys were strengthened with two different structured precipitates. One with body-centered cubic (BCC) based B2 structured needle-shaped precipitates in  $\text{Al}_{05}$ , the other was FCC based  $\text{L}_{12}$  structured spherical- and cuboidal- shaped precipitates in both  $\text{Al}_{02}\text{Ti}_{03}$  and  $\text{Ti}_{05}$  alloys. Transmission electron microscopy (TEM) studies have been performed to confirm the crystal structure of precipitates formed in the aged HEAs. The microstructure observation suggests that the morphology of precipitates varies with the addition of elements (i.e., Ti and Al). The microhardness results show that the  $\text{Ti}_{05}$  alloy has the highest peak hardness compared to  $\text{Al}_{02}\text{Ti}_{03}$  and  $\text{Al}_{05}$  HEAs. These changes were attributed to the finer precipitate distribution within grains.

The effect of different variables, such as aging temperature, quenching medium and pre-deformation (i.e., pre-strain prior to aging) on the microstructure evolution and age-hardening behavior of HEAs have also been investigated. It has been observed that the aging temperature and quenching medium significantly affect the age-hardening behavior, especially for  $\text{Al}_{05}$  and  $\text{Al}_{02}\text{Ti}_{03}$  HEAs. The key factor includes a higher hardness, excellent thermal stability, and a higher number density of precipitates. For 650 °C and 750 °C, a significant age-hardening behavior has been observed compared to 850 °C. It was attributed to the higher number density of precipitates. The precipitation hardening response and precipitate characteristics for brine quenched and water quenched has been found to be significantly different compared to air-cooled samples. The higher hardness value, finer distribution and the higher number density of precipitates were observed in brine quenched and water quenched samples. Further, the precipitation hardening behavior was found to be significantly affected by the pre-deformation prior to the aging



treatment. The key effects include shorter peak-aging time (i.e., from 240 h to 50 h), higher peak hardness, and distinct over-aging behavior. It is attributed to an increased number density of precipitates for all the three HEAs in their solution-treated and pre-deformed (labelled as ST-PS) conditions, than the solution-treated (labelled as ST) conditions. In addition to this, the coarsening kinetics of precipitates for Al<sub>05</sub> and Al<sub>02</sub>Ti<sub>03</sub> HEAs are significantly faster in ST-PS samples than ST samples, while it remained similar for Ti<sub>05</sub> in both sample conditions due to broader precipitate size distribution observed in ST-PS than in ST samples.

Furthermore, the yield stress ( $\sigma_y$ ) of the three HEAs subjected to various treatments such as aging, pre-deformation, different quenching medium and various aging temperatures has been predicted using the Ashby-Orowan model. The yield stresses ( $\sigma_y$ ) of the three HEAs were also estimated using the experimental obtained hardness values following the Tabor's model. These models were used to understand the contributions of precipitates (i.e., Ashby-Orowan model) to the overall strength (i.e., Tabor's model) of the aged samples. The predicted and estimated  $\sigma_y$  values were successfully correlated for the aged HEAs and have been validated with their experimental  $\sigma_y$  values from the literature. The results suggest a good agreement between predicted, estimated, and experimental yield strength values. The observed results emphasize the role of precipitation characteristics in controlling the strength of the aged HEAs.

From the comprehensive studies carried out, it is clear that the Co<sub>1.5</sub>CrFeNi<sub>1.5</sub> alloys with Ti and Al additions present the potential to offer high strength and excellent thermal stability through precipitation strengthening, suitable for several high-temperature applications.

## सार

हार्ड एन्ट्रॉपी एलाय (एचईए) समपरमाण्विक या गैर-समतुल्य अनुपात में पांच या अधिक तत्वों के साथ गठित सामग्री का एक नया वर्ग है। उन्हें बहु-प्रमुख तत्व (एमपीई) मिश्र या जटिल केंद्रित मिश्र (सीसीए) के रूप में भी जाना जाता है। हाल के वर्षों में एचईए ने सामग्री वैज्ञानिकों से उनकी अनूठी रचनाओं, उत्कृष्ट थर्मल स्थिरता, माइक्रोस्ट्रक्चर और समायोज्य गुणों के कारण बहुत ध्यान आकर्षित किया है। यह पी.एच.डी. शोध फेस-सेंटर्ड क्यूबिक (एफसीसी) गैर-समतुल्य  $\text{Co}_{1.5}\text{CrFeNi}_{1.5}$  चतुर्धातुक आधार प्रणाली का उपयोग करके प्रेसिपिटेशन हार्डनिंग हार्ड एन्ट्रॉपी एलाय धातुओं को विकसित करने के लिए किए गए शोध कार्य को प्रस्तुत करता है। बेस सिस्टम में एल्युमिनियम और टाइटेनियम की सामग्री के संकलन से मिश्रधातु एफसीसी मैट्रिक्स में दूसरे चरणों के गठन के द्वारा प्रेसिपिटेशन हार्डनिंग (एजिंग के माध्यम से) के लिए उत्तरदायी हो जाती है। टाइटेनियम का संकलन विशेष रूप से ग्रेन साइज और प्रेसिपिटेशन हार्डनिंग करने वाले कैनेटीक्स को बदल देता है। इसके अलावा इन एलेमेंटल परिवर्धन के कारण होने वाली प्रेसिपिटेशन हार्डनिंग मिश्र धातु के यांत्रिक गुणों को संशोधित करने में महत्वपूर्ण भूमिका निभाती है।

कम्पोजीशन, माइक्रोस्ट्रक्चर और गुण संबंधों का आकलन करने के लिए एक संयोजन दृष्टिकोण का उपयोग किया गया है। वैक्यूम आर्क मेल्टेड  $\text{Al}_x\text{Co}_{1.5}\text{CrFeNi}_{1.5}\text{Ti}_y$  (जहां  $x, y$  ऐटमिक अनुपात में है, जैसे कि  $x + y = 0.5$ ) एचईए का चयन इस अध्ययन के लिए किया गया है। कम्पोजीशन भिन्नता के आधार पर, तीन आशाजनक एफसीसी-आधारित प्रेसिपिटेशन हार्डनिंग मिश्र धातुओं की पहचान की गई है-  $\text{Al}_{0.5}\text{Co}_{1.5}\text{CrFeNi}_{1.5}$  ( $\text{Al}_{0.5}$  के रूप में लेबल),  $\text{Al}_{0.2}\text{Co}_{1.5}\text{CrFeNi}_{1.5}\text{Ti}_{0.3}$  ( $\text{Al}_{0.2}\text{Ti}_{0.3}$  के रूप में लेबल) और  $\text{Co}_{1.5}\text{CrFeNi}_{1.5}\text{Ti}_{0.5}$  ( $\text{Ti}_{0.5}$  के रूप में लेबल) किया गया है। एल्युमिनियम सामग्री के संकलन से अतिरिक्त, सलूशन उपचार के बाद आकार में बड़े और लम्बे ग्रेन देखे गए हैं। जबकि, टाइटेनियम सामग्री में वृद्धि के साथ, मोटे स्तंभ के

आकार के ग्रेन से लगभग समान ग्रेन में धीरे-धीरे परिवर्तन हुआ। इसके अतिरिक्त, एचईए में महत्वपूर्ण लैटिस डिस्टॉरशन के कारण हार्डनेस मूल्य में वृद्धि देखी गई, जो सॉलिड सलूशन हार्डनिंग करने के योगदान को प्रकट करती है, मुख्य रूप से सलूशन उपचार की स्थिति में।

एज्ड  $Al_{05}$ ,  $Al_{02}Ti_{03}$  और  $Ti_{05}$  मिश्र दो अलग-अलग स्ट्रक्चर प्रेसिपिटे के साथ मजबूत किए गए थे। एक बॉडी-सेंटरड क्यूबिक (बीसीसी) आधारित B2 स्ट्रक्चर सुई के आकार का प्रेसिपिटे  $Al_{05}$  में, दूसरा एफसीसी आधारित  $L_{12}$  स्ट्रक्चर गोलाकार प्रेसिपिटे  $Al_{02}Ti_{03}$  में और क्यूबॉइडल आकार के प्रेसिपिटे  $Ti_{05}$  मिश्र धातुओं में थे। एज्ड एचईए में बनने वाले प्रेसिपिटे के क्रिस्टल स्ट्रक्चर की पुष्टि करने के लिए ट्रांसमिशन इलेक्ट्रॉन माइक्रोस्कोपी (टीइम) से अध्ययन किया गया है। माइक्रोस्ट्रक्चर अवलोकन से पता चलता है कि प्रेसिपिटे की आकृति तत्वों (यानी, टाइटेनियम और एल्युमिनियम) के संकलन के साथ बदलता रहता है। माइक्रोहार्डनेस के परिणाम बताते हैं कि  $Ti_{05}$  मिश्र धातु में  $Al_{02}Ti_{03}$  और  $Al_{05}$  एचईए की तुलना में उच्चतम पीक हार्डनेस है। इन परिवर्तनों को ग्रेन के भीतर महीन प्रेसिपिटे वितरण के लिए जिम्मेदार ठहराया गया था।

विभिन्न चरों के प्रभाव, जैसे कि एजिंग टेम्परेचर, केंचीग मीडियम और प्री-डेफोर्म (यानी, एजिंग से पहले डेफोर्म) माइक्रोस्ट्रक्चर एवोलूशन और एचईए के ऐज-हार्डनिंग व्यवहार पर भी जांच की गई है। यह देखा गया है कि एजिंग टेम्परेचर और केंचीग मीडियम ऐज-हार्डनिंग व्यवहार को महत्वपूर्ण रूप से प्रभावित करते हैं, खासकर  $Al_{05}$  और  $Al_{02}Ti_{03}$  एचईए के लिए। मुख्य कारक में उच्च हार्डनेस, उत्कृष्ट तापीय स्थिरता और प्रेसिपिटे की उच्च संख्या घनत्व शामिल है। 650 डिग्री सेल्सियस और 750 डिग्री सेल्सियस के लिए, 850 डिग्री सेल्सियस की तुलना में एक महत्वपूर्ण ऐज-हार्डनिंग व्यवहार देखा गया है। यह प्रेसिपिटे की उच्च संख्या घनत्व के लिए जिम्मेदार ठहराया गया था। एयर कूल्ड सैंपल की तुलना में नमकीन पानी और साधारण पानी में केंचीग में ऐज-हार्डनिंग प्रतिक्रिया और प्रेसिपिटे की विशेषताओं को काफी अलग पाया गया है। उच्च हार्डनेस

मूल्य, महीन वितरण और प्रेसिपिटेट की उच्च संख्या घनत्व को नमकीन पानी और साधारण पानी में केंचीग वाले सैंपल में देखा गया। इसके अलावा, एजिंग के उपचार से पहले प्री-डेफोर्म से प्रेसिपिटेशन हार्डनिंग व्यवहार काफी प्रभावित पाया गया था। मुख्य प्रभावों में कम पीक-एजिंग समय (यानी, 240 घंटे से 50 घंटे तक), उच्च पीक हार्डनेस, और विशिष्ट ओवर-एजिंग का व्यवहार शामिल है। यह सलूशन उपचारित (एसटी के रूप में लेबल) स्थितियों की तुलना में उनके सलूशन-उपचारित और प्री-डेफोर्म (एसटी-पीएस के रूप में लेबल) स्थितियों में सभी तीन एचईए के लिए प्रेसिपिटेट की बढ़ी हुई संख्या घनत्व के लिए जिम्मेदार है। इसके अलावा,  $Al_{105}$  और  $Al_{102}Ti_{103}$  एचईए के लिए प्रेसिपिटेट के कारसेन कैनेटीक्स एसटी नमूनों की तुलना में एसटी-पीएस नमूनों में काफी तेज हैं, जबकि एसटी-पीएस में देखे गए व्यापक प्रेसिपिटेट आकार वितरण के कारण यह दोनों सैंपल स्थितियों में  $Ti_{105}$  के लिए समान रहा एसटी सैंपल की तुलना में।

इसके अलावा, एजिंग, एजिंग टेम्परेचर, केंचीग मीडियम और प्री-डेफोर्म जैसे विभिन्न उपचारों के अधीन तीन एचईए के यील्ड स्ट्रेस ( $\sigma_y$ ) को ओरोवन मॉडल का उपयोग करके प्रेडिक्ट की गई है। ताबोर के मॉडल के बाद प्रयोगात्मक प्राप्त हार्डनेस मूल्यों का उपयोग करके तीन एचईए के  $\sigma_y$  का भी अनुमान लगाया गया था। इन मॉडलों का उपयोग एज्ड सैंपल की समग्र शक्ति (यानी, ताबोर का मॉडल) में प्रेसिपिटेट (यानी, एशबी-ओरोवन मॉडल) के योगदान को समझने के लिए किया गया था। प्रेडिक्ट और अनुमानित  $\sigma_y$  एज्ड एचईए के लिए सफलतापूर्वक सहसंबद्ध थे और साहित्य से उनके प्रयोगात्मक  $\sigma_y$  मूल्यों के साथ मान्य किए गए हैं। परिणाम अनुमानित, प्रेडिक्ट और प्रयोगात्मक यील्ड स्ट्रेस मूल्यों के बीच एक अच्छे समझौते का सुझाव देते हैं। देखे गए परिणाम एज्ड एचईए की स्ट्रेंथ को नियंत्रित करने में प्रेसिपिटेट विशेषताओं की भूमिका पर जोर देते हैं।

किए गए व्यापक अध्ययनों से, यह स्पष्ट है कि टाइटेनियम और एल्युमिनियम संकलन के साथ  $\text{Co}_{1.5}\text{CrFeNi}_{1.5}$  मिश्र कई उच्च तापमान अनुप्रयोगों के लिए उपयुक्त प्रेसिपिटेशन हार्डनिंग के माध्यम से उच्च शक्ति और उत्कृष्ट थर्मल स्थिरता प्रदान करने की क्षमता प्रस्तुत करते हैं।

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