Characterization of Two ODS Alloys: 18Cr ODS and 9Cr ODS

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by

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ABSTRACT

ODS alloys, or oxide dispersion strengthened alloys, are made from elemental or pre-alloyed metal powders mechanically alloyed with oxide powders in a high-energy attritor mill, and then consolidated by either hot isostatic pressing or hot extrusion causing the production of nanometer scale particles within the alloy matrix. Material properties such as creep strength, ductility, corrosion resistance, tensile strength, swelling resistance, and resistance to embrittlement are all observed to be improved by the presence of the nanoparticles in the matrix. The presented research uses various methods to observe and characterize the microstructural and microchemical properties of two developmental ODS steels, 18Cr ODS and 9Cr ODS. The results found aid in assessing the influence of chemical and microstructural variations on the effectiveness of the alloy, and further aid in the optimization of these advanced alloys for future use in cladding and structural applications in Generation IV nuclear reactors. Characterization of these alloys has been conducted in order to identify the second-phase small precipitates through FESEM, TEM, EDS, Synchrotron X-ray diffraction analysis, and CuKα XRD analysis of bulk samples and of extractions. Comparison of results from these methods allows further substantiation of the accuracy of observed nanoparticle composition and identification. Also, TEM samples of the two alloys have been irradiated in-situ with 1 MeV Kr and 300 keV Fe ions to various doses and temperatures at the IVEM-Tandem TEM at Argonne National Laboratory.
Post-irradiated characterization has been conducted and compared to the pre-irradiated characterization results in order to observe the microstructural and microchemical evolution of nanoparticles under irradiation. Overall in the as-received state, the initial Y2O3 is not found anymore and in addition to oxide particles the alloys contain carbides. In both alloys a good correlation between the EDAX and XRD results is found both before and after extraction of the nanoparticles from the matrix. Both alloys show the presence of Y-Ti-O particles as well as Al-containing compounds, and Cr- carbides of the M23C6 type. The oxide particles in 18Cr ODS appear to be stable under irradiation up to 20dpa at 500°C. From SEM analysis of nanoparticle dispersion before and after irradiation there appears to be a decrease in density and increase in average size in both small (10-30nm) and large (100nm-1μm) particles. In the 9Cr ODS alloy, comparison of results from both methods of analysis also shows the presence (in the as-received state) of a combination of carbides and Y- containing oxides, and Al-containing compounds are also found. After irradiation small Y-Ti-O particles appear to be enriched with Chromium. Larger particles, suspected to be carbides, show indications of amorphization at 25°C. Further irradiations on both alloys will provide deeper insight into the structural and chemical stability of the oxide and carbide nanoparticles and the merit of both alloys as structural and cladding materials in future nuclear applications.
TABLE OF CONTENTS

ACKNOWLEDGMENTS........................................................................................................iii

ABSTRACT .......................................................................................................................... iv

TABLE OF CONTENTS ...................................................................................................... vi

LIST OF TABLES ............................................................................................................... viii

LIST OF FIGURES ............................................................................................................. ix

I. BACKGROUND AND MOTIVATIONS ........................................................................ 1
  1.1 MATERIAL CHALLENGES FOR NUCLEAR ENERGY ........................................... 1
  1.2 METALLIC PROPERTIES OF INTEREST IN ODS ALLOY APPLICATION .......... 4
  1.3 COMPOSITION RATIONALIZATION ................................................................ 9
  1.4 SUMMARY ............................................................................................................. 13

II. MATERIALS AND METHODS ...................................................................................... 14
  2.1 MATERIALS ........................................................................................................... 14
  2.2 METHODS ............................................................................................................ 16

III. RESULTS ..................................................................................................................... 21
  3.1 18Cr ODS RESULTS ............................................................................................ 22
  3.2 9Cr ODS RESULTS: ........................................................................................... 54
  3.3 SUMMARY OF RESULTS ................................................................................... 70

IV. DISCUSSION .................................................................................................................. 76
  4.1 FABRICATION METHODS .................................................................................... 76
  4.2 PHASE IDENTIFICATION BY EDS ANALYSIS .................................................. 98
  4.3 ELEMENTAL ADDITIONS ..................................................................................... 107
  4.4 RADIATION STABILITY ....................................................................................... 111
  4.5 LIMITATIONS OF CHARACTERIZATION TECHNIQUES ................................. 119
  4.6 SUMMARY OF ANALYSIS ................................................................................. 124

vi
V. CONCLUSIONS.......................................................................................................................... 129
  5.1 18Cr ODS: .................................................................................................................... 130
  5.2 9Cr ODS: ....................................................................................................................... 133

REFERENCES .................................................................................................................................. 138
LIST OF TABLES

Table 1.1: Nominal Alloy Composition by Weight Percent for 18Cr ODS and 9Cr ODS ..... 15

Table 3.1: 18Cr ODS nanoparticle type and abundance observed through SEM/EDS analysis with corresponding phases extrapolated from XRD Analysis................................................................. 71

Table 3.2: 9Cr ODS nanoparticle type and abundance observed through SEM/EDS analysis with corresponding phases extrapolated from XRD Analysis................................................................. 74

Table 4.1 Relative Abundance of Nanoparticles Observed in 9Cr ODS by Size................. 97
LIST OF FIGURES

Figure 1.1: a) 18Cr ODS extracted nanoparticles on filter after dissolution of the matrix through chemical extraction. b) 9Cr ODS extracted nanoparticles on filter after dissolution from the matrix through chemical extraction................................................................. 18

Figure 1.2: a) 18Cr ODS bulk sample taken from transverse direction of as-fabricated material used for CuKα XRD analysis. b) 18Cr ODS bulk sample taken from longitudinal direction of as-fabricated material used for CuKα XRD analysis......................................................... 18

Figure 3.1: 18Cr ODS Synchrotron X-ray diffraction spectrum collected at APS using 15keV photons. .......................................................................................................................... 22

Figure 3.2: 18Cr ODS Synchrotron X-ray diffraction spectrum collected at APS using 15keV photons. Matrix peaks have been reduced to show second phase peaks from nanoparticles within the alloy matrix............................................................... 23

Figure 3.3: 18Cr ODS CuKα X-ray diffraction spectrum of nanoparticles after chemical extraction from the alloy matrix........................................................................ 24

Figure 3.4: 18Cr ODS CuKα X-ray diffraction spectrum taken on bulk material from the longitudinal direction of the consolidated alloy. ................................................................. 25

Figure 3.5: 18Cr ODS CuKα X-ray diffraction spectrum taken on bulk material from the transverse direction of the consolidated alloy. ................................................................. 25

Figure 3.6: 18Cr ODS X-ray diffraction spectra from Synchrotron bulk, extracted nanoparticle, bulk longitudinal, and bulk transverse samples, aligned to reveal similarities and differences in peak presence and location across methods of XRD analysis........................................ 26

Figure 3.7: 18Cr ODS Synchrotron X-ray diffraction spectrum collected at APS using 15keV photons with peak locations labeled for Y2Ti2O7, Al2O3, and (Cr, Fe)C6 showing their presence in the alloy represented in the collected data................................................ 28

Figure 3.8: 18Cr ODS CuKα X-ray diffraction spectrum of nanoparticles after chemical extraction from the alloy matrix with peak locations labeled for Y2Ti2O7, Al2O3, and (Cr, Fe)C6 showing their presence in the alloy represented in the collected data................................................ 28

Figure 3.9: 18Cr ODS CuKα X-ray diffraction spectrum taken on bulk material from the transverse direction of the consolidated alloy with peak locations labeled for the Iron Chromium (Fe, Cr) matrix and (Cr, Fe)C6 showing their presence in the alloy represented in the collected data. ................................................ 30
Figure 3.10: 18Cr ODS CuKα X-ray diffraction spectrum taken on bulk material from the longitudinal direction of the consolidated alloy with peak locations labeled for the Iron Chromium (Fe, Cr) matrix.

Figure 3.11: 18Cr ODS Peak Fit analysis of phases identified by XRD analysis. (a) shows simulated pattern of peaks from (Cr, Fe)23C6 and Y2Ti2O7 overlaid with the diffraction pattern from extraction to show correlation in peak location and remaining unidentified peaks. (b) Peaks from Y2Ti2O7 within measured 2-Theta values labeled on the extraction diffraction pattern. (c) Peaks from (Cr, Fe)23C6 within measured 2-Theta values labeled on the extraction diffraction pattern.

Figure 3.12: 18Cr ODS (a) Synchrotron X-ray diffraction spectrum collected at APS using 15keV photons with peak locations labeled for Y2Ti2O7, Al2O3, and (Cr, Fe)C6 showing their presence in the alloy represented in the collected data. (b) Peak Fit analysis of phases identified by XRD analysis, shows simulated pattern of peaks from (Cr, Fe)23C6 and Y2Ti2O7 overlaid with the synchrotron diffraction pattern to show correlation in peak location and remaining unidentified peaks.

Figure 3.13: 18Cr ODS (a) CuKα X-ray diffraction spectrum taken on bulk material from the transverse direction of the consolidated alloy with peak locations labeled for the Iron Chromium (Fe, Cr) matrix and (Cr, Fe)23C6 showing their presence in the alloy represented in the collected data. (b) Peak Fit analysis of phases identified by XRD analysis, shows simulated pattern of peaks from (Cr, Fe)23C6 and (Fe, Cr) overlaid with the bulk transverse diffraction pattern to show correlation in peak location and remaining unidentified peaks.

Figure 3.14: 18Cr ODS (a) CuKα X-ray diffraction spectrum taken on bulk material from the longitudinal direction of the consolidated alloy with peak locations labeled for the Iron Chromium (Fe, Cr) matrix showing presence in the alloy represented in the collected data. (b) Peak Fit analysis of phases identified by XRD analysis, shows simulated pattern of peaks from (Fe, Cr) overlaid with the bulk transverse diffraction pattern to show correlation in peak location and remaining unidentified peaks.

Figure 3.15: 18Cr ODS (a) EDS spectrum showing presence of Yttrium, Titanium, and Oxygen in addition to matrix elements overlaid in black. (b) SEM micrograph of capture region for spectrum in (a) showing a Y2Ti2O7 particle in thin foil sample of 18Cr ODS.

Figure 3.16: 18Cr ODS (a) EDS spectrum showing presence of Yttrium and Titanium in addition to background elements. (b) SEM micrograph of capture region for the spectrum in (a) showing Y2Ti2O7 particles after extraction from the alloy matrix.

Figure 3.17: 18Cr ODS (a) EDS spectrum showing presence of Aluminum and Oxygen in addition to matrix elements overlaid in black. (b) SEM micrograph of capture region for spectrum in (a) showing an Al2O3 particle in thin foil sample of 18Cr ODS.

Figure 3.18: 18Cr ODS (a) EDS spectrum showing presence of Aluminum and Oxygen (b) SEM micrograph of capture region for the spectrum in (a) showing Al2O3 particle after extraction from the alloy matrix.

Figure 3.19: 18Cr ODS (a) EDS spectrum showing presence of Chromium and Carbon in addition to matrix elements overlaid in black. (b) SEM micrograph of capture region for spectrum.
in (a) showing M23C6 type particles in thin foil sample of 18Cr ODS that has been irradiated to
20dpa at 500°C. ........................................... 38

Figure 3.20: 18Cr ODS (a) EDS spectrum showing presence of Chromium, Iron, and Carbon. (b)
SEM micrograph of capture region for the spectrum in (a) showing M23C6 particle after
extraction from the alloy matrix ................................................... 39

Figure 3.21: 18Cr ODS (a) EDS spectrum showing presence of Titanium and Oxygen in addition
to matrix elements overlaid in black. (b) SEM micrograph of capture region for spectrum in (a)
showing a TiO2 particle in thin foil sample of 18Cr ODS ...................................... 40

Figure 3.22: 18Cr ODS (a) EDS spectrum showing presence of Aluminum, Titanium, and
Oxygen in addition to matrix elements overlaid in black. (b) SEM micrograph of capture region
for spectrum in (a) showing a AlTiO2 particle in thin foil sample of 18Cr ODS. ............. 40

Figure 3.23: 18Cr ODS (a) EDS spectrum showing presence of Nickel and Molybdenum in
addition to matrix elements overlaid in black. (b) SEM micrograph of capture region for spectrum
in (a) showing accumulation of Ni3Mo on thin foil sample of 18Cr ODS that has been irradiated
to 20dpa at 500°C. ................................................................. 41

Figure 3.24: 18Cr ODS Peak Fit analysis of phases identified by XRD analysis showing
simulated pattern of peaks from (Cr, Fe)23C6 with the diffraction pattern from extraction to show
correlation in peak location and remaining unidentified peaks. The arrow indicates the 100%
relative intensity peak for this phase of (Cr, Fe)23C6 ............................................ 42

Figure 3.25: 18Cr ODS Peak Fit analysis of phases identified by XRD analysis showing
simulated pattern of peaks from (Cr, Fe)23C6 and Y2Ti2O7 with the diffraction pattern from
extraction to show correlation in peak location and remaining unidentified peaks. The arrow
indicates the 100% relative intensity peak for this phase of Y2Ti2O7 ....................... 43

Figure 3.26: 18Cr ODS Peak Fit analysis of phases identified by XRD analysis showing
simulated pattern of peaks from (Cr, Fe)23C6 and two phases of Y2Ti2O7 with the diffraction pattern
from extraction to show correlation in peak location and remaining unidentified peaks. The arrow
indicates the 100% relative intensity peak for the added phase of Y2Ti2O7. ........... 43

Figure 3.27: 18Cr ODS Peak Fit analysis of phases identified by XRD analysis showing
simulated pattern of peaks from (Cr, Fe)23C6, two phases of Y2Ti2O7, and TiO2 with the
diffraction pattern from extraction to show correlation in peak location and remaining
unidentified peaks. The arrow indicates the 100% relative intensity peak for the added phase of
TiO2 ............................................................................................................ 44

Figure 3.28: 18Cr ODS Peak Fit analysis of phases identified by XRD analysis showing
simulated pattern of peaks from (Cr, Fe)23C6, two phases of Y2Ti2O7, TiO2, and Ti2O3 with
the diffraction pattern from extraction to show correlation in peak location and remaining
unidentified peaks. The arrow indicates the 100% relative intensity peak for the added phase of
Ti2O3 ......................................................................................................... 45

Figure 3.29: 18Cr ODS Peak Fit analysis of phases identified by XRD analysis showing a) simulated pattern of peaks from (Cr, Fe)23C6, two phases of Y2Ti2O7, TiO2, Ti2O3, and
AlTiO2 with the diffraction pattern from extraction to show correlation in peak location and
remaining unidentified peaks. The arrow indicates the 100% relative intensity peak for the added
phase of AlTiO2. b) simulated pattern of peaks from (Cr, Fe)23C6, two phases of Y2Ti2O7, TiO2, Ti2O3, AlTiO2, and Ni3Mo with the diffraction pattern from extraction to show correlation in peak location and remaining unidentified peaks. The arrow indicates the 100% relative intensity peak for the added phase of Ni3Mo. c) simulated pattern of peaks from (Cr, Fe)23C6, two phases of Y2Ti2O7, TiO2, Ti2O3, AlTiO2, Ni3Mo, and Al2O3 with the diffraction pattern from extraction to show correlation in peak location and remaining unidentified peaks. The arrow indicates the 100% relative intensity peak for the added phase of Al2O3.

Figure 3.30: 18Cr ODS (a) EDS spectrum showing presence of Yttrium, Titanium, and Oxygen in addition to matrix elements overlaid in black. (b) SEM micrograph of capture region for spectrum in (a) showing Y2Ti2O7 particle in thin foil sample of 18Cr ODS after irradiation to 20dpa at 500°C.

Figure 3.31: 18Cr ODS (a) EDS spectrum showing presence of Aluminum and Oxygen in addition to matrix elements overlaid in black. (b) SEM micrograph of capture region for spectrum in (a) showing an Al2O3 particle in thin foil sample of 18Cr ODS after irradiation to 20dpa at 500°C.

Figure 3.32: 18Cr ODS (a) EDS spectrum showing presence of Aluminum, Titanium, and Oxygen in addition to matrix elements overlaid in black. (b) SEM micrograph of capture region for spectrum in (a) showing an AlTiO2 particle in thin foil sample of 18Cr ODS after irradiation to 20dpa at 500°C.

Figure 3.33: 18Cr ODS (a) EDS spectrum showing presence of Chromium and Carbon in addition to matrix elements overlaid in black. (b) SEM micrograph of capture region for spectrum in (a) showing M23C6 type particles in thin foil sample of 18Cr ODS after irradiation to 20dpa at 500°C.

Figure 3.34: 18Cr ODS Elemental maps of nanoparticle in thin foil sample irradiated to 20dpa at 500°C showing presence of (a) Yttrium, (b) Titanium, and (c) Oxygen.

Figure 3.35: 18Cr ODS SEM micrograph showing appearance of thin foil samples used for SEM analysis. The red circle shows the approximate cross sectional area of the ion beam used for irradiations, the region inside the circle (r~0.5mm) represents the region of the sample that is exposed to radiation during in situ irradiations.

Figure 3.36: 18Cr ODS SEM micrographs showing comparison of microstructure in an irradiated and an un-irradiated sample. The image in (a) shows a region on the sample that has been irradiated to 20dpa at 500°C near the center, within the irradiated radius. (b) Shows a region near the center of the thin foil sample that has not been irradiated. (c) Shows a region on the sample that has been irradiated to 20 dpa at 500°C near the edge, outside of the irradiated radius of the thin foil sample. The image in (d) shows a region near the edge of the thin foil sample that has not been irradiated.

Figure 3.37 18Cr ODS in-situ bright field TEM micrograph showing nanoparticle stability in thin foil sample irradiated to 20dpa at 500°C.

Figure 3.38 18Cr ODS in-situ bright field TEM micrograph showing nanoparticle stability in thin foil sample irradiated to 52dpa at 25°C.
Figure 3.39: 9Cr ODS Synchrotron X-ray diffraction spectrum collected at APS using 15keV photons. ................................................. 54

Figure 3.40: 9Cr ODS Synchrotron X-ray diffraction spectrum collected at APS using 15keV photons. Matrix peaks have been reduced to show second phase peaks from nanoparticles within the alloy matrix................................................................. 55

Figure 3.41: 9Cr ODS Synchrotron X-ray diffraction spectrum collected at APS using 15keV photons with peak locations labeled for all phases showing their presence in the alloy represented in the collected data................................................................. 55

Figure 3.42: 9Cr ODS CuKα X-ray diffraction spectrum of nanoparticles after chemical extraction from the alloy matrix................................................................. 56

Figure 3.43: 9Cr ODS X-ray diffraction spectra from Synchrotron bulk and extracted nanoparticles aligned to reveal similarities and differences in peak presence and location across methods of XRD analysis........................................................................ 57

Figure 3.44: 9Cr ODS CuKα X-ray diffraction spectrum of nanoparticles after chemical extraction from the alloy matrix with peak locations labeled for all phases showing their presence in the alloy represented in the collected data................................................................. 58

Figure 3: 9Cr ODS (a) EDS spectrum showing presence of Iron, Tungsten, and Oxygen in addition to matrix elements overlaid in black. (b) SEM micrograph of capture region for spectrum in (a) showing a tungsten containing oxide particle in thin foil sample of 9Cr ODS................. 58

Figure 3.45: 9Cr ODS (a) EDS spectrum showing presence of Iron, Tungsten, and Oxygen in addition to matrix elements overlaid in black. (b) SEM micrograph of capture region for spectrum in (a) showing particle containing Iron, Tungsten, and Oxygen. ........................................ 59

Figure 3.46: 9Cr ODS (a) EDS spectrum showing presence of Iron, Chromium, Tungsten, and Carbon in addition to matrix elements overlaid in black. (b) SEM micrograph of capture region for spectrum in (a) showing a M23C6 particle in thin foil sample of 9Cr ODS.. ......................... 59

Figure 3.47: 9Cr ODS (a) EDS spectrum showing presence of Iron, Chromium, Tungsten, and Carbon as well as Titanium and Oxygen. (b) SEM micrograph of capture region for spectrum in (a) showing an agglomeration of M23C6 and TiO particles after extraction from the alloy matrix. .................................................. 60

Figure 3.48: 9Cr ODS (a) EDS spectrum showing presence of Aluminum and Oxygen in addition to matrix elements overlaid in black. (b) SEM micrograph of capture region for spectrum in (a) showing an Al2O3 particle in thin foil sample of 9Cr ODS........................................... 61

Figure 3.49: 9Cr ODS (a) EDS spectrum showing presence of Aluminum, Tungsten, and Oxygen in addition to background elements. (b) SEM micrograph of capture region for spectrum in (a) showing an Al2O3 particle as well as other surrounding particles suspected to be tungsten containing oxides after extraction from the alloy matrix.. ........................................ 62

Figure 3.50: 9Cr ODS (a) EDS spectrum showing presence of Aluminum, Yttrium, Titanium, and Oxygen in addition to matrix elements overlaid in black. (b) SEM micrograph of capture region for spectrum in (a) showing an agglomeration of particles in thin foil sample of 9Cr ODS... 62
Figure 3.51: 9Cr ODS (a) EDS spectrum showing presence of Aluminum, Yttrium, and Oxygen in addition to matrix elements overlaid in black. (b) SEM micrograph of capture region for spectrum in (a) showing an agglomeration of particles in thin foil sample of 9Cr ODS. 

Figure 3.52: 9Cr ODS (a) EDS spectrum showing presence of Iron, Chromium, Tungsten, Carbon, Nitrogen, Titanium, Aluminum, and Oxygen in addition to matrix elements overlaid in black. (b) SEM micrograph of capture region for spectrum in (a) showing an agglomeration of particles in thin foil sample of 9Cr ODS. 

Figure 3.53: 9Cr ODS Peak Fit analysis of phases identified by XRD analysis showing simulated pattern of peaks from (Cr, Fe, W, Mo)23Fe21(W, Mo)2C12 with the diffraction pattern from extraction to show correlation in peak location and remaining unidentified peaks. The arrow indicates the 100% relative intensity peak for this phase of (Cr, Fe, W, Mo)23Fe21(W, Mo)2C12. 

Figure 3.54: 9Cr ODS Peak Fit analysis of phases identified by XRD analysis showing simulated pattern of peaks from (Cr, Fe, W, Mo)23Fe21(W, Mo)2C12 and (Cr, Fe)23C6 with the diffraction pattern from extraction to show correlation in peak location and remaining unidentified peaks. The arrow indicates the 100% relative intensity peak for this phase of (Cr, Fe)23C6. 

Figure 3.55: 9Cr ODS Peak Fit analysis of phases identified by XRD analysis showing simulated pattern of peaks from (Cr, Fe, W, Mo)23Fe21(W, Mo)2C12, (Cr, Fe)23C6, and TiO with the diffraction pattern from extraction to show correlation in peak location and remaining unidentified peaks. The arrow indicates the 100% relative intensity peak for the added phase of TiO. 

Figure 3.56: 9Cr ODS Peak Fit analysis of phases identified by XRD analysis showing simulated pattern of peaks from (Cr, Fe, W, Mo)23Fe21(W, Mo)2C12, (Cr, Fe)23C6, TiO, and Y2Ti2O7 with the diffraction pattern from extraction to show correlation in peak location and remaining unidentified peaks. The arrow indicates the 100% relative intensity peak for the added phase of Y2Ti2O7. 

Figure 3.57: 9Cr ODS Peak Fit analysis of phases identified by XRD analysis showing simulated pattern of peaks from (Cr, Fe, W, Mo)23Fe21(W, Mo)2C12, (Cr, Fe)23C6, TiO, Y2Ti2O7, and TiN with the diffraction pattern from extraction to show correlation in peak location and remaining unidentified peaks. The arrow indicates the 100% relative intensity peak for the added phase of TiN. 

Figure 3.58: 9Cr ODS EFTEM Maps of large Yttrium containing particle and very small chromium enriched particles in thin film sample after irradiation to 9dpa at 500°C. 

Figure 3.59: 9Cr ODS In-Situ TEM Images showing particle stability at successive doses in thin film sample during irradiation up to 9dpa at 500°C. 

Figure 4.3: 18Cr ODS TEM micrograph showing dislocations in as-received thin foil sample. Circles indicate locations where there is pinning of dislocations by nanoparticles. 

Figure 4.4: 18Cr ODS TEM micrographs showing dislocation stability under irradiation in thin film sample at successive doses during irradiation up to 10dpa at 25°C.
Figure 4.5: 9Cr ODS TEM micrograph showing dislocations in as-received thin foil sample. Arrows indicate locations where there is pinning of dislocations by nanoparticles.

Figure 4.6: 9Cr ODS TEM micrographs showing dislocation stability under irradiation in thin foil sample at successive doses during irradiation up to 10 dpa at 25°C.

Figure 4.8: 18Cr ODS TEM micrograph of thin foil sample of as-received alloy after thermal treatment to 500°C showing nanoparticle dispersion and accumulation of nanoparticles along grain boundaries.

Figure 4.11: 18Cr ODS: low mag SEM micrographs of as-received thin foil samples showing nanoparticle dispersion with accompanying maps showing outlines of particles used for area calculations in ImageJ for nanoparticle size distributions.

Figure 4.12: 18Cr ODS Distribution of nanoparticle sizes calculated using SEM micrographs and ImageJ on thin foil samples of as-received alloy.

Figure 4.13: 9Cr ODS SEM micrograph of thin foil sample of as-received alloy showing nanoparticle dispersion, size, and composition. 1) EDS spectra and area calculation of Al- and O-containing particle. 2) EDS spectra and area calculation of Al-, Ti-, and O-containing particle. 3) EDS spectra and area calculation of Al-, Y-, and O-containing particle.

Figure 4.14: 9Cr ODS TEM micrograph of thin foil sample after irradiation to about 0.5 dpa at 500°C showing nanoparticle dispersion and accumulation of nanoparticles along grain boundaries.

Figure 4.15: 9Cr ODS TEM micrograph of thin foil sample after irradiation to about 10 dpa at 25°C showing nanoparticle dispersion and accumulation of nanoparticles along grain boundaries.

Figure 4.16: 9Cr ODS low mag SEM micrographs of as-received thin foil samples showing nanoparticle dispersion with accompanying maps showing outlines of particles used for area calculations in ImageJ for nanoparticle size distributions.

Figure 4.17: 9Cr ODS Distribution of nanoparticle sizes calculated using SEM micrographs and ImageJ on thin foil samples of as-received alloy.

Figure 4.18: 9Cr ODS Distribution of nanoparticle sizes with equivalent diameter between 0 and 120 nm calculated using SEM micrographs and ImageJ on thin foil samples of as-received alloy.

Figure 4.19: 9Cr ODS Distribution of nanoparticle sizes with equivalent diameter between 115-270 nm calculated using SEM micrographs and ImageJ on thin foil samples of as-received alloy.

Figure 4.21: 9Cr ODS a) SEM micrographs on thin foil samples of the as-received alloy showing nanoparticles along with corresponding EDS spectra showing the presence of Y-, Ti-, and O-. b) SEM micrographs on thin foil samples of the as-received alloy showing nanoparticles along with corresponding EDS spectra showing the presence of Y-, Al-, Ti-, and O-. c) TEM energy filtering maps of thin foil sample after irradiation up to 18 dpa at 500°C showing large (about 50 nm) Y-, Ti-, and O-containing particle and very small Y-, Ti-, and O-containing particles (<10 nm).
Figure 4.22: 18Cr ODS SEM micrographs on thin foil samples showing nanoparticles along with corresponding EDS spectra showing the presence of Al- and O- as well as particles containing Al-, Ti-, and O- corresponding to Al2O3 precipitates.................................................................104

Figure 4.26: 18Cr ODS a) low mag SEM micrographs of as received thin foil samples showing nanoparticle dispersion with accompanying maps showing outlines of particles used for area calculations in ImageJ for nanoparticle size distributions. b) low mag SEM micrographs of thin foil samples after irradiation to 20dpa at 500°C showing nanoparticle dispersion with accompanying maps showing outlines of particles used for area calculations in ImageJ for nanoparticle size distributions .................................................................113

Figure 4.29: 18Cr ODS TEM micrographs showing grain boundary stability under irradiation in thin foil sample at successive doses during irradiation up to 20 dpa at 25°C. .......................115

Figure 4.30: 18Cr ODS TEM micrographs showing nanoparticle stability under irradiation in thin foil sample at successive doses during irradiation up to 52 dpa at 25°C.................................116

Figure 4.31: 9Cr ODS TEM micrographs showing amorphization of a large particle under irradiation in thin foil sample at successive doses during irradiation up to 10dpa at 25°C... 117

Figure 4.32: 9Cr ODS TEM micrographs showing amorphization before and after tilt of a large particle in a thin foil sample that has been irradiated to 10dpa at 25°C ..............................118
CHAPTER 1

BACKGROUND AND MOTIVATIONS

1.1 MATERIAL CHALLENGES FOR NUCLEAR ENERGY

1.1.1 CURRENT NUCLEAR ENERGY

At this time in the United States nuclear power accounts for about 75% of our emission-free electric power and 20% of the country’s total electrical output. There are currently 104 nuclear power plants in the United States which serve to supply this nuclear contribution to total energy production [1]. All of these plants currently house light water reactors which use zirconium based alloys for both fuel cladding and core internal structures. While these alloys have low neutron capture cross sections for thermal neutrons, good fabric-ability, and strong corrosion resistance at the current operating temperatures of about 300°C; at sufficiently higher temperatures zirconium alloys become prone to extreme oxidation, hybriding, and creep deformation. Certain elemental additions can be made to currently used zirconium based alloys which serve to increase their beneficial microstructural mechanical properties; however the extreme ranges of radiation exposure and temperature in Generation IV nuclear reactors require new materials for application as fuel cladding and core internal structures designed to withstand more hazardous core conditions[2].
1.1.2 Generation IV Reactors

The structural materials and cladding inside a nuclear reactor pressure vessel are vital to containment of the nuclear fuel and fission products as well as the overall reliability and efficiency of energy production. These next generation nuclear reactors increase efficiency, safety, life of operation, proliferation-resistance, and economic viability compared to current nuclear reactors, but will operate at higher neutron doses, higher temperatures, and under extremely corrosive environments [2]. All of these impose strain upon structural materials. Materials used in current light water and boiling water reactors will no longer be sufficient to withstand conditions within the core. The selection of new materials must be carefully studied and tested [1].

Additionally, in order to remain a competitive source of energy nuclear reactors must prove to be affordable to construct and maintain. This requires that the materials used in construction can be utilized for their specific purposes at a reasonable cost, as well as be reliable in the long term, requiring that the damage done to materials is minimal and materials failures are obsolete.

As results emerge from current advanced nuclear materials research Oxide Dispersion Strengthened (ODS) alloys stand out as promising candidates for future nuclear reactor material applications. Many versions of ODS alloys are being developed and tested worldwide for application in Generation IV reactor designs, and current research efforts are aimed at optimization of these ferretic-martensitic, nano-strengthened, steel alloys for environments expected in specific Gen IV reactor designs.
Many new reactor models are emerging under the Generation IV initiative for more efficient, safe, and resilient reactors, however two among these stand out as the most practical for development and application within the US. These are the Sodium-Cooled Fast Reactor (SFR) and the Very High Temperature Reactor (VHTR) [1]. The materials which are the topic of research, ferritic-martensitic ODS steels specifically, are of most importance to the development of the SFR program, they are currently being considered for use as cladding tubes within the reactor pressure vessel (RPV) [3]. The cladding tubes are primarily used to contain nuclear fuel and fission products produced during operation, however they also must be capable of transferring the heat produced by nuclear reactions to the coolant contained within the RPV. The flux through the cladding can reach about 1 MW/m² in current LWRs, requiring fuel cladding materials to have high creep strength while under operation in high temperatures and under exposure to corrosive liquid metal coolant [4]. The cladding must be capable of withstanding this high temperature flux for several years under high mechanical stress, irradiation, and corrosion by the coolant, while also maintaining the integrity to contain fission products and conduct heat efficiently [5]. The primary concerns for materials existing in this environment are oxidation, hydriding, build-up of low thermal conductivity corrosion deposits, and build-up of hydrogen and helium which can lead to further cracking and corrosion [4], however the greatest obstacle for SFR fuel cladding is radiation-induced void swelling due to high neutron fluence under elevated temperatures [5]. Ferritic-Martensitic ODS steels are ideal for this application as they have fine grain structure and fine dispersion of nanoparticles; both act as sinks for point defects and dislocation motion, inhibiting formation of voids which lead to material degradation [6].
1.1.3 Oxide-Dispersion Strengthened Steel Alloys

ODS alloys are typically made from elemental or pre-alloyed metal powders mechanically alloyed with oxide powders in a high-energy attritor mill filled with argon gas, and then consolidated by either hot isostatic pressing or hot extrusion [7], though other fabrication techniques are also being proposed and tested. This process causes the production of nanometer scale oxide and carbide particles within the alloy matrix; these are typically 2-3 nm in size, though the observed range varies almost up to a micrometer in diameter [8]. Crystalline properties such as creep strength, ductility, corrosion resistance, tensile strength, swelling resistance, and resistance to embrittlement are all observed to be improved by the presence of nanoparticles in the matrix, however the science behind these experimental observations is yet to be fully understood, and is crucial to further improvement of reactor materials currently under scrutiny.

1.2 Metallic Properties Of Interest in ODS Alloy Application

1.2.1 Radiation Damage

Radiation damage in crystalline materials, such as that in reactor materials, results from energy transfer from energetic neutrons to the lattice atoms forming primary knock on atoms (PKA), and further damage occurs subsequently from the PKA’s to other lattice atoms. These events can eventually lead to the creation of displacement cascades, causing further damage throughout the material [4].
At the doses and temperatures relevant to fast reactor operation (temperatures ranging from 300°C to greater than 700 °C and doses beyond 200dpa) structural components and cladding experience displacement of atoms by collisions with neutrons at temperatures at which the radiation-induced defects are mobile, resulting in microstructure evolution and overall degradation of material properties [1],[8].

The microstructure of materials within the core evolve by: dislocation loop formation and growth, microchemistry changes due to radiation-induced segregation, radiation-induced precipitation, destabilization of the existing precipitate structure, and in some cases void formation and growth. These do not occur independently, their evolution is highly interlinked and neither the evolution of these processes nor their coupling has been sufficiently examined under the conditions required for materials performance in fast reactors [8].

The stability of these oxide nanoparticles under irradiation is crucial to the benefits of ODS alloys and is the primary property being researched. Results from a neutron irradiation up to 18dpa at 725-825K on an Fe-11Cr-0.4Ti-2.7W-0.40Y2O3 ODS alloy have shown that the particle size is relatively unchanged throughout a wide span of doses and temperatures; however the density of particles tends to be reduced, possibly due to ballistic ejection from interaction with the beam ions [1]. The degree to which particle number is reduced appears to depend on the composition and microstructure, detailed characterization of each alloy provides insight into why particles are dissipating, and which changes can be made to improve stability.
The nanoparticles contained in the matrix of ODS alloys are the primary source of the observed enhanced mechanical properties. The existence of these particles not only serve to inhibit the motion of dislocations and thus loop formation, but also increase resistance to other forms of degradation relevant to reactor core conditions, the theory behind these mechanisms, and their inhibition caused by the presence of nanoparticles, is outlined in the following paragraphs:

1.2.2 Creep

Creep is time-dependent plastic deformation of a material. There are several types of creep which occur in metallic materials however the sort of primary interest in nuclear environments is irradiation creep. As pressure builds up inside fuel cladding during operation along with increasing dose, and defect formation and accumulation, the creep rate increases and occurs more quickly over reactor cycle. Irradiation creep is expected to be important in Generation IV nuclear reactors where operating temperatures are above 500°C as it is both a temperature and stress dependent property. Current research shows that ODS alloys have an exceptional creep vs. stress rate. Meaning that under the same amount of stress (from irradiation, temperature, etc.), there is overall less plastic deformation than in other reactor materials. This is a result of the nature of the interaction between the nanoscale oxide particles and mobile dislocations present. Specifically the particles act as obstacles, pinning the dislocations and greater energy is required for mobility, as the dislocation must climb, or glide around each particle. Also the nanoscale particles act as sinks, such that radiation-produced defects are pulled away from dislocations reducing ability to climb and thus dislocation mobility or creep [9].
The processing method of the alloy has an effect on the creep strength as well, in early samples there was a tendency toward a non-uniform distribution of nanoparticles, as well as irregular elongated grains, which caused in some cases grain boundary sliding and absences of dislocation obstacles in some areas. Through modification of processing technique as well as composition adjustment, these problems have been largely solved; however theoretical calculations of the threshold stress for deformation have shown that the strength should be even higher than currently obtained experimental results. So, while ODS alloys already have a far superior creep strength to traditional cladding materials it is clear that there is still room for improvement [10].

1.2.3 Helium Embrittlement and Void Swelling

Void swelling in nuclear reactor materials occurs due to helium bubbles formed inside the structural materials during transmutation reactions. The helium gathers at grain boundaries and forms bubbles which then become sinks for further produced helium and begin to grow, causing cracks at the grain boundaries, this cracking is sometimes referred to as helium embrittlement. The nanoparticles aid in reducing formation of these bubbles by acting as sinks themselves, keeping the dispersion of helium away from grain boundaries and reducing overall void growth. Experimental results show that void swelling in ODS alloys seems to be independent of the level of radiation dose, confirming the theory that the nanoparticles serve to disperse helium accumulation [1], [2], [8].
1.2.4 ULTIMATE TENSILE STRENGTH

Under high temperature observation ODS alloys are shown to have an increased ultimate tensile strength as well as a more uniform elongation when compared to conventional reactor materials (without oxide-particle dispersion). This improvement is particularly evident at temperatures above 600 °C, and most likely results from pinning of the dislocations by nanoparticles, which slows recovery rates and hastens work-hardening in the material. ODS alloys have also been shown to have resistance to radiation hardening, with ductility (total strain) relatively unaffected by dose level under radiation exposure [11].

1.2.5 CORROSION RESISTANCE

Various cooling agents will be used in Generation IV nuclear reactor designs in place of water. The contact of these cooling agents with fuel cladding and reactor structure materials will lead to fuel cladding chemical interaction. Direct interaction with the cooling agents can lead to corrosion of the material as can helium embrittlement which occurs through fission product accumulation in the fuel during irradiation which migrates to the cladding/fuel interface producing a reaction zone leading to degradation of the cladding [4]. The presence of the oxides in ODS alloys helps to raise resistance to corrosion from both of these modes of interaction.

1.2.6 THERMAL STABILITY

The primary evidence of increased thermal stability is shown through the resistances of ODS alloys to microstructure evolution under high temperature exposure. Many aspects are considered in order to maintain high-temperature strength and ductility without jeopardizing other beneficial properties.
The thermal efficiency of ODS alloys is enhanced through controlling the grain boundary structure during processing and consolidation; small homogenous grains are desired for optimal mechanical performance, and through stability of nanoparticles. The nanoparticles have been observed to remain stable, without dissolution or coarsening, at temperatures up to 1300°C for several hours [1].

1.3 Composition Rationalization

1.3.1 Effects of Elemental Additions

Variations of ODS alloys are developed with differing chemical compositions and consolidation techniques which affect the microstructural properties lending to the beneficially resilient properties of these alloys. Some of the properties which can be manipulated by small adjustments in composition and consolidation are corrosion resistance, grain size, morphology, particle size, and spacial distribution. These can be optimized to resist radiation and temperature induced damage such as that seen within a nuclear reactor pressure vessel. For example, the addition of pure Y2O3 during fabrication shows an initial increase in alloy’s mechanical properties when compared to conventional steel. Each additional element included as well as any purposeful step taken during fabrication further serves to supply, enhance, or decrease some physical property of the alloy. The most common elemental additions and fabrication methods used for these purposes are presented and expanded upon below:
1.3.2 **Yittria and Titanium**

$\text{Y}_2\text{O}_3$ and Ti are added to improve mechanical strength as they play a role in the forming mechanisms of the very small Y-Ti-O particles. As already mentioned, the addition of pure $\text{Y}_2\text{O}_3$ shows the greatest increase in mechanical properties and isotropy of particle distribution, but it has been shown that the addition of titanium reduces the oxide particles to around 3 nm in size from an average size of about 10 nm in the absence of titanium. This decrease in size causes a significant improvement of the creep rupture strength and serves to be worth the subsequent loss of enhanced properties that is achieved from the addition of pure $\text{Y}_2\text{O}_3$. However, the precipitated Y-Ti-O particles have been observed to undergo dissolution under certain welding [12].

1.3.3 **Tungsten**

Tungsten is responsible for solution hardening; however more than 2 wt% can cause concern with irradiation/thermal embrittlement due to precipitation of laves phases. Results have shown that tungsten should be used in place of molybdenum, one of the previously used additions, in order to improve isotropy and activation properties of the alloy [1].

1.3.4 **Aluminum**

Addition of aluminum has been shown to be beneficial to corrosion resistance of ODS alloys, but can also have detrimental effects to the alloy’s resistance to irradiation embrittlement and high-temperature strength. [11].
1.3.5 Chromium and Phase Control

Chromium content is involved in phase control, for example a 9wt%Cr-ODS is martensitic while 12wt%Cr-ODS alloys are usually fully ferritic. It is apparent that to maintain high corrosion resistance the ideal range for chromium concentration is between \( \sim 13-18 \) wt% as the \( \alpha \)-Ferritic BCC phase is dominant throughout all temperatures in that region [13]. However a lower chromium concentration, such as 9Cr ODS, allows for a ferritic-martensitic microstructure which has an improved resistance to high temperatures and void swelling. The choice of high chromium ferritic ODS material results from different compromises. High concentrations of chromium lead to thermal embrittlement due to the formation of the \( \alpha' \)-phase at temperatures between \( 400^\circ\text{C} \) and \( 550^\circ\text{C} \). The degree of thermal embrittlement related to the phase separation was clearly shown to increase with increasing chromium content in a comparison of 14 Cr, 16 Cr, and 19 Cr ferritic ODS steels [12]. For application at temperatures below \( 800^\circ\text{C} \) fully martensitic steels can be used, but at higher temperatures they exhibit a phase transformation as well as being susceptible to corrosion due to lower chromium concentration.

The microstructure of martensitic steel is usually isotropic with a low ductile to brittle transition temperature (DBTT), so a Fe–9Cr martensitic material is advantageous to some regard, however, the corrosion resistance in service and especially inside the cladding tube seems correlated to the chromium content of the material. From that point of view, a ferritic material with high chromium content is preferred. Conventional ferritic steels generally exhibit a higher DBTT when compared to martensitic ones. In the case of a ferritic ODS material consolidated by hot extrusion and unrecrystallized with a very fine microstructure, the DBTT can be similar to one of a good martensitic material (around \( 50^\circ\text{C} \)) [3].
An ODS material, martensitic or ferritic, can exhibit excellent creep properties and both types of material could be retained for the application. In some cases an extra step is taken during processing to change the ferritic (bcc) alloy into martensitic (fcc), by heating. This transformation causes a decrease in average grain size as well as more homogeneous grain distribution due to the impedance of grain growth by the Y2O3 particles during heating. This structure is an advantage for application of the material in fuel pin applications, particularly emergency applications such as fuel cladding being rapidly heated during a loss of coolant flow event. However BCC structures tend to be more advantageous as they serve to have a higher resistance to void swelling.

Chromium also serves to enhance corrosion resistance, but can lead to embrittlement at high concentrations (>20%) due to the formation of the α’-phase [12]. This is advantageous for certain nuclear applications which do not induce embrittlement, such as in spent nuclear fuel refining which requires the dissolution of uranium or plutonium oxide in nitric acid, high chromium alloys are resistant to the corrosion caused by the nitric acid on containment materials [3].

There are two ODS alloys analyzed in this research; both have a structure that can be either ferritic or martensitic. This structure was chosen for its excellent resistance to void swelling, and as the nano-particles serve to inhibit dislocation motion in all ODS alloys, having a BCC structure they are able to have high resistance to both void swelling and creep.
1.4 **SUMMARY**

As interest in the applications of ODS steels develops, determination of the structure, character, and particle stability of nanometer scale Y-Ti-O precipitate clusters needs to be further studied. Consolidation of the significance of these results can then be applied to the development of advanced structural materials for long-term, elevated temperature irradiation in future reactor applications.

However, recent observations have shown the true need for further research, as new ODS alloys are being developed. Some experiments show a dissolution and reduction in average size of precipitates under neutron and ion irradiation, a detriment to the beneficial qualities of ODS steel alloys, while other results show that the thermal stability of the nanoparticles is very good, with no discernible sign of coarsening or dissolution up to 1,300°C. Other evidence of the need for further understanding of the characterization and stability of the nanoparticles is the apparent non-homogeneity of nanoparticle distribution after processing which causes a decrease in creep and ductility properties. More research needs to be done to determine the cause of these phenomena, and why they are only present under certain conditions.

The presented research uses various methods to characterize the microstructural and micro-chemical properties of two ODS alloys, 18Cr ODS and 9Cr ODS. The results found will aid in displaying the influence of chemical and structural variations on the effectiveness of the alloy, and further, will aid in the optimization of these advanced alloys for future use in nuclear cladding and structural applications in Generation IV nuclear reactors.
CHAPTER 2

MATERIALS AND METHODS

2.1 MATERIALS

The alloys presented in this research are Fe-18wt% Cr and Fe-9wt% Cr, these are supplied with certain elemental additions and prescribed processing techniques which result in a precipitation of nanometer-scale oxide particles.

In Table 1 the nominal compositions by weight percent of 18Cr ODS and 9Cr ODS are listed, these are the initial elements added in proportion by weight percent.
### Table 1.1: Nominal Alloy Composition by Weight Percent for 18Cr ODS and 9Cr ODS

<table>
<thead>
<tr>
<th>Element</th>
<th>18Cr ODS</th>
<th>9Cr ODS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>Bal.</td>
<td>Bal.</td>
</tr>
<tr>
<td>Cr</td>
<td>18</td>
<td>8.67</td>
</tr>
<tr>
<td>W</td>
<td>1</td>
<td>1.96</td>
</tr>
<tr>
<td>Ti</td>
<td>0.25</td>
<td>0.23</td>
</tr>
<tr>
<td>Mn</td>
<td>0.3</td>
<td>0.05</td>
</tr>
<tr>
<td>Si</td>
<td>0.3</td>
<td>0.048</td>
</tr>
<tr>
<td>Ni</td>
<td>0.19</td>
<td>0.06</td>
</tr>
<tr>
<td>C</td>
<td>0.027</td>
<td>0.14</td>
</tr>
<tr>
<td>P</td>
<td>-</td>
<td>&lt;0.005</td>
</tr>
<tr>
<td>S</td>
<td>-</td>
<td>0.003</td>
</tr>
<tr>
<td>N</td>
<td>-</td>
<td>0.017</td>
</tr>
<tr>
<td>Ar</td>
<td>-</td>
<td>0.004</td>
</tr>
<tr>
<td>Y</td>
<td>-</td>
<td>0.27</td>
</tr>
<tr>
<td>O</td>
<td>0.11</td>
<td>0.14</td>
</tr>
<tr>
<td>Y2O3</td>
<td>0.56</td>
<td>0.34</td>
</tr>
<tr>
<td>Ex. O</td>
<td>-</td>
<td>0.07</td>
</tr>
</tbody>
</table>

#### 2.1.1 18Cr Fabrication

18Cr ODS is manufactured at CEA. Alloying is performed using pre-alloyed (Y2O3) powder and the remaining additions as elementary powders. These are combined and mechanically milled in an attritor. It is during this stage that dissolution of the oxides is observed. After mechanical alloying, the powders are sieved at 150 μm, consolidated, and hot extruded at 1100°C where precipitation of the final nano-clusters occurs. Finally the alloy is formed into the desired dimensions through hot rolling 20% at 650°C and annealing for 1 h at 1050°C. This process controls the final microstructure and allows for very fine grain structures. The alloy is typically shaped into long tubes, and then cut into thin plates about 4 mm thick, 30 mm wide and 2000 mm long, which allows for ease of most basic studies of this type of semi-final product.
This shape permits machine tensile and small impact testing of specimens in different directions in order to study the anisotropy of the material due to processing technique [3].

2.1.2 **9Cr Fabrication**

The 9Cr ODS was fabricated at JAEA by a similar process with annealing at 1050°C for 60 minutes and subsequent tempering at 800°C for 60 minutes. The precipitation of the nano-clusters occurs during the consolidation process. This process also controls the final microstructure and to get very fine structures it is necessary to use the hot extrusion process instead of the hot isostatic pressure [14].

2.2 **Methods**

2.2.1 **Synchrotron X-ray Diffraction Analysis**

In order to identify the matrix and nano-particle composition, phase, and relative abundance the alloys were analyzed using Synchrotron X-ray diffraction analysis at the Advanced Photon Source at Argonne National Laboratory. Synchrotron XRD allows for higher energy photons and higher brilliance than the typically utilized Cu-Kα photon source, which enables observance of signal from low volume fraction precipitates. The diffraction pattern was taken using 15 keV photons and analyzed using the PDF 4+ ICDD database, PeakFit, and Sieve data analysis software in order to gather data from the resulting diffraction patterns.
2.2.2 CuKa XRD Analysis

The XRD pattern resulting from the Synchrotron source still had a vast difference between the overall volume fraction of the matrix peaks versus the peaks from the nano-scale precipitates. In order to further substantiate the phases identified, chemical extractions of precipitates were characterized using CuKα radiation. Also, bulk samples of 18Cr ODS were subject to CuKα XRD analysis in order to compare data acquisition techniques and to substantiate results.

The metallic matrices of the specimens were dissolved in a Berzelius type solution. The Berzelius reagent was prepared by dissolving 47.7 g of copper (II) chloride dihydrate (Acros Organics, code 206532500), 41.7 g of potassium chloride (Fisher Scientific P217-500), and 2.9 g of tartaric acid (Acros Organics, code 137860250) in 275 ml of water and 22.4 ml of concentrated hydrochloric acid (Fisher Scientific A144S-500). The salts were added one at a time in the described order and they had to be stirred to be dissolved. The Berzelius reagent was vacuum filtered through a 0.02 µm Whatman Anodisc 25 filter, to remove any impurities that could be present after the reagent preparation.

Alloy samples of about 2 g were weighed and the matrix dissolved at room temperature. Mixing was aided by an electromagnetic stirrer. The solution was filtered through a 0.02 µm Whatman Anodisc 25 filter. After filtering, the precipitates were cleaned with a 0.2 N hydrochloric wash, and dried for two hours at 105 °C before being weighed.
The nanoparticles were then analyzed using a Rigaku Ultima IV Powder X-ray diffraction system (CuKa radiation) with a diffracted beam graphite monochromator in order to obtain a diffraction pattern without the obstruction of peaks from the matrix.

The images below show the nanoparticles after extraction from the matrix.

Figure 1.1: a) 18Cr ODS extracted nanoparticles on filter after dissolution of the matrix through chemical extraction. b) 9Cr ODS extracted nanoparticles on filter after dissolution from the matrix through chemical extraction.

Additionally bulk samples taken from both the transverse and longitudinal directions were analyzed using the Rigaku Ultima IV Powder X-ray diffraction system in order to compare with the pattern obtained from the bulk sample used for Synchrotron analysis. Images of the samples used are shown below.

Figure 1.2: a) 18Cr ODS bulk sample taken from transverse direction of as-fabricated material used for CuKα XRD analysis. b) 18Cr ODS bulk sample taken from longitudinal direction of as-fabricated material used for CuKα XRD analysis.
The resulting patterns were analyzed using PDF 2 ICDD database, Peak Fit, and SIeve data analysis software and the results compared with findings from the Synchrotron XRD data in order to substantiate peak identifications and methods.

2.2.3 FIELD EMISSION SCANNING ELECTRON MICROSCOPY

FESEM analysis was first conducted using thin foil samples of the two alloys. In order to form thin foils from the bulk samples, the alloys were first cut and polished down to a thickness of about 1μm using a polishing wheel and increasingly fine grit polishing sheets. The foils were then punched into discs approximately 3 mm in diameter, and electropolished using 95:5 electrolyte solution of methanol and perchloric acid. The discs were characterized using a Zeiss Ultra plus FESEM in order to observe both matrix and nanoparticle composition using EDS analysis and to observe nanoparticle size and distribution. Nanoparticles from the dissolution experiment were also analyzed using SEM EDS with similar methods for comparison with XRD results. Comparison of the composition analysis from the XRD methods and results from SEM EDS analyses were made in order to consolidate and verify the presence, composition, and character of nanoparticles in specific phases dispersed within the Fe-Cr matrices as well as after extraction.

2.2.4 IRRADIATION AND IN-SITU TEM ANALYSIS

Thin disk samples of these alloys were used for irradiation studies at the IVEM-Tandem TEM at Argonne National Lab. This facility is equipped with a Hitachi 9000 NAR Transmission Electron Microscope with an operating voltage of 100-300 kV with the capability of reached a maximum resolution of 0.25 nm.
The TEM is interfaced with an ion accelerator. The assemblage provides control over the ion type used for in-situ irradiation (i.e. Ar, Kr, Fe), as well as the ion energy, dose rate, and irradiation temperature (20-1200 K).

In-situ evaluation allows for damage to be observed directly as it proceeds in the material providing information on the kinetics and processes of the phenomena so that the mechanisms and driving forces can be understood in detail. The effects of irradiation can be observed over a shorter time span using ion irradiation as it enables high doses to be reached much more quickly than with neutron irradiation.

These runs were carried out at various temperatures and to multiple doses in order to observe nanoparticle stability as well as microstructural and microchemical evolution under irradiation. 18Cr ODS samples were irradiated with 1 MeV Kr ions to 2, 10, 30, and 52 dpa at 25°C, to 30dpa at 300°C, and to 20dpa at 500°C. 9Cr ODS irradiations were carried out with 300keV Fe ions to 6 dpa at 25°C and to 9 dpa at 500°C; 9Cr was also irradiated with 1 MeV Kr ions to 30 dpa at 500°C. All dpa calculations were made using SRIM-2008 code. TEM images of both samples were taken in-situ throughout irradiation at successive doses on a set of predetermined regions in order to track and record the effects of the radiation and temperature on the material. After irradiation, EFTEM energy filtering maps were taken in-situ of the 9Cr ODS to observe nanoparticle composition after irradiation. The 18Cr ODS sample irradiated to 20dpa at 500°C was characterized in the post-irradiated state using the Zeiss Ultra plus FESEM in order to observe any irradiation induced changes in the composition, appearance, or nanoparticle distribution in comparison to pre-irradiated analysis.
CHAPTER 3

RESULTS

These alloys have been fabricated by methods which are shown to produce the desired mechanical properties in the consolidated alloy, however characterization of the as fabricated microstructure is lacking. This purpose of characterization is to substantiate or disprove the methods of fabrication used by observing whether the desired results are achieved in the consolidated microstructure. Results of characterization can also be compared with testing of mechanical properties to better understand the formation and degradation mechanisms occurring during fabrication and testing. In this section, we report the results of characterization that has been carried out on developmental alloys 18Cr ODS and 9Cr ODS through Synchrotron and CuKα XRD, FESEM, EDS, in situ TEM, and EFTEM analyses as well as the results of preliminary irradiations that have been carried out to study the stability of as fabrication microstructure.
3.1 18Cr ODS Results

3.1.1 Synchrotron XRD

An image of the raw XRD spectrum obtained from the Advanced Photon source is shown in the figure above. The matrix peaks were reduced before analysis in order to observe the smaller peaks from second phase particles which comprise a much smaller volume fraction of the bulk sample and thus are dwarfed by the peaks from the matrix.
The reduction was made by first normalizing the total counts collected by the minimum count observed, and then capping data, for the matrix peaks only, slightly above the maximum second phase peak height; the edited data is displayed in the figure below.

It should be noted that due to the normalization of data and reduction of the peaks, the count scale on the y-axis does not represent the actual counts recorded during analysis and the values are not used in any quantitative analysis.

The 2-Theta values and relative height of peaks remain consistent and are the focus of this research; from the image above it is clear that the smaller peaks from second-phase precipitates are more easily observed after the matrix peaks are reduced and the two theta values for peak location more discernible.

Figure 3.2: 18Cr ODS Synchrotron X-ray diffraction spectrum collected at APS using 15keV photons. Matrix peaks have been reduced to show second phase peaks from nanoparticles within the alloy matrix.
3.1.2 CuKα XRD Analysis on Extracted Nanoparticles

Additional methods of XRD analysis allow us to substantiate both the method and results of the data collected at APS. The nanoparticles, which were separated from the matrix through chemical dissolution, were analyzed using CuKα radiation in order to obtain a diffraction pattern without the obstruction of peaks from the matrix; the raw data obtained is shown in the figure below.

![18Cr ODS Extraction](image)

Figure 3.3: 18Cr ODS CuKα X-ray diffraction spectrum of nanoparticles after chemical extraction from the alloy matrix.

Additionally a pattern was obtained from each of two bulk samples, taken from different regions of the consolidated alloy (longitudinal and transverse), using CuKα radiation. The raw data obtained is displayed in the following figures:
The spectra obtained by all XRD methods are compared in order to observe any discrepancies in peak count or location in the figure below:

Figure 3.4: 18Cr ODS CuKα X-ray diffraction spectrum taken on bulk material from the longitudinal direction of the consolidated alloy.

Figure 3.5: 18Cr ODS CuKα X-ray diffraction spectrum taken on bulk material from the transverse direction of the consolidated alloy.

The spectra obtained by all XRD methods are compared in order to observe any discrepancies in peak count or location in the figure below:
The energies of the two sources (Synchrotron and CuK\(\alpha\)) were used to calibrate the two-theta values using Bragg’s law. First the d-spacing was calculated for each peak in the Synchrotron data using:

\[
d = \frac{\lambda}{2\sin \theta}
\]

and using \(\lambda=0.826667 \text{ Å}\) for the 15keV photon source. The d-values could then be used to calculate two theta values for the same data using the energy of the CuK\(\alpha\)-source which has an energy of about 8.05keV and corresponding wavelength \(\lambda=1.54 \text{ Å}\).

Using Bragg’s law again:

\[
2\theta = 2 \cdot \sin^{-1} \frac{\lambda}{2d}
\]

gave us the values of two theta used to compare the Synchrotron data with that from the CuK\(\alpha\) source.
In comparing the peaks present, it is clear that there is strong correlation in pattern, particularly between the synchrotron and extraction spectra. There were slight variances observed in beam energies from the CuKα diffraction patterns, the wavelengths were adjusted from the standard $\lambda=1.54$ Å correspondingly. These corrections allow for better comparison as alignment of the peak locations in all patterns highlights similarities and differences observed by multiple methods of XRD analysis. However, as numeric 2-Theta values are insufficient to substantiate peak positions between CuKα XRD patterns the peaks were identified for each spectrum individually using the PDF2 database and PeakFit in order to show correlation. The results of analyses are displayed in the next section.

3.1.3 Peak Identification

In order to identify the peaks present in each of the four diffraction patterns obtained on 18Cr ODS, Sleve XRD peak identification software was used to find the possible phases present in each spectrum. Initially identified phases are displayed in the following images for each spectrum.
The phases identified using XRD software and the PDF database are shown above overlaid on the edited synchrotron and extraction diffraction patterns in order to show that the peaks in the pattern are closely matched with those identified by Siieve, although not all peaks are identified.

Figure 3.7: 18Cr ODS Synchrotron X-ray diffraction spectrum collected at APS using 15keV photons with peak locations labeled for Y2Ti2O7, Al2O3, and (Cr, Fe)C6 showing their presence in the alloy represented in the collected data.

Figure 3.8: 18Cr ODS CuKα X-ray diffraction spectrum of nanoparticles after chemical extraction from the alloy matrix with peak locations labeled for Y2Ti2O7, Al2O3, and (Cr, Fe)C6 showing their presence in the alloy represented in the collected data.
Present in the Synchrotron pattern, in addition to the (Fe, Cr) Matrix, are an Iron Chromium Carbide of the form M23C6 (PDF# 01-078-1501), and Yttrium Titanium Oxide of the form Y2Ti2O7 (PDF# 01-074-9631).

The same phases which were identified in the synchrotron pattern are overlaid on the extraction pattern. It can be seen that all peaks from phases previously identified on the un-extracted particles are reasonably represented in this diffraction pattern; however there are a few smaller peaks present which were not as obvious in the synchrotron pattern, and thus are not represented in the accepted phases.

The Patterns collected from bulk samples using CuKα radiation have much fewer peaks present, this should be expected as only phases with relatively high volume fraction in the alloy are observable. The figures below show that the (Fe, Cr) Matrix (PDF # 01-077-7599) is most easily observable in both directions; in the transverse direction we see the M23C6-Iron Chromium Carbide (PDF# 01-078-1501), in addition to the matrix and in the longitudinal sample there is only the matrix identified, the smaller low angle peaks present in the longitudinal sample are most likely contaminate peaks from the stage used during XRD analysis, the peaks are too large relative to the matrix peaks to be from any second phase nanoparticle and do not correspond with peaks in any other obtained pattern.
Figure 3.9: 18Cr ODS CuKα X-ray diffraction spectrum taken on bulk material from the transverse direction of the consolidated alloy with peak locations labeled for the Iron Chromium (Fe, Cr) matrix and (Cr, Fe)C6 showing their presence in the alloy represented in the collected data.

Figure 3.10: 18Cr ODS CuKα X-ray diffraction spectrum taken on bulk material from the longitudinal direction of the consolidated alloy with peak locations labeled for the Iron Chromium (Fe, Cr) matrix.
Additionally analysis was made using Peak Fit, which uses Gaussian peaks to approximate the patterns obtained, this aids in locating exact peak locations for comparing with peak locations listed on the PDF cards for the phases identified using Sieve.

Figure 3.11: 18Cr ODS Peak Fit analysis of phases identified by XRD analysis. (a) shows simulated pattern of peaks from (Cr, Fe)23C6 and Y2Ti2O7 overlaid with the diffraction pattern from extraction to show correlation in peak location and remaining unidentified peaks. (b) Peaks from Y2Ti2O7 within measured 2-Theta values labeled on the extraction diffraction pattern. (c) Peaks from (Cr, Fe)23C6 within measured 2-Theta values labeled on the extraction diffraction pattern.
Above are pattern simulations created in PeakFit using the diffraction pattern from extraction, the peaks present on the lower line in image (a) are from only the M23C6 and Y2Ti2O7 phases identified with Sieve between 25° and 85° for CuKα radiation. The line on the top compares the simulated pattern with the actual data; the actual data is in yellow and the simulated pattern in white. Image (b) shows the peaks from Y2Ti2O7 alone and (c) shows those from (Cr, Fe)23C6. It is evident that these are of the highest volume fraction in the sample as these two phases alone account for all but a few minor peaks. Simulations were also done for the Synchrotron data and for the two bulk samples in order to verify findings.

Figure 3.12: 18Cr ODS (a) Synchrotron X-ray diffraction spectrum collected at APS using 15keV photons with peak locations labeled for Y2Ti2O7, Al2O3, and (Cr, Fe)C6 showing their presence in the alloy represented in the collected data. (b) Peak Fit analysis of phases identified by XRD analysis, shows simulated pattern of peaks from (Cr, Fe)23C6 and Y2Ti2O7 overlaid with the synchrotron diffraction pattern to show correlation in peak location and remaining unidentified peaks.
Peaks here do correspond well to the pattern however in many cases, particularly the remaining unmatched peaks, it is difficult to discern between background noise and actual peak location, for this reason the primary PeakFit analysis is carried out with the extraction data, which has no signal from the matrix and much less background noise due to lower source strength.

Figure 3.13: 18Cr ODS (a) CuKα X-ray diffraction spectrum taken on bulk material from the transverse direction of the consolidated alloy with peak locations labeled for the Iron Chromium (Fe, Cr) matrix and (Cr, Fe)23C6 showing their presence in the alloy represented in the collected data. (b) Peak Fit analysis of phases identified by XRD analysis, shows simulated pattern of peaks from (Cr, Fe)23C6 and (Fe, Cr) overlaid with the bulk transverse diffraction pattern to show correlation in peak location and possible remaining unidentified peaks.
From PeakFit analysis of the phases identified for the longitudinal and transverse bulk samples, it is seen that the pattern is well simulated in both cases. In the transverse direction an iron chromium carbide of the M23C6 type is observed in addition to the (Fe, Cr) matrix, and in the longitudinal direction only the (Fe, Cr) matrix is observed. The unidentified low angle peaks in the longitudinal bulk pattern are likely contamination from the sample substrate as they represent a very large volume fraction due to having similar relative intensity as the (Fe, Cr) matrix peaks in the pattern.
3.1.3 Field Emission Scanning Electron Microscopy

Scanning electron microscopy was conducted on the alloy both before and after extraction of the nanoparticles from the matrix. This allowed both preliminary observation of the dispersion, size, and appearance of the nanoparticles, as well as EDS analysis to further validate the presence of the phases identified using XRD-analysis. The figures below show examples of each of the phases identified using XRD analyses which are identified here using EDS taken on the pictured nanoparticles which were observed in the alloy matrix prior to and after extraction as indicated.

Figure 3.15: 18Cr ODS (a) EDS spectrum showing presence of Yttrium, Titanium, and Oxygen in addition to matrix elements overlaid in black. (b) SEM micrograph of capture region for spectrum in (a) showing a Y2Ti2O7 particle in thin foil sample of 18Cr ODS.
Above is a Y-Ti-O particle observed in the alloy after the particles were extracted from the matrix; the EDS spectrum shows the enriched presence of Yttrium and Titanium in this region, though this is most likely an agglomeration as the micrograph shows what appear to be a large angular particle type and a second small rounded type of particle. The size (~20-60 nm) and shape of the smaller particle type correlate more closely with Y-Ti-O particles observed before extraction and these are most likely the source of the Yttrium, and Titanium present in the EDS spectrum and the larger angular particle type is most likely an M23C6 type carbide as indicated by the elemental presences in the EDS spectrum in addition to Yttrium and Titanium.
Above is an Aluminum Oxide particle observed in the matrix, the micrograph shows that the particle is several microns in size, much larger than that of Y-Ti-O particles observed, and the surface appears to be smooth and rounded, though less spherical than in observed Y-Ti-O. Aluminum is not included in the nominal composition of 18Cr ODS or 9Cr ODS, however aluminum containing oxides are identified through EDS and XRD analysis for both alloys, the cause and implication of Aluminum contamination is further discussed in the following chapter.

Figure 3.17: 18Cr ODS (a) EDS spectrum showing presence of Aluminum and Oxygen in addition to matrix elements overlaid in black. (b) SEM micrograph of capture region for spectrum in (a) showing an Al2O3 particle in thin foil sample of 18Cr ODS.
The Al-O particles observed after extraction are very large, several microns in length and width, and less rounded than the particle observed prior to extraction. It is likely that parts of the particle were obscured by the matrix before extraction, however this could also be a slightly different phase of Al2O3 than the one observed prior to extraction.

Figure 3.18: 18Cr ODS (a) EDS spectrum showing presence of Aluminum and Oxygen (b) SEM micrograph of capture region for the spectrum in (a) showing Al2O3 particle after extraction from the alloy matrix.

Figure 3.19: 18Cr ODS (a) EDS spectrum showing presence of Chromium and Carbon in addition to matrix elements overlaid in black. (b) SEM micrograph of capture region for spectrum in (a) showing M23C6 type particles in thin foil sample of 18Cr ODS that has been irradiated to 20dpa at 500°C.
The particles shown above contain Chromium and Carbon according to the EDS spectrum collected on their surface. These appear as large flake-like particles which are partially obscured by the alloy matrix; it is difficult to determine size though it is clear that a single “flake” can be larger than a micron in span. These are predicted to be representative of the (Cr,Fe)23C6 phase identified with XRD analysis, however the EDS spectrum shows the presence of some Tungsten and a greater enrichment of Chromium; the phase present here may be closer to (Cr, W)23C6.

Figure 3.20: 18Cr ODS (a) EDS spectrum showing presence of Chromium, Iron, and Carbon. (b) SEM micrograph of capture region for the spectrum in (a) showing M23C6 particle after extraction from the alloy matrix.

After Extraction a Chromium Carbide is again observed, however this time clearly showing the presence of Iron. The particle still appears flake-like and the size is again hard to determine from a 2D image, the length of this particular protrusion is approximately 900nm.
These three phases were the most commonly observed particles using SEM analysis which leads us to again assume that they are most likely the most common particles or of the greatest volume fraction in the alloy as was also evidenced by XRD analysis for the M23C6 and Y2Ti2O7 phases. The other particles types observed in 18Cr ODS by SEM and EDS analysis may aid in identification of the unmatched peaks in the diffraction pattern. The following are the less commonly observed particles identified by EDS analysis:

![Figure 3.21](image1.png)

**Figure 3.21:** 18Cr ODS (a) EDS spectrum showing presence of Titanium and Oxygen in addition to matrix elements overlaid in black. (b) SEM micrograph of capture region for spectrum in (a) showing a TiO2 particle in thin foil sample of 18Cr ODS.

![Figure 3.22](image2.png)

**Figure 3.22:** 18Cr ODS (a) EDS spectrum showing presence of Aluminum, Titanium, and Oxygen in addition to matrix elements overlaid in black. (b) SEM micrograph of capture region for spectrum in (a) showing a AlTiO2 particle in thin foil sample of 18Cr ODS.
These images show the presence of an Aluminum Titanium Oxide and a Titanium Oxide as well as a Nickel and Molybdenum containing compound which is most likely a contaminant as Molybdenum is not present in the nominal composition of 18Cr ODS. All of these were used to aid in identifying the small peaks still unidentified in the XRD spectrum from the extracted particles.

### 3.1.4 Correlation of XRD and SEM Analysis

The following images show PeakFit analysis to see if the particles observed in SEM analysis can also be identified in the XRD spectrum obtained on extracted particles. Using Sieve, phases containing elements identified with EDS analysis were compared with the extraction XRD pattern to find the closest match. The phases identified were AlTiO2, TiO2, and Ni3Mo. The peak locations for these phases are displayed in the PeakFit analysis below. The phases were added one by one to show progressive fitting of the pattern.
The images each consist of two parts; the configuration on the lower half of each image shows the diffraction pattern obtained from XRD analysis of the extracted particles in light blue and the peaks overlaid in white correspond to the major peaks for the phase(s) indicated in each image. The top configuration displays three overlaid patterns: the collected data from XRD analysis of the extracted particles is shown in yellow as data points, a simulated pattern constructed from the collected data is shown in white, and the light blue pattern is a simulated pattern constructed from the peaks present in the lower configuration for the designated phases.

![Figure 3.24: 18Cr ODS Peak Fit analysis of phases identified by XRD analysis showing simulated pattern of peaks from (Cr, Fe)23C6 with the diffraction pattern from extraction to show correlation in peak location and remaining unidentified peaks. The arrow indicates the 100% relative intensity peak for this phase of (Cr, Fe)23C6.](image)

The (Cr, Fe)23C6 phase (PDF# 01-078-1501) overlaid above is clearly present in the alloy as all peaks above 1% relative intensity listed in the PDF card are clearly represented in the extraction diffraction pattern. Additionally, this phase appears to be of the largest volume fraction from the extracted particles as the 100% intensity peak corresponds with the 100% intensity peak of the extraction diffraction pattern indicated by the arrow in the image above.
The simulated pattern above shows the presence of the (Cr, Fe)₂₃C₆ shown previously in addition to Y₂Ti₂O₇ (PDF# 01-074-9631) with the arrow indicating the 100% intensity peak for the Y₂Ti₂O₇ phase. Below a second phase of Y₂Ti₂O₇ (PDF# 01-077-9940) has been added which allows for a closer simulation of the collected data, particularly in the 100% intensity peak for cubic Y₂Ti₂O₇ indicated with the arrow.

The simulated pattern above shows the presence of the (Cr, Fe)₂₃C₆ shown previously in addition to Y₂Ti₂O₇ (PDF# 01-074-9631) with the arrow indicating the 100% intensity peak for the Y₂Ti₂O₇ phase. Below a second phase of Y₂Ti₂O₇ (PDF# 01-077-9940) has been added which allows for a closer simulation of the collected data, particularly in the 100% intensity peak for cubic Y₂Ti₂O₇ indicated with the arrow.

Figure 3.25: 18Cr ODS Peak Fit analysis of phases identified by XRD analysis showing simulated pattern of peaks from (Cr, Fe)₂₃C₆ and Y₂Ti₂O₇ with the diffraction pattern from extraction to show correlation in peak location and remaining unidentified peaks. The arrow indicates the 100% relative intensity peak for this phase of Y₂Ti₂O₇.

Figure 3.26: 18Cr ODS Peak Fit analysis of phases identified by XRD analysis showing simulated pattern of peaks from (Cr, Fe)₂₃C₆ and two phases of Y₂Ti₂O₇ with the diffraction pattern from extraction to show correlation in peak location and remaining unidentified peaks. The arrow indicates the 100% relative intensity peak for the added phase of Y₂Ti₂O₇.
The two phases of Y2Ti2O7 account for the only remaining major peak in the diffraction pattern, the remaining unidentified peaks are of very small relative intensity and should be from phases which are of very small volume fraction in the alloy. Below TiO2 (PDF# 01-071-4809) has been added and the 100% intensity peak indicated, the peak is very small, however all peaks above 40% relative intensity for the phase are represented in the extraction diffraction pattern.

![Figure 3.27: 18Cr ODS Peak Fit analysis of phases identified by XRD analysis showing simulated pattern of peaks from (Cr, Fe)23C6, two phases of Y2Ti2O7, and TiO2 with the diffraction pattern from extraction to show correlation in peak location and remaining unidentified peaks. The arrow indicates the 100% relative intensity peak for the added phase of TiO2.](image-url)

A second phase of titanium oxide is added, below Ti2O3 (PDF # 01-073-1780) is added and the 100% intensity peak labeled. All peaks above 30% intensity for this phase appear to be represented in the pattern, and enhance the similarity between the simulated and collected patterns.
Figure 3.28: 18Cr ODS Peak Fit analysis of phases identified by XRD analysis showing simulated pattern of peaks from (Cr, Fe)23C6, two phases of Y2Ti2O7, TiO2, and Ti2O3 with the diffraction pattern from extraction to show correlation in peak location and remaining unidentified peaks. The arrow indicates the 100% relative intensity peak for the added phase of Ti2O3.
The same method is used for the addition of AlTiO2 (PDF# 00-052-1557), Ni3Mo (PDF# 00-017-0572), and Al2O3 (PDF# 00-002-1227) in the images below:

Figure 3.29: 18Cr ODS Peak Fit analysis of phases identified by XRD analysis showing a) simulated pattern of peaks from (Cr, Fe)23C6, two phases of Y2Ti2O7, TiO2, Ti2O3, and AlTiO2 with the diffraction pattern from extraction to show correlation in peak location and remaining unidentified peaks. The arrow indicates the 100% relative intensity peak for the added phase of AlTiO2. b) simulated pattern of peaks from (Cr, Fe)23C6, two phases of Y2Ti2O7, TiO2, Ti2O3, AlTiO2, and Ni3Mo with the diffraction pattern from extraction to show correlation in peak location and remaining unidentified peaks. The arrow indicates the 100% relative intensity peak for the added phase of Ni3Mo. c) simulated pattern of peaks from (Cr, Fe)23C6, two phases of Y2Ti2O7, TiO2, Ti2O3, AlTiO2, Ni3Mo, and Al2O3 with the diffraction pattern from extraction to show correlation in peak location and remaining unidentified peaks. The arrow indicates the 100% relative intensity peak for the added phase of Al2O3.
While the presence of all phases other than (Cr, Fe)23C6 and Y2Ti2O7 are not greatly represented in the XRD pattern for 18Cr ODS, low volume fraction presences of TiO2, Ti2O3, AlTiO2, Ni3Mo, and Al2O3 (all compounds observed through SEM analysis) do enhance the correspondence between the pattern simulated using PeakFit and peaks from the identified phases and the XRD pattern obtained from the extracted nanoparticles.

In summary, the nanoparticles identified in 18Cr ODS through SEM and XRD analysis appear to be largely Iron Chromium Carbide of the M23C6 type and the desired Yttrium Titanium Oxide of the Y2Ti2O7 type. Additionally Al2O3, AlTiO2, TiO2, Ti2O3, and Ni3Mo are evidenced to be present in the alloy; however their relatively small appearance in the XRD spectrum shows that they are of small volume fraction in the alloy.

3.1.5 Irradiation and In-Situ TEM Analysis
18Cr ODS samples were irradiated with 1 MeV Kr ions to 2, 10, 30, and 52 dpa at 25°C, to 30dpa at 300°C, and to 20dpa at 500°C.

The sample irradiated to 20dpa at 500°C was then characterized in the post-irradiated state using a Zeiss Ultra plus FESEM in order to observe any irradiation induced changes in the composition, appearance, or nanoparticle distribution.

Below are SEM images of particles in the 18Cr ODS sample irradiated to 20dpa at 500°C showing that these families of particles are still present in the alloy after irradiation.
Figure 3.30: 18Cr ODS (a) EDS spectrum showing presence of Yttrium, Titanium, and Oxygen in addition to matrix elements overlaid in black. (b) SEM micrograph of capture region for spectrum in (a) showing Y2Ti2O7 particle in thin foil sample of 18Cr ODS after irradiation to 20dpa at 500°C.

Figure 3.31: 18Cr ODS (a) EDS spectrum showing presence of Aluminum and Oxygen in addition to matrix elements overlaid in black. (b) SEM micrograph of capture region for spectrum in (a) showing an Al2O3 particle in thin foil sample of 18Cr ODS after irradiation to 20dpa at 500°C.
Figure 3.32: 18Cr ODS (a) EDS spectrum showing presence of Aluminum, Titanium, and Oxygen in addition to matrix elements overlaid in black. (b) SEM micrograph of capture region for spectrum in (a) showing an AlTiO$_2$ particle in thin foil sample of 18Cr ODS after irradiation to 20dpa at 500°C.

Figure 3.33: 18Cr ODS (a) EDS spectrum showing presence of Chromium and Carbon in addition to matrix elements overlaid in black. (b) SEM micrograph of capture region for spectrum in (a) showing M23C6 type particles in thin foil sample of 18Cr ODS after irradiation to 20dpa at 500°C.
SEM analysis after irradiation of the 18Cr ODS indicates that the nanoparticle composition remains relatively stable, with nanoparticle relative compositions similar to pre-irradiated findings and no severe change in shape or dispersion. The Cr- and C-containing particles assumed to be of the M23C6 type are represented by the same image used previously as this was the only occurrence of their observation by SEM prior to extraction. The oxides Y2Ti2O7, Al2O3, and AlTiO2 were the vast majority of the particles observed in SEM analysis prior to radiation as well, and these families were the focus of results analysis as carbides have been shown to be less stable under irradiation and are thus a less desirable precipitate. Image 3.30 showing a large Y-Ti-O containing particle appears to exhibit preferred sputtering at the matrix particle interface, as was seen in other post-irradiated SEM observation of 18Cr ODS. Additionally elemental mapping was done on one of the larger Y2Ti2O7 particles to substantiate the presence of these elements by another method.

Figure 3.34: 18Cr ODS Elemental maps of nanoparticle in thin foil sample irradiated to 20dpa at 500°C showing presence of (a) Yttrium, (b) Titanium, and (c) Oxygen.
Post-irradiation SEM analysis was carried on a thin foil sample that has been irradiated to 20dpa at 500°C and resultant images are compared with as fabricated microstructure from similar regions on an un-irradiated thin foil sample. The SEM micrograph below shows the appearance of the samples used and the red circle distinguishes the two regions that were imaged on both the irradiated and un-irradiated sample.

Figure 3.35: 18Cr ODS SEM micrograph showing appearance of thin foil samples used for SEM analysis. The red circle shows the approximate cross sectional area of the ion beam used for irradiations, the region inside the circle (r~0.5mm) represents the region of the sample that is exposed to radiation during in situ irradiations.

The side by side micrographs below are captured both within and outside of the approximate irradiated radius of 0.5mm from the center of the two 18Cr samples in order to compare the basic microstructure of the alloy in the irradiated and un-irradiated states.
Figure 3.36: 18Cr ODS SEM micrographs showing comparison of microstructure in an irradiated and an un-irradiated sample. The image in (a) shows a region on the sample that has been irradiated to 20 dpa at 500°C near the center, within the irradiated radius. (b) Shows a region near the center of the thin foil sample that has not been irradiated. (c) Shows a region on the sample that has been irradiated to 20 dpa at 500°C near the edge, outside of the irradiated radius of the thin foil sample. The image in (d) shows a region near the edge of the thin foil sample that has not been irradiated.

The SEM micrographs comparing irradiated (3.36a) and unirradiated (3.36b, c, and d) microstructure show an apparent separation between grain boundaries when compared to micrographs of unirradiated samples indicating preferred sputtering at grain boundary and precipitate interfaces. There was even preferred sputtering observed near the edge after irradiation (3.36c), where the area has not been irradiated but the sample has undergone heat treatment, though the observed separation is not as pronounced as in the images taken within the irradiated radius (3.36a). The dispersion of nanoparticles seems to be less dense and consisting of larger average size in both regions of the irradiated disc (3.36a and c). Further analysis of these phenomena is presented in chapter four.
Below are in-situ bright field TEM images of an area of an 18Cr ODS sample dispersed with particles. Successive doses illustrate the stability of nanoparticles up to 20dpa at 500°C.

Figure 3.37 18Cr ODS in-situ bright field TEM micrograph showing nanoparticle stability in thin foil sample irradiated to 20dpa at 500°C.

The imaging conditions begin to deteriorate after 10dpa, however it is evident between 15 and 20 dpa that the nanoparticles within the grain are still present and do not appear to have changed in size or dispersion. This is seen also for a nanoparticle aligned along the grain boundary in the images below.

Figure 3.38 18Cr ODS in-situ bright field TEM micrograph showing nanoparticle stability in thin foil sample irradiated to 52dpa at 25°C
The 18Cr ODS sample imaged above was irradiated up to 52dpa at 25°C with no apparent change in the size or shape of the nanoparticle. Further analysis of nanoparticle stability under irradiation will be presented in chapter four.

3.2 9Cr ODS RESULTS:

3.2.1 SYNCHROTRON XRD

The same methods were applied in analyzing the synchrotron diffraction pattern obtained on 9Cr ODS from the Advanced Photon Source as were used with 18Cr ODS. The raw data is shown below:

![9Cr ODS Synchrotron X-ray diffraction spectrum collected at APS using 15keV photons.](image)

Figure 3.39: 9Cr ODS Synchrotron X-ray diffraction spectrum collected at APS using 15keV photons.

Here again the matrix peaks were too large in comparison to the second phase precipitate peaks, and the figure below shows the data after the matrix peaks have been capped in order to show the smaller peaks.
Figure 3.40: 9Cr ODS Synchrotron X-ray diffraction spectrum collected at APS using 15keV photons. Matrix peaks have been reduced to show second phase peaks from nanoparticles within the alloy matrix.

Figure 3.41: 9Cr ODS Synchrotron X-ray diffraction spectrum collected at APS using 15keV photons with peak locations labeled for all phases showing their presence in the alloy represented in the collected data.
The phases identified through the same analysis methods already detailed for 18Cr ODS are shown overlaid on the edited synchrotron diffraction pattern on the image above. Here we see oxides, a nitride, and again Iron Chromium Carbides of the M23C6 type, including an additional phase which contains Tungsten. The phases identified are: Chromium Iron Tungsten Carbide ((Cr, Fe, W, Mo)23Fe21(W, Mo)2C12) PDF# 00-005-0721, Chromium Iron Carbide ((Cr, Fe)23C6) PDF# 01-078-1501, Titanium Oxide (TiO) PDF# 00-002-1196, Titanium Nitride (TiN) PDF# 03-065-0965, and Yttrium Titanium Oxide (Y2Ti2O7) PDF# 01-074-9633.

3.2.2 CuKa XRD Analysis on Extracted Nanoparticle

Figure 3.42: 9Cr ODS CuKα X-ray diffraction spectrum of nanoparticles after chemical extraction from the alloy matrix.
Above is the raw diffraction pattern obtained on the extracted particles using CuKα radiation; this spectrum is overlaid with the synchrotron data in the figure below:

![9Cr ODS X-ray diffraction spectra from Synchrotron bulk and extracted nanoparticles aligned to reveal similarities and differences in peak presence and location across methods of XRD analysis.](image)

The two theta scale was calibrated in the same fashion detailed above for 18Cr. Again the peaks correspond closely for overlapping regions of the two data sets substantiating the validity of both methods.
The same phases that were identified with the synchrotron data are displayed below overlaid on this spectrum.

![9Cr ODS CuKα Extraction](image)

Figure 3.44: 9Cr ODS CuKα X-ray diffraction spectrum of nanoparticles after chemical extraction from the alloy matrix with peak locations labeled for all phases showing their presence in the alloy represented in the collected data

Here again it is seen that the phases identified closely match the peaks from both XRD methods.

3.2.3 FIELD EMISSION SCANNING ELECTRON MICROSCOPY

Scanning electron microscopy was conducted both before and after extraction of the nanoparticles from the matrix. This allowed both preliminary observation of the dispersion, size, and appearance of the nanoparticles, as well as EDS analysis to further validate the presence of the phases identified using XRD-analysis. These will be displayed, as previously, in figures showing images and corresponding EDS patterns.
An Iron, Tungsten, and Oxygen containing particle is shown above, seen in SEM analysis prior to extraction, the particle is about 200nm by 400nm and appears somewhat smooth and in an oblong rounded shape. The EDS spectrum shows the presence of Iron, Tungsten, and Oxygen in red; the black overlaid spectrum is from the alloy matrix.

Figure 3.45: 9Cr ODS (a) EDS spectrum showing presence of Iron, Tungsten, and Oxygen in addition to matrix elements overlaid in black. (b) SEM micrograph of capture region for spectrum in (a) showing particle containing Iron, Tungsten, and Oxygen.

An Iron, Tungsten, and Oxygen containing particle is shown above, seen in SEM analysis prior to extraction, the particle is about 200nm by 400nm and appears somewhat smooth and in an oblong rounded shape. The EDS spectrum shows the presence of Iron, Tungsten, and Oxygen in red; the black overlaid spectrum is from the alloy matrix.

Figure 3.46: 9Cr ODS (a) EDS spectrum showing presence of Iron, Chromium, Tungsten, and Carbon in addition to matrix elements overlaid in black. (b) SEM micrograph of capture region for spectrum in (a) showing a M23C6 particle in thin foil sample of 9Cr ODS.
The micrograph shows that the Cr-, Fe-, W-, and C- containing particle is approximately 300 nm in diameter and appears to have smooth flattened surface. The EDS pattern shows the presence of Chromium, Iron, Tungsten, and Carbon which are labeled. Based on elemental presences in the EDS spectrum this is predicted to correspond with the M23C6 type particle of the form \((\text{Cr}, \text{Fe}, \text{W}, \text{Mo})_{23} \text{Fe}_{21} (\text{W}, \text{Mo})_{2} \text{C}_{12}\) identified through XRD analysis.

The presences of the M23C6 phase after extraction is confirmed by the EDS spectrum above. As seen previously, in 18Cr ODS, there are other peaks present due to interference from surrounding particles, here these appear to be Titanium and Oxygen containing particles which correlate to the TiO phase identified with the XRD analysis.

Figure 3.47: 9Cr ODS (a) EDS spectrum showing presence of Iron, Chromium, Tungsten, and Carbon as well as Titanium and Oxygen. (b) SEM micrograph of capture region for spectrum in (a) showing an agglomeration of M23C6 and TiO particles after extraction from the alloy matrix.
Above is an Aluminum Oxide particle observed in the 9Cr matrix, the micrograph shows that the diameter is almost 500nm in diameter and the surface appears to be somewhat smooth and rounded. This type of particle was also seen after extraction and is displayed below. Again there is interference from surrounding particles which appear to identify a second phase present of those identified with XRD analysis. Both Aluminum Oxide and a Tungsten containing phase appear to be present.

Figure 3.48: 9Cr ODS (a) EDS spectrum showing presence of Aluminum and Oxygen in addition to matrix elements overlaid in black. (b) SEM micrograph of capture region for spectrum in (a) showing an Al2O3 particle in thin foil sample of 9Cr ODS.
Agglomerations of particles were abundant in this alloy, both before and after extraction of the nanoparticles. The following are all images which appear to contain multiple particle types before extraction.

Figure 3.49: 9Cr ODS (a) EDS spectrum showing presence of Aluminum, Tungsten, and Oxygen in addition to background elements. (b) SEM micrograph of capture region for spectrum in (a) showing an Al2O3 particle as well as other surrounding particles suspected to be tungsten containing oxides after extraction from the alloy matrix.

Figure 3.50: 9Cr ODS (a) EDS spectrum showing presence of Aluminum, Yttrium, Titanium, and Oxygen in addition to matrix elements overlaid in black. (b) SEM micrograph of capture region for spectrum in (a) showing an agglomeration of particles in thin foil sample of 9Cr ODS.
This agglomeration appears to be a combination of Al2O3 and Y2Ti2O7 particulates as indicated by the labeled EDS spectrum. Below is a second agglomeration observed with a similar EDS spectrum.

Figure 3.51: 9Cr ODS (a) EDS spectrum showing presence of Aluminum, Yttrium, and Oxygen in addition to matrix elements overlaid in black. (b) SEM micrograph of capture region for spectrum in (a) showing an agglomeration of particles in thin foil sample of 9Cr ODS.

Figure 3.52: 9Cr ODS (a) EDS spectrum showing presence of Iron, Chromium, Tungsten, Carbon, Nitrogen, Titanium, Aluminum, and Oxygen in addition to matrix elements overlaid in black. (b) SEM micrograph of capture region for spectrum in (a) showing an agglomeration of particles in thin foil sample of 9Cr ODS.

The Titanium Nitride and Aluminum Oxide phases were seen prior to extraction in the image above. There is also Cr-, Fe-, W-, and C- present, which is likely represented in the micrograph above as a flat particle similar to the image showing the M23C6 type particle of the form (Cr , Fe , W , Mo )23 Fe21 ( W , Mo )2 C12.
3.2.4 Correlation of XRD and SEM Analysis

The following images display PeakFit analysis substantiating the presence of low volume fraction particles and phases observed through comparison of peak locations and intensities with the XRD spectrum obtained on extracted particles. Using the PDF 2 database, phases containing elements identified with EDS analysis were compared with the extraction XRD pattern to find the closest match. The peak locations for the selected phases are displayed in the PeakFit analysis below. The phases were added one by one to show progressive fitting of the pattern. The images each consist of two parts as previously; the configuration on the lower half of each image shows the diffraction pattern obtained from XRD analysis of the extracted particles in light blue and the peaks overlaid in white correspond to the major peaks for the phases indicated in each image. The top configuration displays three overlaid patterns: the collected data from XRD analysis of the extracted particles is shown in yellow as data points, a simulated pattern constructed from the collected data is shown in white, and the light blue pattern is a simulated pattern constructed from the peaks present in the lower configuration for the designated phases.

Figure 3.53: 9Cr ODS Peak Fit analysis of phases identified by XRD analysis showing simulated pattern of peaks from (Cr, Fe, W, Mo)23Fe21(W, Mo)2C12 with the diffraction pattern from extraction to show correlation in peak location and remaining unidentified peaks. The arrow indicates the 100% relative intensity peak for this phase of (Cr, Fe, W, Mo)23Fe21(W, Mo)2C12.
The (Cr, Fe, W, Mo)\textsubscript{23}Fe\textsubscript{21}(W, Mo)\textsubscript{2}C\textsubscript{12} phase (PDF\# 00-005-0721) overlaid above is clearly present in the alloy as all peaks above 1\% relative intensity listed in the PDF card are clearly represented in the extraction diffraction pattern. Additionally, this phase appears to be of the largest volume fraction from the extracted particles as the 100\% intensity peak corresponds with the 100\% intensity peak of the extraction diffraction pattern indicated by the arrow in the image above. Below a second phase of M\textsubscript{23}C\textsubscript{6} is added of the form (Cr, Fe)\textsubscript{23}C\textsubscript{6}. This is the same phase that was observed in 18Cr ODS (PDF\#01-078-1501) and it appears to be present in addition to (Cr, Fe, W, Mo)\textsubscript{23}Fe\textsubscript{21}(W, Mo)\textsubscript{2}C\textsubscript{12}. Many peaks from these two phases overlap, however those which are only from (Cr, Fe)\textsubscript{23}C\textsubscript{6} have a lower relative intensity than they would if only this phase were present.

Figure 3.54: 9Cr ODS Peak Fit analysis of phases identified by XRD analysis showing simulated pattern of peaks from (Cr, Fe, W, Mo)\textsubscript{23}Fe\textsubscript{21}(W, Mo)\textsubscript{2}C\textsubscript{12} and (Cr, Fe)\textsubscript{23}C\textsubscript{6} with the diffraction pattern from extraction to show correlation in peak location and remaining unidentified peaks. The arrow indicates the 100\% relative intensity peak for this phase of (Cr, Fe)\textsubscript{23}C\textsubscript{6}. 
Below TiO (PDF# 00-002-1196) has been added and the 100% intensity peak indicated, all peaks above 60% relative intensity for the phase are represented in the extraction diffraction pattern as shown below.

Figure 3.55: 9Cr ODS Peak Fit analysis of phases identified by XRD analysis showing simulated pattern of peaks from (Cr, Fe, W, Mo)23Fe21(W, Mo)2C12, (Cr, Fe)23C6, and TiO with the diffraction pattern from extraction to show correlation in peak location and remaining unidentified peaks. The arrow indicates the 100% relative intensity peak for the added phase of TiO.

The simulated pattern below shows the presence of both of the M23C6 phases shown previously and TiO in addition to Y2Ti2O7 (PDF# 01-074-9633) with the arrow indicating the 100% intensity peak for the Y2Ti2O7 phase.

Figure 3.56: 9Cr ODS Peak Fit analysis of phases identified by XRD analysis showing simulated pattern of peaks from (Cr, Fe, W, Mo)23Fe21(W, Mo)2C12, (Cr, Fe)23C6, TiO, and Y2Ti2O7 with the diffraction pattern from extraction to show correlation in peak location and remaining unidentified peaks. The arrow indicates the 100% relative intensity peak for the added phase of Y2Ti2O7.
Y2Ti2O7 accounts for the only significant peak in the diffraction pattern that was still to be matched; the only remaining phase that was added based on the remaining unmatched peaks and SEM analysis was a phase of Titanium Nitride (PDF# 03-065-0965) which is shown below along with all other phases.

![Diffraction Pattern](image)

Figure 3.57: 9Cr ODS Peak Fit analysis of phases identified by XRD analysis showing simulated pattern of peaks from (Cr, Fe, W, Mo)23Fe21(W, Mo)2C12, (Cr, Fe)23C6, TiO, Y2Ti2O7, and TiN with the diffraction pattern from extraction to show correlation in peak location and remaining unidentified peaks. The arrow indicates the 100% relative intensity peak for the added phase of TiN

While the presence of all phases other than the M23C6 phases are not greatly represented in the XRD pattern for 9Cr ODS, low volume fraction presences of TiO, Y2Ti2O7, and TiN (all compounds observed through SEM analysis) do enhance the correspondence between the pattern simulated using PeakFit and peaks from the identified phases and the XRD pattern obtained from the extracted nanoparticles.
In summary the nanoparticles identified in 9Cr ODS through SEM and XRD analysis appear to be largely Iron Chromium Carbides of the M23C6 type with or without tungsten. Additionally TiO, Y2Ti2O7, and TiN are evidenced to be present in the alloy; however their relatively small appearance in the XRD spectrum shows that they are of small volume fraction in the alloy. Aluminum Oxide particles were observed through SEM/EDS analysis however they are not represented in the diffraction pattern indicating that, while they are relatively large in size (diameter ~1μm), they are of too small volume fraction to be represented in XRD analysis. The results again show that both X-ray diffraction techniques and SEM/EDS analysis serve as viable identification methods for identifying the second phase precipitates which form within the matrices of these alloys.

### 3.2.5 Irradiation and In-Situ TEM Analysis

Fe-9Cr irradiations were carried out with 300keV Fe ions to 6 dpa at 25°C and to 9 dpa at 500°C; also with 1 MeV Kr ions to 30 dpa at 500°C.

After irradiation of the 9Cr ODS, EFTEM energy filtering maps were taken of a small region displayed in the figure below showing the nucleation of a large Y-Ti-O particle, as well as many 3-4 nm Y-Ti-O particles that are still present in 9Cr ODS after being irradiated to 9 dpa at 500 °C with 300KeV Fe ions. The small particles also appear to be enriched with chromium and possibly carbon.
The EFTEM images above demonstrate the importance of technique in observing nanoparticles, as the small Y-Ti-O rich particles are not visible in the bright field TEM micrograph until energy filtering maps reveal the compositional differences between microstructural components.

In situ TEM images taken of the same sample show the stability of large and mid-size particles at successive doses up to 9dpa at 500°C.
3.3 SUMMARY OF RESULTS

3.3.1 18Cr ODS RESULTS

XRD analysis of 18Cr ODS revealed a strong correlation in patterns obtained through various methods, particularly between the synchrotron and extraction spectra. It was seen that all peaks from the Synchrotron pattern are reasonably represented in the extraction diffraction pattern; however there are a few smaller peaks present in the extraction pattern that are not as obvious in the synchrotron pattern due to obstruction by the matrix peaks, thus extraction served to be the most comprehensive source for phase identification. Primary PeakFit analysis and peak identification was conducted with the extraction data, which has no contamination from the matrix and much less background noise due to lower source strength. The phases identified through these methods are an Iron Chromium Carbide of the form M23C6 and Yttrium Titanium Oxide of the form Y2Ti2O7. Peak Fit analysis of these identifications showed that the peaks from Y2Ti2O7 and (Cr, Fe)23C6 are of the highest volume fraction in the sample as these two phases alone account for all but a few minor peaks.

The Patterns collected from bulk samples using CuKα radiation have much fewer peaks than from the other methods; this was expected as only phases with relatively high volume fraction in the alloy should be observable. Peak identification of the bulk samples showed that the Matrix is most easily observable in both directions, however in the transverse direction we also see the M23C6-Iron Chromium Carbide.

SEM analysis of 18Cr ODS allowed substantiation of XRD results through EDS analysis along with imaging of nanoparticles and microstructure of the alloy.
The nanoparticles identified in 18Cr ODS through these methods are listed in the table below along with the number of the type observed and the phase identified by XRD analysis that most closely corresponds with the elemental composition identified by EDS analysis.

Table 3.1: 18Cr ODS nanoparticle type and abundance observed through SEM/EDS analysis with corresponding phases extrapolated from XRD Analysis.

<table>
<thead>
<tr>
<th>Elements</th>
<th>Number Observed</th>
<th>Phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y</td>
<td>9</td>
<td>Y2Ti2O7</td>
</tr>
<tr>
<td>Ti</td>
<td></td>
<td></td>
</tr>
<tr>
<td>O</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al</td>
<td>6</td>
<td>Al2O3</td>
</tr>
<tr>
<td>O</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ti</td>
<td>2</td>
<td>AlTiO2</td>
</tr>
<tr>
<td>Al</td>
<td></td>
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<tr>
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<td>3</td>
<td>TiO2 or Ti2O3</td>
</tr>
<tr>
<td>O</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni</td>
<td>1</td>
<td>Ni3Mo</td>
</tr>
<tr>
<td>Mo</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The nanoparticles identified in 18Cr ODS through SEM and XRD analysis appear to be largely Iron Chromium Carbide of the M23C6 type and the desired Yttrium Titanium Oxide of the Y2Ti2O7 type. Additionally Al2O3, AlTiO2, TiO2, Ti2O3, and Ni3Mo are evidenced to be present in the alloy; however their relatively small appearance in the XRD spectrum shows that they are of small volume fraction in the alloy.
Irradiations with 18Cr ODS were carried out with 1 MeV Kr ions at 25°C to 2, 10, 30, and 52 dpa, to 30dpa at 300°C, and to 20dpa at 500°C. SEM analysis after irradiation to 20dpa at 500°C indicated that the nanoparticle composition remains relatively stable, with nanoparticle relative compositions similar to pre-irradiated findings and no severe change in shape or dispersion. The oxides Y2Ti2O7, Al2O3, and AlTiO2 were the majority of the particles observed in SEM analysis prior to and after radiation, and these families were the focus of results analysis; carbides have been shown to be less stable under irradiation. Post-irradiation SEM analysis of microstructure showed apparent preferred sputtering at grain boundaries and larger particle interfaces when compared to micrographs of unirradiated samples. From the SEM micrographs taken from similar regions of one irradiated and one unirradiated sample of 18Cr ODS, the dispersion of nanoparticles seems to be less dense and consisting of larger average size after irradiation to 20 dpa at 500°C. In-situ TEM analysis during irradiation revealed that between 15 and 20 dpa at 25°C nanoparticles within the grain are still present and do not appear to have changed in size or dispersion.

During irradiation up to 52dpa at 25°C there was no apparent change in the size or shape of small particles, however at a lower temperatures amorphization of carbides was observed.
3.3.2 9Cr ODS Results

XRD analysis of 9Cr ODS revealed that both synchrotron and extraction X-ray diffraction techniques serve as viable identification methods for identifying the second phase precipitates which form within the matrices, however the extraction allows for better peak identification as there is no obstruction from matrix peaks. Again the peaks correspond closely for overlapping regions of the two data sets substantiating the validity of both methods.

The phases identified are: Chromium Iron Tungsten Carbide ((Cr, Fe, W, Mo)23Fe21(W, Mo)2C12), and a Chromium Iron Carbide ((Cr, Fe)23C6), Titanium Oxide (TiO), Titanium Nitride (TiN), and Yttrium Titanium Oxide (Y2Ti2O7). The phases identified with the extraction pattern were shown to closely match the peaks from the Synchrotron pattern. PeakFit analysis of the phases identified revealed that M23C6 is by far of the highest volume fraction within the extracted nanoparticles, however the presence of all lower volume fraction particulates are reflected in the pattern; this method exemplifies how the combination of very small peaks simulate the collected pattern.

SEM and EDS analysis of 9Cr ODS SEM analysis allowed substantiation of XRD results, the nanoparticles identified in 9Cr ODS are listed in the table below along with the number of the type observed and the phase identified by XRD analysis that most closely corresponds with the elemental composition identified by EDS analysis.
Table 3.2: 9Cr ODS nanoparticle type and abundance observed through SEM/EDS analysis with corresponding phases extrapolated from XRD Analysis.

<table>
<thead>
<tr>
<th>Elements</th>
<th>Number Observed</th>
<th>Phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
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<tr>
<td>O</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>7</td>
<td>M23 C6</td>
</tr>
<tr>
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<td></td>
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<td></td>
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<tr>
<td>Ti</td>
<td>3</td>
<td>Al2O3</td>
</tr>
<tr>
<td>Al</td>
<td></td>
<td>TiO</td>
</tr>
<tr>
<td>O</td>
<td></td>
<td>Y2Ti2O7</td>
</tr>
<tr>
<td>Y</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ti</td>
<td>3</td>
<td>Al2O3</td>
</tr>
<tr>
<td>Al</td>
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<td>TiO</td>
</tr>
<tr>
<td>O</td>
<td></td>
<td></td>
</tr>
<tr>
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<td>1</td>
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</tr>
<tr>
<td>N</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al</td>
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<td>Al2O3</td>
</tr>
<tr>
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<td></td>
<td></td>
</tr>
<tr>
<td>Cr</td>
<td></td>
<td>M23C6</td>
</tr>
<tr>
<td>Fe</td>
<td></td>
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<tr>
<td>C</td>
<td></td>
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</table>
Correlation of these results proves slightly more difficult than with 18Cr ODS as there are far more particle types present and many agglomerations of particles observed through SEM analysis. Consequently, identifying a corresponding phase is less certain as it could be several different combinations of phases identified through XRD analysis. Additionally Y2Ti2O7 was not observed through SEM analysis of 9Cr ODS, however it is clearly present in the alloy as evidenced through XRD analysis and through in-situ TEM energy filtering maps. The sizes of the Y2Ti2O7 particles are likely too small to be resolvable through SEM and thus are not reflected in these results. Oppositely, Aluminum Oxide is identified through SEM/EDS analysis, but is not clearly represented in the diffraction spectrum for 9Cr ODS.

9Cr ODS irradiations were carried out with 300keV Fe ions to 6 dpa at 25°C and to 9 dpa at 500°C; also with 1 MeV Kr ions to 30 dpa at 500°C. EFTEM energy filtering maps were taken after irradiation showing the nucleation of a large Y-Ti-O particle, as well as many 3-4 nm Y-Ti-O particles that are still present in 9Cr ODS after being irradiated to 9 dpa at 500 °C with 300KeV Fe ions. The small particles also appear to be enriched with chromium and carbon. Apparent amorphization of larger particles (most likely carbides) was observed in contrast with the stability of smaller surrounding nanoparticles. The implications of nanoparticle composition in both 18Cr ODS and 9Cr ODS alloys, as well as as-fabricated microstructure and radiation stability, will be discussed further in the following chapter.
CHAPTER 4

DISCUSSION

The experimental alloys which have been selected for evaluation in this work, 18Cr ODS and 9Cr ODS, have been characterized based on composition, both nominal and as-fabricated, in order to find the effects of alloying elements and fabrication techniques on the microstructure and nucleation of nanoparticles which serve to enhance the mechanical properties of the alloys required for operation in Generation IV reactors. Discussion of the results found, within the framework of proceeding research efforts, will be presented in the following paragraphs.

4.1 FABRICATION METHODS

4.1.1 MICROSTRUCTURE:

The processing methods used during fabrication of 18Cr ODS and 9Cr ODS serve to not only support the nucleation of nano-meter scale precipitates, but also to enhance the material properties of the alloys through control of phase and microstructure of the Fe-Cr matrix. For both alloys a ferritic-martensitic structure was chosen as it has been shown to perform well under irradiation and to avoid the swelling problems which can be met with austenitic steels [3].
The 18Cr ODS alloy is manufactured with a ferritic structure which has been shown to have high corrosion resistance due primarily to high-chromium content. In addition to enhanced corrosion resistance, ferritic alloys are stable at very high temperatures. However, ferritic alloys have also been observed to be somewhat non-homogenous after consolidation, difficult to manufacture, and susceptible to embrittlement under irradiation and high temperatures due to the formation of the α’-phase in high chromium alloys [12], [10]. By contrast, martensitic steels such as 9Cr ODS are usually more isotropic, easier to manufacture, and exhibit a beneficial residual ferrite phase transformation above 800–850°C, but their corrosion resistance is lower compared to high chromium ferritic ODS alloys, such as 18Cr ODS [10]. In the case of a ferritic ODS material consolidated by hot extrusion and prior to any recrystallization, a very fine microstructure is obtained which allows for a DBTT similar to one of a good martensitic material (around 50 °C), showing that a ferritic ODS materials could display the advantages of both classes of materials [3].

9Cr ODS is unique in that there is the observed formation of a non-equilibrium phase, designated as the residual ferrite, which serves to greatly enhance several vital mechanical properties in comparison to both standard RAFM alloys and the fully ferritic 18Cr ODS. For example: the yield strength of the residual (or α-) ferrite phase itself has been determined to be as high as 1360MPa at room temperature.

The creep strength is shown to be enhanced by the minimization of the number of packet boundaries which is induced by the martensitic phase transformation and creep strain occurs at a lower stress than that necessary for deformation of intra-grain areas.
This is most likely due to an interaction between nanometer-scale oxide particles and dislocations [15]. This is theorized to be further enhanced by sliding at weaker regions such as at the grain boundaries and packet boundaries; behaving as a fiber composite material comprising the harder residual ferrite and the softer tempered martensite. [15]

The α-ferrite phase remains in the ferrite phase even at a hot-extrusion temperature of up to 1423 K, rather than transforming to austenitic. The formation mechanism of the α-ferrite is presumed to be enabled by the pinning force for boundary movement caused by oxide particles and dislocations, inhibiting the driving forces for phase transformation. However this competitive force is strongly affected by excess oxygen, as oxygen serves to both aid in the nucleation of small Y-Ti-O particles and to moderate the matrix carbon content which is linked to the free energy difference between the ferrite and austenite phases [15]. This Ferrite phase forms due solely to the addition of Y2O3 to the nominal composition and the degree of formation depends upon the extent of addition. The α-ferrite phase also differs from the δ-ferrite phase which forms in equilibrium with the γ-martensite phase and is not as beneficial to strengthening mechanisms. Chromium content plays a role in controlling the formation of α versus δ ferrite phases; a nominal carbon content above 0.08 mass% causes the δ-ferrite phase to become unstable and is therefore favorable to strengthening mechanisms [16].

The question whether a ferritic or a martensitic alloy is a better starting place for application in a nuclear reactor depends upon the strains which would be imposed on the consolidated structure.
A martensitic alloy, such as 9Cr ODS, would be best utilized in areas exposed to high temperatures, neutron doses, and mechanical strain, such as fuel cladding within the reactor pressure vessel. 18Cr ODS would be more valuable for application as structural components that are in contact with coolant, as the high chromium content lends to good resistance to corrosion.

4.1.2 Grain size:

The fabrication methods also have control over the grain structure produced in the observed alloys. The desired result is to get very fine grains, as these serve as sinks for defects and as inhibitors for dislocation motion associated with irradiation creep. In order to obtain small grain sizes it is necessary to use the hot extrusion process instead of the hot isostatic pressure [3]. The resultant microstructure consists of very fine grains or “fibers” which are elongated along the hot extrusion direction [3].

The grain structure of 18Cr ODS observed through SEM analysis is shown in the figures below:

Figure 4.1: 18Cr ODS a) low mag SEM image of thin foil sample of as received alloy showing grain structure b) SEM image of thin sample after irradiation to 20dpa at 500°C showing grain structure.
Most of the grains observed do not appear to have elongation along the hot extrusion direction; other studies on this alloy have found that grains along the hot extrusion axis exhibit an aspect ratio of 4:1 with a mean length of 1.2 μm and mean width of about 300 nm [10]. Here the grains appear to be primarily equiaxed, only in rare cases are elongated grains observed, this could be due to the direction in which the observed samples were taken. Samples taken from the longitudinal direction may exhibit a more pronounced elongation of grains. This more homogeneous microstructure consisting of equiaxed grains has been achieved by annealing the alloy after hot extrusion which allows for recrystallization of the material.

The recrystallized grain structure is vital as it greatly increases the high-temperature strength and ductility in the hoop direction (perpendicular to the hot extrusion and rolling direction) which is otherwise weakened due to a primary stress mode in the cladding of the fission gas pressurized fuel pins [14].

The equiaxed grains are preferred for increased corrosion resistance and prevention of crack initiation which assures that both internal creep strength and ductility are increased; all of these properties have been observed to correlate with homogeneous grain morphology [14].

The extent of recrystallization has also been seen to be dependent upon the yttria content, and must be restricted to a content less than 0.25 mass% in order to maintain small equiaxed grain sizes. For similar high-chromium ferritic ODS alloys, such as 14Cr ODS, grains as large as 20μm have been observed after consolidation [17]. The images above have inadequate contrast to make a good estimation of grain size, however from TEM images of 18Cr ODS it is observed that grain sizes are well below 1μm.
The presence of much smaller grains in this 18Cr ODS alloy verifies that the fabrication method used was effective in creating the desired homogeneous, fine, equiaxed grain structure required for application in Gen IV reactors.

The grain structure observed in the as-fabricated 9Cr ODS is shown in the SEM micrographs below:

![Figure 4.2: 9Cr ODS a) low mag SEM image of thin foil sample of as received alloy showing grain structure b) SEM image of thin foil sample showing grain fine structure and accumulation of nanoparticles at grain boundaries.](image)

The grain size is observed in this sample to be smaller than observed in 18Cr ODS with average grain sizes of only a few hundred nm in width with an observed maximum size of only about 1 μm. This corresponds to observations in other work with 9Cr ODS alloys which show elongated grains with a mean length of 1.2 μm and mean width of 550 nm [18]. Again it is desired to have a more homogeneous equiaxed grain structure in order to minimize loss of creep rupture strength in the hoop direction. The SEM micrographs show that there is a minimization of elongated grains in the examined 9Cr ODS alloy, these more equiaxed grains are achieved through the formation of the residual ferrite phase after the martensitic transformation [14].
The combination of small yttria particles and the residual α-ferrite phase serve to produce a very fine grain structure without the additional step of recrystallization, consequently 9Cr ODS alloys are easier to fabricate than 18Cr ODS and appear to have an even finer grain size [14].

4.1.3 DISLOCATION MICROSTRUCTURE:

The primary result of dislocation-nanoparticle interaction in ODS alloys is strengthening of the alloy, this is caused by decreased mobility of dislocations through the various modes of interactions with dispersoids [19]. Below is a TEM image of as received 18Cr ODS showing the presence of nanoparticles and dislocations on a few grains.

Figure 4.3: 18Cr ODS TEM micrograph showing dislocations in as-received thin foil sample. Circles indicate locations where there is pinning of dislocations by nanoparticles.
The circled regions show areas where there is clear pinning of the dislocations by nanoparticles. The goal is to maximize the occurrence of dislocations within grains through fabrication techniques and to minimize loss of dislocations due to irradiation creep and thermal treatment. The images below show the dislocation structure in as-received 18Cr ODS and at successive doses up to 10 dpa at 25°C.

Figure 4.4: 18Cr ODS TEM micrographs showing dislocation stability under irradiation in thin film sample at successive doses during irradiation up to 10dpa at 25°C.

It is clear that there are intra grain dislocations in the as fabricated alloy and after irradiation. The in-situ images also show the presence and stability of very small particles dispersed in the imaging region.
An example of the as received dislocation structure of 9Cr ODS is displayed in the image below.

![Image of 9Cr ODS TEM micrograph showing dislocations in as-received thin foil sample. Arrows indicate locations where there is pinning of dislocations by nanoparticles.]

Figure 4.5: 9Cr ODS TEM micrograph showing dislocations in as-received thin foil sample. Arrows indicate locations where there is pinning of dislocations by nanoparticles.

Again we do see dislocations pinned by particles indicated on the image, there is also an observed higher nanoparticle density around dislocation locations as expected. This region was followed during irradiation up to 10 dpa at 25°C and the in-situ TEM images are shown below:
It seems that particles tend to occur in grains which are greater in dislocation density and that there is a strong dislocation network in as fabricated and irradiated samples of 18Cr ODS and 9Cr ODS.

4.1.4 Nanoparticle dispersion:

The dispersion of nanoparticles throughout the matrices of these alloys is crucial to the beneficiary qualities of the nanoparticles. Here the discussion involves location of dispersed particles as well as their general size and composition.

Below is an image showing several particles types within an area of 18Cr ODS, EDS spectra show the composition of the labeled particles and nanoparticle outlines with the calculated area are shown for size analysis.
In general the strings of small, rounded particles, such as those observed in the image above, have been observed to be either Ti- rich particulates with sizes of 100nm-200nm and below, corresponding to the sizes observed here. The larger (>1μm) bright rounded particles appear to be Al- containing particles [7]. Smaller (<50nm) particles are most likely $Y_2Ti_2O_7$ and are seen in the TEM micrograph below to also accumulate along grain boundaries.

Figure 4.7: 18Cr ODS SEM micrograph of thin foil sample after irradiation to 20dpa at 500°C showing nanoparticle dispersion, size, and composition. 1) EDS spectra and area calculation of Al- and O-containing particle. 2) EDS spectra and area calculation of Al- and O-containing particle. 3) EDS spectra and area calculation of Al-, Ti-, and O-containing particle. 4) EDS spectra and area calculation of Al-, Ti-, and O-containing particle. 5) EDS spectra and area calculation of Ti- and O-containing particle. 1) EDS spectra and area calculation of Y-, Ti-, and O-containing particle.

Figure 4.8: 18Cr ODS TEM micrograph of thin foil sample of as received alloy after thermal treatment to 500°C showing nanoparticle dispersion and accumulation of nanoparticles along grain boundaries.
It is clear from the TEM image above showing 18Cr ODS microstructure and previous images that there is an apparent accumulation of particles at the grain boundaries. An observance of the nucleation of these small particles along grain boundaries in the extrusion direction has been made in other studies of ODS alloys and is discussed further shortly.

The general dispersion of particles in 18Cr ODS is shown in the figures below, first at a low magnification showing distribution throughout the material.

![Image](image.png)

Figure 4.9: 18Cr ODS a) low mag SEM of as received thin foil sample showing nanoparticle dispersion b) outlines of particles in a) used for area calculations in ImageJ for nanoparticle size distributions

The image on the left is a low-mag SEM micrograph taken of a region of 18Cr ODS, the image on the right was obtained using ImageJ, showing an outline of all particles visible in that region. The same analysis using a higher magnification is displayed below:
Figure 4.10: 18Cr ODS a) SEM of as received thin foil sample showing nanoparticle dispersion b) outlines of particles in a) used for area calculations in ImageJ for nanoparticle size distributions

It is imperative to have an homogeneous dispersion of very small oxides at all scales, with no oxide free strips, however at both magnifications we do observe regions that are free of small particles within the grain boundary [10]. The structure of nanometer-sized particles analyzed in other ODS research have been observed to show a strong correlation between the crystallographic orientation of the particle and the matrix lattice, such that imaging conditions ideal for a particular grain orientation would allow visibility of particles only on grains in that region with the same orientation [11], [20]. Additionally, these SEM images only exhibit the surface of the alloy and particles under the surface are not visible. More analysis needs to be carried out in order to discover whether or not there actually are depleted zones within this alloy. If in fact there are bands present in 18Cr ODS which lack the fine yttria particle dispersion it is a sign that mechanical alloying was not sufficient and would need to be more extensive in future batches [3].
Other results on 18Cr ODS have shown that oxides are uniformly distributed inside all grains and that different classes of oxides are observed, the size of the largest is few hundreds nanometers and the small spherical particles which are densely packed (up to 1023 particles/m^3) with diameters smaller than 3 nm are observed in nano-clusters all around the material [10]. There may be some variability of as fabricated microstructure between batches leading to discrepancies in observations made here and results from other studies on 18Cr ODS.

The appearance of these nanoclusters is clear in the micrographs above showing nanoparticle dispersion in 18Cr ODS.

In order to show the general size dispersion of nanoparticles in 18Cr ODS, nanoparticle maps were made of multiple regions and magnifications throughout the alloy. The image below shows the mapped regions.

Figure 4.11: 18Cr ODS: low mag SEM micrographs of as received thin foil samples showing nanoparticle dispersion with accompanying maps showing outlines of particles used for area calculations in ImageJ for nanoparticle size distributions
The areas of the outlined nanoparticles were calculated using ImageJ based on the image scale and the distribution of sizes is displayed in the distribution below:

![18Cr ODS Nanoparticle Size Distribution](image.png)

Figure 4.12: 18Cr ODS Distribution of nanoparticle sizes calculated using SEM micrographs and ImageJ on thin foil samples of as-received alloy.

The distribution shows that most nanoparticles observed within the sample are very small with an equivalent diameter less than about 70 nm. There are only a few “spikes” at other size bins likely showing distinct particle types characterized by size. The most dominant spikes for nanoparticles larger than 70 nm occur at bins corresponding to equivalent diameters of about 150 nm and about 215 nm; these possibly correspond to larger Aluminum/Titanium Oxides or Carbide particles most predominately observed in both SEM and XRD analysis.
This relatively small sample size and limitations of the analysis method used give rise to results which are not representative of the nanoparticle dispersion in full. The presented data only reflects particles observed in the images shown which only represent a very small sample of dispersion in the consolidated alloy; samples taken from different regions or directions of as fabricated 18Cr ODS may yield different results. The FESEM used for analysis has an ideal resolution of 0.8nm-4nm depending on beam voltage and experimental resolution was closer to a minimum of 10-15nm, consequently any particles smaller than approximately 10 nm would not be observed by this analysis. Additionally, scanning electron microscopy only reveals the particle dispersion on the surface of the alloy; particles fully obscured within the alloy matrix are not properly represented as they are not observed or counted at all and particles partially obscured result in inaccurate calculated area estimates. However from this sample of nanoparticle sizes in 18Cr ODS it is observed that 60% of nanoparticles are very small with an average diameter less than 35nm and that 82% have a diameter under about 70nm. Particles smaller than 70nm are most likely the very small Y2Ti2O7 particles or other small Titanium containing oxides, this nanometric size is beneficial for strengthening mechanisms desired for optimal alloy durability and performance.

A similar analysis for nanoparticle distribution was conducted for 9Cr ODS. The image below shows a few nanoparticles in a selected region of 9Cr ODS as well as their respective composition by EDS analysis and the area calculated using ImageJ:
Here again we see that the largest particles are Al-containing oxides while the smaller more rounded particles tend to be Y-containing.

Another example showing nanoparticle distribution in 9Cr ODS is shown below in a TEM bright field micrograph taken on a few grains.

Figure 4.14: 9Cr ODS TEM micrograph of thin foil sample after irradiation to about 0.5 dpa at 500°C showing nanoparticle dispersion and accumulation of nanoparticles along grain boundaries.
The variance in nanoparticle size and apparent type is much larger than that observed in 18Cr ODS, and while we do see a fine dispersion of very small yttria particles, they are only observed on a few grains. This could be a result of imaging conditions under which the image was taken, however it has been seen in other studies that oxide particles are more densely dispersed in the elongated residual α-ferrite grains than in the tempered martensite equiaxed grains [21]. There is apparent nucleation of nanoparticles along the grain boundaries as was seen in 18Cr ODS. The larger elongated particles, seen primarily in 9Cr ODS as in the TEM micrograph below, have been observed to be Cr-carbides [8].

![TEM micrograph of thin foil sample after irradiation to about 10 dpa at 25°C showing nanoparticle dispersion and accumulation of nanoparticles along grain boundaries.](image)

Figure 4.15: 9Cr ODS TEM micrograph of thin foil sample after irradiation to about 10 dpa at 25°C showing nanoparticle dispersion and accumulation of nanoparticles along grain boundaries.

The carbon necessary to form these carbide precipitates can be mainly attributed to a pick-up during the mechanical alloying due to wear of high carbon-containing milling balls, as carbon included in the nominal composition (0.14 wt% for 9Cr ODS and 0.027 wt% for 18Cr ODS) is not sufficient to form carbides of the size and quantity observed in these alloys after consolidation.
These carbides have been considered as main reason for the degradation in tensile ductility, impact properties, and resistance as unlike oxide particles carbides have been observed to amorphize at room temperature under irradiation [22]. The heat treatment used both for recrystallization in ferritic alloys and phase transformation in martensitic alloys have been shown to cause the coherency of the particles to be lost and their size to increase up to as much as 10 nm [10]. Accumulation of particles at grain boundaries at all leads to degradation of the materials, and should be reduced as much as possible.

The size distribution of nanoparticles in 9Cr ODS was analyzed in the same way as for 18Cr ODS, the SEM micrographs used in ImageJ for area calculations are displayed below:

![SEM micrographs of 9Cr ODS](image)

Figure 4.16: 9Cr ODS low mag SEM micrographs of as received thin foil samples showing nanoparticle dispersion with accompanying maps showing outlines of particles used for area calculations in ImageJ for nanoparticle size distributions

In every region the particles appear larger and more numerous than in 18Cr ODS, based on these size distributions 9Cr ODS, appears to have a more densely packed dispersion of particles than 18Cr ODS, though these results may not be representative of actual dispersion. The size distribution calculated from these maps is displayed below:
The variety in nanoparticle sizes is much larger and analysis of the distribution will be displayed in two regions. First the smallest nanoparticles with an equivalent diameter smaller than about 120nm are shown in the distribution below:

Figure 4.17: 9Cr ODS Distribution of nanoparticle sizes calculated using SEM micrographs and ImageJ on thin foil samples of as-received alloy.

Figure 4.18: 9Cr ODS Distribution of nanoparticle sizes with equivalent diameter between 0 and 120nm calculated using SEM micrographs and ImageJ on thin foil samples of as-received alloy
Nanoparticles in this size range account for about 30% of the total measured particles. The sizes are not as clearly defined here as with 18Cr ODS due to either greater variance in size or to greater particle types present. The highest occurring diameter is between about 35nm-40nm; however these only account for about 4% of the total analyzed.

The “mid-size” range is displayed below showing the dispersion for particles with a diameter between the sizes of about 115nm and 270nm.

![9Cr ODS Nanoparticle Size Distribution](image)

Figure 4.19: 9Cr ODS Distribution of nanoparticle sizes with equivalent diameter between 115-270 nm calculated using SEM micrographs and ImageJ on thin foil samples of as-received alloy

Nanoparticles analyzed in this range make up for about 56% of the total observed, here there are also clearly “spikes” which most likely are associated with a particular particle type. The bins for these “spikes” as well as the fraction they represent of the total number of particles are displayed in the accompanying table below:
While it is unclear which particle types are associated with each of these sizes, a more comprehensive study of the composition and size of individual particles dispersed in the alloy could elucidate the correlation. Additional methods of analysis would be necessary as well in order to show particles obscured by the matrix and particles which are too small to be resolved through SEM analysis.

<table>
<thead>
<tr>
<th>Area Range (nm²)</th>
<th>Equivalent Diameter Range (nm)</th>
<th>% (of total particles analyzed)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10600-10800</td>
<td>37</td>
<td>5.6</td>
</tr>
<tr>
<td>14200-14400</td>
<td>43</td>
<td>4.8</td>
</tr>
<tr>
<td>17800-18000</td>
<td>48</td>
<td>3.7</td>
</tr>
<tr>
<td>21400-21600</td>
<td>52</td>
<td>3.5</td>
</tr>
<tr>
<td>25000-25200</td>
<td>56-57</td>
<td>2.1</td>
</tr>
<tr>
<td>28600-28800</td>
<td>60-61</td>
<td>1.7</td>
</tr>
<tr>
<td>32200-32400</td>
<td>64</td>
<td>1.9</td>
</tr>
<tr>
<td>35800-36000</td>
<td>68</td>
<td>1.4</td>
</tr>
<tr>
<td>39400-39600</td>
<td>71</td>
<td>1.4</td>
</tr>
<tr>
<td>43000-43200</td>
<td>74</td>
<td>1.0</td>
</tr>
<tr>
<td>46600-46800</td>
<td>77</td>
<td>1.1</td>
</tr>
<tr>
<td>50200-50400</td>
<td>80</td>
<td>0.7</td>
</tr>
<tr>
<td>53800-54000</td>
<td>83</td>
<td>0.9</td>
</tr>
<tr>
<td>57400-57600</td>
<td>86</td>
<td>0.9</td>
</tr>
</tbody>
</table>
The distribution does show that the average sizes of nanoparticles observed by this small sample of 9Cr ODS are both larger and more varied than those observed by SEM analysis in 18Cr ODS and that there are more than twice as many particles observed in 9Cr ODS than in 18Cr ODS from approximately equal regions selected from each alloy.

The lower concentration of very small particles observed in 9Cr ODS is most likely not representative of the actual dispersion, in other ODS research yttria nanoparticles in 9Cr ODS have been observed with a mean size of about 2.3 nm and spatial density $5 \times 10^{22} \text{ m}^3$, leading to a mean spacing between particles equal to 27 nm. This is smaller than what is resolvable with SEM analysis and the observance of these small Y-Ti-O particles must be carried out using TEM or other higher resolution analysis techniques such as Atom Probe Tomography (APT), similar very small particles were observed in this 9Cr ODS using EFTEM energy filtering maps shown in figure 3.58 from chapter three [18].

4.2 Phase Identification by EDS Analysis

Based on the nominal compositions of the alloys and fabrication methods used we expect to find nanoparticles imbedded within the matrix: carbides (especially tungsten carbides, titanium carbides, etc.), and oxides (Ti, Y oxides, Al oxides etc.). These oxides are essential to the functionality of the alloy and the basis of the research presented.
4.2.1 Y-Ti-O Rich Particles:

As was expected there are several oxide and carbide particles identified in both alloys, including Y-Ti-O containing particles which are expected to greatly enhance the strength of ODS materials and the desired result of the elemental additions Y2O3 and Ti, listed in the initial composition. In 18Cr ODS there were several different Y-Ti-O containing particles identified.

The images below were all confirmed by EDS analysis to contain Yttrium, Titanium, and Oxygen:

![Figure 4.20: 18Cr ODS SEM micrographs on thin foil samples showing nanoparticles along with corresponding EDS spectra showing the presence of Y-, Ti-, and O- corresponding to Y2Ti2O7 precipitates.](image)

The top three images all appear to be the same phase, with an average size of about 40 nm and a bright spherical appearance. There is also a particle of about the same size and shape but with a dark appearance; another with the same texture, color, and size, but with an elongated shape, and a forth type which is much larger, several hundred nanometers, which has a gray elongated appearance.

The contrast of particles observed by SEM analysis depend upon the atomic number of the region being imaged, in general regions with an average high atomic number appear brighter relative to regions with a lower atomic number [23].
However, the thickness of the sample and specific methods used effect the reliability of this correlation, and the “color” of the particles in SEM images is not a reliable indicator of composition.

There has elsewhere been observed two types of Y-Ti-O phases; a non-stoichiometric Y-, Ti-, O- enriched cluster containing particles from 2 to 15 nm with a Ytttrium-Titanium ratio less than 1, and stoichiometric Y2Ti2O7 with sizes from 15 to 35 nm [12]. The phases identified by XRD analysis to be present in our alloy are cubic Y2Ti2O7; however these are most likely only two of four phases present as is concluded from the appearance of particles observed by SEM analysis.

Investigations have indicated that smaller Y-, Ti-, and O-rich nano-clusters, such as those observed in the top row of images above, are not residual remnants of the original Y2O3 but a constituent of Ti-O, as there is more titanium present than yttrium and the metal-to-oxygen ratio has been observed to be approximately 1:1 in these nano-cluster particles. However as indicated above, these smaller Y–Ti–O nano-particles with a diameter of several nanometers have been identified as cubic Y2Ti2O7 also, concluding that the growth process of oxides is not apparent. The Y-, Ti-, and O- rich clusters grow into stoichiometric oxides through processing methods used in fabrication. Both the fine nano-clusters and larger nanoparticles containing Y-, Ti-, and O- substantially contribute to the mechanical strength of ODS steels, and the stability of these oxides is vital to the mechanical properties of the fabricated alloy [24].
From other results on 18Cr ODS alloys, it has been concluded that the composition of Y-Ti-O particles is related to the particle size and within the PDF database there exist six different Y–Ti–O compositions with different stoichiometry and crystallographic structures; in our case many only pyrochlore Y2Ti2O7 is observed to be present in the alloy based on XRD analysis however there are several forms of Y2Ti2O7 which are closely matched to the XRD spectrum from 18Cr ODS. The best match is most likely of the highest volume fraction within the alloy [11].

Images of particles containing Y-, Ti-, and O- identified by EDS and TEM Energy Filtering maps on 9Cr ODS are shown below:
There appear to be three different types present: the first are very small, ~20nm, bright, and spherical; these most likely correspond to the Y2Ti2O7 phase identified through XRD analysis and are not used previously in SEM results due to low elemental presence of Y-, Ti-, and O- in the EDS spectra. The second are very large agglomerations of particles which have been speculated to be combinations of Y-Ti-O, Ti-O, and Al-O; however both agglomerations are Y-, Ti- and O- rich.

These first two observations were made using SEM and EDS analysis which is limited in observation ability due to an instrument minimum resolvable size of about 10nm.
The third image set was obtained by EFTEM which has a higher resolution than SEM and shows both a large (>50nm) particle containing Y-, Ti-, and O- and in the surrounding matrix it is apparent that extremely fine (~1-5nm) Y-Ti-O particles are present which were not resolved through SEM analysis.

Other analysis on 9Cr ODS has revealed as many as three types of Y-, Ti-, O- precipitates: non-stoichiometric very small particles less than about 10 nm with Y/Ti < 1, stoichiometric Y2Ti2O7 with Y/Ti=~1 and particles about 15 nm in size, and aggregated coarse oxides of about 100 nm in size and consisting of Y–Ti–O system oxide and Al–O system oxide [12]. These results correlate well with the observations found on our 9Cr alloy, the very fine dispersion is most likely made up of the very small non-stoichiometric Y-Ti-O particles, the stoichiometric Y2Ti2O7 are most likely the small spherical particles of about 20nm, and the agglomerations seen can be paralleled with the aggregated coarse oxides observed in other studies. The larger (~50nm) particle observed in EFTEM is bigger than Y-, Ti-, O- rich particles observed in other studies on 9Cr ODS which report the observation of only the very small (<20nm) Y-Ti-O containing particles and coarse aluminum containing compounds.

Y2O3 and Ti additions prove to lead to the formation of a fine dispersion of Y-Ti-O particles within the matrix of both 18Cr ODS and 9Cr ODS; however they are shown to nucleate in multiple different phases in both alloys. This corresponds well with other observations made on a Fe–14Cr–0.3Mo–1.0Ti–0.25Y2O3 ODS alloy, however the goal is to have the vast majority of Yttrium dispersed into very small particles of only a few nanometers in size [12].
Dispersoids containing a non-negligible content of Al, such as those observed in 9Cr ODS, could strongly affect the formation of Y2Ti2O7, as much of the free oxygen is absorbed in the formation of these much larger particles [22]. Reduction of Aluminum contamination is vital to the formation Y2Ti2O7 in both alloys and must be minimized in future alloys.

4.2.2 Al-O RICH PARTICLES:
In both alloys very large Al-O particles were observed and are shown in the images below:

Figure 4.22: 18Cr ODS SEM micrographs on thin foil samples showing nanoparticles along with corresponding EDS spectra showing the presence of Al- and O- as well as particles containing Al-, Ti-, and O- corresponding to Al2O3 precipitates.

Figure 4.23: 9Cr ODS SEM micrographs on thin foil samples showing nanoparticles along with corresponding EDS spectra showing the presence of Al- and O- as well as particles containing Al-, Ti-, and O- corresponding to Al2O3 precipitates.
While the appearance of the Al- and O-containing particles vary slightly, they are all very large (100nm-1μm) and have a smooth rounded shape.

These have appeared in other ODS research to be Al2O3 particles and of coarse micrometric size [12]. These Al-O particles have been observed to nucleate mostly on grain boundaries aligned along the extrusion direction with a mean size of about 100–200 nm, with a maximum of 1μm [18].

XRD analysis revealed that the Al-O present is in the Al2O3 configuration for 18Cr ODS and is suspected to be the same phase for 9Cr ODS. In both cases the particles are of the same size and appearance as those observed elsewhere to in 9Cr ODS [25]. Aluminum is a contaminate from fabrication methods in 18Cr ODS and 9Cr ODS and is undesirable for both mechanical properties and nucleation of smaller oxides. Alternative methods for ball milling should be considered in future experimental alloys to avoid the nucleation of these large oxides

4.2.3 Cr-C Rich Precipitates:
Chromium containing carbides of the M23C6 type are observed in both alloys, examples are shown in the following images:

![Figure 4.24: 18Cr ODS SEM micrographs on thin foil samples showing nanoparticles along with corresponding EDS spectra showing the presence of Fe-, Cr-, and C- corresponding to M23C6 precipitates.](image-url)
The images show Fe-Cr-Carbide particles in 18Cr ODS both before and after extraction from the matrix. These appear flake-like and were not commonly observed in SEM analysis of 18Cr. In studies on a Fe–13.5Cr–2W–0.4Ti–0.3Y2O3 ODS alloy these have been observed to align preferentially along the grain boundary with a typical length and thickness of 1–4 μm and 0.2–0.5 μm, respectively, correlating well with the particles observed here in 18Cr ODS [22].

Figure 4.25: 9Cr ODS SEM micrographs on thin film samples showing nanoparticles along with corresponding EDS spectra showing the presence of Fe-, Cr-, W-, and C- corresponding to M23C6 precipitates.

There are two different particle types which were observed to be Fe-Cr-W-carbides in 9Cr ODS. The first appear dark, flat, and “plate-like” against the matrix with sizes around 200-300 nm, and the second are bright rounded and elongated particles around 100nm by 400nm in size. The appearance of particles observed may be affected by sample prep used prior to SEM analysis. The samples imaged through SEM analysis have undergone grinding, punching into thin foils, and electropolishing prior to observation.
XRD analysis of 9Cr ODS, revealed the presence of both (Cr, Fe)\textsubscript{23}C\textsubscript{6} and (Cr, Fe, W, Mo)\textsubscript{23}Fe\textsubscript{21} (W, Mo)\textsubscript{2}C\textsubscript{12} (or M\textsubscript{23}C\textsubscript{6}) phases correlating well with SEM/EDS results. The appearance appears to reflect differing tungsten concentration, as the flat “plate-like” particles appear to have a larger W- content based on EDS analysis which is shown above. Again these are observed in other 9Cr ODS alloys as large M\textsubscript{23}C\textsubscript{6} type precipitates nucleated along grain boundaries [17]. The nucleation of these large carbide particles is undesirable and leads to quicker degradation of the material, the carbon necessary to form these particles is picked up during fabrication (as with aluminum contamination) and should be reduced as much as possible in future batches of 18Cr and 9Cr ODS.

4.3 **Elemental Additions**

The nominal composition for the presented alloys are displayed in table one of chapter two, the addition of alloying elements primarily lends to the precipitation of oxide nanoparticles within the matrix. However, apart from the addition of Y\textsubscript{2}O\textsubscript{3} and Ti, other elements such as W and Cr are added for the optimization of mechanical resilience in the alloy, and for environmental reasons the use of low activation elements such as C, Cr, W, Ti, Mn, Si and Fe are required [26].

4.3.1 **Y-addition:**

Yttria is commonly used as a dispersed oxide, but its particle size increases during the consolidation and thermal treatment of ODS steel. Some additional elements are necessary to make the dispersed oxides finer, and for this, titanium and aluminum are frequently used to form complex oxides with Yttria [24].
For our alloys titanium has been used, and it is observed that yttria particles within 9Cr ODS and 18Cr ODS which contain titanium are much finer than those paired solely with oxygen or aluminum. These fine particles are selected as the primary dispersion particles to strengthen ODS ferritic steels [24].

4.3.2 Ti-ADDITION:
Results have shown that the appropriate increase of titanium content compared to yttrium content in ODS alloys modifies the chemical composition allowing a finer dispersion of oxide particles to be formed in the matrix [12]. The dependence of mean particle size on Ti content has been evaluated in previous work and has been found that refinement is achieved by shifting the average diameter from 11.48 nm for the non-Ti ODS alloy to 3.73 nm with the addition of 0.3% Ti. Further increase in Ti content does not seem very effective in particle refinement as the influence of grain structure on the particle size distribution begins to work against the refinement process at higher concentrations [22]. The titanium content in 18Cr ODS and 9Cr ODS are 0.25wt% and 0.23wt% respectively, and are within the desired range of concentration.

The addition of Ti has also been observed to affect the nucleation of Cr- oxides in material, in studies on Fe–13.5Cr–2W–0.4Ti–0.3Y2O3 ODS alloy it has been seen that the addition of Ti- resulted in the formation of spherical Ti oxides rather than Cr oxides owing to the stronger affinity of Ti [22]. As we have not observed any Chromium Oxides in either alloy it is likely that this mechanism has taken place, inhibiting their precipitation.
Additionally the creep strength is considerably improved in ODS alloys by increasing titanium concentrations from 0.2 wt% to either 0.3 wt% or 0.35 wt% and is highest when titanium concentration is 0.30–0.35 wt%. The hardness of ODS alloys has also been seen to increase consistently with increasing Ti content. Again, alloying with 0.3% Ti exhibited the highest strength due to the optimum refinement of mean ODS particle size [21]. It has yet to be seen whether an increase in Ti concentration, from 0.25 wt% in 18Cr ODS and 0.23 wt% in 9Cr ODS, would be beneficial to the mechanical properties of either of these alloys.

4.3.3 O-CONTENT:
It has been seen that the amount of excess oxygen in an ODS alloy strongly effects the nucleation of small Y-Ti-O particles. This directly affects the high-temperature strength and microstructure of ODS alloys and is moderated through control of the excess oxygen (Ex.O) content. This is best achieved through a more controlled fabrication process as oxygen is easily picked up in powder particles during the milling process. Oxygen content is highly dependent on the milling conditions (grinding medium, grinding bowl, milling time, milling intensity, etc.) and the atmosphere under which the powder is being milled [13].

4.3.4 Al-CONTENT
Aluminum is not included in the nominal composition of either 18Cr ODS or 9Cr ODS, and most likely has two main sources: the steel-powders manufacturing where Al is commonly used as deoxidizers to reduce the dissolved oxygen to a desired level, or from contamination due to ball milling during the mechanical alloying process [27].
However in both alloys there are particles containing a non-negligible content of Al identified through both XRD and EDS analysis. Nucleation of these particles could strongly affect the formation of Y2Ti2O7 within the alloy matrix as the presence of Al may prevent Ti from acting as catalyst for the formation of Y2Ti2O7 and be prone to form different Y–Al–O types [22].

The effect of the aluminum contamination has been observed in both alloys as large Al-O particles, and in 9Cr ODS with the formation of large agglomerations. This contamination should be avoided as much as is possible in future versions of these alloys as it inhibits Y-Ti-O formation and thus degradation of the material properties otherwise enhanced by the fine dispersion of small scale yttria precipitates.

4.3.5 Cr-content:
Chromium inclusion is strongly tied to both phase control and corrosion resistance in ODS alloys. The effects of phase control have already been discussed as the formation of fine grains in recrystallized ferritic 18Cr ODS and the residual α-ferrite in 9Cr ODS. The corrosion resistance has been found to be optimized in ODS ferritic steels containing 16 to 19 wt% Cr, such that 18Cr ODS is in the ideal range, while 9Cr ODS requires further development for increasing corrosion resistance to the desired level for certain applications in future Gen IV reactors [13].
4.3.6 W-ADDITION:

Tungsten is added to ODS alloys primarily for activation properties, as it has been shown to distribute more isotropically than molybdenum or other alloying elements used for this purpose[1]. Tungsten has been seen; particularly in 9Cr ODS, to form in carbide particles within the matrix. Other research has seen that tungsten is concentrated in elongated areas parallel to extrusion direction which is considered to be the residual-a ferrite, as tungsten is a ferrite-forming element having a higher partitioning ratio into ferrite [4]. Further analysis would be required in order to confirm that the tungsten containing particles in 9Cr ODS are formed preferentially in ferrite regions.

Further analysis and mechanical testing needs to be carried out on these 18Cr ODS and 9Cr ODS alloys in order to determine the degree to which manipulation of the microstructure and particle nucleation mechanisms have affected the mechanical properties relevant to application as cladding materials in Gen IV reactors.

4.4 RADIATION STABILITY

The small size and high number density of Y-Ti-O nanoclusters in ODS alloys are responsible for their superior tensile strengths and creep resistance compared to conventional ferritic and martensitic alloys. This high number density of nanoclusters also provides effective trapping centers for point defects and transmutation products produced during irradiation, mitigating their effect on bulk ODS material properties.

Previous high-temperature annealing studies have shown nanoclusters are remarkably stable at high temperatures and do not appreciably coarsen or decrease in number density after isothermal aging up to 1300 °C for 24 h [17] and that nanoclusters do not change after ion irradiation up to 0.7 dpa at 300°C [24].
In this work, preliminary irradiations have been conducted on 18Cr ODS and 9Cr ODS in order to evaluate the effects of temperature and radiation on precipitate stability.

The 18Cr ODS alloy was evaluated using SEM analysis before and after irradiation to 20dpa at 500°C in order to observe nanoparticle size, distribution, and composition as well as grain structure. The figure below displays analyses of the nanoparticle size before and after irradiation, these were measured using ImageJ to outline individual particles in SEM micrographs.

The limitations of this analysis are the same as those discussed previously for SEM analysis of the as fabricated nanoparticle dispersion. The presented data only reflects particles observed in the images shown; only representing a very small sample of dispersion in the consolidated alloy. The resolution of the SEM limits observations to particles of 10nm or larger and scanning electron microscopy only reveals the particle dispersion on the surface of the alloy; particles fully obscured within the alloy matrix are not properly represented as they are not observed or counted at all and particles partially obscured result in inaccurate calculated area estimates.

The maps used for these analyses are displayed below followed by the resultant distributions; there were 2087 particles measured before irradiation and 5493 after irradiation.
Figure 4.26: 18Cr ODS a) low mag SEM micrographs of as received thin foil samples showing nanoparticle dispersion with accompanying maps showing outlines of particles used for area calculations in ImageJ for nanoparticle size distributions. b) low mag SEM micrographs of thin foil samples after irradiation to 20dpa at 500°C showing nanoparticle dispersion with accompanying maps showing outlines of particles used for area calculations in ImageJ for nanoparticle size distributions.
Figure 4.27: 18Cr ODS Distribution of nanoparticle sizes calculated using SEM micrographs and ImageJ on thin foil samples both before and after irradiation to 20dpa at 500°C to show any changes in nanoparticle dispersion or size.

The figure below is a zoom in on smaller scale data presented in the previous figure, this shows the distribution of particle sizes with an equivalent diameter of about 100nm or less.

Figure 4.28: 18Cr ODS Distribution of nanoparticle sizes for nanoparticles with a calculated diameter less than 100nm, areas were calculated using SEM micrographs and ImageJ on thin foil samples both before and after irradiation to 20dpa at 500°C to show any changes in nanoparticle dispersion or size.

114
These results show a greater division in nanoparticle size after irradiation, with a greater concentration of both very fine particles (<20 nm) and in particles between about 50-150 nm. It is clear that the “spikes” observed which are most likely associated with a particular particle type are at different size values before and after irradiation and do not appear to occur preferentially at either extreme, which leads to the assumption that there is an effect on the average size, though the effect may be different based on the composition of the particle. Further analysis taking into account particle composition, alternate imaging methods, and a greater sample size to increase the statistical reliability of results must be done in order to extrapolate the dependence of particle size on irradiation and thermal treatment.

From images 3.35 and 3.36 in chapter three it is observed that the number density of small particles appears to decrease in the irradiated region. There also appear to be craters present associated with sputtering of particles in that region. Previous irradiation studies with an 18Cr ODS observe stability of Y-Ti-O containing particles up to 45 dpa at 500°C however there is observed amorphization of some particles at temperatures below 780K [10], [20].

The images below of 18Cr ODS under irradiation to 20dpa at 25°C show grain stability under irradiation.

Figure 4.29: 18Cr ODS TEM micrographs showing grain boundary stability under irradiation in thin foil sample at successive doses during irradiation up to 20 dpa at 25°C.
There is an apparent loss of imaging conditions due to bending of the sample under irradiation, but it is clear that the grains from the as received sample are still present and the alloy has not undergone recrystallization.

An irradiation conducted at 25°C up to 52 dpa on 18Cr ODS showed nanoparticle stability up to 52 dpa, the TEM images below show the same very small nanoparticle (about 20nm) at successive doses with no apparent change in size or shape.

Figure 4.30: 18Cr ODS TEM micrographs showing nanoparticle stability under irradiation in thin foil sample at successive doses during irradiation up to 52 dpa at 25°C.
Precipitate stability of 9Cr ODS under irradiation was conducted using TEM analysis at successive doses during in-situ irradiation; this is shown in the figure below:

![TEM micrographs showing amorphization of a large particle under irradiation in thin foil sample at successive doses during irradiation up to 10dpa at 25°C.](image)

Figure 4.31: 9Cr ODS TEM micrographs showing amorphization of a large particle under irradiation in thin foil sample at successive doses during irradiation up to 10dpa at 25°C.

Here it is seen that the large particle, indicated in the image by an arrow, appears to undergo amorphization as evidenced by an increasingly diffuse appearance at successive doses. The particle in the image is suspected to be a carbide based on prior observations through SEM analysis, as the size and appearance correlates most closely with other carbides observed in 9Cr ODS. After irradiation the sample was tilted to ensure loss of crystalline structure and the comparison is displayed below:
The particle still appears milky, with no defined structure after tilt showing amorphization, this is only observed at room temperature. High temperature stability is evidenced in figure 3.59 of chapter three; the large particles do not change in appearance or structure during irradiation to 9dpa at 500°C. It is crucial that oxide particles are stable at all temperatures and doses as these are the primary strengthening mechanism for ODS materials; it is clear that the very small particles in figures 4.31 and 4.32, which are likely Y- and Ti- rich oxides, remain stable throughout irradiation. The amorphization of carbides is less injurious to mechanical properties as these particles are largely considered to be contaminants in ODS alloys, however any strengthening they may serve is lost if the particles lose their crystalline structure. Amorphization as well as other observed forms of radiation damage are detrimental to radiation-resistant properties; further investigation needs to be done to determine the cause and mechanisms of prevention of such phenomena.

Figure 4.32: 9Cr ODS TEM micrographs showing amorphization before and after tilt of a large particle in a thin foil sample that has been irradiated to 10dpa at 25°C.
Figure 3.58 shows the dispersion of very small oxides which are not otherwise observed in bright field TEM showing that they are still finely dispersed within the alloy and mid-range Y-Ti-O particles are still present after irradiation up to 9 dpa at 500 °C. Irradiation studies on a 13Cr ODS have revealed a re-precipitation of oxides around the larger oxides after irradiation [10], and the observance of these small particles surrounding a much larger precipitate after irradiation in figure 3.58 could be related to this phenomena.

In preliminary studies of both alloys under irradiation it has been seen that there is apparent decrease in nanoparticle size and dispersion. More work is required to determine the extent to which this dissolution is happening and whether there is any dependence on composition or coherency of the nanoparticles within the matrix.

4.5 LIMITATIONS OF CHARACTERIZATION TECHNIQUES.

The two alloys used for this research, 18Cr ODS and 9Cr ODS, are developed at national laboratories as developmental alloys. The purposes of these alloys are for optimization of properties for specified applications based on the imposed strains associated with operating environments. Characterization of the developmental alloys was carried using SEM, EDS, TEM, and XRD analysis in order to evaluate grain size, dislocation microstructure, matrix microstructure and composition, and nanoparticle size, dispersion, and composition.
The conclusions derived from various methods in this body of work must be considered within the framework of the limitations of the techniques used. While the results serve to enhance the knowledge base about the microstructural and microchemical properties of 18Cr and 9Cr ODS, there is further work necessary for comprehensive and statistically significant characterization.

The first limitation to be discussed is the detection limit of particle size, it is impossible to obtain reliable overall particle size statistics especially for the extremely fine (<10nm) nanoclusters, while they have been observed through TEM and SEM analysis, the resolution associated with techniques used limit the ability to make compositional analysis of these very small particles. The FESEM used for analysis has an ideal resolution of 0.8nm-4nm depending on beam voltage [28], though the experimental resolution was closer to 10nm-20nm. SEM analysis also only shows particles which are on the surface of the thin foil sample after electropolishing. This limits the statistical reliability of results gathered through observation by SEM alone to particles on the surface of the thin foil sample that are about 10nm or larger.

TEM observation has a higher resolution, with a maximum resolution of 0.25nm [29], and a higher penetration depth and thus has the ability to reveal particles of only a few nanometers in size on the surface and within the alloy matrix. However, TEM observation is strongly dependent on sample orientation and the occurrence of particles or dislocations may not be apparent until additional steps are taken such as tilting or energy filtering. This is seen in image 3.58, where small particles are not visible in the region until energy filtering maps reveal the differences in elemental composition.
A combination of SEM, EDS, TEM (EFTEM), XRD, and atom probe analyses would be necessary to form a comprehensive imaging record of as fabricated and irradiated microstructure, nanoparticle size, dispersion, and composition for 18CrODS and 9Cr ODS.

The combination of very small grain sizes and dislocation densities in some regions limit the visibility of particles to those of about 4–10 nm in diameter, particularly along grain boundaries [22]. In examinations of the extracted particles, it is important to keep in mind that it has been reported that Y2O3 completely dissolves in hydrochloric acid–methanol, which is traditionally used for chemical extraction of steels, and Y–Ti–O system oxides like Y2Ti2O7 have been observed to be unstable in solutions using hydrochloric acid which would affect the reliability of analysis made after extraction as hydrochloric acid has been used both in the Berzelius solution and to clean particles after filtering [12]. However, Y2O3 dissolves completely during fabrication and is not expected to still be present in the alloy, and the presence of Y2Ti2O7 in both XRD and SEM after extraction confirms that it does not dissolve under the conditions used for extraction.

Grain size estimations were made using SEM and TEM images, however etching and optical microscopy would give greater contrast between grains leading to a better estimate of average grain size from distributions of measured sizes from optical micrographs. Dislocation density calculations could be made through comprehensive in-situ TEM analysis, allowing for a greater understanding of the dislocation networks present in the as-fabricated alloys.
SEM and EDS analysis revealed the presence of large M23C6 type carbides and Al2O3 alumina particles in both alloys. The presence of these particles is a product of contamination of aluminum and carbon during ball milling of elementary powders and is undesirable to strengthening mechanisms of these ODS alloys. While there is significant carbon added to the nominal composition of 9Cr ODS (0.14wt%) to aid in the formation of a martensitic structure, the carbides found in 9Cr ODS are too large and numerous to be products of initially added carbon and are most likely representative of carbon contamination. Fabrication of future batches should involve measures to reduce contamination during fabrication to prevent the nucleation of these large particles.

XRD and PeakFit analyses were used to identify the specific phases of nanoparticles present as well as to substantiate the matrix composition and estimate relative volume fraction of the phases identified. Several methods of XRD analysis were used in order to substantiate the effectiveness of techniques and results of analyses.

Synchrotron XRD was effective in observing peaks from second phase precipitates; however the peaks from the matrix have a very large relative intensity and obscure some of the smaller peaks which occur at similar 2-theta values. Identification of peaks using the Synchrotron data involves some uncertainty as it cannot be known whether or not there should be second-phase peaks present at 2-theta values surrounding matrix peak locations. For this reason CuKα XRD analysis was carried out on the nanoparticles alone, after extraction from the alloy matrix. Comparison of the spectra substantiated results from both methods as the peak locations for second-phase precipitates are closely matched for both alloys, the only discrepancies occur in areas where matrix peaks occur in the synchrotron data.
In bulk samples, the results of CuKα XRD analysis were shown to be dependent on the orientation of the 18Cr ODS alloy; in the transverse direction there were some small peaks present correlating to an M23C6 carbide that were not present in the same analysis on a sample from the longitudinal direction of the alloy. Bulk CuKα XRD analysis also showed the true effectiveness of using synchrotron radiation in lieu of CuKα for detection of signal from second-phase peaks. The Synchrotron pattern represented the second-phase peaks as well as CuKα analysis on the extracted nanoparticles alone, whereas bulk CuKα analysis was only effective in producing peaks from the matrix and the highest volume fraction precipitate, an M23C6 type carbide.

Comparison of spectra obtained from the various XRD techniques used shows that both extraction and bulk synchrotron XRD analysis are effective in showing signal from Y-containing small volume fraction oxides, however the low volume fraction representation of Y-containing oxide phases in the XRD spectra is likely not representative of the actual dispersion in the alloys, as the filter used after extraction had a grid spacing of 20nm, so particles smaller than 20nm (likely Y2Ti2O7 particles) are mostly lost after filtering and are only captured if they settle on top of larger particles. The low intensity representation of Y2Ti2O7 in the synchrotron patterns indicates that signal from very small particles (<20nm) is likely not picked up through bulk synchrotron analysis, and only larger particles are clearly represented in the resultant diffraction pattern.
4.6 Summary of Analysis

18Cr ODS is manufactured with a ferritic structure which has been shown to have high corrosion resistance due primarily to high-chromium content and can be utilized at temperatures up to 1100°C without exhibiting any phase transformation [3].

However, ferritic alloys have also been observed to have a somewhat non-uniform nanoparticle dispersion, be difficult to manufacture, and susceptible to embrittlement at high temperatures due to an undesirable phase transformation between 400°C and 550°C [12], [10]. 9Cr ODS is unique in that there is the observed formation of a non-equilibrium phase, designated as the residual ferrite, which serves to greatly enhance several vital mechanical properties in comparison to both standard RAFM alloys and the fully ferritic 18Cr ODS. This is theorized to be further enhanced by sliding at weaker regions such as at the grain boundaries and packet boundaries; behaving as a fiber composite material comprising the harder residual ferrite and the softer tempered martensite. [15] A martensitic alloy, such as 9Cr ODS, would be best utilized in areas exposed to high temperatures, neutron doses, and mechanical strain, such as fuel cladding within the reactor pressure vessel. 18Cr ODS would be more valuable for application as structural components that are in contact with coolant, as the high chromium content lends to good resistance to corrosion.

18Cr ODS exhibits two different types of grain sizes observed, as has been seen in other ferritic alloys after recrystallization such as Fe–13.5Cr–2W–0.4Ti–0.3Y2O3 ODS, RAFM Eurofer-ODS, and 13–14% Cr ODS ferritic steels, from TEM observation it is observed that grain sizes in 18Cr ODS are well below 1 µm in diameter [22].
The grains appear to be primarily equiaxed, only in rare cases are elongated grains observed. The presence of much smaller grains in this 18Cr ODS alloy verifies that the fabrication method used was effective in creating the desired homogeneous, fine, equiaxed grain structure required for application in Gen IV reactors.

In 9Cr ODS the grain size is observed to be smaller than in 18Cr ODS with average sizes of only a few hundred nm in width with an observed maximum size of only about 1 μm. There is a minimization of elongated grains in the examined 9Cr ODS alloy; these more equiaxed grains are achieved through the formation of the residual ferrite phase after the martensitic transformation [14]. The combination of small yttria particles and the residual α-ferrite phase serve to produce a very fine grain structure without the additional step of recrystallization, as a result 9Cr ODS alloys are easier to fabricate than 18Cr ODS and appear to have an even finer grain size [14].

The nanoparticle dispersion observed in 18Cr ODS in general consists of three particle types: small, rounded particles observed to be Ti-rich particulates with an average size of 100nm-200nm. Larger (>1μm) rounded particles appear to be Al-containing particles [7], and smaller (<50nm) particles are most likely Y2Ti2O7. There is also an apparent accumulation of particles at the grain boundaries. It is imperative to have a homogeneous dispersion of very small oxides at all scales, with no oxide free strips; however at both magnifications we do observe regions that are free of small particles within the grain boundary. The distribution shows that most nanoparticles are very small with an equivalent diameter less than about 70nm. There are only a few “spikes” at other size bins likely showing distinct particle types characterized by size.
The most dominant spikes for nanoparticles larger than 70nm occur at about 150nm and 215nm, these possibly correspond to larger Aluminum/Titanium Oxides or Carbide particles most predominately observed in both SEM and XRD analysis. The particles smaller than 70nm are most likely the very small Y2Ti2O7 particles or other small Titanium containing oxides, this distribution serves to show that 60% of nanoparticles are very small with an average diameter less than 35nm and that 82% have a diameter under about 70nm, this nanometric size is beneficial for strengthening mechanisms desired for optimal alloy durability and performance.

Analysis of nanoparticle dispersion in 9Cr ODS reveals that the largest particles are Al- containing oxides while the smaller more rounded particles tend to be Y-containing. The variance in nanoparticle size and apparent type is much larger than that observed in 18Cr ODS, and while we do see a fine dispersion of very small yttria particles, they are again only observed on a few grains. There is a nucleation of nanoparticles along the grain boundaries as was seen in 18Cr ODS. Larger elongated particles, seen primarily accumulated along grain boundaries, have been observed to be Cr- carbides [8] Accumulation of particles at grain boundaries at all leads to degradation of the materials, and should be reduced as much as possible.

The distribution shows that the average sizes of nanoparticles in 9Cr ODS, of the areas observed, appear both larger and more varied than those in 18Cr ODS and with more than twice as many particles observed in 9Cr ODS than in 18Cr ODS from approximately equal regions selected from each alloy.
The lower concentration of very small particles observed in 9Cr ODS is most likely not representative of the actual dispersion, as dispersion analysis was carried out using SEM analysis which is unable to resolve particles of only a few nanometers in size. The presence of the very small Y2Ti2O7 particles in 9Cr ODS is confirmed through both XRD and TEM analysis.

Nanoparticle dispersion distributions made using SEM and ImageJ before and after irradiation on 18Cr ODS show that there is a greater division in nanoparticle size after irradiation with a greater concentration of both very fine particles (<20 nm) and of larger particles between 40-150 nm. The “spikes” observed are most likely associated with a particular particle type are at different size values before and after irradiation and do not appear to occur preferentially at either extreme, which leads to the assumption that there is an effect on the average size, though the effect may be different based on the composition of the particle.

Dispersion analysis in both alloys before and after irradiation is not representative of the nanoparticle dispersion at large due to limitations of the techniques used; only nanoparticles within the resolvable range of the SEM used for this analysis are observed, and the amount of data collected is not statistically significant enough to state conclusions with confidence. The results of dispersion analyses only show the nanoparticle dispersion as evidenced through SEM analysis from a small sample of data.

Analysis of nanoparticle stability under irradiation in 9Cr ODS reveals that large particles, likely carbides, appear to undergo increasing amorphization under irradiation at room temperature.
Very small oxides are still finely dispersed within the alloy and mid-range Y-Ti-O particles are still present after irradiation up to 9 dpa at 500 °C. In preliminary studies of both alloys under irradiation it has been seen that there is apparent effect on nanoparticle size and dispersion. More work is required to determine the extent to which radiation induced damage is occurring and whether there is any dependence on composition or coherency of the nanoparticles within the matrix.
CHAPTER 5

CONCLUSIONS

Current ODS research focuses on relevant mechanical properties such as tensile strength, toughness, fatigue, and creep rupture at a wide range of temperatures and irradiation doses. However, detailed information concerning the crystalline structure of ODS nanoparticles, orientation with respect to the alloy matrix, and individual elementary composition is still lacking and is important for improving ODS alloys by means of targeted nanostructural tailoring. Additionally, detailed knowledge about ODS particles and their interaction with the matrix aids in development of nanoscale theory and modeling with simulation approaches that will be designed specifically to address material structures and properties in the nanoscale regime.

For this reason characterization is necessary for advanced understanding of mechanisms guiding the mechanical properties of these alloys. Characterization serves to check the homogeneity of the material, to verify the size of the grains or laths and to confirm the presence of a homogeneous dispersion of nano-clusters which are all required to remain stable at conditions relevant to Gen IV reactor operation.
In this work, two developmental alloys, 18Cr ODS from CEA and 9Cr ODS from JAEA, have been characterized in the as fabricated and irradiated states in order to evaluate the microstructure and composition. In order to evaluate the merit of ODS alloys for their intended use, the microstructural and microchemical state of these alloys, including nanoparticle stability under irradiation at various temperatures was considered. Chemical composition and microstructure have been studied prior to and after irradiation through FESEM, TEM, EDAX and Synchrotron X-ray diffraction analysis on 9Cr ODS and 18Cr ODS alloys.

5.1 18Cr ODS:

18Cr ODS is manufactured with a ferritic structure which has been shown to have high corrosion resistance due primarily to high-chromium [3]. 18Cr ODS grain sizes are observed by TEM to be well below 1 µm in diameter. The grains appear to be primarily equiaxed, only in rare cases are elongated grains observed, though samples taken from a different direction of the alloy may yield different results as elongation tends to occur along the extrusion direction.

The presence of much smaller grains in this 18Cr ODS alloy in comparison to previous versions of high chromium ferritic ODS alloys (with grain sizes as large as 20µm), verifies that the fabrication method used was effective in creating the desired fine, equiaxed grain structure required for application in Gen IV reactors.
TEM analysis of the dislocation microstructure observed in 18Cr ODS shows areas with pinning of the dislocations by nanoparticles in the as-received alloy, this is desirable for reduction of irradiation creep. There is an apparent correlation observed between nanoparticle density and dislocation density as expected; grains with a high density of nanoparticles are observed to also have high intra grain dislocation density.

XRD analysis of 18Cr ODS revealed a strong correlation in patterns obtained through various methods, particularly between the synchrotron and extraction spectra. The phases identified through analysis are the Matrix (Fe, Cr), in addition to an Iron Chromium Carbide of the form M23C6 and Yttrium Titanium Oxide of the form Y2Ti2O7. Peak Fit analysis of these identifications showed that the peaks from Y2Ti2O7 and (Cr, Fe)23C6 are of the highest volume fraction in the sample as these two phases alone account for all but a few minor peaks. SEM analysis of 18Cr ODS allowed substantiation of XRD results through imaging of nanoparticles and microstructure of the alloy along with EDS analysis. SEM analysis revealed the presence of Al2O3, AlTiO2, TiO2, Ti2O3, and Ni3Mo particles in 18Cr ODS and substantiated the presence of (Cr, Fe)23C6 and Y2Ti2O7 identified through XRD analysis.

The nanoparticle dispersion in 18Cr ODS, observed by SEM and EDS analysis, in general consists of three particle types: strings of small, rounded particles observed to be Ti-rich particulates with sizes of 100nm-200nm or smaller. Larger (>1μm) bright rounded particles appear to be Al-containing oxides, and smaller (<50nm) particles are most commonly Y2Ti2O7.
There is also an apparent accumulation of particles at the grain boundaries and non-uniform distribution of particles. It is imperative to have a homogeneous dispersion of very small oxides at all scales, with no oxide particle free strips; however at large and small magnifications using SEM we do observe regions that are free of small particles within the grain boundaries.

Nanoparticle size distributions made using SEM images and imageJ area calculations revealed that 60% of nanoparticles observed by SEM are very small with an average diameter less than 35nm and that 82% have a diameter under about 70nm, this nanometric size is beneficial for strengthening mechanisms desired for optimal alloy durability and performance. Nanoparticle dispersion distributions made using SEM and ImageJ before and after irradiation on 18Cr ODS seems to show that there is a greater division in nanoparticle size after irradiation with a greater concentration of both very fine particles (<20 nm) and of larger particles between 40-150 nm.

However, all analyses on nanoparticle distribution were made using SEM analysis which is limited in observation capabilities as the minimum resolvable size here was around 10nm and any smaller particles were not observed through these methods. Also the samples used for analysis only represent a small sample of the total alloy microstructure.

In order to obtain statistically significant and comprehensive nanoparticle dispersion characterization, further analysis using TEM and APT imaging would be necessary as they provide higher resolution capabilities as well as detection of particles below the surface of the alloy sample.
TEM and APT allow observation of very small (<10nm) particle dispersion which are primarily responsible for good strength of ODS alloys, and is not resolvable through SEM analysis. However large particles (up to 1-2\(\mu\)m) that are shown to be a large volume fraction of precipitates through XRD analysis are not observed through TEM or APT, and so the combination of SEM, TEM, and APT analyses are required in order to gain information on the full spectrum of nanoparticle sizes and dispersion in 18Cr and 9Cr ODS.

Irradiations with 18Cr ODS were carried out with 1 MeV Kr ions at 25°C to 2, 10, 30, and 52 dpa, to 30dpa at 300°C, and to 20dpa at 500°C. Post-irradiation SEM analysis of microstructure seemed to show preferred sputtering at grain boundaries and at interfaces of large particles intersecting the surface when compared to micrographs of unirradiated samples. In-situ TEM analysis during irradiation revealed that between 15 and 20 dpa at 25°C nanoparticles within grains are still present and do not appear to have changed in size or dispersion. During irradiation up to 52dpa at 25°C there was no apparent change in the size or shape of a small particle on the grain boundary.

5.2 9Cr ODS:

9Cr ODS is fabricated with a largely martensitic structure, however the addition of Y2O3 during fabrication leads the formation of a non-equilibrium phase, designated as the residual ferrite, which serves to greatly enhance several vital mechanical properties in comparison to both standard RAFM alloys and the fully ferritic 18Cr ODS.
In 9Cr ODS the grain size is observed by SEM images to be on average only a few hundred nm in width with an observed maximum size of only about 1 μm. There is a minimization of elongated grains in the examined 9Cr ODS. The combination of small oxide particles and the residual α-ferrite phase serve to produce the observed very fine grain structure without the additional step of recrystallization. SEM analysis of dislocation microstructure in 9Cr ODS revealed the presence of dislocations pinned by particles within grains and an apparent higher nanoparticle density around dislocations locations as expected.

XRD analysis of 9Cr ODS revealed that both synchrotron and extraction X-ray diffraction techniques serve as viable identification methods for identifying the second phase precipitates which form within the matrices, however the extraction allows for better peak identification as there is no obstruction in the pattern from matrix peaks. The phases identified through XRD analysis are: Chromium Iron Tungsten Carbide ((Cr, Fe, W, Mo)23Fe21(W, Mo)2C12), and a Chromium Iron Carbide ((Cr, Fe)23C6). SEM and EDS analysis substantiated the presence of these Iron Chromium carbides as well as the presence of Titanium Oxide (TiO), Titanium Nitride (TiN), and Yttrium Titanium Oxide (Y2Ti2O7). The Y2Ti2O7 phase was represented in the XRD pattern, however the relative intensity of the correlating peaks were very low in both the extraction and synchrotron data indicating a low volume fraction abundance in the alloy. The low representation of Y-Ti-O phases in the XRD spectra is not representative of the actual dispersion in the alloy, as the filter used after extraction had a grid spacing of 20nm, so particles smaller than 20nm (likely Y2Ti2O7 particles) are mostly lost after filtering and are only captured if they settle on top of larger particles.
The low intensity representation of Y2Ti2O7 in the synchrotron pattern indicates that signal from very small particles (<20nm) is likely not picked up through bulk synchrotron analysis, and only larger particles are clearly represented in the resultant diffraction pattern. PeakFit analysis of the phases identified revealed that M23C6 is by far of the highest volume fraction within the extracted nanoparticles, however the presence of all lower volume fraction particulates identified through SEM are reflected in the pattern; this method exemplifies how the combination of very small peaks simulate the collected pattern.

SEM analysis of nanoparticle dispersion in 9Cr ODS reveals that the largest particles are Al- containing oxides while smaller (<20nm) more rounded particles tend to be Y- containing. Nanoparticle dispersion observed by SEM images and ImageJ area calculations in as fabricated 9Cr ODS seems to show a greater variance in nanoparticle size and apparent type than that observed in 18Cr ODS. A fine dispersion of very small Y- containing oxide particles was observed, however they are only observed on a few grains. This is most likely due to limitation of imaging techniques, using TEM and APT for further analysis would reveal a more accurate and statistically significant approximation of nanoparticle dispersion in 9Cr ODS. There is a nucleation of nanoparticles along the grain boundaries as was seen in 18Cr ODS. Larger elongated particles, seen primarily accumulated along grain boundaries have been observed to be Cr- carbides Accumulation of particles at grain boundaries at all leads to degradation of the materials, and should be reduced as much as possible.
Analysis of nanoparticle stability under irradiation in 9Cr ODS revealed that large particles, suspected to be carbides, appear to undergo increasing amorphization at successive doses at room temperature and that very small particles and mid-range particles are stable at doses up to 10dpa. Additionally very small Y-containing oxides were observed to be stable after irradiation up to 9 dpa at 500 °C and EFTEM images taken after irradiation showed possible enrichment of chromium in the very small oxides.

Preliminary analysis of radiation stability of the microstructure and nanoparticles was carried using in-situ TEM analysis at the IVEM Tandem In-situ TEM at Argonne National Laboratory. Results from these irradiations revealed the suspected amorphization of carbides at room temperature and the stability of oxides under irradiation for doses from 2-52 dpa at temperatures from 25°C to 500°C. SEM analysis after irradiation suggested the presence of apparent sputtering at grain boundaries and particle-matrix interfaces, an apparent decrease in nanoparticle density, and an increase in average particle size after irradiation. Degradation of the microstructure or nanoparticle dispersion in any way is detrimental to the long term stability of these alloys, and further analysis is required to understand the specific doses and temperatures at which these mechanisms are occurring, and how they can be prevented in future batches of 18Cr and 9Cr ODS.
Characterization of the developmental alloys was carried using SEM, EDS, TEM, and XRD analysis in order to evaluate grain size, dislocation microstructure, matrix microstructure and composition, and nanoparticle size, dispersion, and composition. The presented data only reflects particles observed in the images collected through the analysis techniques utilized; this only represents a very small sample of the microstructure and nanoparticle dispersion in the consolidated alloy. The resolution of SEM limits observations to particles of 10nm or larger and scanning electron microscopy only reveals the particle dispersion on the surface of the alloy; particles fully obscured within the alloy matrix are not properly represented as they are not observed or counted at all and particles partially obscured result in inaccurate calculated area estimates. A combination of SEM, EDS, TEM (EFTEM), XRD, and atom probe analyses would be necessary to form a comprehensive imaging record of as fabricated and irradiated microstructure, nanoparticle size, dispersion, and composition for 18CrODS and 9Cr ODS.

Results from this work allow a deeper understanding of as-fabricated microstructural and microchemical properties of 18Cr ODS and 9Cr ODS, however further analysis using additional methods and more comprehensive examination will reveal a more detailed and inclusive understanding of the properties evaluated and the effectiveness of fabrication methods used to create these developmental ODS alloys that are intended for future use in Generation IV nuclear reactors.
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