Modeling and Validation of Irradiation Damage in Ni-based Alloys for Long-Term LWR Applications

Reactor Concepts Research Development and Demonstration

Julie Tucker
Oregon State University

Collaborators
University of Michigan

Alison Hahn, Federal POC
Tom Rosseel, Technical POC
Project Title: Modeling and Validation of Irradiation Damage in Ni-based Alloys for Long-Term LWR Applications

Reporting Frequency: Final Report, March 2019
Recipient: Oregon State University
Award number CFA-15-8489
Awarding Agency: U.S. DOE, NEUP
Working Partners: Oregon State University
University of Michigan – Ann Arbor
Idaho National Laboratory
University of Manchester

Principal Investigator: Julie Tucker, School of Mechanical, Industrial and Manufacturing Engineering, Oregon State University
Title: Assistant Professor
Phone: 737-541-5840
Email: Julie.Tucker@oregonstate.edu

Collaborators: Emmanuelle Marquis - University of Michigan – Ann Arbor
Benjamin Spencer - Idaho National Laboratory
Grace Burke - University of Manchester
Table of Contents

1 Project Overview ...................................................................................................................................... 3
  1.1 Proposal abstract ................................................................................................................................. 3
  1.2 Milestone deliverables outlined by DOE Work Package ................................................................. 3
  1.3 Collaboration roles and responsibilities ............................................................................................ 4

2 Project Status ........................................................................................................................................ 6
  2.1 Executive summary of achievements ................................................................................................. 6
  2.2 Budget status .................................................................................................................................... 6
  2.3 Communication and reporting status ................................................................................................. 6
    2.3.1 Peer-reviewed publications .......................................................................................................... 6
    2.3.2 Presentations ............................................................................................................................... 7
    2.3.3 Student theses ............................................................................................................................. 8

3 Technical Review .................................................................................................................................. 9
  3.1 Materials .......................................................................................................................................... 9
    3.1.1 As-received characterization of commercial alloys ...................................................................... 9
  3.2 Isothermal Aging and Characterization of Model and Commercial Alloys ............................ 10
    3.2.1 Test matrix .................................................................................................................................. 10
    3.2.2 Model alloy aging results .......................................................................................................... 11
    3.2.3 Commercial alloy aging results ............................................................................................... 23
  3.3 Irradiation of Model and Commercial Alloys ................................................................................... 32
    3.3.1 Test matrix .................................................................................................................................. 32
    3.3.2 Model Alloys ............................................................................................................................... 33
    3.3.3 Alloy 690 .................................................................................................................................. 36
    3.3.4 Alloy 625 and 625 Plus .............................................................................................................. 38
    3.3.5 Summary .................................................................................................................................... 51
  3.4 Modeling of Thermal and Irradiation Degradation ........................................................................... 52
    3.4.1 Thermal Aging Model .................................................................................................................. 53
    3.4.2 Crystal plasticity model for thermal aging and irradiation ......................................................... 57
    3.4.3 Summary .................................................................................................................................... 68

4 References .......................................................................................................................................... 70

Appendix A. IMR Composition Confirmation Report ................................................................................. 73
1 PROJECT OVERVIEW

1.1 PROPOSAL ABSTRACT

As light water reactor (LWR) plant lives are extended, the need for predictive modeling tools for materials degradation increase in order to ensure safe operation and plan for component replacements. The Grizzly code, which is built on the MOOSE multi-physics simulation environment, is being developed for exactly this purpose. To extend Grizzly to include capabilities for modeling Ni-based alloys, we propose a US/UK integrated program to address thermal and irradiation-induced transformations mechanisms of Alloys 690 and 625. Alloy 690 is widely used in existing LWR plants due to its superior stress corrosion cracking (SCC) resistance compared to Alloy 600. Alloy 625 is used in more limited applications but offers the benefits of both high strength (in the aged condition) and corrosion/SCC resistance [1]. Research has shown that both alloys can undergo phase changes due to thermal or irradiation exposure. In the precipitation-hardened condition, Alloy 625 “softens” during neutron irradiation as the strengthening precipitates decompose and metastable precipitates form [2, 3]. However, the nature and rates of these transformations as a function of exposure conditions are not well understood. Similarly, the effects of these thermal and irradiation-induced microstructural changes on mechanical properties require evaluation. The proposed program combines thermal and irradiation experiments, mechanical testing, microstructural characterization using state-of-the art analytical techniques, atomistic modeling, micro-and macro-scale modeling via Grizzly. This multi-pronged approach yields several benefits: 1) atomistic scale models capture the physics of the mechanisms of phase transformations, which can be generalized to other systems, 2) the modeling results (from atomistic to continuum) will be validated experimentally to ensure the predictive aspect, 3) the microstructure/property relationships captured with mechanical testing provides information at the engineering scale that is needed to validate the integration of the proposed new capability into Grizzly.


1.2 MILESTONE DELIVERABLES OUTLINED BY DOE WORK PACKAGE

This project combined thermal and irradiation experiments, mechanical testing, microstructural characterization using state-of-the art analytical techniques, atomistic modeling, micro-and macro-scale modeling via Grizzly. This multi-pronged approach yields several benefits: 1) atomistic scale models capture the physics of the mechanisms of phase transformations, which can be generalized to other systems, 2) the modeling results (from atomistic to continuum) will be validated experimentally to ensure the predictive aspect, 3) the microstructure/property relationships captured with mechanical testing provides information at the engineering scale that is needed to validate the integration of the proposed new capability into Grizzly. This project had three major objectives:
1. Thermal and irradiation-induced ordering in Alloy 690 and model alloys
2. Thermal and irradiation-induced damage/phase transformations in Alloy 625
3. Development of physics-based predictive models for degradation in Alloys 690/625

The major and minor milestones for the project are:

1. Final Report
2. Year 1 Report
3. Year 2 Report
4. Planning Meeting
5. Procure/Fabricate Material
6. Thermal Aging
7. As Received Characterization
8. Thermal Aging Characterization
9. Irradiation of 690 and Model Alloys
10. Irradiated 690/Model Alloy Characterization
11. Thermal Model in Grizzly
12. Irradiation 690 Model in Grizzly
13. Irradiation of Alloy 625
14. Characterization of Alloy 625
15. Irradiation Model for 625 in Grizzly
16. Model benchmarking and validation

1.3 Collaboration roles and responsibilities

Dr. Julie Tucker (US Lead-PI) is an Assistant Professor in the School of Mechanical, Industrial and Manufacturing Engineering at Oregon State University. She was the lead for the thermal aging, microhardness testing, XRD characterization, model alloy fabrication, and mechanical testing experiments. She was also responsible for developing models for thermal and irradiation degradation for input in Grizzly.

Dr. Emmanuelle Marquis is an Associate Professor in the Materials Science Department at the University of Michigan. She was responsible for proton irradiation of specimens in the U.S., characterization via TEM, APT, and micro-mechanical testing. Additionally, her team helped with the identification of the physics that needed to be incorporated in the degradation models.

Dr. Benjamin Spencer is a computational scientist in the Fuel Modeling and Simulation Department at Idaho National Laboratory. He is the lead developer of the Grizzly code for modeling component aging, and is heavily involved in development of the Bison nuclear fuel performance modeling code. He was responsible for the integration of the thermal and irradiation models into Grizzly in order to predict mechanical property degradation.

Dr. M. Grace Burke (UK Lead-PI) is the Director of the Materials Performance Centre and Director of the Electron Microscopy Centre at the University of Manchester. She was responsible for leading an irradiation and characterization effort in parallel with the US effort. Her team
utilized state-of-the-art analytical transmission electron microscopy and electron diffraction analyses to identify phase transformations, precipitation and ordering phenomena as a function of thermal and irradiation history, complementing the state-of-the-art atom probe analyses at the University of Michigan.
2  PROJECT STATUS

2.1 EXECUTIVE SUMMARY OF ACHIEVEMENTS

This report summarizes the progress made during DOE NEUP project titled “Modeling and Validation of Irradiation Damage in Ni-based Alloys for Long-Term LWR Applications”. Through this project we performed isothermal aging and irradiation of Ni-Cr model alloys and commercial alloys 690, 625 and 625 Plus. Through state-of-the-art characterization techniques we have revealed the degradation that occurs in these alloys under accelerated plant conditions. In addition to the experimental testing, we have developed a crystal plasticity-based deformation model for implementation into the Grizzly code within the MOOSE framework.

2.2 BUDGET STATUS

All budgeting items were kept valid.

2.3 COMMUNICATION AND REPORTING STATUS

Communication of the research that evolved within this project was a critical component for advancing nuclear materials understanding. It allowed for development and understanding of experiment techniques, and opened discussion for the impact and direction of these materials. The primary methods for dissemination under this project included journal publications and conference proceedings.

2.3.1  Peer-reviewed publications


### 2.3.2 Presentations


9) "Role of Stoichiometry on Ordering in Ni-Cr Alloys", F. Teng, J.D. Tucker. TMS, Nashville, TN, February 16 (2016).


12) “Precipitation in an Irradiated 625 plus alloy”, L.-J. Yu and EA Marquis, Microscopy & Microanalysis, St Louis, MO, August (2016) [Poster] (awarded Best Poster Award).


2.3.3 Student theses

1) "Investigation of thermal degradation in structural alloys for nuclear power systems.” Fei Teng, Master of Science, Doctor of Philosophy, Oregon State University, December 07, (2018).

2) “Role of Stoichiometry on Ordering in Ni-Cr Alloys." Fei Teng, Master of Science, Materials Science, Oregon State University, May 17, (2016).

3) “Phase stability in Ni alloys under irradiation” Li-Jen Yu, PhD, University of Michigan, planned graduation date 2020.

4) “Modeling and Simulation of Microstructure Evolution and Deformation in an Irradiated Environment.” Stephanie Pitts, Doctor of Philosophy, Washington State University, April 02 (2019).


3 TECHNICAL REVIEW

3.1 MATERIALS

The materials in this study include both model and commercial alloys. Table 1 provides a complete list of materials under investigation. Alloy 690 samples are from Special Metals Heat NX7075HK11. Alloy 625 and 625+ samples are from Carpenter, heats 602051 and 215846, respectively. The commercial alloy chemistries are based on vender certs and most alloying compositions were identified by x-ray fluorescence (XRF). The four binary Ni-Cr model alloys have different Ni:Cr stoichiometries (1.8, 2.0, 2.2 and 2.4). Their compositions have been confirmed by IMR Test Lab (see Appendix A). Test method comes from CAP-017N (ICP-AES) and ASTM E 1019-11 (Comb./IGF).

Table 1. Alloy compositions (wt.%) for thermal aging studies.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Ni</th>
<th>Cr</th>
<th>Fe</th>
<th>Mo</th>
<th>Nb</th>
<th>Co</th>
<th>Mn</th>
<th>P</th>
<th>S</th>
<th>others</th>
</tr>
</thead>
<tbody>
<tr>
<td>690</td>
<td>59.37</td>
<td>29.42</td>
<td>10.36</td>
<td>0.01</td>
<td>&lt;0.01</td>
<td>0.009</td>
<td>0.15</td>
<td>0.004</td>
<td>&lt;0.001</td>
<td>*</td>
</tr>
<tr>
<td>625</td>
<td>58.0</td>
<td>20.0-</td>
<td>5.0</td>
<td>8.0-</td>
<td>3.15-</td>
<td>1.0</td>
<td>0.50</td>
<td>0.015</td>
<td>0.015</td>
<td>**</td>
</tr>
<tr>
<td></td>
<td>min</td>
<td>max</td>
<td>max</td>
<td>max</td>
<td>max</td>
<td>max</td>
<td>max</td>
<td>max</td>
<td>max</td>
<td></td>
</tr>
<tr>
<td>625+</td>
<td>60.28</td>
<td>20.99</td>
<td>NR</td>
<td>8.02</td>
<td>3.40</td>
<td>NR</td>
<td>0.02</td>
<td>0.001</td>
<td>0.0005</td>
<td>+</td>
</tr>
<tr>
<td>Ni:Cr 1.8</td>
<td>67.03</td>
<td>32.95</td>
<td>&lt;0.01</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.007</td>
<td>0.002</td>
<td>-</td>
</tr>
<tr>
<td>Ni:Cr 2.0</td>
<td>69.36</td>
<td>30.62</td>
<td>&lt;0.01</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.006</td>
<td>0.002</td>
<td>-</td>
</tr>
<tr>
<td>Ni:Cr 2.2</td>
<td>71.40</td>
<td>28.58</td>
<td>&lt;0.01</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.006</td>
<td>0.002</td>
<td>-</td>
</tr>
<tr>
<td>Ni:Cr 2.4</td>
<td>72.58</td>
<td>27.36</td>
<td>0.04</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.006</td>
<td>0.001</td>
<td>-</td>
</tr>
</tbody>
</table>

*C=0.030, Cu=0.01, Si=0.05, Al=0.27, Ti=0.28, Mg=0.001, B<0.001, O<0.01
**C=0.1max. Al=0.4max. Ti=0.4max. Si=0.5max.
+ Al=0.20
NR=Not reported

3.1.1 As-received characterization of commercial alloys

3.1.1.1 Atom Probe Tomography

3.1.1.1 Procedure

Alloys were solution treated at 1100 °C for 1 hour, followed by water quenching. Samples were electropolished using a 10% perchloric acid + 90% methanol electrolyte at -30 °C. APT specimens were prepared using a standard lift-out and Ga ion beam thinning process on both FEI Nova 200 and FEI Helios 650 Nanolab dual scanning electron microscope (SEM)/focus ion beam (FIB) instruments. APT data was collected on both Cameca LEAP 4000X HR and 5000 XR instruments operated in laser mode using a pulse energy of 50 pJ, 200 kHz pulse rate, and a target detection rate of 0.5% at 50 K. For compositional measurements, a background subtraction was applied and peak deconvolutions of Ti and Cr, Cr and Fe, Fe and Ni, Ni and Mo, and Ni and Nb were performed based on isotopic natural abundances.

3.1.1.2 Results

The measured compositions of the alloys is consistent with the nominal compositions, Table 2.
Table 2. Chemical composition (at.%) of the commercial alloys. Compositions measured by APT listed in parentheses are compared to the nominal values.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Ni</th>
<th>Cr</th>
<th>Mo</th>
<th>Fe</th>
<th>Nb</th>
<th>Ti</th>
<th>Al</th>
<th>Si</th>
<th>Co</th>
<th>Mn</th>
<th>P</th>
<th>S</th>
<th>C</th>
<th>Ta</th>
</tr>
</thead>
<tbody>
<tr>
<td>625</td>
<td>61.8</td>
<td>25.6</td>
<td>5.4</td>
<td>3.7</td>
<td>2.3</td>
<td>0.29</td>
<td>0.37</td>
<td>0.17</td>
<td>0.03</td>
<td>0.06</td>
<td>0.29</td>
<td>0.37</td>
<td>0.17</td>
<td>0.03</td>
</tr>
<tr>
<td></td>
<td>(61.6)</td>
<td>(26.1)</td>
<td>(5.5)</td>
<td>(3.8)</td>
<td>(2.2)</td>
<td>(0.29)</td>
<td>(0.33)</td>
<td>(0.15)</td>
<td>(0.01)</td>
<td>(0.06)</td>
<td>(0.29)</td>
<td>(0.33)</td>
<td>(0.15)</td>
<td>(0.01)</td>
</tr>
<tr>
<td>625 Plus</td>
<td>60.8</td>
<td>23.9</td>
<td>4.9</td>
<td>6.0</td>
<td>2.2</td>
<td>1.58</td>
<td>0.44</td>
<td>0.06</td>
<td>-</td>
<td>0.02</td>
<td>0.02</td>
<td>0.02</td>
<td>0.02</td>
<td>0.02</td>
</tr>
<tr>
<td></td>
<td>(61.1)</td>
<td>(23.9)</td>
<td>(5.1)</td>
<td>(5.5)</td>
<td>(2.2)</td>
<td>(1.59)</td>
<td>(0.37)</td>
<td>(0.09)</td>
<td>(0.01)</td>
<td>(0.02)</td>
<td>(-)</td>
<td>(-)</td>
<td>(0.01)</td>
<td>(0.03)</td>
</tr>
<tr>
<td>690</td>
<td>56.6</td>
<td>31.7</td>
<td>&lt;0.01</td>
<td>10.4</td>
<td>&lt;0.01</td>
<td>0.41</td>
<td>0.48</td>
<td>0.10</td>
<td>&lt;0.01</td>
<td>0.15</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td></td>
<td>(56.6)</td>
<td>(31.9)</td>
<td>(-)</td>
<td>(10.4)</td>
<td>(-)</td>
<td>(0.33)</td>
<td>(0.45)</td>
<td>(0.12)</td>
<td>(0.02)</td>
<td>(0.17)</td>
<td>(-)</td>
<td>(-)</td>
<td>(0.02)</td>
<td>(0.04)</td>
</tr>
</tbody>
</table>

3.2 Isothermal Aging and Characterization of Model and Commercial Alloys

3.2.1 Test matrix

In this project, model alloy samples were given isothermal heat treatments at three temperatures as shown in Table 3. The heat treatment for model alloys is complete. Table 4 shows the test matrix for commercial alloys. This project only includes isothermal aging out to 10,000 hours, however, longer aging treatments are planned with this test matrix.

Table 3. Test matrix of isothermal aging for model alloys

<table>
<thead>
<tr>
<th>Time(hrs)</th>
<th>Temp(°C)</th>
<th>500</th>
<th>1000</th>
<th>3000</th>
<th>5000</th>
<th>10000</th>
</tr>
</thead>
<tbody>
<tr>
<td>475</td>
<td></td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>418</td>
<td></td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>373</td>
<td></td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>2</td>
</tr>
</tbody>
</table>

Table 4. Test matrix of isothermal aging for commercial alloys

<table>
<thead>
<tr>
<th>Time(hrs)</th>
<th>Temp(°C)</th>
<th>5000</th>
<th>10,000</th>
<th>20,000</th>
</tr>
</thead>
<tbody>
<tr>
<td>475</td>
<td></td>
<td>2</td>
<td>2</td>
<td>4</td>
</tr>
<tr>
<td>418</td>
<td></td>
<td>2</td>
<td>2</td>
<td>4</td>
</tr>
<tr>
<td>360</td>
<td></td>
<td>2</td>
<td>2</td>
<td>4</td>
</tr>
<tr>
<td>333</td>
<td></td>
<td>2</td>
<td>2</td>
<td>4</td>
</tr>
</tbody>
</table>
3.2.2 Model alloy aging results

3.2.2.1 TEM

3.2.2.1.1 Sample preparation and procedure
Specimens to be characterized by TEM were first sectioned by low speed diamond saw into ~1 mm thick slices. The slices were then ground to thin foil with the thickness less than 120 µm with 1200 grit SiC sandpaper finished surface on both sides. The foils were punched into 3 mm diameter disks and jet electro-polished in 20% HClO4 – 80% CH3OH at -40°C and 15V using a Struers Tenupol 5 with a Julabo FP50 closed-cycle refrigeration system.

TEM characterization was performed by using the FEI Tecnai TF30-FEG transmission electron microscope located in Center for Advanced Energy Studies (CAES) at 300 kV voltage. To best reveal the size of precipitation, [112] zone axis was selected for dark field imaging.

3.2.2.1.2 Results
Figure 1 shows the evolution of MoPt2-type ordered precipitates with time snapshots of 3000 h, 5000 h, and 10,000 h ageing at 475°C in [112] zone axis. In dark field mode, both 1/3 [220] and 1/3 [131̅] spots were captured for Figure 2(a). The 2/3 [311] and 2/3 [220] spots were selected for Figure 2(b) and 2(c).

The selected-area electron diffraction patterns indicate the existence of the ordered phase after isothermal ageing and the corresponding dark field images reveal the distribution of Ni2Cr-ordered precipitates in samples. TEM dark field images generally reveal the evolution of ordering transition in quality as ageing going. After 3000 h ageing (Figure 1(a)), small ordered precipitates can be observed, and some precipitates start growing into an early stage superlattice structure with a size ~10 nm. As ageing continues, ordered precipitates with larger coherent particle size (p-size) of ~13 nm can be observed after 5,000 h isothermal heat treatment and the superlattice structure is more obvious (Figure 1(b)). P-size keeps growing at ~20 nm as ageing time comes to 10,000 h (Figure 1(c)). The superlattice structure of thermal induced Ni2Cr ordered structure can be observed in some area clearly. Figure 1 shows the boundary between precipitates appears clearer with increasing aging time. No clear precipitates can be observed in Figure 1(a) (3000 h). Dark area between precipitates start showing in Figure 1(b) (5,000 h) and precipitates can be imaged clearly in Figure 1(c) (10,000h). However, it is difficult to calculate ordered phase fraction from TEM darkfield images because of the low contrast between matrix and ordered precipitates. More precise, robust, and larger volume characterization method, such as synchrotron XRD, is needed to determine precise ordered phase fractions.
Figure 1. The evolution of ordering from 3000 to 10,000 h under TEM at [112] zone axis. (a) and (d) Darkfield image of Ni/Cr = 2.0 sample aged at 475°C for 3000 h and the corresponding diffraction pattern. (b) and (e) Darkfield image of Ni/Cr = 2.0 sample aged at 475°C for 5000 h and the corresponding diffraction pattern. The Ni2Cr superlattice structure is marked out and zoomed in. (c) and (f) Darkfield image of Ni/Cr = 2.0 sample aged at 475°C for 10,000 h and the corresponding diffraction pattern. Results shows that precipitation size for 3000 and 5000 h are similar, which is about 12 nm. The size of precipitation for 10,000 h aged sample is larger. Some precipitates are about 20 nm.
3.2.2.2 Microhardness

3.2.2.2.1 Sample prep
For microhardness tests, the bulk specimens (in dimension of 10×10×5 mm³) were polished using SiC papers from 240 to 800 grit followed by 0.05 µm colloidal alumina polishing to create flat surfaces. Microhardness measurements were performed by using MicroMaterials NanoTest Vantage nanoindenter with a Berkovich diamond tip and a load of 500 mN.

3.2.2.2.2 Procedure
The load was chosen to balance degradation of indenter tip, sensitivity for vibration from environment during testing, resistance on effect of grain orientation, effect of grain boundary on indentation, and the accuracy level of the result. A larger load causes faster tip damage, which changes the dynamic area function that is used to calculate microhardness. A smaller load requires lower environmental vibration. Considering these effects on standard deviation of measurement, microhardness measurements using a grid of (4×5) were performed twice (total 40 indents) on the sample surface with 600 µm between indentations in each direction. Considering the effect of grain orientation and grain boundary on data variance, all 40 data points are ranked from low to high and the lowest 10 and highest 10 points were removed from the data set. Only the remained middle 20 data points were analyzed for hardness.

3.2.2.2.3 Results
We define embrittlement here as the difference of Berkovich microhardness at current ageing time (GPa) and the microhardness of same sample at as-received condition (GPa). The average change in Berkovich microhardness, which is the difference of microhardness before and after isothermal ageing, from 500 to 10,000 h isothermal heat treatment as function of stoichiometry at three temperatures are shown in Figure 2. The result shows that the relationship of embrittlement at three temperatures is generally 475°C > 418°C > 373°C during the whole ageing time.

In the first 500 and 1,000 h ageing, the change in microhardness as a function of temperature is 475°C > 418°C > 373°C. The change on microhardness as a function of stoichiometry at 475°C is 2.0 ≈ 2.2 > 1.8 ≈ 2.4. The role of stoichiometry at 418°C and 373°C on embrittlement is not obvious; the four stoichiometries reveal similar microhardness changes at both temperatures. When the ageing time extends after 3,000 h, role of stoichiometry starts to become more obvious at 475°C. The relationship of embrittlement as a function of stoichiometry is 2.0 > 2.2 ≈ 1.8 > 2.4 at 475°C. This relationship keeps stable at 418°C compared to the relationship before 1,000 h. For the embrittlement at 373°C, the 2.2 sample is of slightly larger embrittlement than other compositions. Compared to the embrittlement before 1,000 h, no obvious change in the relationship of embrittlement can be observed at 373°C. However, the degree of embrittlement, which is between 0.3 and 0.75 GPa, is much larger than that of 500 h and 1,000 h, which is between 0 and 0.25 GPa. When the ageing time equals to 10,000 h, the relationship of embrittlement at all temperatures is close to 2.0 > 2.2 ≈ 1.8 > 2.4. Compared to the tendency at 3,000 h and 5,000 h, the embrittlement at 475°C is similar. For 418°C, the embrittlement increases to 1 GPa at all stoichiometry, which is larger than 5,000 h. For 373°C, the change of microhardness is of obvious increasing compared to that of 5,000 h.

The size of nanoindentation is ~20 µm, which is smaller than the grain size (~150 µm). The size difference may cause the measurement of microhardness is heavily dependent on grain properties,
such as grain orientation. The uncertainty revealed in the hardness measurements, indicates microhardness needs to be combined with another more reliable technique to clarify the evolution of ordering as a function of temperature and stoichiometry.

Figure 2. Change in microhardness as function of stoichiometry three temperatures when isothermal ageing comes to a) 500 h, b) 1,000 h, c) 3,000 h, and d) 10,000 h. The result shows that higher temperature is of earlier saturation on microhardness. 475°C starts showing the saturation behavior. 373°C and 418°C have not reached saturation point, but the faster kinetic can be observed at 418°C heat ageing. Ni/Cr = 2.0 samples are of highest value of change in hardness. Further distance from Ni/Cr =2.0 causes a smaller change in hardness.

3.2.2.3  Synchrotron X-ray Diffraction

3.2.2.3.1  Sample preparation and procedure

All samples for XRD characterization are prepared into slides by using low speed diamond blade followed by grinding. A slide of specimen was cut from the parent bulk sample with the thickness
of ~1.5 mm, then the specimen was grinded by 800 sandpaper with the final thickness of 300 to 500 μm.

XRD measurements were performed using the high-energy X-rays available the X-ray Powder Diffraction beamline of the National Synchrotron Light Source-II (NSLS-II) [41, 42]. All measurements were performed in transmission mode with an amorphous Silicon-based flat panel detector (Perken-Elmer) mounted orthogonal to and centered on the beam path. The sample-to-detector distances and tilts of the detector relative to the beam were refined using a LaB6 powder standard (NIST standard reference material 660c). The wavelength of the incident X-rays was 0.2370 Å (52.3149 keV). The sample-to-detector distance was calculated to be 1351.94 mm. Samples were continuously rotated during acquisition to improve the powder averaging. Multiple patterns were collected to avoid saturation of the detector. Typical count times were 0.5-1 sec (depending on the sample). All raw two-dimensional patterns were background corrected by subtracting the dark current image and any air scattering. Noticeable artefact regions of the detector (like the beam stop, dead pixels) were masked. The corrected and masked two-dimensional detector images were then radially integrated to obtain the one-dimensional powder diffraction patterns. The background subtracted XRD patterns were Rietveld refined with the TOPAS software package (BRUKER). The peak profiles were modeled by a modified pseudo-Voigt function. The instrument contribution to the broadening of the measured profiles was quantified by fitting a LaB6 NIST powder standard, with known crystallite-domain size and negligible strain contribution. The Gaussian and Lorentzian-based instrument broadening parameters were subsequently fixed during the analysis of the alloys under investigation.

Table 5 shows the test matrix for XRD characterization. To best reveal the evolution of ordered phase, Ni/Cr = 2.0 samples aged at 475℃ were chosen to perform the test. Ni/Cr = 2.0 samples aged at 373℃ and 418℃ for 10,000 h were also tested for exploring the role of temperature in ordering transition. Moreover, Ni/Cr = 1.8, 2.2, and 2.4 samples were chosen to reveal the evolution of ordering as a function of stoichiometry.

<table>
<thead>
<tr>
<th>Time (h)</th>
<th>Temperature (℃)</th>
<th>500</th>
<th>1000</th>
<th>3000</th>
<th>5000</th>
<th>10,000</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>373</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2.0</td>
</tr>
<tr>
<td></td>
<td>418</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2.0</td>
</tr>
<tr>
<td></td>
<td>475</td>
<td>2.0</td>
<td>2.0</td>
<td>2.0</td>
<td>2.0</td>
<td>1.8, 2.0, 2.2, 2.4</td>
</tr>
</tbody>
</table>

3.2.3.2 Results
Considering the challenge of measuring ordered phase fraction by TEM and grain properties influenced microhardness, XRD is the ideal technique to precisely quantify the evolution of ordered precipitation. Also, previous research from Gwalani et al. [1] shows the efficiency of XRD on identifying ordered precipitation.

The XRD patterns are shown in Figure 3 (phases are included for references), confirming the formation of the Ni2Cr ordered phase. All samples show the cubic FCC Ni-Cr matrix (higher peaks
indicated by the blue tick marks). All samples, with the exception of the “as-received” sample, show peaks from the orthorhombic phase Ni$_2$Cr (red tick marks). The peaks from the Ni2Cr phase vary in height and width between samples due to varying concentration and coherent particle size (p-size). There does not appear to be any diffraction peaks for BCC Cr in the current samples. In Figure 3(a), compared to as-received 2.0 sample, both 2.0-475-5000 and 2.0-475-10,000 samples show Ni2Cr diffraction and the corresponding intensity increases with ageing time, as confirmed by quantitative analysis (Table 6). Figure 3(b) reveals diffraction patterns that confirm the formation of the Ni2Cr ordered phase in all four stoichiometries. Figure 3(c) shows the diffraction pattern from samples with different ageing temperatures (373°C, 418°C, and 475°C). Significant peak broadening can be observed in the Ni2Cr precipitates at lower temperatures, indicative of small precipitate sizes. The lattice parameters (and volume of unit cell) also appear to be temperature dependent and increase with increasing temperature.

The structural results from the Rietveld fitting are shown in Table 6 and Figure 3 for the phase fraction, lattice parameter (for both matrix and precipitates), size of ordered precipitation (p-size) and strain (numbers in parentheses () are errors from the refinements). The blue (dash line) plot of Figure 3 shows the evolution of p-size as a function of ageing time for Ni/Cr = 2.0 samples aged at 475°C. The p-size increases rapidly in the beginning period of heat treatment then starts slowing down after 1,000 h. A similar but reversed trend can be observed on the change of lattice parameters in same sample as shown in the green (dots line) plot in Figure 3. The matrix lattice parameter contracts rapidly in the beginning 1,000 h from 3.567 Å, and then plateaus around 3.558 Å. The pink (dash-dot line) plot in Figure 3 shows the evolution of ordered phase fraction. Different from the tendency of other parameters, ordered phase goes to ~ 6% rapidly (at 500 h) and keeps going down till 5000 h. The ordered phase fraction keeps stable at ~5% after 5000 h. The black (solid line) in Figure 5 shows the evolution of microhardness on the same samples for comparison. Figure 3 shows change of the strain on Ni/Cr = 2.0 jet-polished samples from 3000 h to 10,000 h. A significant jump on strain can be observed between 5000 h and 10,000 h. Figure 3 shows the evolution of strain, p-size, and change in microhardness as a function of stoichiometry. The Ni/Cr = 2.0 and 2.4 samples have the largest and smallest values on all parameters correspondingly, which means the farther distance from 2.0, the smaller p-size/strain/change in microhardness can be observed in the sample. Ni/Cr = 1.8 sample is of slightly larger size on precipitates than Ni/Cr = 2.2.
Figure 3. Synchrotron X-ray diffraction of Ni-Cr model alloys. Plot (a) indicates the evolution of ordering of Ni/Cr=2.0 alloy after aging at 475°C for 0, 5000, and 10,000 h. Phase identification is overlaid for the FCC matrix (blue ticks) and for the orthorhombic Ni2Cr phase (red ticks). Plot (b) indicates the evolution of ordering as a function of stoichiometry after 10,000 h ageing at 475°C. Plot (c) indicates the evolution of ordering as a function of ageing temperature on the Ni/Cr=2.0 alloy after aging 10,000 h. The peak broadening occurs as ageing temperature decreases, which indicates the changing of strain caused by ordered phase.
Table 6. Summary and comparison of Rietveld refinements.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Phase</th>
<th>a (Å)</th>
<th>±</th>
<th>b (Å)</th>
<th>±</th>
<th>c (Å)</th>
<th>±</th>
<th>Phase Fraction (%)</th>
<th>±</th>
<th>p-size (nm)</th>
<th>±</th>
<th>strain</th>
<th>±</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.0 As-received</td>
<td>Fm-3m</td>
<td>3.56720</td>
<td>0.00005</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.28</td>
<td>0.01</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.0-500hr-475°C</td>
<td>Fm-3m</td>
<td>3.56031</td>
<td>0.00013</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.23</td>
<td>0.02</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Immm</td>
<td>2.50639</td>
<td>0.00069</td>
<td>7.52024</td>
<td>0.02264</td>
<td>3.59554</td>
<td>0.00638</td>
<td>6.0</td>
<td>0.2</td>
<td>9</td>
<td>0.5</td>
<td>0.2</td>
<td>6.0</td>
</tr>
<tr>
<td>2.0-1,000hr-475°C</td>
<td>Fm-3m</td>
<td>3.55875</td>
<td>0.00010</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.39</td>
<td>0.01</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Immm</td>
<td>2.50923</td>
<td>0.00253</td>
<td>7.50987</td>
<td>0.00845</td>
<td>3.59472</td>
<td>0.00258</td>
<td>5.8</td>
<td>0.2</td>
<td>12.9</td>
<td>1.0</td>
<td>0.2</td>
<td>6.0</td>
</tr>
<tr>
<td>2.0-3,000hr-475°C</td>
<td>Fm-3m</td>
<td>3.55860</td>
<td>0.00016</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.24</td>
<td>0.02</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Immm</td>
<td>2.50747</td>
<td>0.01200</td>
<td>7.53310</td>
<td>0.03940</td>
<td>3.56688</td>
<td>0.01598</td>
<td>5.6</td>
<td>0.6</td>
<td>12.4</td>
<td>2.0</td>
<td>0.2</td>
<td>6.0</td>
</tr>
<tr>
<td>2.0-5,000hr-475°C</td>
<td>Fm-3m</td>
<td>3.55853</td>
<td>0.00009</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.23</td>
<td>0.01</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Immm</td>
<td>2.50323</td>
<td>0.00834</td>
<td>7.50819</td>
<td>0.02548</td>
<td>3.60427</td>
<td>0.00721</td>
<td>4.7</td>
<td>0.2</td>
<td>15.0</td>
<td>2.0</td>
<td>0.2</td>
<td>6.0</td>
</tr>
<tr>
<td>2.0-10,000hr-475°C</td>
<td>Fm-3m</td>
<td>3.55790</td>
<td>0.00010</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.54</td>
<td>0.01</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Immm</td>
<td>2.50816</td>
<td>0.00311</td>
<td>7.50204</td>
<td>0.00940</td>
<td>3.59506</td>
<td>0.00239</td>
<td>4.9</td>
<td>0.2</td>
<td>19.0</td>
<td>1.1</td>
<td>0.2</td>
<td>6.0</td>
</tr>
<tr>
<td>1.8-10,000hr-475°C</td>
<td>Fm-3m</td>
<td>3.56387</td>
<td>0.0001</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.5</td>
<td>0.01</td>
<td>1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Immm</td>
<td>2.51294</td>
<td>0.00213</td>
<td>7.5324</td>
<td>0.00659</td>
<td>3.5855</td>
<td>0.0023874</td>
<td>6.0</td>
<td>0.3</td>
<td>15.0</td>
<td>2.0</td>
<td>0.2</td>
<td>6.0</td>
</tr>
<tr>
<td>2.2-10,000hr-475°C</td>
<td>Fm-3m</td>
<td>3.55598</td>
<td>0.00013</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.47</td>
<td>0.01</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Immm</td>
<td>2.50852</td>
<td>0.00240</td>
<td>7.51625</td>
<td>0.00910</td>
<td>3.58372</td>
<td>0.00250</td>
<td>12.1</td>
<td>0.5</td>
<td>12.7</td>
<td>1.0</td>
<td>0.2</td>
<td>6.0</td>
</tr>
<tr>
<td>2.4-10,000hr-475°C</td>
<td>Fm-3m</td>
<td>3.55570</td>
<td>0.00012</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.39</td>
<td>0.01</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Immm</td>
<td>2.51187</td>
<td>0.00480</td>
<td>7.57838</td>
<td>0.01850</td>
<td>3.57230</td>
<td>0.00540</td>
<td>6.8</td>
<td>0.5</td>
<td>8.0</td>
<td></td>
<td>0.2</td>
<td>6.0</td>
</tr>
<tr>
<td>2.0-10,000hr-373°C</td>
<td>Fm-3m</td>
<td>3.56158</td>
<td>0.00010</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.24</td>
<td>0.01</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Immm</td>
<td>2.48545</td>
<td>0.01000</td>
<td>7.52002</td>
<td>0.03100</td>
<td>3.63926</td>
<td>0.00800</td>
<td>6.6</td>
<td>0.2</td>
<td>4.0</td>
<td></td>
<td>0.2</td>
<td>6.0</td>
</tr>
<tr>
<td>2.0-10,000hr-418°C</td>
<td>Fm-3m</td>
<td>3.55954</td>
<td>0.00009</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.29</td>
<td>0.01</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Immm</td>
<td>2.50636</td>
<td>0.00637</td>
<td>7.52694</td>
<td>0.02159</td>
<td>3.59439</td>
<td>0.00592</td>
<td>9.5</td>
<td>0.3</td>
<td>6.7</td>
<td>1.0</td>
<td>0.2</td>
<td>6.0</td>
</tr>
</tbody>
</table>

3.2.2.4  In situ micropillar compression testing and post-characterization by TEM

3.2.2.4.1  Sample preparation and procedure

For each single slide specimen, EBSD characterization was performed on the edge of the sample to find grains in [100] and [111] orientation by using FEI Quanta 3D FEG dual beam SEM/FIB. Three pillars with the dimension of 2 μm × 2 μm × 4 μm were fabricated inside each grain with known grain orientation on top surface. The pillars on both 2.0-AR and 2.0-475-10,000 specimens were compressed by Hysitron PI 88 SEM Picoindenter to perform in situ micro compression testing. To confirm the LRO induced deformation behavior inside the pillar, TEM characterization was performed on compressed pillars. After the compression testing, TEM lamellas were lift out in [100] and [111] pillars on 2.0-475-10,000 aged sample in the direction that parallel to loading
direction from compressed pillars by using FIB. Beside FIB prepared lamella, a 3 mm TEM disk was also prepared by twin jet polishing with the etchant of 90% ethanol and 10% perchloric acid at -30 °C and 20V. Both FIB prepared lamellas and jet polished disk were characterized by FEI Tecnai TF30-FEG and FEI Titan TEM.

3.2.2.4.2 Results

We noticed significant change in deformation mode between aged and as-received sample when each sample was compressed in [001] and [111] grain orientation. Figure 4 shows the SEM images of compressed pillars, which has the dimension of 2 µm x 2 µm x 4 µm, in all conditions. For unaged 2.0-AR pillars, all pillars in [100] and [111] compressed grain orientation were failure by slipping (Figure 4 (a)). The shear bands from one or more slip system can be observed on the surface of pillar. For the pillars on aged sample 2.0-475-10,000, change of surface contrast can be observed during compressing. The contrast change regime can be observed in steps of initiation, growing, and merging during loading (shown in video). Twinning deformation was suspected to be observed in [100] grain orientation here. Aged [111] pillars were still failed by slipping as expected.

Figure 5 shows TEM characterization result for aged samples including TEM disk and FIB prepared lamellas. Figure 5 (a) show the dark field (DF) TEM micrograph on jet polished disk of 2.0-475-10,000 specimen and corresponding selected area electron diffraction (SAED) in Figure 5 (b). The DF image (Figure 5 (a)) shows the distribution of LRO-Ni2Cr precipitates in matrix. Diffraction spot for dark field imaging is circled out in yellow in SAED (Figure 5 (b)). Figure 5 (a) indicates that the LRO precipitates were uniformly distributed in matrix. The size of precipitation is much smaller than the dimension of micro pillar, which avoids the effect of ununiform microstructure in the mechanical behavior of micropillars. Secondary diffraction pattern in Figure 5 (b) indicates the existing of LRO-Ni2Cr in aged Ni at%33Cr binary model alloy. Figure 5 (c) – (e) show DF images and the corresponding SAED of [001] compressed pillar in zone axis of [001], which confirms the forming of twin during deformation in [100] compression orientation. Figure 5 (f) – (h) show the DF image and the SAED of [111] grain orientation compressed pillar in [011] zone axis. The result indicates the coexisting of matrix, LRO precipitates, and twin. The maximum width of twin can reach ~0.3 µm. The deformation behavior in 2.0-475-10,000-[111] pillar can be confirmed to be slipping only as no LRO precipitates can be observed in slipping band area (Figure 4(g)). No twinning can be observed in SAED in Figure 5 (h). Compared to jet polished disk, the secondary reflection of LRO in FIB prepared sample is much weaker.
Figure 4. Micro pillars of aged Ni2-Cr sample that compressed in (a) [001], (b) [111] orientation and the corresponding schematics, which shows ordered MoPt2 superlattice structure (solid-line cubic) with fcc structure (dash-line cubic) in Ni-Cr system. Schematic of twinning direction [112] (solid line with arrow) and slipping direction [011]/[101] (dash lines with arrow) in (111) plane (triangular surface with red outline) of fcc crystal referenced to bct LRO crystal structure. Schematic of fcc/bct is after [1].
3.2.2.5 Atom probe tomography

3.2.2.5.1 Procedure
APT specimens were prepared using a standard lift-out and Ga ion beam thinning process on both FEI Nova 200 and FEI Helios 650 Nanolab dual scanning electron microscope (SEM)/focus ion beam (FIB) instruments. TEM specimens were characterized on a JEOL 3011 transmission electron microscope. APT data was collected on both Cameca LEAP 4000X HR and 5000 XR instruments operated in laser mode using a pulse energy of 50 pJ, 200 kHz pulse rate, and a target detection rate of 0.5% at 50 K. APT data was analyzed using the IVAS 3.8.2 software, and the radius evolution of the reconstructed dataset was based on voltage evolution using the evaporation
field of Ni (35 nm/V [2]). The reconstruction parameters (image compression factor and field factor kf) were adjusted to minimize the matrix atomic density variations along the longitudinal and radial directions. The image compression factor and kf value ranged between 1.3 and 1.8, and between 2.9 and 3.5, respectively. The spatial resolution of APT along the specimen axis has been shown to be sufficient to resolve atomic planes and ordering. Therefore, EBSD mapping was used to select (110) oriented grains, from which APT samples were prepared, as shown in Figure 6.

3.2.2.5.2 Results
The lack of obvious compositional difference between the expected Pt2Mo-type ordered Ni2Cr precipitates and the matrix challenges any quantification of precipitate size, volume fraction and density from APT data. Strong evaporation and reconstruction artefacts are present as evidenced by the density variations in the reconstructed data. We hypothesized that the different evaporation fields between ordered and disordered phases affect the surface of the specimen and the ion trajectories leading to macroscopic variations in the detected atomic densities. Periodic plane structures are locally resolved and correspond to one of the 6 variants of the Pt2Mo-type phase. Specifically, the variant with its [100] direction parallel the [110] direction of FCC matrix. The other variants are not resolvable due to limited spatial resolution. Density map suggests a correlation between the periodic plane structures and high density regions. The high density regions also exhibit higher Cr concentration than the stoichiometric value of 33 at.%. The 4 Ni-Cr binary alloys exhibited similar density and compositional variations, as illustrated in Figure 7. The use of Hough transformations did not lead to any satisfactory analysis of the data that remains strongly limited by its poor spatial resolution.

Figure 6. (a) EBSD map showing the \{110\} grain orientation chosen for APT sample preparation. APT ion maps showing (b) density variations and (c) periodic plane structures possibly corresponding to the ordered region. (d) APT density map showing the correlation.
Figure 7. 2-nm slices of APT ion maps showing density variations in (a) Ni:Cr = 1.8, (b) Ni:Cr = 2.0, (c) Ni:Cr = 2.2, and (d) Ni:Cr = 2.4 alloys after thermal aging at 475 °C for 10,000 h.

3.2.3 Commercial alloy aging results

3.2.3.1 Microhardness testing

3.2.3.1.1 Methods
For the microhardness tests, the bulk specimens (in dimensions of 10x12x120 mm) were sectioned into (10x12x5 mm samples) and polished using SiC papers from 120 to 1200 grit followed by 0.5 μm colloidal alumina polishing to create flat surfaces. The surfaces of all tested materials were prepared to minimize the alterations of the characteristic of the material being indented [3]. Microhardness measurements were performed by using a model M 400-A Leco hardness tester with a pyramidal diamond tip. A load of 500 gf was applied for a 15 sec duration for each indentation. A minimum of five indentations were completed on each sample surface. Standard
calculation of the Vickers hardness were completed with optical measurements of indentation size with 55x magnification light microscope measurements as outlined in the standard [3]. This report has conducted hardness testing on Alloy 690, 625, and 625 Plus. The alloys were isothermally aged for ~10,000, and ~17,000 h. The alloys were aged for both of these times at four temperatures; 330, 360, 418, and 470 °C.

3.2.3.1.2 Results
The average Vickers hardness for each ageing time across the four temperatures is graphed in Figure 8. The average size of indentation from the Vickers hardness testing is ~50 µm. The results show an increase in hardness with exposure to tested isothermal aging conditions. It is hypothesized that the increased hardness is due to the formation of the Ni2Cr phase.

![Figure 8. Vickers Hardness for Alloy 690, 625, and 625 Plus at aging times AR, 10,000, and 17,000 h averaged for all ageing temperatures 330, 360, 418, and 470 °C. The result shows that each alloy has increased in hardness in response to isothermal aging.](image)

3.2.3.2 High temperature aging of Alloy 625 and 625 Plus

3.2.3.2.1 Methods
Both alloys were solution treated at 1100 °C for 1 hour, followed by water quenching, and aged at 650 °C for 8, 25 and 100 hours in order to investigate the evolution of γ” precipitates. Longer aging times (200, 300, 400 and 1000 hours) were applied to Alloy 625 Plus in order to characterize the precipitation of γ’ phase.

APT and TEM samples were electropolished using a 10% perchloric acid + 90% methanol electrolyte at -30 °C. APT and transmission electron microscopy (TEM) specimens were prepared
using a standard lift-out and Ga ion beam thinning process on both FEI Nova 200 and FEI Helios 650 Nanolab dual scanning electron microscope (SEM)/focus ion beam (FIB) instruments. TEM specimens were characterized on a JEOL 3011 transmission electron microscope. APT data was collected on both Cameca LEAP 4000X HR and 5000 XR instruments operated in laser mode using a pulse energy of 50 pJ, 200 kHz pulse rate, and a target detection rate of 0.5% at 50 K. APT data was analyzed using the IVAS 3.8.2 software, and the radius evolution of the reconstructed dataset was based on voltage evolution using the evaporation field of Ni. The reconstruction parameters (image compression factor and field factor k) were adjusted to minimize the matrix atomic density variations along the longitudinal and radial directions. The image compression factor and kf value ranged between 1.3 and 1.8, and between 2.9 and 3.5, respectively.

3.2.3.2.2 Results

3.2.3.2.2.1 Alloy 625

The evolution of γ” precipitates (as revealed by the depletion of Cr and partitioning of Nb and Ti in Figure 9) during aging at 650 °C is shown in Figure 9. Mo exhibited a neutral in partitioning behavior, and Al slightly partitioned to the γ” phase (Figure 10). The compositions of γ matrix and γ” precipitates as a function of aging time are listed in Table 7. The measured precipitate compositions are consistent with the Ni₃(Nb, Ti, Mo, Al) γ” phase. The presence of γ” precipitates was also confirmed by the superlattice diffraction spots at {1 0 0}, {1 1/2 0} and {1 1 0} positions in the <001>-zone TEM diffraction patterns (Figure 11 (a)), which correspond to body-centered tetragonal (BCT) structure [4]. The sizes of γ” precipitates in TEM dark-field image (Figure 11(b)) are consistent with the observation in APT results.

3.2.3.2.2.2 Alloy 625 Plus

The evolution of γ” and γ’ precipitates in Alloy 625 during aging at 650 °C was characterized by APT, as shown in Figure 12. The formation of γ” precipitates was first observed after aging at 650 °C for 8 hours, as shown by the very faint depletion of Cr, and the γ” precipitates grew larger as increasing aging time. For aging periods shorter than 300 hours, only γ” precipitates were observed. However, as aging time exceeded 300 hours, Ti and Al-rich γ’ precipitates were observed but with much lower density compared to γ” precipitates. For both γ” and γ’ phases, Ni, Nb and Ti partitioned to the precipitates, while Cr and Fe partitioned to the γ matrix (Figure 13). As opposed to the γ” phase that exhibited slight Al enrichment and no Mo partitioning, Al strongly partitioned to the γ’ phase, while Mo is significantly depleted (Figure 13). The measured matrix composition became stable after 300-hour aging. The measured γ” composition was close to Ni₃(Nb, Ti, Mo, Al), and the γ’ composition was measured to be Ni₃(Ti, Al, Nb). The compositions of the γ matrix, γ” and γ’ precipitates as a function of aging time are listed in Table 8.

The γ” phase precipitated with a disk shape, while γ’ precipitates formed with a cuboid morphology, as illustrated in Figure 14. All the observed γ’ precipitates were attached to the flat surface of the disk-shaped γ” precipitates. The γ”-γ’ duplets were more frequently observed than the γ”-γ’-γ” triplets (sandwich structure). TEM bright-field images displayed comparable sizes of precipitates after 1000-hour aging as observed in APT results, and the <001>-TEM diffraction pattern confirmed the presence of precipitates (Figure 15). The TEM dark-field images illustrated the different variants of γ” precipitates. The morphology of γ”-γ’-γ” triplets was also observed in dark-
field image taken by selecting (010) superlattice diffraction spot, as highlighted by the yellow circle in Figure 15 (c).

Figure 9. APT ion maps Alloy 625 after (a) solution treatment and thermal aging at 650 °C for (b) 8 h and (c) 25 h. The thickness of ion map slice is 1, 2, 10, 10, 20, 20 and 20 nm for Ni, Cr, Mo, Fe, Nb, Ti, and Al, respectively, and the same thickness will be used in this article.

Figure 10. Proximity histograms [5] (proxigrams), generated from Cr iso-concentration interfaces at 16 at%, of γ” precipitates in Alloy 625 after 650 °C aging for 25 h. The error bars are based on the counting error $\sqrt{c_i(1 - c_i)/N_{bin}}$, where $c_i$ is the atomic fraction of element $i$ and $N_{bin}$ is the total number of atoms in the bin.
Table 7. Chemical composition (at.%) of the γ matrix and γ” precipitates in Alloy 625. The counting errors are listed in the parentheses.

<table>
<thead>
<tr>
<th>Phase</th>
<th>Aging time (h)</th>
<th>Ni</th>
<th>Cr</th>
<th>Mo</th>
<th>Fe</th>
<th>Nb</th>
<th>Ti</th>
<th>Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>γ matrix</td>
<td>8</td>
<td>59.9 (0.02)</td>
<td>28.5 (0.02)</td>
<td>5.19 (0.01)</td>
<td>3.77 (0.01)</td>
<td>1.85 (0.01)</td>
<td>0.25 (&lt;0.01)</td>
<td>0.31 (&lt;0.01)</td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>58.5 (0.03)</td>
<td>30.4 (0.03)</td>
<td>5.35 (0.01)</td>
<td>4.00 (0.01)</td>
<td>1.16 (0.01)</td>
<td>0.14 (&lt;0.01)</td>
<td>0.24 (&lt;0.01)</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>57.8 (0.03)</td>
<td>29.9 (0.02)</td>
<td>5.88 (0.01)</td>
<td>3.96 (0.01)</td>
<td>1.48 (0.01)</td>
<td>0.15 (&lt;0.01)</td>
<td>0.09 (&lt;0.01)</td>
</tr>
<tr>
<td>γ” precipitates</td>
<td>8</td>
<td>73.7 (0.90)</td>
<td>4.77 (0.39)</td>
<td>6.24 (0.47)</td>
<td>0.59 (0.18)</td>
<td>12.3 (0.73)</td>
<td>1.16 (0.23)</td>
<td>0.79 (0.17)</td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>74.3 (0.23)</td>
<td>3.65 (0.10)</td>
<td>5.27 (0.12)</td>
<td>0.60 (0.06)</td>
<td>13.2 (0.20)</td>
<td>1.87 (0.07)</td>
<td>0.89 (0.04)</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>73.0 (0.29)</td>
<td>3.67 (0.13)</td>
<td>6.07 (0.15)</td>
<td>0.75 (0.08)</td>
<td>13.5 (0.25)</td>
<td>1.52 (0.08)</td>
<td>0.55 (0.05)</td>
</tr>
</tbody>
</table>

Figure 11. (a) <001>-zone TEM diffraction patterns showing the corresponding superlattice diffraction spots of γ” precipitates, and (b) TEM dark-field image showing γ” precipitates in Alloy 625 after thermal aging for 25 hours.
Figure 12. APT ion maps Alloy 625 Plus after (a) solution treatment and thermal aging at 650 °C aging for (b) 8 h, (c) 25 h, (d) 100 h, (e) 300 h, (f) 400 h, and (g) 1000 h, respectively.
Figure 13. (a) Proximity histograms, generated from Cr iso-concentration interfaces at 16 at%, of \( \gamma'' \) precipitates in Alloy 625 Plus after 650 °C aging for 1000 h. (b) Proximity histograms, generated from Al iso-concentration interfaces at 5 at%, of \( \gamma' \) precipitates in Alloy 625 Plus after 650 °C aging for 1000 h.
Table 8. Chemical composition (at.%) of the $\gamma$ matrix, $\gamma''$, and $\gamma'$ precipitates in Alloy 625 Plus.

The counting errors are listed in the parentheses.

<table>
<thead>
<tr>
<th>Phase</th>
<th>Aging time (h)</th>
<th>Ni</th>
<th>Cr</th>
<th>Mo</th>
<th>Fe</th>
<th>Nb</th>
<th>Ti</th>
<th>Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\gamma$ matrix</td>
<td>25</td>
<td>57.6</td>
<td>29.1</td>
<td>4.71</td>
<td>6.08</td>
<td>1.10</td>
<td>0.84</td>
<td>0.37</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>57.7</td>
<td>29.5</td>
<td>4.92</td>
<td>6.24</td>
<td>0.72</td>
<td>0.54</td>
<td>0.24</td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>55.6</td>
<td>31.4</td>
<td>4.84</td>
<td>6.59</td>
<td>0.67</td>
<td>0.48</td>
<td>0.18</td>
</tr>
<tr>
<td></td>
<td>400</td>
<td>56.1</td>
<td>31.0</td>
<td>4.90</td>
<td>6.48</td>
<td>0.61</td>
<td>0.43</td>
<td>0.22</td>
</tr>
<tr>
<td></td>
<td>1000</td>
<td>55.9</td>
<td>31.1</td>
<td>4.89</td>
<td>6.67</td>
<td>0.61</td>
<td>0.43</td>
<td>0.14</td>
</tr>
<tr>
<td>$\gamma''$ precipitates</td>
<td>25</td>
<td>74.7</td>
<td>3.16</td>
<td>4.94</td>
<td>0.79</td>
<td>9.42</td>
<td>5.99</td>
<td>0.70</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>74.9</td>
<td>2.38</td>
<td>5.51</td>
<td>0.61</td>
<td>9.44</td>
<td>6.41</td>
<td>0.46</td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>74.9</td>
<td>1.79</td>
<td>5.61</td>
<td>0.67</td>
<td>9.34</td>
<td>6.96</td>
<td>0.48</td>
</tr>
<tr>
<td></td>
<td>400</td>
<td>74.8</td>
<td>2.04</td>
<td>5.45</td>
<td>0.63</td>
<td>9.76</td>
<td>6.59</td>
<td>0.49</td>
</tr>
<tr>
<td></td>
<td>1000</td>
<td>74.7</td>
<td>1.96</td>
<td>5.44</td>
<td>0.60</td>
<td>9.65</td>
<td>6.88</td>
<td>0.51</td>
</tr>
<tr>
<td>$\gamma'$ precipitates</td>
<td>300</td>
<td>70.6</td>
<td>0.93</td>
<td>0.63</td>
<td>0.90</td>
<td>5.42</td>
<td>10.5</td>
<td>10.5</td>
</tr>
<tr>
<td></td>
<td>400</td>
<td>71.1</td>
<td>0.63</td>
<td>0.96</td>
<td>0.72</td>
<td>4.60</td>
<td>11.1</td>
<td>10.5</td>
</tr>
<tr>
<td></td>
<td>1000</td>
<td>71.5</td>
<td>0.78</td>
<td>0.80</td>
<td>1.01</td>
<td>4.82</td>
<td>10.5</td>
<td>10.1</td>
</tr>
</tbody>
</table>
Figure 14. APT ion maps showing (a) the $\gamma''$-$\gamma'$ duplets and (b) the $\gamma''$-$\gamma'$-$\gamma''$ triplets. Only Al and Mo were displayed for clarity.

Figure 15. (a) TEM bright-field image showing $\gamma''$ and $\gamma'$ precipitates in Alloy 625 Plus after thermal aging for 1000 hours. (b) $<001>$-zone TEM diffraction patterns. TME dark-field images taken from (c) (010), and (d) (100) superlattice diffraction spots. The $\gamma''$-$\gamma'$-$\gamma''$ triplets structure is highlighted by the yellow circle in (c).
3.2.3.2.3 Summary

Despite the similar composition of Alloy 625 and Alloy 625 Plus, their aging behavior at 650 °C revealed significant differences. In addition to the γ” phase forming in Alloy 625, the γ’ phase subsequently formed in Alloy 625 Plus. The γ” phase compositions were different with the Nb concentration being higher than Ti for Alloy 625, while being comparable for Alloy 625 Plus. Higher number density of smaller γ” precipitates were observed in Alloy 625 Plus after the same thermal aging condition and slower coarsening rates were also measured in Alloy 625 Plus.

3.3 IRRADIATION OF MODEL AND COMMERCIAL ALLOYS

3.3.1 Test matrix

Sample surfaces for proton and ion irradiations were prepared by electropolishing at 30 V in a 10% perchloric acid + 90% methanol electrolyte at -30 °C. As-quenched and aged samples of both alloys were irradiated at the Michigan Ion Beam Laboratory using a 2 MeV proton beam, at an estimated dose rate of 10^{-5} dpa/s at 300 °C. Ion irradiations were performed at 300 °C using a 5 MeV Ni ion beam, at a dose rate of 10^{-4} dpa/s. Following the suggestions in [6], SRIM calculation [7] was performed to estimate the damage profile using the Kinchin–Pease model [8] with the displacement energy of 25 eV [9]. The irradiation conditions are summarized in Table 9.

APT and transmission electron microscopy (TEM) specimens were prepared using a standard lift-out and Ga ion beam thinning process on both FEI Nova 200 and FEI Helios 650 Nanolab dual scanning electron microscope (SEM)/focus ion beam (FIB) instruments. TEM specimens were characterized on a JEOL 3011 transmission electron microscope, and bright field scanning transmission electron microscopy (STEM) images were obtained using a JEOL 2100F microscope. APT data was collected on a CAMECA LEAP 5000 XR instrument operated in laser mode using a pulse energy of 50 pJ, 200 kHz pulse rate, and a target detection rate of 0.5% at 50 K. APT data was analyzed using the IVAS 3.8.2 software, and the radius evolution of the reconstructed dataset was based on voltage evolution using the evaporation field of Ni (35 nm/V [2]). The reconstruction parameters (image compression factor and field factor k_f) were adjusted to minimize the matrix atomic density variations along the longitudinal and radial directions. The image compression factors ranged between 1.4 and 1.8 and the k_f values between 2.9 and 3.8.

<table>
<thead>
<tr>
<th>Table 9. Irradiation conditions</th>
<th>Proton irradiation (2 MeV)</th>
<th>Ion irradiation (5 MeV Ni)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alloy 690</td>
<td>300 °C, 10^{-5} dpa/s, 1.5, 6, 11 dpa</td>
<td>300 °C, 10^{-4} dpa/s, 1.5 dpa</td>
</tr>
<tr>
<td>Alloy 625</td>
<td>300 °C, 10^{-5} dpa/s, 1.5, 6, 11 dpa</td>
<td>300 °C, 10^{-4} dpa/s, 1.5 dpa</td>
</tr>
<tr>
<td>Alloy 625+</td>
<td>300 °C, 10^{-5} dpa/s, 1.5, 6, 11 dpa</td>
<td>300 °C, 10^{-4} dpa/s, 1.5 dpa</td>
</tr>
<tr>
<td>Model alloys</td>
<td>300 °C, 10^{-5} dpa/s, 1.5, 6 dpa</td>
<td>300 °C, 10^{-3} dpa/s, 1.5 dpa for NiCr 2.0 only</td>
</tr>
</tbody>
</table>
3.3.2 Model Alloys

3.3.2.1 In Situ Micropillar compression

In situ SEM micropillar compression testing was also performed on 6 dpa and 300 °C proton irradiated NiCr 2.0 binary model alloy with a rate of 10⁻³ dpa/s. The sample was first characterized by EBSD to identify grains with [001] orientation on the edge of the specimen for pillar fabrication and compression.

The change of contrast of pillar front surface can be observed during compression in Figure 16, which indicates the formation of deformation twin during compression based on the previous analysis of thermal aged model alloy. The phenomenon indicates that 1) ordered precipitates were formed during proton irradiation. 2) The effect of proton irradiation induced ordered precipitates on the changing of deformation mode in Ni-Cr system is similar to that of thermal induced ordered precipitates.

![Figure 16. In situ micropillar compression indicates the formation of twinning in proton-irradiated Ni-Cr 2.0 model alloy in [001] grain orientation.](image)

3.3.2.2 Atom probe tomography and transmission electron microscopy

3.3.2.2.1 Methods

APT and TEM specimens were prepared using a standard lift-out and Ga ion beam thinning process on both FEI Nova 200 and FEI Helios 650 Nanolab dual scanning electron microscope (SEM)/focus ion beam (FIB) instruments. TEM specimens were characterized on a JEOL 3011 transmission electron microscope. APT data was collected on both Cameca LEAP 4000X HR and 5000 XR instruments operated in laser mode using a pulse energy of 50 pJ, 200 kHz pulse rate, and a target detection rate of 0.5% at 50 K. APT data was analyzed using the IVAS 3.8.2 software. The fine-scale clustering revealed in some of the APT data was analyzed using radial distribution functions. The normalized concentration fluctuation curves were fitted using the following equation [10]:

\[
\frac{c_i(r)}{c_i^0} = A \cos \left(\frac{2\pi r}{\lambda}\right) \exp \left(-\frac{r}{\xi}\right) + 1
\]

Equation 1
where $C_i(r)$ is the average concentration of element $i$ at the distance of $r$ from an $i$ atom, $C_i^0$ is the bulk concentration of element $i$ in the analyzed volume, $A$ is the amplitude of the normalized concentration fluctuations, $\lambda$ is the wavelength of the fluctuation, and $\xi$ is the correlation length that describes the attenuation of the fluctuation. The cluster size can be approximated as the correlation length ($\xi$), and $\lambda^{-3}$ roughly represents the number density of the clusters.

3.3.2.2.2 Results

Both ion and proton irradiation were performed to investigate how different irradiation conditions affect the microstructural evolution in Ni-Cr binary alloys. The NiCr 2.0 sample remained as solid solution after ion irradiation at the dose rate of $10^{-3}$ dpa/s, as shown by the uniform distribution of Ni and Cr atoms in Figure 17. However, proton-irradiated NiCr 2.0 alloy exhibited density and compositional variations, as illustrated in Figure 18. Periodic plane structures similar to those observed in aged samples were found. TEM diffraction patterns further confirmed the formation of Pt$_2$Mo-type ordered precipitates after proton irradiation at 1.5 and 6 dpa, as revealed by the superlattice diffraction spots in Figure 19 (a) and (c). Voids and dislocation loops were also observed in proton-irradiated NiCr 2.0 alloy (Figure 19 (b) and (d)-(e)). The void size (diameters) and density at 6 dpa was $6.7 \pm 2.5$ nm and $2.9 \pm 0.6 \times 10^{21}$ m$^{-3}$, and dislocation loop size and density was $13.3 \pm 7.9$ nm and $7.8 \pm 1.6 \times 10^{21}$ m$^{-3}$, respectively. Due to the challenging analysis of Pt$_2$Mo-type ordered precipitates in APT data, STEM characterization was attempted to capture the morphology and distribution of Pt$_2$Mo-type ordered precipitates. <001>-zone STEM images revealed the formation of voids and dislocation loops simultaneously, as shown in Figure 20. The small black dots, pointed out by the yellow arrows in the STEM bright-field image (Figure 20 (a)) may require further investigation to confirm whether they correspond to the Pt$_2$Mo-type ordered precipitates or other defects generated during irradiation.

Figure 17. 2-nm slices of APT ion map showing uniform distribution of Ni and Cr atoms in Ni:Cr = 2.0 alloy after 1.5 dpa ion irradiation at the dose rate of $10^{-3}$ dpa/s at 300 °C.
Figure 18. 1-nm slice APT ion map showing density variations and periodic plane structures in Ni:Cr = 2.0 alloy after 1.5 dpa proton irradiation at the dose rate of 10^{-5} dpa/s at 300 °C.

Figure 19. (a) TEM diffraction pattern and (b) TEM bright-field image showing the presence of Pt₂Mo-type ordered phase and void formation in Ni:Cr = 2.0 alloys after 1.5 dpa proton irradiation at the dose rate of 10^{-5} dpa/s at 300 °C. (c) TEM diffraction pattern, (d) TEM bright-field image, and (e) TEM rel-rod dark-field image showing the presence of Pt₂Mo-type ordered phase, void formation, and dislocation loop formation in Ni:Cr = 2.0 alloys after 6 dpa proton irradiation at the dose rate of 10^{-5} dpa/s at 300 °C.
Figure 20. (a) <001>-zone STEM bright-field and (b) STEM LAADF image showing void formation (pointed out by white arrows) and black dot features (pointed out by the yellow arrows) in Ni:Cr = 2.2 alloys after 6 dpa proton irradiation at the dose rate of $10^{-5}$ dpa/s at 300°C.

3.3.3 Alloy 690
The proton-irradiated samples were characterized using APT and TEM. Voids were observed at all three doses with increasing average diameter and number density with increasing dose. At 11 dpa, a bimodal distribution of voids is present (Figure 21). High densities of dislocation loops were also observed with average loop diameter increasing with dose (Figure 21). Measured average sizes and number densities are summarized in Table 10. The superlattice diffraction spots of Pt$_2$Mo-type ordered phase were present at all doses from 1.5 to 11 dpa (Figure 22). However, the intensity of these spots appeared to be weaker as compared to the other two alloys (Alloy 625, 625Plus) under equivalent irradiation conditions. APT analysis revealed Al and Ti co-clustering, Si-rich clusters, and segregation of Ni and Si to dislocation loops (Figure 22). The evolution of the Al and Ti clustering behavior as a function of dose is quantified in Figure 23 (a). The location of Al-rich clusters corresponded well to Ti-rich clusters (Figure 23 (b)), and these clusters evolved from a fine scale and uniform distribution at 1.5 dpa to larger sizes and a non-uniform distribution that is anti-correlated with dislocation loops as dose increased (Figure 22). The Al-rich clusters are enriched in Ni, Ti and Al while depleted in Cr and Fe, as shown in Figure 23 (c).
Figure 21. (a)-(c) TEM bright-field images showing the formation of voids in Alloy 690 after proton irradiation at 1.5, 6 and 11 dpa, respectively. (d) the void size distribution at 6 and 11 dpa. (e)-(g) TEM rel-rod dark field images showing the formation of dislocation loops in Alloy 690 after proton irradiation at 1.5, 6 and 11 dpa, respectively. (h) loop size distribution at 1.5, 6 and 11 dpa.

Figure 22. <001>-zone TEM diffraction patterns and APT ion maps and of Alloy 690 after proton irradiation to (a) 1.5 dpa, (b) 6 dpa, and (c) 11 dpa.
Figure 23. (a) The evolution of concentration fluctuation amplitude, wavelength and correlation length of Ti and Al in Alloy 690 after proton irradiation. (b) A 20-nm slice of APT ion maps showing the spatial distribution of Ti-rich and Al-rich clusters. (c) The proxigram of Al-rich clusters calculated from Al 1.2 at.% iso-concentration surfaces.

Table 10. Summary of void and dislocation loop size and number density in Alloy 625, 625 Plus, and 690 under proton irradiation.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Dose (dpa)</th>
<th>Voids</th>
<th>Dislocation loops</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Average size (nm)</td>
<td>Number density (×10^{21} m^{-3})</td>
</tr>
<tr>
<td>625</td>
<td>1.5</td>
<td>4.2</td>
<td>0.14</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>4.9 ± 1.4</td>
<td>11.0 ± 1.7</td>
</tr>
<tr>
<td></td>
<td>11</td>
<td>5.9 ± 1.8</td>
<td>17.2 ± 1.5</td>
</tr>
<tr>
<td>625 Plus</td>
<td>1.5</td>
<td>2.9 ± 0.6</td>
<td>0.17 ± 0.1</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>6.4 ± 1.9</td>
<td>1.8 ± 0.4</td>
</tr>
<tr>
<td></td>
<td>11</td>
<td>18.2 ± 2.6</td>
<td>1.6 ± 0.3</td>
</tr>
<tr>
<td>690</td>
<td>1.5</td>
<td>3.9 ± 0.6</td>
<td>0.23 ± 0.1</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>9.9 ± 1.9</td>
<td>1.0 ± 0.2</td>
</tr>
<tr>
<td></td>
<td>11</td>
<td>14.1 ± 5.0</td>
<td>2.9 ± 0.5</td>
</tr>
</tbody>
</table>

3.3.4 Alloy 625 and 625 Plus

3.3.4.1 Microstructures prior irradiation
Alloy microstructures in the as-quenched and aged conditions were first characterized before irradiation. In the as-quenched conditions, both alloys exhibited uniform elemental distributions, and the <001>-zone TEM diffraction patterns only showed the spots of face-centered cubic matrix (Figure 24). Following thermal aging, γ” precipitation was evident in both alloys, as illustrated by
the superlattice spots at \{1 \ 0 \ 0\}, \{1 \ 1/2 \ 0\} and \{1 \ 1 \ 0\} positions in the \langle001\rangle-zone TEM diffraction patterns (Figure 24). The elements, Ni, Nb and Ti partitioned to the \gamma'' phase, whereas Cr and Fe partitioned to the \gamma matrix in both alloys. The concentrations of Mo remained nearly the same in the matrix and \gamma'' precipitates, and a slight partitioning of Al to the \gamma'' phase was observed in both alloys (Figure 25). The measured compositions of the different phases are summarized in Table 7 and Table 8.

Figure 24. APT ion maps and \langle001\rangle zone TEM diffraction patterns of (a) Alloy 625 and (b) Alloy 625 Plus after solution treatment, and (c) Alloy 625 and (d) Alloy 625 Plus after aging at 650 °C aging for 25 h and 100 h, respectively. The thickness of ion map slice is 1, 2, 10, 10, 20, 20 and 20 nm for Ni, Cr, Mo, Fe, Nb, Ti, and Al, respectively, and the same thickness will be used in subsequent figures.
Figure 25. Proximity histograms, generated from Cr iso-concentration interfaces at 16 at% of γ’’ precipitates in (a) Alloy 625 after 650 °C aging for 25 h, and (b) Alloy 625 Plus after 650 °C aging for 100 h (solid lines) and post-aging ion irradiation to 1.5 dpa (dashed lines). The error bars are based on the counting error \( \sqrt{c_i(1 - c_i)/N_{bin}} \), where \( c_i \) is the atomic fraction of element \( i \) and \( N_{bin} \) is the total number of atoms in the bin. Error bars are removed in (b) for clarity.

3.3.4.2 Alloy 625

3.3.4.2.1 Proton irradiation

Microstructure characterization revealed the formation and evolution of voids, dislocation loops and solute clusters. Voids were observed at all three doses (1.5, 6, and 11 dpa) using the bright-field under-focused condition (Figure 26). While number density increased with dose, the average void diameters barely increased. Dislocation loops were quantified using the rel-rod dark-field imaging condition [11] (Figure 26). The distribution of dislocation loop sizes became broader with increasing doses. Since only one quarter of the total number of loops was imaged, the number density of dislocation loops was adjusted accordingly, assuming the same number of dislocation loops on each of the \{111\} crystallographic planes. The average size and number density of voids and dislocation loops as a function of dose are summarized in Table 10. Dislocations were also revealed by APT via Si segregation (Figure 27). At 1.5 dpa, the small Si-rich features are too small to distinguish Si-rich clusters from small dislocation loops. At 6 and 11 dpa, dislocation loops could be clearly noted and were enriched in Ni and Si while depleted in Cr, Mo, and Fe, as shown in Figure 27. In addition to Al-rich clusters and nanoscale Si-rich clusters evident in the APT data, the superlattice diffraction spots at \{2/3 2/3 0\}, \{4/3 4/3 0\} and \{2/3 4/3 0\} positions in the <001>-zone TEM diffraction patterns at all three doses (1.5, 6 and 11 dpa) indicated the formation of Pt\textsubscript{5}Mo-type ordered phase, as shown in Figure 28.
Figure 26. (a)-(c) TEM bright-field images showing the formation of voids in Alloy 625 after proton irradiation at 1.5, 6 and 11 dpa, respectively. (d) the void size distribution at 6 and 11 dpa. (e)-(g) TEM refl-dark field images showing the formation of dislocation loops in Alloy 625 after proton irradiation at 1.5, 6 and 11 dpa, respectively. (h) loop size distribution at 1.5, 6 and 11 dpa.

Figure 27. (a) APT Si ion maps of proton-irradiated Alloy 625 at 1.5, 6, and 11 dpa. The ion maps are displayed in the style of the whole dataset. (b) the proximity histogram (proxigram) of dislocation loops calculated from Si 0.8 at% iso-concentration surfaces.
The evolution of the solute clusters is summarized in Figure 29. The Al cluster composition and size increased while number density decreased as dose increased. No prominent clustering of Nb and Ti was observed. In the 6 and 11 dpa irradiation conditions, the distribution of Al-rich clusters became non-uniform and the Al-rich clusters depleted regions were observed near the Si-rich regions, as illustrated in Figure 29. The Al-rich clusters are enriched in Ni, Al, Nb and Ti while depleted in Cr, Mo and Fe, as displayed by the proxigrams of Al-rich clusters defined by 1.2 at% Al iso-concentration surfaces in Figure 29.

Si-rich clusters with an average radius of ~1.6 ± 0.6 nm were observed at 1.5 dpa, and grew larger as dose was increased to 6 dpa (radius ~1.7 ± 0.9 nm) and 11 dpa (radius ~2.0 ± 0.9 nm), as shown in Figure 30. The clusters are either near dislocation loops or isolated and their composition is close to the Ni3Si phase, as shown in Figure 30 (b). However, no superlattice spots corresponding to an L12 ordered phase were observed in the TEM diffraction patterns. Voids were also captured within the APT datasets as evidenced by the dark pink 76 atom/nm³ iso-density surfaces, which is approximated two times higher than the matrix atomic density.
Figure 29. (a) the evolution of concentration fluctuation amplitude of Nb, Ti and Al, the evolution of wavelength and correlation length of Al in Alloy 625 after proton irradiation. (b) a 15-nm slice of APT ion maps showing the spatial distribution of Al-rich clusters. (c)-(d) the proxigrams of Al-rich clusters calculated from Al 1.2 at% iso-concentration surfaces.

Figure 30. (a) APT ion map showing the spatial distribution of Si-rich clusters, delineated by the grey Si 3.9 at% iso-concentration surfaces. Voids were also presented by the dark pink 76 atom/nm$^3$ iso-density surfaces to distinguish from Si-rich clusters. (b) Proxigram of Si-rich clusters calculated from Si 3.9 at% iso-concentration surfaces.
3.3.4.2.2  Dose rate effects: ion and proton irradiation on solution annealed and aged microstructure

Different microstructures were observed after ion and proton irradiations. As illustrated in Figure 31, ion irradiation tended to homogenize solute distributions, with the exception of Si that exhibited some clustering. Pre-existing γ” precipitates in the aged samples dissolved so that only the γ phase is present in both as-quenched and aged samples after irradiation. In both as-quenched and aged samples, proton irradiation led to precipitation of the Pt2Mo-type ordered phase, Al clustering, Si clustering and segregation. The Pt2Mo-type ordered phase is evidenced by the superlattice spots at \{2/3 2/3 0\}, \{4/3 4/3 0\} and \{2/3 4/3 0\} positions in the <001>-zone TEM diffraction patterns [2]. The absence of γ” superlattice spots in the TEM diffraction pattern of the aged condition (Figure 31 (d)) indicated the disordering of pre-existing γ” precipitates.

Clustering of Al, Nb and Ti was quantified using radial distribution functions. The number density of the clusters is approximated by \(\lambda^{-3}\). The evolution of the clusters after proton irradiation is summarized in Figure 32. For the as-quenched conditions, the amplitude and correlation length of Al increased while number density decreased as dose increased. No significant clustering of Nb and Ti was observed. For the aged conditions, the decrease of the Nb and Ti amplitudes is consistent with the dissolution of pre-existing γ” precipitates, while significant Al clustering was detected.

Si segregation to line features, presumably dislocation loops, and Si-rich clusters are observed in both as-quenched and aged conditions, (Figure 31). The composition at center of Si-rich clusters is close to Ni3Si, as illustrated by the proxigram that was calculated using 3.9 at.% Si iso-concentration surfaces (Figure 33).
Figure 31. APT ion maps and <001> zone TEM diffraction patterns of Alloy 625 after (a) solution treatment + Ni ion irradiation to 1.5 dpa, (b) 650 °C aging for 25 h + Ni ion irradiation to 1.5 dpa, (c) solution treatment + proton irradiation to 11 dpa, and (d) 650 °C aging for 25 h + proton irradiation to 5 dpa. Si ion maps are displayed in the style of the whole dataset rather than slices.

Figure 32. (a) the evolution of concentration fluctuation amplitude (represented by diamonds) of Nb, Ti and Al in Alloy 625 after proton irradiation for as-quenched (solid symbols) and aged (hollow symbols) conditions. (b) the evolution of wavelength (represented by disks) and correlation length (represented by squares) of Al in Alloy 625 after proton irradiation for as-quenched (solid symbols) and aged (hollow symbols) conditions.
Figure 33. Proximity histogram, generated from Si iso-concentration interfaces at 3.9 at%, of nano-sized Si-rich clusters in Alloy 625 after proton irradiation to 11 dpa. The error bars are based on the counting error \( \sqrt{c_i(1-c_i)/N_{bin}} \), where \( c_i \) is the atomic fraction of element \( i \) and \( N_{bin} \) is the total number of atoms in the bin.

3.3.4.3 Alloy 625 Plus

3.3.4.3.1 Proton irradiation

Similar to Alloy 625, the microstructures of proton-irradiated Alloy 625 Plus after proton irradiation exhibited high densities of voids and dislocation loops (Figure 34). The average void diameter increased with dose. The void number density increased as dose increased from 1.5 to 6 dpa (from 0.14 ± 0.1 to 1.8 ± 0.4 \( \times \)10\(^{21} \) m\(^{-3} \)), and maintained nearly the same as dose further increased to 11 dpa (1.6 ± 0.3 \( \times \)10\(^{21} \) m\(^{-3} \)). Dislocation loops were observed at 1.5 dpa, and their average sizes increased with longer irradiation exposure to 6 and 11 dpa, (Figure 34). The number density of dislocation loops increased monotonically as dose increased. The average sizes and number density of voids and dislocation loops as a function of dose are summarized in Table 10. Solute segregation of Si to dislocation loops were also observed by APT ion maps (Figure 35).

The Pt\(_2\)Mo-type ordered phase formed during irradiation as evidenced by the corresponding superlattice diffraction spots (Figure 36). The \( \gamma'' \) superlattice diffraction spots at \( \{2/3 \ 2/3 \ 0\} \), \( \{4/3 \ 4/3 \ 0\} \) and \( \{2/3 \ 4/3 \ 0\} \) positions in the \( <001> \)-zone TEM diffraction patterns were observed at 6 dpa (Figure 36). The APT ion maps also revealed the presence of the \( \gamma'' \) phase. Indeed, at 6 dpa, uniformly distributed Nb and Ti clusters were observed (Figure 36). These Nb-rich clusters, delineated by Nb iso-concentration surfaces, were distributed uniformly and were enriched in Ni, Nb, and Ti, and slightly in Al while depleted in Cr and Fe (Figure 37). Another type of clusters developed, mostly visible by the level of Al clustering. Al iso-concentration surfaces were used to define these Al-rich clusters and their locations did not correlate with the Nb-rich clusters, as shown in the 11 dpa condition. The Al-rich clusters were enriched in Ni, Al, Ti and Nb while depleted in Cr, Fe, and Mo. The Al-rich clusters are presumably embryos for the \( \gamma' \) phase. The clustering behavior in terms of amplitude, wavelength and correlation length of both Nb-rich and Al-rich clusters is summarized in Figure 37 (g).

Si-rich clusters (radius \(~1.4 \pm 0.6 \) nm) were observed in Alloy 625 Plus at 1.5 dpa (Figure 35), and their sizes increased as dose increased with dose (radius \(~2.3 \pm 0.8 \) and \(~2.0 \pm 0.9 \) nm at 6 and 11
The composition measured from larger Si-rich clusters at the 11 dpa condition revealed a stoichiometry consistent with that of the Ni₃Si phase.

Figure 34. (a)-(c) TEM bright-field images showing the formation of voids in Alloy 625 Plus after proton irradiation at 1.5, 6 and 11 dpa, respectively. (d) the void size distribution at 6 and 11 dpa. (e)-(g) TEM rel-rod dark field images showing the formation of dislocation loops in Alloy 625 Plus after proton irradiation at 1.5, 6 and 11 dpa, respectively. (h) loop size distribution at 1.5, 6 and 11 dpa.

Figure 35. APT Si ion maps of proton-irradiated Alloy 625 Plus at 1.5, 6, and 11 dpa.
Figure 36. <001>-zone TEM diffraction patterns and APT ion maps and of Alloy 625 Plus after proton irradiation to (a) 1.5 dpa, (b) 6 dpa, and (c) 11 dpa.
Figure 37. 20-nm slices of APT ion maps of (a) Nb-rich clusters and (b)-(c) their corresponding proxigrams calculated from Nb 2.8 at\% iso-concentration surfaces, and (d) Al-rich clusters and (e)-(f) their corresponding proxigrams calculated from Al 1.2 at\% iso-concentration surfaces. (g) the evolution of concentration fluctuation amplitude, wavelength and correlation length of Nb, Ti and Al in Alloy 625 Plus after proton irradiation.

3.3.4.3.2 Dose rate effects: ion and proton irradiation on solution annealed and aged microstructure

After ion irradiation, the spatial distribution of solute atoms in the as-quenched samples remained uniform, as shown in Figure 38. Pre-existing $\gamma''$ precipitates in the aged samples disordered as evidence by the absence of superlative spots. Compositionally, they also started to dissolve, with the $\gamma''$ precipitates/matrix interface becoming wider, as illustrated by the proxigram in Figure 25.
Proton irradiation of the as-quenched and aged samples resulted in precipitation of the Pt\textsubscript{2}Mo-type ordered phase and γ” phase, Si clustering and Si segregation to dislocation loops (Figure 38). APT ion maps showed not only Al but also Nb and Ti clustering for both conditions. For the as-quenched condition, quantitative analyses of the clusters showed the increase of the correlation lengths with dose. The correlation length increased from 1.5 to 6 dpa and subsequently decreased from 6 to 11 dpa, while the number density steadily decreased with dose (Figure 39). For the aged condition, the Nb and Ti amplitudes and correlation lengths decreased, while the number density of Nb and Ti increased. Superlattice spots of both the Pt\textsubscript{2}Mo-type ordered phase and γ” phase were observed in both as-quenched and aged samples.

The presence of dislocation loops after ion and proton irradiation was confirmed by STEM imaging and APT analysis (Figure 40). After ion irradiation to 1.5 dpa, the average loop diameter was 7 ± 2 nm, as measured from STEM images. Faint to no segregation was observed in the APT data (Figure 38). After proton irradiation to 5 dpa, the average loop diameter was 23 ± 6 nm, as measured from STEM images. Clear Si segregation is also observed in the APT datasets and the average size measured from full loops is 22 ± 3 nm, consistent with STEM results.

![Figure 38. APT ion maps and <001> zone TEM diffraction patterns of Alloy 625 Plus after (a) solution treatment + Ni ion irradiation to 1.5 dpa, (b) 650 °C aging for 100 h + Ni ion irradiation to 1.5 dpa, (c) solution treatment + proton irradiation to 6 dpa, and (d) 650 °C aging for 100 h + proton irradiation to 5 dpa. Si ion maps are displayed in the style of the whole dataset rather than slices.](image)
3.3.5 Summary

Microstructural evolution and phase transformation in three commercial Ni-based alloys, Alloy 625, Alloy 625 Plus, and Alloy 690, under proton irradiation at 300 °C were analyzed using TEM and APT. Common features were observed including:

- Voids and dislocation loops form at low dose in all three alloys, and the sizes of both voids and loops increase as dose increases. The number density of voids appears to saturate at around 6 dpa and the number density of dislocation loops seems to be relatively stable throughout the three dose conditions.
- Pt₂Mo-type ordered phase forms in all three alloys at 1.5 dpa (~42 hours), which indicates a faster ordering rate under irradiation.
- The segregation of Ni and Si, and depletion of Cr, Mo, Fe and Nb (no Nb in Alloy 690) at
dislocation loops are observed in all three alloys, and Si-rich clusters, with composition near to Ni3Si are found.

- In the three alloys, high number densities of nanoscale Al-rich clusters form. These clusters may be precursors of the γ’ Ni3Al phase. Clusters free zones near defect sinks are observed, which may suggest that defect sinks prevent the formation of clusters. These clusters are also rich in Ti.

- Finally, the γ’’ phase is only observed in Alloy 625 Plus.

In addition, Alloy 625 and Alloy 625 Plus, in solution treated and thermally aged conditions, were irradiated using ions and protons at different dose rates (10^{-4} and 10^{-5} dpa/s) at 300 °C. Under ion irradiation where cascade mixing dominates, both alloys irrespective of their starting microstructure, converge to solid solutions with small dislocation loops slightly segregated with Si and any pre-existing γ’’ precipitates that were formed during thermal aging first disordered and then chemically dissolve. Under proton irradiation where radiation-enhanced diffusion can play a significant role, both the microstructures also converge irrespective of their starting microstructure. Pt2Mo-type precipitates and Si decorated dislocation loops form in both alloys. However, any pre-existing γ’’ precipitates dissolve in Alloy 625, while appear stable in Alloy 625Plus.

### 3.4 Modeling of Thermal and Irradiation Degradation

Engineering scale behavior of materials are strongly impacted by the underlying microstructure. The distribution, evolution, and interaction of dislocations and defects within the individual grains dictate how the engineering scale material will perform under different loading and environmental conditions. Mesoscale models can connect microstructure evolution models to engineering models of the ductile-brittle transition temperature (DBTT) curve and fracture. The toughness of a material, which governs the engineering scale fracture behavior, is a function of both elastic deformation and plastic deformation. While the yield stress measurements capture the elastic contribution to a material's toughness, information about the dislocation movement is required to understand the plastic component of toughness.

Crystal plasticity models predict dislocation density evolution and thereby connect microstructure evolution to engineering scale behavior predictions. These models calculate the plastic strain within a metal as a function of dislocations and other crystal defects, including precipitates and interstitial loops, among others, by tracking dislocation movement and the interaction of these dislocations with the crystal defects. Within NiCr alloys, long-range ordered (LRO) precipitates form under aging conditions. These precipitates act as barriers to dislocation motion and either are sheared by dislocations, or act to pin dislocations and prevent dislocation movement. Under irradiation Ni-based alloys form voids, as discussed in previous sections of this report. These defects also impede dislocation motion in the alloys, thus contributing to embrittlement of the materials.

A crystal plasticity model for Ni-based alloys which accounts for the impact of these defects on microscale dislocation evolution has been implemented in the Grizzly code at Idaho National Laboratory (INL). This section describes the current efforts to implement a model to predict the engineering scale behavior of irradiated and aged Ni-based alloys, particularly Alloy 690 Alloy
625, into the Grizzly software. Grizzly is a multiphysics simulation code under development at INL to simulate aging mechanisms and their effects on the integrity of critical LWR components. This section includes a description of the theoretical models incorporated into the Grizzly crystal plasticity code. We begin by first discussing the methods used to characterize the theoretical representation of microstructure at the start of the crystal plasticity simulation. We introduce a set of material specific Avrami equations to estimate the number density of LRO precipitates formed after aging at a given temperature. Next we provide an overview of the dislocation evolution models used in the crystal plasticity simulations. The dislocation evolution models predict how various states of thermal aging and irradiation exposure will affect the strength and ductility of the Ni-based alloys. These theoretical dislocation evolution models include mechanisms for dislocation glide and twinning as well as dislocation-defect interaction relationship for the LRO precipitates, dislocation loops, and voids. We have selected these models based on the deformation mechanisms observed in experimental micropillar compression tests conducted on the Ni<sub>2</sub>Cr model alloy. We compare the simulation predictions to these experimental micropillar measurements to better align the simulation predictions with the experimental measurements. We conclude this section with a discussion of the theoretical model for irradiation voids and outline the procedure for extending the crystal plasticity model of the binary alloy to the Alloy 690 and Alloy 625 materials.

### 3.4.1 Thermal Aging Model

The Avrami equation can be used to represent the evolution of LRO particles which are used as an input for continuum level models. The parameters for the Avrami equation are determined from a set of experimental measurements of the evolution of hardening as a function of aging time at a range of different aging temperatures.

The Avrami equation, also known as the Kolomogorov-Johnson-Mehl-Avrami (KJMA) equation [12], is used to estimate the fraction of precipitate concentration, assuming random and homogeneous nucleation and isotropic precipitate growth:

\[
f = 1 - \exp\left[-(kt)^n\right], \quad k = k_o \cdot \exp\left[\frac{-Q}{RT}\right] \tag{Equation 2}
\]

where \(f\) is the fraction transformed, \(k\) is the ordering constant, \(t\) is the aging time, \(k_o\) is the initial ordering constant, \(Q\) is the activation energy, \(R\) is the universal gas constant, and \(T\) is the aging temperature. The Avrami equation also assumes that the fraction transformed is related to either the change in hardness, \(H\) or the change in the lattice parameter, \(a\), [12] both of which can be experimentally measured.

\[
f = \left(\frac{H - H_o}{H_{max} - H_o}\right) \tag{Equation 3}
\]

As Young et al. [12] note, the complete fraction transformation to the ordered phase \((f = 1)\), does not indicate that the entire material sample has transformed to the LRO phase. Instead the complete transformation indicates that a two-phase type equilibrium among the ordered and disordered (original alloy lattice structure) has been achieved; thus, a value of \((f = 1)\), indicates that the maximum phase fraction of LRO precipitates in the alloy has been reached.
Young and Eno [13] have shown that the Avrami equation can be used to estimate the transformed fraction of LRO precipitates in NiCr alloys under various cooling treatments. Significantly more work has been completed to understand the rate of LRO phase formation and growth in the model binary Ni$_2$Cr alloy than in the more complex Ni-based superalloys [14-16].

Our approach in implementing an Avrami relation for Alloy 690 and Alloy 625 has been to leverage the Avrami equations developed by Young and Eno [13] for the binary Ni$_2$Cr alloy. The function, named AvramiTransformedFractionFunction, implemented in Grizzly includes calculations for binary Ni$_2$Cr, Alloy 690, estimated Alloy 625, and estimated ternary Ni$_2$(Cr$_{1-x}$Mo$_x$). The constants used in the Avrami equation for the various alloys are given in Table 11.

3.4.1.1.1 Alloy 690

Based on research by Stephan et al. [17] we apply the same Avrami constants $k_0$, $Q$, and $n$ for Alloy 690 as Young and Eno [18] determined for the binary Ni2Cr model alloy. Stephan et al. [17] compared the Avrami equation for the binary model alloy to the behavior of ternary NiCrFe alloys with increasing amounts of Fe and found reasonable agreement with the Avrami equation constants for aging temperatures below 500°C. Increasing the iron content does not appear to impact the kinetics of the ordering formation but does strongly affect the temperature range in which the ordered phase forms [12].

The inclusion of Fe in a NiCr alloy is known to depress the disordering temperature, which is the temperature at which the ordered phases disorder back to the original alloy lattice structure. Mougiont et al. [19] studied the evolution of hardness, an indication of the volume fraction of the LRO phase [13], in Alloy 690 under different aging conditions. They found a maximum hardness after aging at 420°C with some hardening observed at 475°C; thus, we have restricted the long range ordered phase forming temperature bounds from 300°C to 450°C for the Alloy 690 Avrami equation.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Initial Prefactor Constant $k_0$ (hr$^{-1}$)</th>
<th>Activation Energy $Q$ (kJ/mol)</th>
<th>Exponent n (-)</th>
<th>Temperature Range (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Binary Ni$_2$Cr,</td>
<td>3.0 x 10$^{15}$</td>
<td>2.44 x 10$^{5}$</td>
<td>0.65</td>
<td>573 - 863</td>
</tr>
<tr>
<td>Furnace cooled</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Binary Ni$_2$Cr,</td>
<td>3.5 x 10$^7$</td>
<td>1.47 x 10$^5$</td>
<td>0.6</td>
<td>573 - 863</td>
</tr>
<tr>
<td>Water Quenched</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Alloy 690, Furnace</td>
<td>3.0 x 10$^{15}$</td>
<td>2.44 x 10$^5$</td>
<td>0.65</td>
<td>573 – 723</td>
</tr>
<tr>
<td>cooled</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Alloy 690,</td>
<td>3.5 x 10$^7$</td>
<td>1.47 x 10$^5$</td>
<td>0.6</td>
<td>573 - 723</td>
</tr>
<tr>
<td>Water Quenched</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Alloy 625,</td>
<td>3.12 x 10$^8$</td>
<td>1.47 x 10$^5$</td>
<td>0.65</td>
<td>673 - 873</td>
</tr>
<tr>
<td>Water Quenched,</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>estimated</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Estimated Ternary</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni$<em>2$(Cr$</em>{1-x}$Mo$_x$) Water Quenched</td>
<td>(1.47 x 10$^9$) x + 4.738 x 10$^7$</td>
<td>1.47 x 10$^5$</td>
<td>0.65</td>
<td>673 - 873</td>
</tr>
</tbody>
</table>
Data concerning the evolution of the LRO phase in Alloy 625 is more difficult to obtain, with the majority of aging studies characterizing Alloy 625 after 50,000 to 70,000 hours of in-service time [20-22]. Young and Eno [13] presented a comparison of the Avrami equation for binary Ni2Cr to a set of two aged ternary Ni2(Cr1−x Mox). alloys, with a 0.15at% and a 1.42at% Mo content, respectively. While the Mo content of these two alloys is much lower than that of Alloy 625 (5.39at% [22]), the trends observed in the literature provide a useful direction for estimating the long range ordering kinetics of Alloy 625. Young and Eno’s comparison of the ternary NiCrMo alloys demonstrate a shift of the ordering kinetics and thus the corresponding Avrami equation towards faster aging with increasing Mo content. Verma et al. [23] conducted a study of ternary Ni2(Cr1−x Mox) alloys, varying the relative composition of Cr and Mo. This group found an increase in the ordering kinetics with increasing relative Mo content using DSC measurements.

In light of these trends, we have estimated an initial prefactor constant, ko, for an Alloy 625 expression from the ternary NiCrMo alloy aging data given in Young and Eno [13]. We retain the same activation energy, Q, and Avrami exponent, n, as determined for the water quenched binary Ni2Cr alloy, see Table 12. This approach follows from the treatment of Alloy 690 [17] and is justified by the observations of the ordering kinetics shift [18]. Using the curve fit functionality of SciPy [24], we determined the ko value for both ternary NiCrMo alloys presented by Young and Eno [13] at the 418°C and 470°C aging temperatures; these values are given in Table 12. The comparison of the predicted hardness using the curve fit values of ko against the experimental data [13] is shown in Figure 41 and Figure 42.

Table 12. Avrami initial prefactor constant values curve fit for the ternary NiCrMo alloys aging data presented in Young and Eno [13] using the values for the Avrami exponent, n, and activation energy, Q, for water quenched binary Ni2Cr alloy.

<table>
<thead>
<tr>
<th>Alloy at.% Mo</th>
<th>Stoichiometric ratio in Ni2(Cr1−x Mox)</th>
<th>Curve fit ko value</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.15</td>
<td>0.005</td>
<td>6.87 x 10^7</td>
</tr>
<tr>
<td>1.42</td>
<td>0.043</td>
<td>1.09 x 10^8</td>
</tr>
</tbody>
</table>

We propose a function for the initial ordering constant as a function of Mo content, with the stoichiometric relationship given as Ni2(Cr1−x Mox), by fitting a linear function to the combination of the data listed in Table 12 with the ko value for the water quenched binary alloy (x = 0) [18]. This proposed function is

\[
k_o = 1.471 \times 10^9 \cdot x + 4.738 \times 10^7 \quad \text{Equation 4}
\]

where x is the stoichiometric ratio of Ni to Cr, and the R^2 value from the linear regression is 0.872. From this function, we estimated the ko value for Alloy 625 to be 3.12×108. The predicted LRO volume fraction curves from our proposed Avrami equation constants for Alloy 625 are shown in Figure 42.

These predicted curves are reasonable in light of the observation of LRO in ternary Ni2(Cr0.5Mo0.5) alloy after only two hours of aging at 525°C [23]. The temperature range for the formation of LRO
phases shown in Table 11 is based on DSC experiments conducted by Verma et al. [23] and characterizations of Alloy 625 after several thousand hours of operation [20-22].

3.4.1.1.3 Use in crystal plasticity mechanical behavior models

The output of the Avrami equation, the transformed fraction of long range ordered precipitates, can be used to calculate the number density of these precipitates in an alloy exposed to a conditioning temperature for a given amount of time. The precipitate number density, along with an average diameter is a required initial condition for continuum level models of the Ni-based alloys hardening response. Based on observations made by Marucco and Nath [25] of the uniform distribution of LRO precipitates, we treat the LRO number density as uniform in the entire material sample.

Figure 41: Fitted Avrami equation predictions for 0.15% Mo content ternary NiCrMo alloy with the comparison of experimentally measured hardness [18].

Figure 42: Fitted Avrami equation predictions for 1.42% Mo content ternary NiCrMo alloy with the comparison of experimentally measured hardness [18].

Figure 43: The predicted LRO volume fraction curves for Alloy 625 using the Avrami constants listed in Table 11 are consistent with expected trends published in the literature for increasing Mo content in Ni-based alloys with the volume fraction occurring sooner than in the binary Ni2Cr alloy.
We calculate the number density of LRO precipitates by assuming spherical particles:

\[ N = \frac{f \cdot P}{V_{\text{LRO-sphere}}} = \frac{f \cdot P}{\frac{4}{3}\pi r^3} \]  

Equation 5

where \( P \) is the equilibrium phase fraction of the LRO precipitates in the alloy and \( r \) is the radius. Based on TEM experiments conducted by other experimenters in this project, we assume an equilibrium phase fraction for LRO of 0.05136. The average diameter in the binary Ni2Cr alloy is taken as 2.5nm [26] and the average diameter of LRO precipitates in a ternary NiCrMo alloy was measured as 3.0nm [23]. We assume that the LRO diameter for Alloy 690 is the same as for the binary Ni2Cr and that the LRO precipitate diameter for Alloy 625 is equivalent to the ternary NiCrMo alloy diameter.

### 3.4.2 Crystal plasticity model for thermal aging and irradiation

Following Asaro [27] the crystal plasticity model implemented in Grizzly uses a multiplicative decomposition of the deformation gradient into elastic and plastic components:

\[ \mathbf{F} = \mathbf{F}^e \mathbf{F}^p \]  

Equation 6

The change in the crystal shape due to dislocation motion is accounted for in the plastic deformation gradient tensor, \( \mathbf{F}^p \), while the elastic deformation gradient tensor, \( \mathbf{F}^e \), accounts for recoverable elastic stretch and rotations of the crystal lattice. The evolution of the plastic deformation is given as:

\[ \dot{\mathbf{F}}^p = \mathbf{L}^p \mathbf{F}^p \]  

Equation 7

where \( \mathbf{L}^p \) is the plastic velocity gradient. The plastic deformation gradient rate is used to calculate the increment of the Lagrangian strain. The plastic velocity gradient is defined as the sum of the slip increments from dislocation motion on all of the slip systems. As in the approach of Wu et al. [28] we additively decompose the plastic velocity gradient to account for the various mechanisms of dislocation movement in the Ni alloy crystal.

\[ \mathbf{L}^p = \sum_{\alpha}^\gamma \dot{\gamma}_{\text{glide}}^\alpha \mathbf{s}_\alpha^\alpha \otimes \mathbf{m}_\alpha^\alpha + \sum_{\beta}^\gamma \dot{\gamma}_{\text{twin}}^\beta \mathbf{s}_\beta^\beta \otimes \mathbf{m}_\beta^\beta \]  

Equation 8

where \( \dot{\gamma}_{\text{glide}}^\alpha \) is the slip rate due to dislocation glide and \( \dot{\gamma}_{\text{twin}}^\beta \) is the dislocation slip rate from twinning. Note that the slip direction and slip plane normal unit vectors, \( \mathbf{s}_\alpha \) and \( \mathbf{m}_\alpha \), are defined in the reference configuration.

#### 3.4.2.1 Glide dislocation evolution model

The plastic dislocation glide slip on each slip system, \( \dot{\gamma}_{\text{glide}}^\alpha \), is connected to the behavior of the mobile glide dislocations through Orowan’s relation, where only dislocation glide is considered.
where $\rho^\alpha_{\text{mobile}}$ is the mobile dislocation density on each slip system $\alpha$, $b$ is the burgers vector of the crystal, and $v^\alpha$ is the glide velocity of the mobile dislocations. In this implementation we apply a power law glide expression for the dislocation glide velocity,

$$v^\alpha_{\text{glide}} = v_0 b \left| \frac{\tau^\alpha}{g^\alpha} \right|^{1/m} \text{sign}(\tau^\alpha) \quad \text{if} \quad \tau^\alpha \geq g_o^\alpha$$

Equation 10

where $v_0$ is the initial dislocation velocity, $\tau^\alpha$ is the applied resolved shear stress on each slip system $\alpha$, and $g^\alpha$ is the slip system resistance or strength. As a consequence of the decision to use the slip direction and plane normal unit vectors from the initial crystal orientation, the second Piola-Kirchhoff stress is used to determine the applied resolved shear stress.

The constitutive relationship for dislocation glide is based on the Continuum Dislocation Dynamics (CDD) framework [29], with separate terms used to describe each of the specific physical glide mechanisms in the dislocation evolution rate terms. The rate of the mobile dislocation evolution rate is also fully coupled to the immobile dislocation evolution rate. The mobile dislocation evolution is governed by six terms: each term in the equation represents a specific physical dislocation-interaction mechanism.

$$\dot{\rho}^\alpha_{\text{mobile}} = \dot{\rho}^\alpha_{\text{generation}} - \dot{\rho}^\alpha_{\text{mobile-annihilation}} - \dot{\rho}^\alpha_{\text{locking}}$$

$$+ \dot{\rho}^\alpha_{\text{freed}} - \dot{\rho}^\alpha_{\text{immobile-annihilation}}$$

Equation 11

Mobile dislocation generation is considered to occur by Orowan looping. Dislocation annihilation of two dislocations of opposite sign can occur between two mobile dislocations or between an immobile dislocation and a mobile dislocation. The annihilation interaction among dislocations is assumed to occur only within a capture radius, $R_c$, which is defined as a factor of the burgers vector.

The mobile dislocation evolution rate is coupled to the immobile dislocation evolution rate through evolution terms for dislocation locks and dislocations freed from locks. These terms also appear in the evolution rate equation for immobile dislocations

$$\dot{\rho}^\alpha_{\text{immobile}} = \dot{\rho}^\alpha_{\text{locking}} - \dot{\rho}^\alpha_{\text{freed}} - \dot{\rho}^\alpha_{\text{immobile-annihilation}}$$

Equation 12

The locked dislocations term, which is negative in the mobile dislocation evolution equation acts as the source term for the immobile dislocations.

3.4.2.1.2 Hardening models

In this crystal plasticity model we consider both defects and other dislocations as barriers to dislocation motion [30]. Here the resistance of the slip systems to dislocation motion is considered
as the additive sum of the physical barriers to dislocation motion, including dislocation forests, aged long-range ordered precipitates, and irradiation defects.

\[ g^{(\alpha)} = g_o^{(\alpha)} + g_{\text{dislocations}}^{(\alpha)} + g_{\text{precipitates}}^{(\alpha)} + g_{\text{defects}}^{(\alpha)} \]  \hspace{1cm} \text{Equation 13}

where \( g_o \) represents the intrinsic lattice friction, \( g_{\text{dislocations}} \) models the hardening of slip systems due to the accumulation of other dislocations on all of the slip systems, \( g_{\text{precipitates}} \) accounts for the hardening due precipitates to the long-range ordered precipitates, and \( g_{\text{defects}} \) is used to capture the effect of irradiation lattice defects on the slip system hardening.

The intrinsic resistance of a crystal to dislocation motion is due to friction forces, and the measure of this resistance is termed the Peierls strength of the material. Because NiCr alloys are low stacking fault materials compared to pure Ni, the spreading of the dislocation core will play a role in the intrinsic lattice friction of the alloy. Molecular dynamics simulations have estimated the Peierls strength for Ni to be a function of the shear modulus, following the work of Szelestey et al. [31]:

\[ g_o^{(\alpha)} = 10^{-4} \cdot \mu \]  \hspace{1cm} \text{Equation 14}

where \( \mu \) is the shear modulus of the alloy. While this function provides a guideline for the commercial alloys Peierls strength, the lower values reduces the predicted strength response of the simulated material. First principle calculations for the binary Ni2Cr alloy are available [32]. This study gives separate values of the Peierls stress for edge dislocations and screw dislocations [32]; since we do not distinguish between edge and screw dislocations in our crystal plasticity framework, we use the average of these two Peierls stress values.

The slip system resistance due to dislocation forest-type accumulation on all slip systems is modeled with a modified Bailey-Hirsch approach following Ohashi [33]:

\[ g_{\text{dislocations}}^{(\alpha)} = \alpha_{mbh} b \mu \sqrt{\sum_{\beta} \Omega^{(\alpha\beta)} \left( \rho_{\text{mobile}}^{(\beta)} + \rho_{\text{immobile}}^{(\beta)} \right)} \]  \hspace{1cm} \text{Equation 15}

where the hardening is termed self-hardening when \( \alpha = \beta \) and latent-hardening when \( \alpha \neq \beta \). The coefficient \( \alpha_{mbh} \) is a fitting parameter, \( b \) is the burgers vector, \( \mu \) is the shear modulus of the material, and \( \Omega \) is the interaction matrix containing the hardening due to self- and latent-hardening parameters. For simplicity, in this work we assume all components of the interaction matrix to be unity.

The hardening due to LRO \( \gamma' \) precipitates is accounted for with anti-phase boundary (APB) particle shearing. The hardening mechanism was selected from the review provided by Kozar et al. [34] for the small tertiary \( \gamma' \) precipitates experimentally observed in the Ni2Cr alloy. The Alloy 690 and Alloy 625 microstructures contain larger primary and secondary \( \gamma' \) precipitates. The Ni2Cr model alloy only demonstrates tertiary LRO precipitates, under 10nm in size. Based on this size, we have implemented a model for weakly coupled APB shearing Kozar et al. [34]. The effective spacing between two LRO precipitates is modeled in a manner that accounts for the radii of the precipitates.
Equation 16

\[ g_{ab}^{(\alpha)} = \frac{\gamma_{apb}}{2b} \left[ \left( \frac{\gamma_{apb}d_s}{\mu} \right)^{1/2} \frac{d_s}{bL_s} - \frac{\pi}{4} \left( \frac{3\pi f}{8} \right) \right] \]

where \( \gamma_{apb} \) is the energy of the anti-phase boundary, \( b \) is the burgers vector, \( d_s \) is the mean planar diameter of the precipitate, \( \mu \) is the shear modulus, \( L_s \) is the effective spacing between precipitates, and \( f \) is the volume fraction of the tertiary precipitates. The effective spacing between precipitates takes into account the diameter of the precipitates [34]:

\[ L_s = \left( \frac{8}{3\pi f} \right)^{1/2} d_s - d_s \]

Equation 17

The weakly coupled terminology refers to the ability of the precipitate to contain only a single dislocation partial at a time; larger precipitates which can contain both partials of a dislocation are said to undergo strongly coupled APB shearing.

### 3.4.2.2 Model benchmarking and validation

Micropillar compression experiments were first introduced by Uchic et al. [35] and Dimiduk et al. [36] as a way to study the effect of smaller sample size on the stress response of a material. Micropillar experiments have contributed to the understanding of how different deformation mechanisms control the material behavior as the sample size changes. Simulations have also been applied to micropillar compression problems. Because of the limited amount of the 10,000 hour aged binary alloy, micropillar compression testing was selected as the method to mechanically test single crystals of both aged and unaged Ni\(_2\)Cr alloy. Crystal plasticity is a useful simulation tool in this situation to extend information from experimental data sets limited by available material to polycrystalline structures. We have therefore focused on replicating the micropillar compression tests with our CDD crystal plasticity model as a first step towards the prediction of engineering scale mechanical behavior based on the evolution of the thermally aged microstructure of Ni-based alloys.

Generally, simulation studies of micropillars agree on the importance of boundary conditions to correctly model the micropillar. Recent studies have demonstrated the importance of including the substrate geometry on the predicted stress-strain curve from the simulation for an isotropic plastic material [37]. Other crystal plasticity simulations of micropillar compression tests have included the substrate within the meshed problem geometry, despite the additional computational load introduced [38]. These crystal plasticity studies have addressed the computational load associated with including the substrate geometry by reducing the number of elements in the mesh through mesh coarsening. The aggressive mesh coarsening employed in these studies, could, however, fail to fully capture the interactions of the substrate and the micropillar.

Beyond the study of size-dependence of material strength, micropillar compression tests are useful for determining material properties such as yield stress and work hardening behavior [36]. In cases where limited amounts of material are available, as is the case with the 10,000 hours thermally
aged Ni$_2$Cr alloy, micropillar compression tests offer the ability to determine the stress-strain behavior in a more direct approach than through nanoindentation, another common experimental technique. Furthermore, Cruzado et al. [39] argue that for a nickel-based alloy with a deformation behavior governed by dislocation-particle interactions, micropillar compression tests can be used to directly calibrate a crystal plasticity model. We have elected to employ micropillar compression experiment and simulation comparisons to verify our crystal plasticity framework for the binary Ni$_2$Cr model alloys.

3.4.2.2.1 Deformation twinning model implementation

Experimental data on a set of [111] and [100] oriented micropillars was collected on both unaged and 10,000 hrs aged single crystals of Ni$_2$Cr alloy. During the experimental testing of these micropillars, twinning was observed in the [100] orientation micropillars during testing. Thus, in order to model the active physical deformation mechanisms active in the Ni$_2$Cr alloy, we must add a deformation twinning model to our CDD crystal plasticity framework.

In low stacking fault metals, twinning is another common deformation mechanism. Both twinning and microtwinning have been observed in NiCr alloys; microtwinning is described as thin twins only a few atomic planes wide Kovarik et al. [40]. We justify the use of the simplistic twinning model [41] over other twinning models developed for Ni-based alloys [42, 43] with the small size of the LRO precipitates. Because the average diameter of the LRO precipitates is under 20 nm these precipitates cannot hold both the tail and lead partials of a dislocation in order to nucleate a microtwin within the precipitate [34].

Following Wu et al. [28] we incorporate the deformation twinning into the plastic velocity gradient as a pseudo-slip mechanism. We implement a variation of the twinning model introduced by Kalidinidi with an additive decomposition of the plastic velocity gradient.

$$L^P = (1 - f_t) \sum_{\alpha} \gamma^\alpha s^\alpha_o \otimes m^\alpha_o + \sum_{\beta} \gamma^\beta s^\beta_o \otimes m^\beta_o$$

Equation 18

where $f_t$ is the total volume fractions of the twins on all of the twin systems, and the superscript $\alpha$ indicates the glide slip systems and the superscript $\beta$ indicates the twinning system. Implicit is the assumption that the twinned portions of the crystal do not undergo additional dislocation glide, as applied by Salem et al. [44]. The twin slip increment model we have implemented is the power law type model first proposed by Kalidindi [45]. In incremental form the shear slip due to twinning is

$$\Delta \gamma^\beta = \dot{\gamma}_0 \left( \frac{g^\beta}{g_{twin}} \right)^{1/m} \Delta t \text{ if } \tau^\beta > 0 \text{ and } f_T < f_{\text{limit}}$$

Equation 19

where we use the same shear reference rate $\dot{\gamma}_0$ and power law exponent m as in the glide dislocation velocity model as suggested by Kalidindi [41]. The resistance of the system to twinning, $g_\beta$ is given below. We introduce coupling to the CDD glide dislocations through the twinning system resistance. The total twin volume fraction, $f_T$, used in the calculation of the plastic velocity gradient is calculated directly from the twin slip increment.
where $\gamma_{tw}$ is the characteristic twin shear. For an FCC material, which we consider here, the characteristic twin shear is the inverse of the square root of two [46].

Interactions between glide dislocations and twins increase the resistance of the crystal to the motion and growth of both dislocation types. In light of this observation we have introduced coupling of the twin dislocation and glide dislocation evolution through the resistance components of the two evolution models. We treat the resistance of twin slip as an additive decomposition

$$g_{twin}^\beta = g_{tw-o} + g_{forest} + g_{forest-twin}$$

Equation 21

where $g_{tw-o}$ represents the lattice friction contribution to the twin resistance, $g_{forest}$ is the forest hardening from glide dislocations, and $g_{tw-forest}$ is a forest hardening type term to account for the accumulation of twins. The lattice friction twin system hardening has the simple form of

$$g_{tw-o} = \alpha_{twin-ps} \cdot g_o$$

Equation 22

where, following the summary of Roters et al. [47], the coefficient $\alpha_{twin-ps}$ is set to unity and $g_o$ is the Peierls strength. The third term in Eq (21) represents the hardening due to twins. Twins are known to increase the system hardening for noncoplanar systems over other coplanar systems [47]; thus several crystal plasticity models introduce twinning resistance models with different treatments for coplanar and noncoplanar systems [41]. In our model we have adopted a simpler approach in which we treat the contributions from all twin systems equally,

$$g_{forest-twin} = \alpha_{tiff} \mu \sqrt{f_T}$$

Equation 23

which is similar to the approach used to calculate the forest hardening from glide dislocations. We acknowledge that this form of slip resistance on the twin systems calculates an equal value of resistance for all twin systems, both active and inactive.

The influence of the twins on the evolution of the glide dislocation is incorporated into the calculation of the mean free glide path rather than directly into the glide resistance. We modify the mean free glide path with a correction factor that is a function of the total twin volume.

$$l_{inv}^{(\alpha)} = \beta_{path} \left( \sum_\beta \omega^{(\alpha\beta)} \left( \rho^{(\beta)}_{mobile} + \rho^{(\beta)}_{immobile} \right) \right) / \left( 1 - f_T \right)$$

Equation 24

where the denominator is the twin volume correction factor [48]. We account for the additional obstacles to glide dislocation only in the mean free glide path to avoid artificially over hardening the glide slip systems. The combination of the glide forest hardening term in the twin resistance
expression allows us to complete the two-way coupling of these two different deformation mechanisms.

3.4.2.2 Single crystal CDD simulations

FCC materials are known to twin in the [100] orientation when loaded in compression but not in tension; conversely, tensile loading in the [111] orientation demonstrates twinning while compression does not [49]. This expected behavior is a consequence of the unidirectional nature of twins. We use a set of four loading directions and orientations, [100] in compression, [100] in tension, [111] in compression, and [111] in tension, to verify our general implementation of the twin model addition to the CDD crystal plasticity framework. The single crystal simulations were performed on a 1 mm$^3$ cube mesh consisting of 216 Hex8 elements. Symmetric boundary conditions were used and a displacement loading rate corresponding to a strain rate of $\pm 1.0 \times 10^{-3}$ s$^{-1}$ was applied, depending on the specified loading direction. The elastic constants and material parameters used in this set of simulations are given in Table 13.

The [111] orientation compression loading case demonstrates a minimal amount of twin volume growth while the tensile [100] loading shows no twin volume growth, as expected. We note that in both cases with twin volume fraction growth, Figure 44 and Figure 47, the effective stress response is around 10 MPa higher than for the cases without twin growth, Figure 45 and Figure 46. This increased stress effect is more pronounced in the [111] orientation where fewer glide dislocation systems are active. The change of the effective stress response indicates that the twin slip increment implementation has been included in the calculation of the stress through the plastic velocity gradient modification.

The twinning model addition to the CDD crystal plasticity framework demonstrates the formation of twins only in the loading directions known to twin in FCC materials: compression loading in [100] and tensile loading in [111]. These results indicate the proper implementation of the twinning model.

Table 13. The elasticity tensor and hardening material parameter values used in the CDD crystal plasticity for twinning model addition simulations of single crystal Alloy 690.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_{11}$</td>
<td>$332 \times 10^3$ MPa</td>
<td>Elastic constant, Blaziot et al. [50]</td>
</tr>
<tr>
<td>$C_{12}$</td>
<td>$187 \times 10^3$ MPa</td>
<td>Elastic constant, Blaziot et al. [50]</td>
</tr>
<tr>
<td>$C_{44}$</td>
<td>$72.8 \times 10^3$ MPa</td>
<td>Elastic constant, Blaziot et al. [50]</td>
</tr>
<tr>
<td>$\mu$</td>
<td>$72.8 \times 10^3$ MPa</td>
<td>Shear modulus, Blaziot et al. [50]</td>
</tr>
<tr>
<td>$b$</td>
<td>$2.52 \times 10^{-7}$ mm</td>
<td>Burgers vector</td>
</tr>
<tr>
<td>$a_{mbh}$</td>
<td>0.4</td>
<td>Forest hardening coefficient</td>
</tr>
<tr>
<td>$\Omega^{aa}, \Omega^{ab}$</td>
<td>1.0</td>
<td>Self and latent hardening coefficients</td>
</tr>
<tr>
<td>$\omega^{aa}, \omega^{ab}$</td>
<td>1.0</td>
<td>Mean free glide path coefficient</td>
</tr>
<tr>
<td>$g_0$</td>
<td>$3.64$ MPa</td>
<td>Estimated isotropic Peierls strength</td>
</tr>
<tr>
<td>$T$</td>
<td>298 K</td>
<td>Temperature</td>
</tr>
</tbody>
</table>
3.4.2.2.3 Micropillar compression Ni$_2$Cr alloy simulations

With the successful benchmark simulations of our twin slip implementation, we turn to the simulation of Ni$_2$Cr alloy micropillars, both aged and unaged. To align with the experimental procedure, we simulate a set of micropillars, with aged and unaged Ni$_2$Cr. We adopt a nominal micropillar height of 4 μm with a nominal width and depth of 2 μm, as shown in Figure 44. In our simulations we model both the micropillar and the substrate with crystal plasticity with a uniform mesh element size.

We have applied zero displacement boundary conditions normal to all of the substrate surfaces except the surface with the micropillar. These zero displacement boundary conditions capture the inability of the modeled substrate component to move. The displacement rate boundary condition of -0.01 μm/s was applied to the top of the micropillar, as shown in Figure 48.
Figure 48. The micropillar compression test geometry used in the crystal plasticity simulations.

The micropillar width and depth have the same dimension, and the substrate width and depth are the same length. The bottom of the micropillar substrate is fixed in the x direction, the front and back sides of the substrate cube are fixed in the y direction as are the right and left sides fixed in the z direction, and a compressive displacement is applied to the top of the micropillar.

Although we relied on elastic constants for a specific Ni-based Alloy, 690, for our twinning verification problems, we have elected to apply Ni2Cr alloy-specific elastic constants in the micropillar compression simulations calculated rather than measured from experimental work. We employ a set of anisotropic elastic constants calculated from first principles specifically for Ni2Cr Chan et al. [2006]. The list of elastic properties used in our micropillar compression simulations is given in Table 14.

Table 14. The elasticity tensor and hardening material parameter values used in the CDD crystal plasticity for the micropillar Ni2Cr simulations. The characteristics of the LRO precipitates for the aged micropillar simulations are also listed.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>C11</td>
<td>230.7 x 10³ MPa</td>
<td>Elastic constant, Chan et al. [32]</td>
</tr>
<tr>
<td>C12</td>
<td>78.8 x 10³ MPa</td>
<td>Elastic constant, Chan et al. [32]</td>
</tr>
<tr>
<td>C44</td>
<td>71.7 x 10³ MPa</td>
<td>Elastic constant, Chan et al. [32]</td>
</tr>
<tr>
<td>µ</td>
<td>74.5 x 10³ MPa</td>
<td>Shear modulus, Chan et al. [32]</td>
</tr>
<tr>
<td>b</td>
<td>2.16 x 10⁻⁷ mm</td>
<td>Burgers vector, Chan et al. [32]</td>
</tr>
<tr>
<td>αmbh</td>
<td>0.4</td>
<td>Forest hardening coefficient</td>
</tr>
<tr>
<td>Ωαα, Ωαβ</td>
<td>1.0</td>
<td>Self and latent hardening coefficients</td>
</tr>
<tr>
<td>ωαα, ωαβ</td>
<td>1.0</td>
<td>Mean free glide path coefficient</td>
</tr>
<tr>
<td>g₀</td>
<td>191.5 x 10³ MPa</td>
<td>Peierls strength, Chan et al. [32]</td>
</tr>
<tr>
<td>T</td>
<td>298K</td>
<td>Temperature</td>
</tr>
<tr>
<td>dLRO</td>
<td>2.5 x 10⁻⁶mm</td>
<td>Average LRO diameter, Gwalani et al. [26]</td>
</tr>
<tr>
<td>fLRO</td>
<td>0.033</td>
<td>Volume fraction of LRO, Gwalani et al. [26]</td>
</tr>
<tr>
<td>γabp</td>
<td>2.0 x 10⁻⁴</td>
<td>Energy of the anti-phase boundary</td>
</tr>
</tbody>
</table>
Following the assumption of a low initial dislocation density for the micropillars, similar to that of a well-annealed crystal, we apply an initial dislocation density of $1.0 \times 10^6 \text{ mm}^{-2}$ [51] and split the initial dislocation density evenly among the mobile and immobile dislocation densities.

We have completed two sets of micropillar compression simulations: on unaged binary Ni$_2$Cr alloy and the same binary alloy after 10,000 hours of thermal aging at 475°C. We present a simulation of the unaged binary alloy in the [321] orientation and simulations of the 10,000 hours thermally aged alloy in both the [100] orientation and in the [111] orientation, corresponding to the experimental micropillar compression data collected. To capture the impact of the thermal aging, we introduce a population of uniformly distributed LRO precipitates, as listed in Table 14.

3.4.2.2.4 Micropillar simulation results
Calculating the stress-strain curve from micropillar compression experiments is not straightforward: the contribution of the substrate to the overall response must be separated from the response of the micropillar alone. The Sneddon correction is often applied to extract the stress-strain response [37, 39]. In our study we avoid the need for a correction factor by directly comparing the force-displacement experimental measurement to the simulation results. In Figure 49 and Figure 50 we present the results of our CDD simulations with preliminary experimental micropillar compression data. Because these experimental micropillar data are preliminary, we do not expect to see exact alignment of the simulations and experimental measurements in the elastic or plastic regions; instead we use these experimental data to qualitatively access the results of our crystal plasticity simulations. For the unaged micropillar we compare the CDD crystal plasticity simulation results against a force-displacement data collected from a [213] orientated micropillar, Figure 49, and for the thermally aged simulations experimental measurements in the corresponding loading orientations are available, Figure 50.

The significant differences in the force measured during the experimental micropillar compression tests and the force predicted by the crystal plasticity simulations indicates that not all of the relevant
physics active in the micropillar are captured by our bulk material crystal plasticity model. We suggest further developments to the model or experimental testing of larger diameter micropillars to bring the measured and simulation results into alignment.

The underprediction of the force response by the simulations indicates that our crystal plasticity framework does not capture all of the physics relevant to this problem. The CDD crystal plasticity models we have employed in these simulations are suitable for bulk materials. Experimental studies of pure nickel micropillars found that a minimum micropillar diameter of 20 μm was required to replicate bulk material properties [36]. Since the micropillar geometry we are attempting to replicate here is an order of magnitude smaller than this threshold, it is reasonable that size effects may play a role in the simulation underpredictions. In particular, for small diameter micropillars, the forest-type hardening model used to capture dislocation interactions in crystal plasticity models is not sufficient to capture the increase in strength of micropillars [36]. Several crystal plasticity studies have suggested the use of strain gradient terms, including geometrically necessary dislocations [52], although the applicability of these terms to micropillars remains a subject of some disagreement in the field [36].

Beyond the difference likely due to size effects, the simulations of the thermally aged micropillar also underpredict the hardening observed in the micropillar experiment force response, Figure 50. Furthermore, we note that the thermally aged micropillar force response demonstrates a larger hardening slope than does the unaged micropillar force measurement. Allowing for the different loading orientations, this difference in hardening behavior raises the possibility that the thermally aged LRO precipitates contribute to the work hardening. This slight predicted increase in hardening for the thermally aged materials indicates that our crystal plasticity simulation has not fully captured the interaction of the LRO precipitates with the dislocations. To capture this work hardening contribution of the LRO precipitates, the interactions between these precipitates and dislocations should be investigated further. Among the potential interaction mechanisms to consider are bowing of dislocations around precipitates or the pinning of dislocation segments by a pair of precipitates to create a new glide dislocation source, such as the Frank-Read source. Additionally, our proposed twinning resistance model does not include a contribution from the LRO precipitates. The contributions of the tertiary LRO precipitates to the twinning resistance should also be incorporated into the crystal plasticity model.

The apparent softening in the force response of the thermally aged micropillar simulations is the result of improper boundary conditions, which have allowed the top micropillar surface to slide out. To prevent movement of the top surface, we will explore the use of frictional and zero displacement boundary conditions for the displacements tangential to the top micropillar surface. We expect that these boundary conditions will prevent the softening we observe in the current simulation results.

The inclusion of the substrate portion in the simulation geometry does impact the overall predicted force response. We inspect two glide dislocation systems: one that is active in the micropillar, Figure 51, and one that is mostly inactive in the pillar while being active in the region of the substrate near the pillar, Figure 52. The evolution of mobile dislocations within the substrate at the base of the pillar demonstrate the importance of including the model of the substrate in our micropillar crystal plasticity simulations.
The distribution of the mobile dislocations on the [-101](111) slip system shows the importance of including the crystal plasticity model in the substrate. While the [-101](111) slip system is not active in the micropillar itself, the evolution of the dislocations on this system at the base of the micropillar will harden the overall response of the micropillar to the applied displacement. We conclude that the inclusion of the substrate and the boundary conditions applied to the substrate portion are appropriate to this micropillar problem.

3.4.2.2.5 Irradiation defect modeling
The use of these nickel-based alloys in nuclear power plant applications requires the inclusion of irradiation defects in the strengthening model terms. As discussed previously, a primary radiation defect observed in these alloys is voids. We propose a modified Orowan impenetrable barrier model, similar to the model used for irradiation caused stacking fault tetrahedra in other FCC materials [53]:

\[ g_{\text{defects}}^{(\alpha)} = \alpha_{db} b \mu \sqrt{N_v d_v} \]  

Equation 25

where \( \alpha_{db} \) is a coefficient, \( b \) is the burgers vector, \( \mu \) is the shear modulus, \( N_v \) is the number density of the voids and \( d_v \) is the average size of the void. The value of the coefficient \( \alpha_{db} \) depends on the manner in which dislocations bypass the voids: for voids which are cut by dislocations shear, a value of \( 0.3 \leq \alpha_{db} \leq 0.5 \) is used while for voids which pin dislocations and cause dislocation bowing the coefficient value is set to unity [54].

3.4.3 Summary
In this section we have presented the implementation of a simplified twinning evolution model, suitable for use in binary model Ni_2Cr alloy. Although simple, this twinning model includes
coupling among the glide dislocation evolution models and the twin growth model. This twinning model addition to the CDD crystal plasticity framework has been verified with a series of benchmark problems developed from conventional knowledge of twin formation under specific loading conditions in FCC materials. Additionally, we have incorporated a hardening model specific for LRO precipitates, which form in thermally aged Ni$_2$Cr and nickel-based alloys and proposed a model for hardening due to irradiation damage.

We have applied these twinning and LRO precipitate hardening models to the study of micropillar compression tests. These results demonstrate that the crystal plasticity models we have presented here underpredict the micropillar response. We attribute this underprediction to a combination of an ill-posed loading boundary condition and an incomplete capture of the relevant physics for the 2 μm diameter pillar. We propose as future work additional models to address the underprediction. To extend these crystal plasticity models from the binary Ni$_2$Cr alloy that we have focused on modeling here to the more complex Alloy 690 and Alloy 625 materials, we propose a set of future modifications. The anisotropic elastic constants should be updated for the alloy of interest, along with the lattice parameter and lattice friction Peierls strength. Additional terms for the interaction mechanisms between the larger γ' precipitates and the dislocations, such as strongly coupled particle shearing and microtwinning, should be added to the existing crystal plasticity model. The simulation work we have performed with the binary Ni2Cr alloy ensures that our crystal plasticity model has a verified foundation that will allow further work to proceed smoothly to the modeling of Alloy 690 and Alloy 625.
4 REFERENCES


APPENDIX A. IMR COMPOSITION CONFIRMATION REPORT

August 22, 2014

Julie Tucker
Oregon State University
204 Rodgers Hall
Corvallis, OR 97331

TEST REPORT
IMR Report Number 201410486

PO Number
P0096352

Date Received
August 15, 2014

Sample ID
Ni/Cr 1.6
Ni/Cr 1.8
Ni/Cr 2.0
Ni/Cr 2.2
Ni/Cr 2.4

SUMMARY

Five samples were received for chemical analysis.

The results are on the following page(s).

Reviewed by
Cheryl Downey
Report Review Specialist

Reviewed by
Andrew Ensign, Supervisor
Chemistry Department
### CHEMISTRY

<table>
<thead>
<tr>
<th>Element</th>
<th>N\textsubscript{ij}/Cr 1.6</th>
<th>N\textsubscript{ij}/Cr 1.8</th>
<th>N\textsubscript{ij}/Cr 2.0</th>
<th>N\textsubscript{ij}/Cr 2.2</th>
<th>N\textsubscript{ij}/Cr 2.4</th>
</tr>
</thead>
<tbody>
<tr>
<td>C\textsuperscript{1}</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
</tr>
<tr>
<td>Cr</td>
<td>31.17</td>
<td>32.95</td>
<td>30.62</td>
<td>28.58</td>
<td>27.36</td>
</tr>
<tr>
<td>Fe</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>0.04</td>
</tr>
<tr>
<td>P</td>
<td>0.006</td>
<td>0.007</td>
<td>0.006</td>
<td>0.006</td>
<td>0.006</td>
</tr>
<tr>
<td>S\textsuperscript{2}</td>
<td>0.002</td>
<td>0.002</td>
<td>0.002</td>
<td>0.002</td>
<td>0.001</td>
</tr>
<tr>
<td>Ni\textsuperscript{3}</td>
<td>68.51</td>
<td>67.03</td>
<td>69.36</td>
<td>71.40</td>
<td>72.55</td>
</tr>
</tbody>
</table>

\textsuperscript{1} Determined by combustion-infrared absorbance.
\textsuperscript{2} Determined by difference.
Other elements tested (<0.01%): Al, As, Au, B, Be, Bi, Ca, Cd, Co, Cu, Hf, La, Li, Mg, Mn, Mo, Nb, Pb, Sb, Se, Si, Sn, Ta, Ti, V, W, & Zr.

Results in weight percent unless otherwise indicated.
Method(s): CAP-017N (ICP-AES) and ASTM E 1019-11 (Comb./IGF)