Effects of Zr or Hf on Radiation Induced Segregation in 316SS

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Background

- Next generation (Gen IV) nuclear power plants will operate at higher temperatures under more demanding conditions than our current nuclear fleet
- Effects of radiation damage in structural materials will be magnified
- New structural materials must be developed in order to support an advanced reactor fleet

Radiation Damage

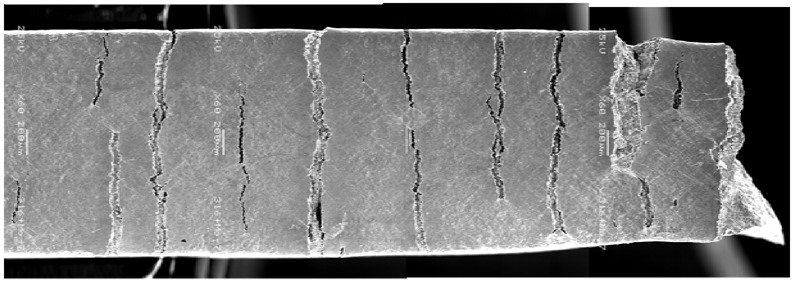
Point Defects

Dislocation Loops

Radiation-Induced Segregation

Voids

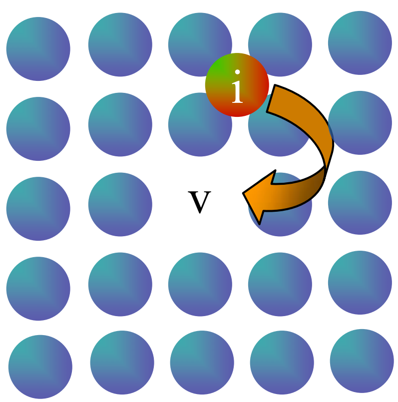
Irradiation-Assisted Stress Corrosion Cracking



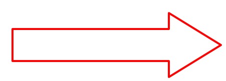
MJ Hackett and GS Was, 12th Int'l Conf. Env. Deg. (2005)

Decreasing Radiation Damage

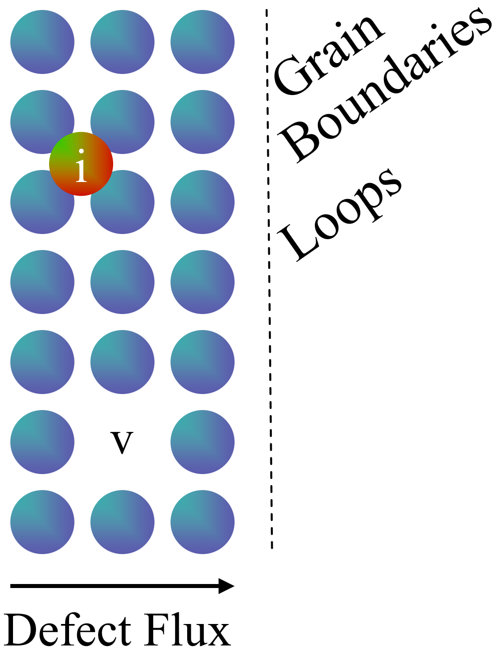
An Increase in Recombination



Results in



A Decrease in Flow of Defects to:



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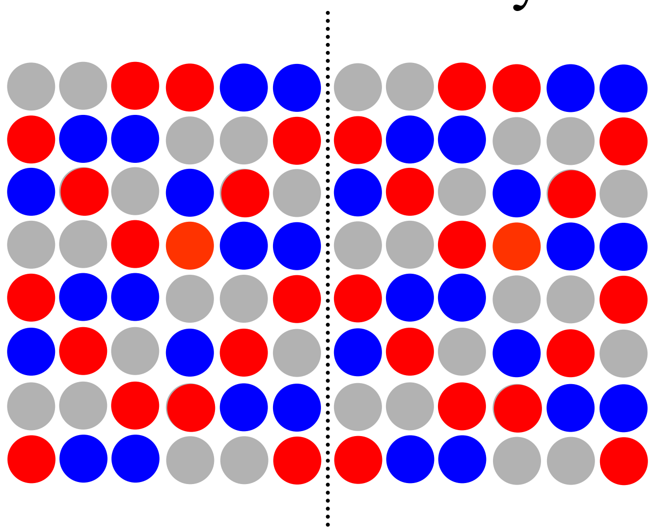
RIS in Austenitic Stainless Steels

Grain Boundary



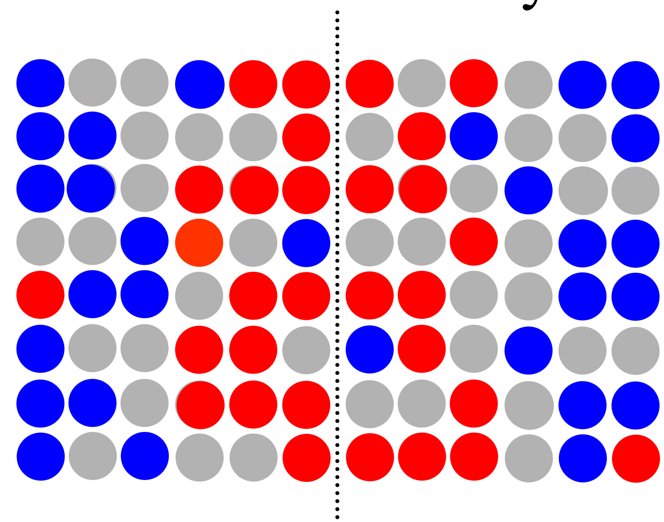
Before Irradiation

Fe, Cr, Ni

Ni enriches

Cr depletes

Grain Boundary



After Irradiation

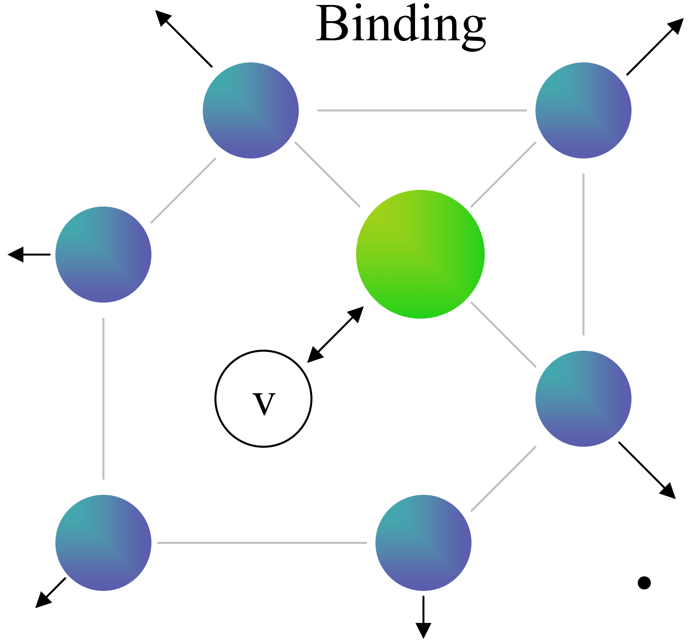
Ni: Migrates preferentially as interstitials

Cr: Exchanges preferentially with vacancies

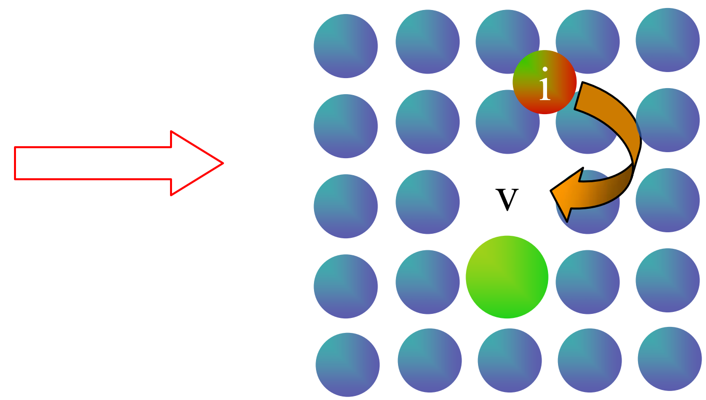
Oversized Solutes – Theory

$$\Omega_{solute} > \Omega_{matrix}$$

Solute-Vacancy Binding



Enhanced Recombination



- Solute-vacancy binding energy must be large for an observable effect
- Assumes oversized solute acts as immobile trap (solute remains in solution)

Oversized Solutes – Results

- Past results generally show a reduction in Cr depletion and Ni enrichment in oversized solute alloys; however, some results are contradictory and no comprehensive studies have been performed[1-8]
- Purpose here is to conduct a systematic study over a range of temperatures, doses and alloys (solute type) to understand conflicting results

[1] Kato, T., et al., *JNM*, 189 (1992) 167

[2] Shigenaka, N., et al., *JNST*, 33 (1996) 577

[3] Kasahara, S., et al., *JNM*, 239 (1996) 194

[4] Fournier, L., et al., *JNM*, 321 (2003) 192

[5] Sakaguchi, N., et al, *Nuc. Inst. Meth. Phys. Res. B*, 153 (1999) 142

[6] Gan, J., et al., *JNM*, 325 (2004) 94

[7] Dumbill, S., et al., *6th Int'l Conf. Env. Deg. Mat. in Nuc. Pw. Sys.*, (1993) 521

[8] Allen, T., et al., DOE Progress Report, Grant No. DE-FG07-03ID14542 (2005)

Approach

- Because of their large size, Zr and Hf additions in varying concentrations are made to 316-type SS

Sample Composition (wt%)

Alloy ID	Fe	Cr	Ni	Mo	C	Mn	Si	Zr	Hf
316-Zr-Ref	Bal.	14.34	13.45	0.16	0.05	1.21	0.38	-	-
316+LoZr	bal.	14.40	13.55	0.18	0.050	1.30	0.38	**0.310**	-
316+HiZr	bal.	13.91	13.48	0.17	0.050	1.18	0.40	**0.450**	-
316-Hf-Ref	bal.	17.65	13.85	2.23	0.022	1.00	0.12	-	-
316+LoHf	bal.	17.42	13.45	2.18	0.025	1.01	0.14	-	**0.16**
316+HiHf	bal.	17.03	13.6	2.18	0.028	1.01	0.10	-	**1.17**

Linear Size Factor

$$l_{sf} = \left\{ \left(\frac{\Omega_{solute}}{\Omega_{matrix}} \right)^{1/3} - 1 \right\} \times 100(\%)$$ [1]

Element	Atomic Density (atoms/cm^3)	Atomic Volume (Å^3/atom)
Fe	8.49E+22	11.8
Cr	8.27E+22	12.1
Ni	9.13E+22	10.9
Zr	4.29E+22	23.3
Hf	4.48E+22	22.3

Size Factor (%)	**Zr**	**Hf**
Fe-Cr-Ni	**25.7**	**23.9**

Zr and Hf have the same size so similar RIS results are expected

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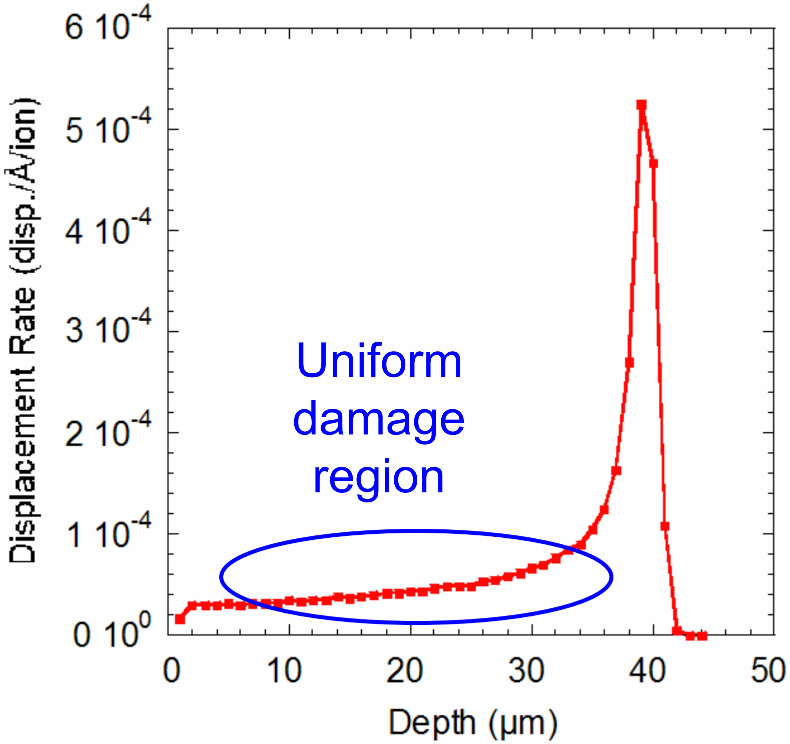
[1] H.W. King, *Journal of Materials Science*, 1 (1966), 79

Proton Irradiation

- Irradiation with 3.2 MeV H^+ with the tandem accelerator at the Michigan Ion Beam Laboratory (MIBL) at University of Michigan
- Irradiation at 400°C ±10°C to doses of 3, 7, 10 dpa
- Damage layer in first 40 µm
- Nearly uniform damage ~ from 5 - 35 µm; analysis done in this damage region



Objectives of SHaRE Work

- Use STEM-EDS to study grain boundary microchemistry
  - Show that additions of the oversized solutes Zr and Hf to austenitic SS reduce Cr depletion
- Use FIB and LEAP to study matrix composition
  - Verify that oversized solutes remain in solution for the purpose of vacancy trapping to enhance recombination
  - Changes to grain boundary microchemistry can be attributed to oversized solutes only if they are in solution

Results

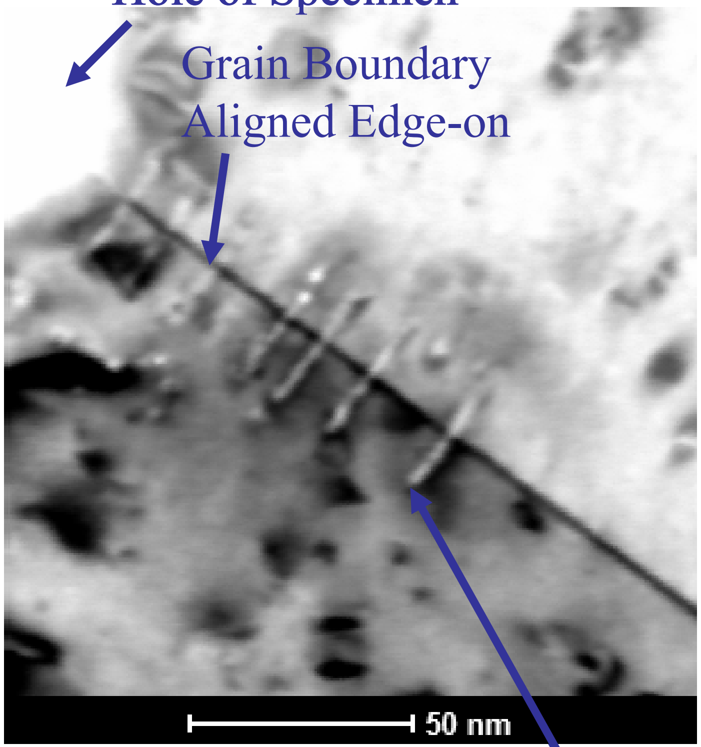
Transmission Electron Microscopy

- Use the Philips CM200 at ORNL to measure grain boundary chemistry and determine RIS
  - Instrument must be equipped with a field emission gun (FEG) for high intensity, capable of scanning mode (STEM), and paired with electron dispersive X-ray spectroscopy (EDS)

Microchemistry Measurements

Hole of Specimen

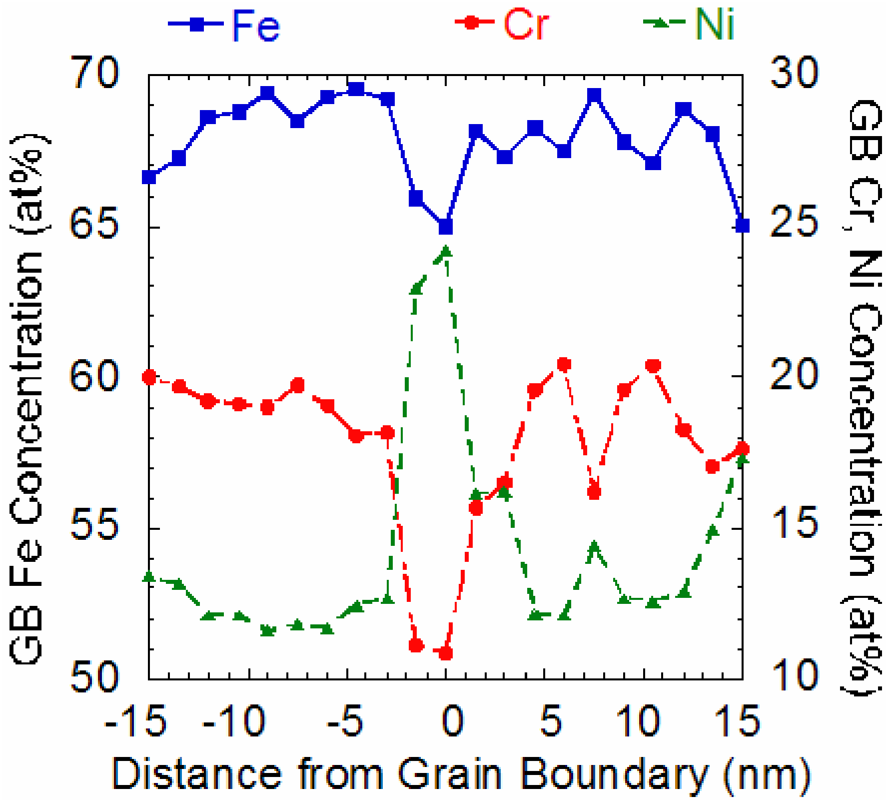
Grain Boundary Aligned Edge-on



700,000 X Magnification

e^- beam damage from RIS profile

Concentration from Single RIS Profile



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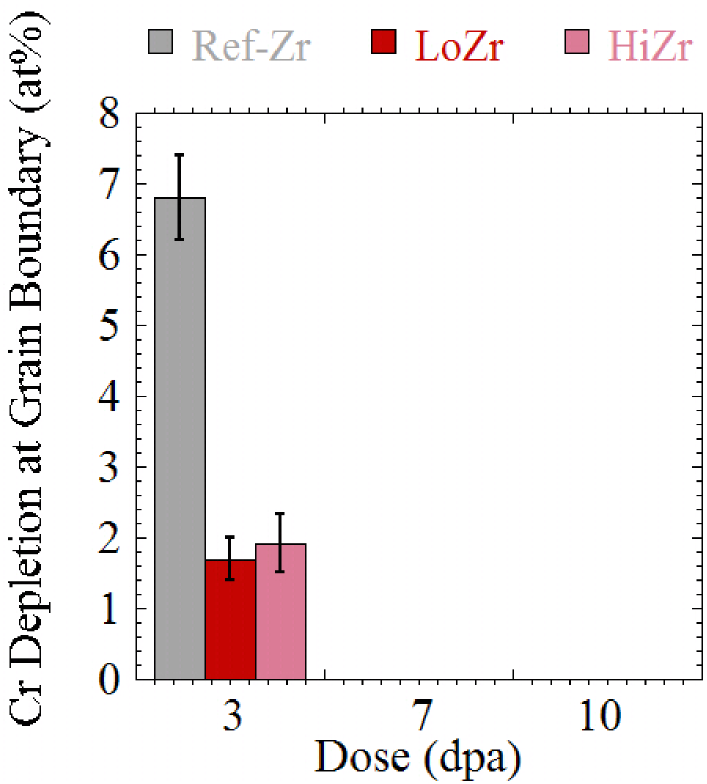
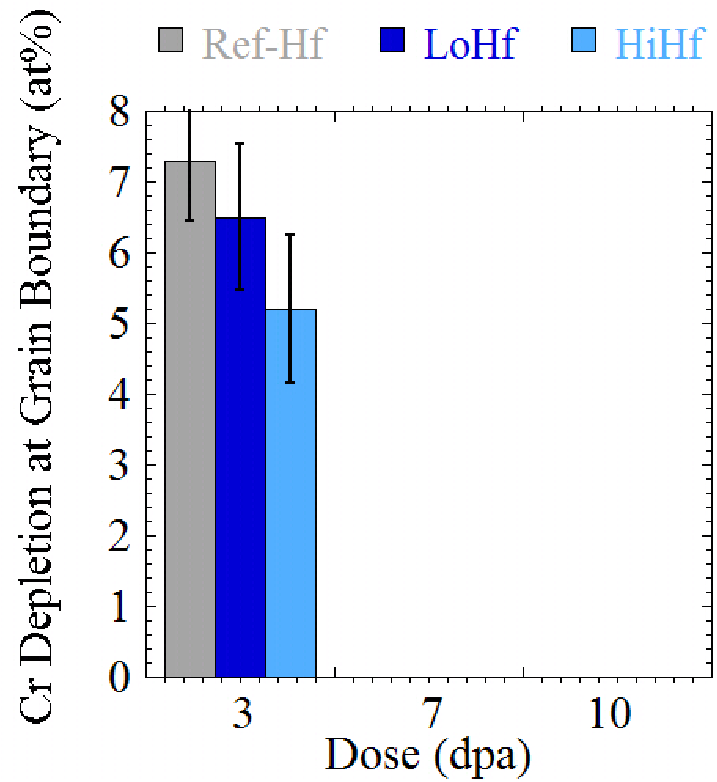
RIS Results (I)





- At 3 dpa, Zr addition results in greater reduction in Cr depletion than Hf addition

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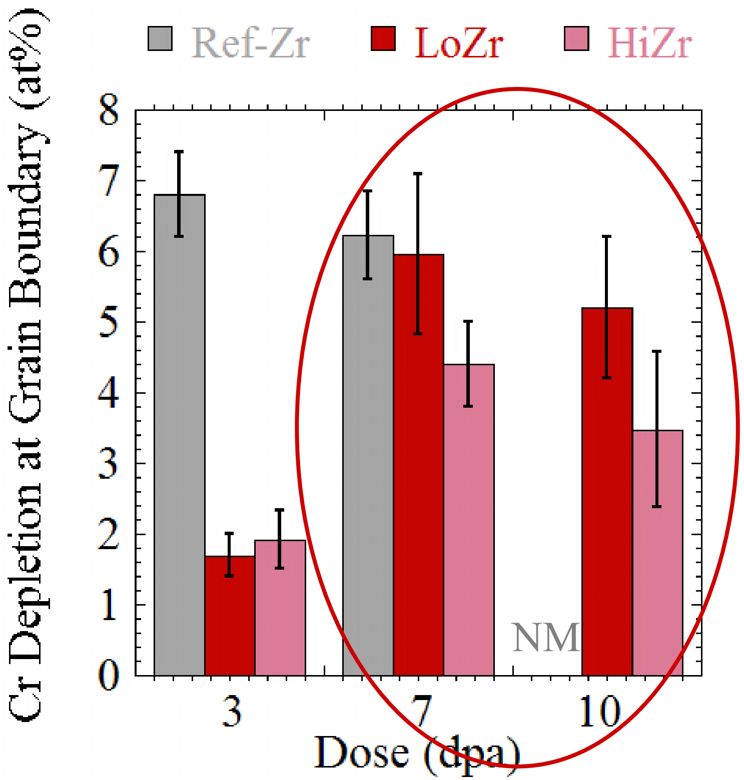
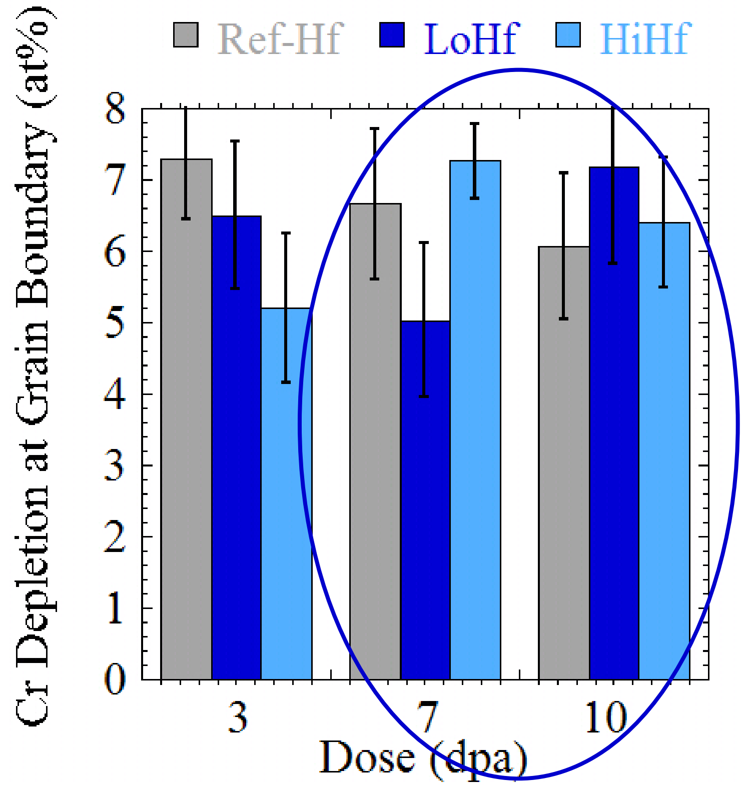
RIS Results (II)





- By 7 and 10 dpa, reduction in Cr depletion less substantial for Zr addition; no effective difference in Cr depletion between Hf alloys and reference
- Fournier et al. saw large (transient) reduction in Cr depletion at 2.5 dpa for Hf addition to 316SS; only small reduction at 5 dpa

[4] Fournier, L., et al., *JNM*, 321 (2003) 192

RIS Results (III)

Why the difference in RIS results between Zr and Hf?

→

Turn to first principles calculations

Ab initio Calculations

- Vienna *Ab initio* Simulation Package (VASP)
- VASP is a first-principles quantum-mechanical code where an atom nucleus is treated in a classical sense and the electrons are treated quantum mechanically
- VASP can be used to determine fundamental interaction energies between atoms and with defects
- Calculations performed with 108-atom cells

- Size factor → lattice parameter for fcc Fe, Zr, Hf
- Solute-vacancy binding energy → effect on RIS

Atom Species	Lattice Parameter (Å)	Size Factor (%)
Fe (fcc)	3.447	-
Zr (fcc)	4.531	31.42
Hf (fcc)	4.467	29.58

Hf Binding Energy = 0.69 eV

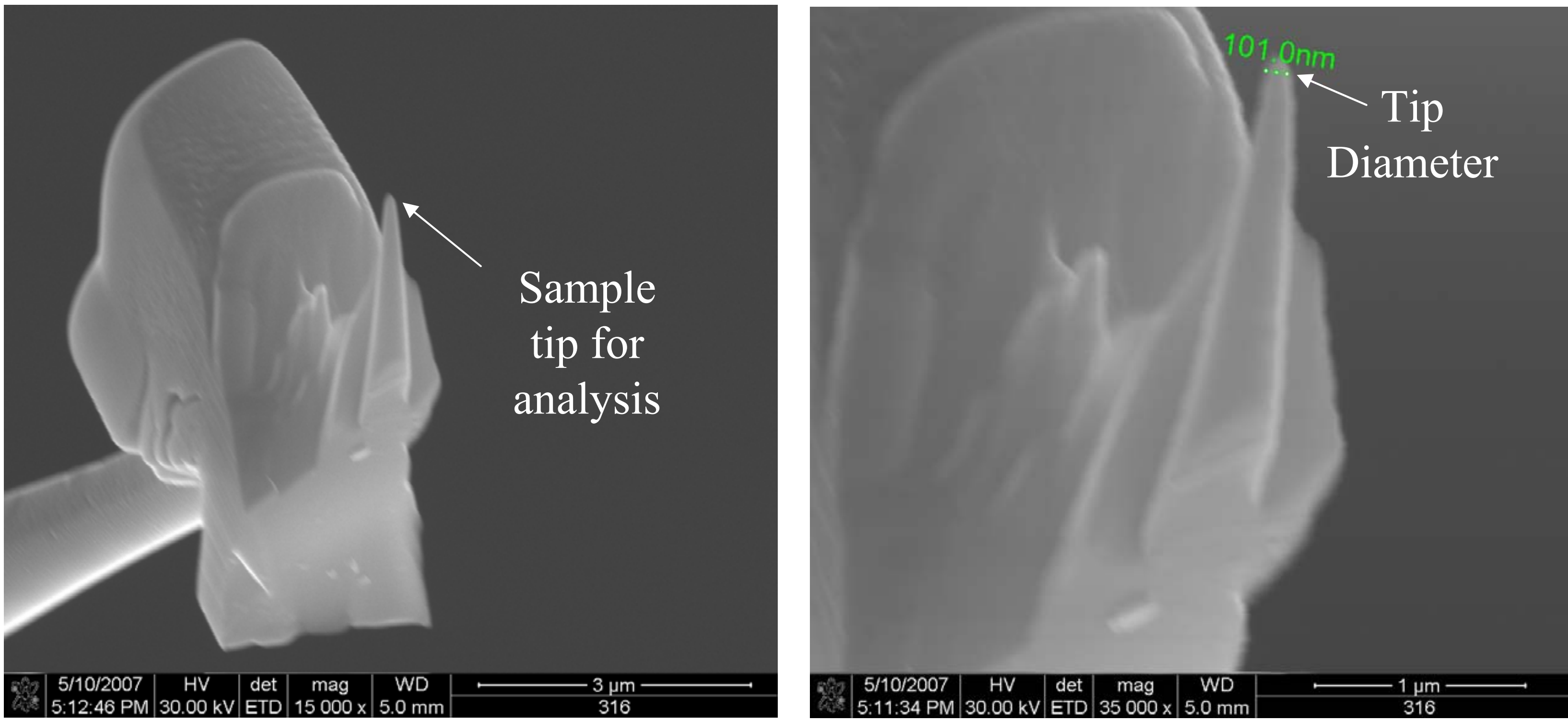
Zr Binding Energy = 1.05 eV

Hackett, M. J., et al., *Metall. Mat. Trans. A*, In Publication, (2007)

Local Electrode Atom Probe (LEAP)

- All methods for identification of matrix oversized solute – including TEM, SEM, WDS, XPS and X-ray Diffraction – were inconclusive because of low concentration and presence of small precipitates
- The Imago Scientific LEAP™ at ORNL can sample small volumes for elemental identification with atomic resolution

Specimen Preparation



Focused Ion Beam (FIB) milling of sample tip

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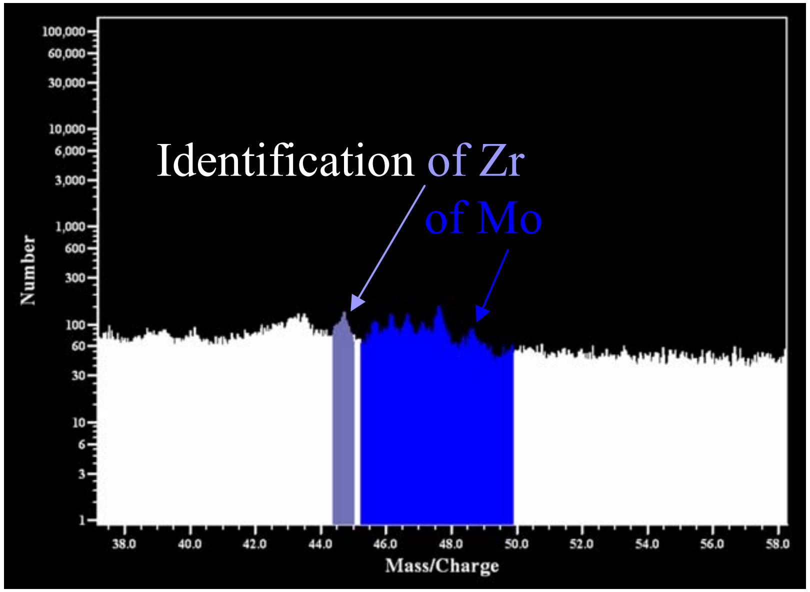
Oversized Solute Detection

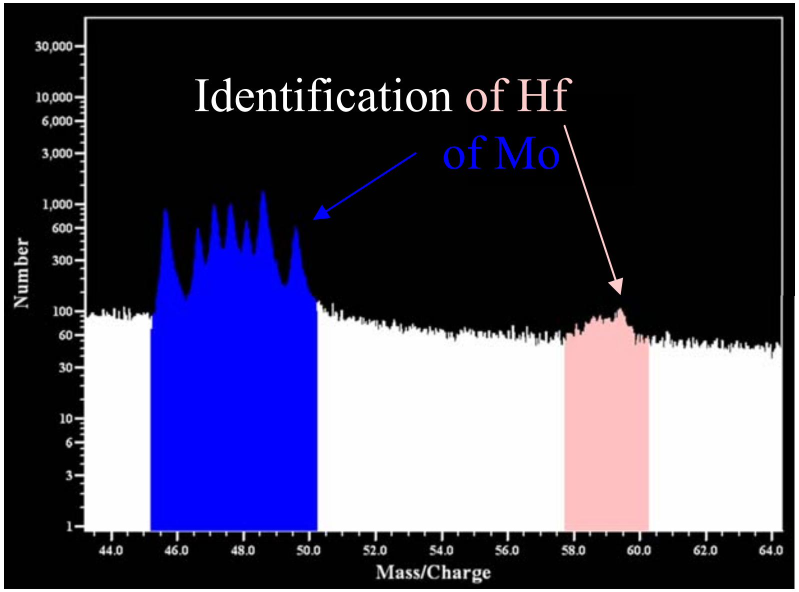
- Samples of the oversized solute alloys were prepared in the unirradiated and irradiated conditions, both 3 and 7 dpa
- Results generally verified the presence of Zr or Hf in the matrix
  - Absence of a peak for oversized solute does not preclude its presence, but means it was below the detection limit

Mass/Charge Spectra

- Oversized solute identified in 7 of 12 samples and did not appear to be dependent upon radiation dose



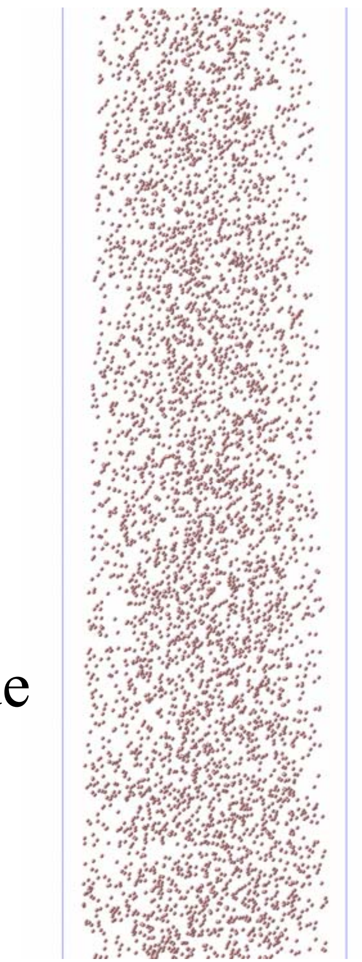
Mass/Charge spectrum showing Zr^{2+} and Mo^{2+}

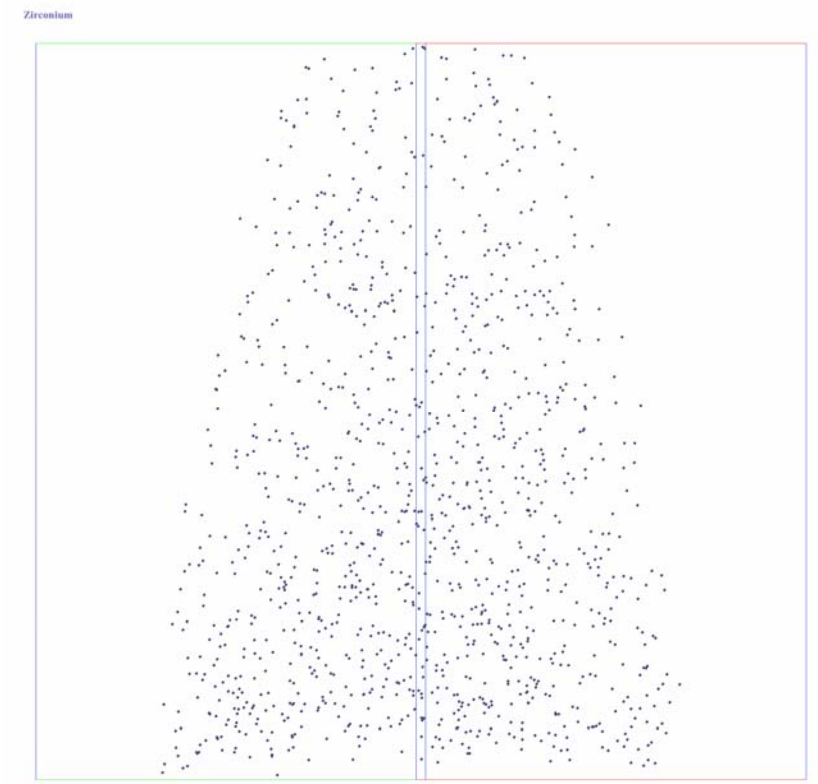


Mass/Charge spectrum showing Hf^{3+} and Mo^{2+}

Hf, Zr in Solution

- Hf appears to be uniformly distributed
- No Hf-rich precipitates visible; Hf peaks in mass/charge spectra are due only to Hf remaining in solution

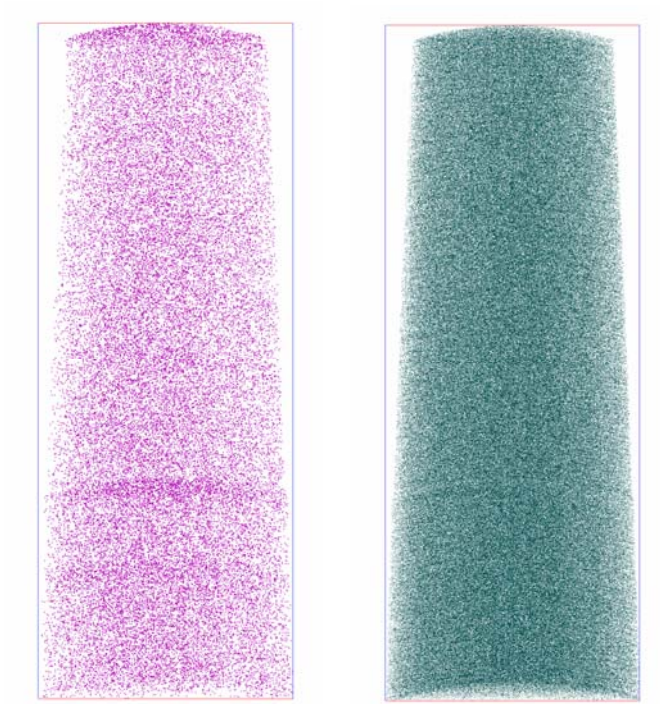




- Zr is also uniformly distributed
- Effort to verify oversized solute remaining in solution was successful

Precipitation of Ni and Si

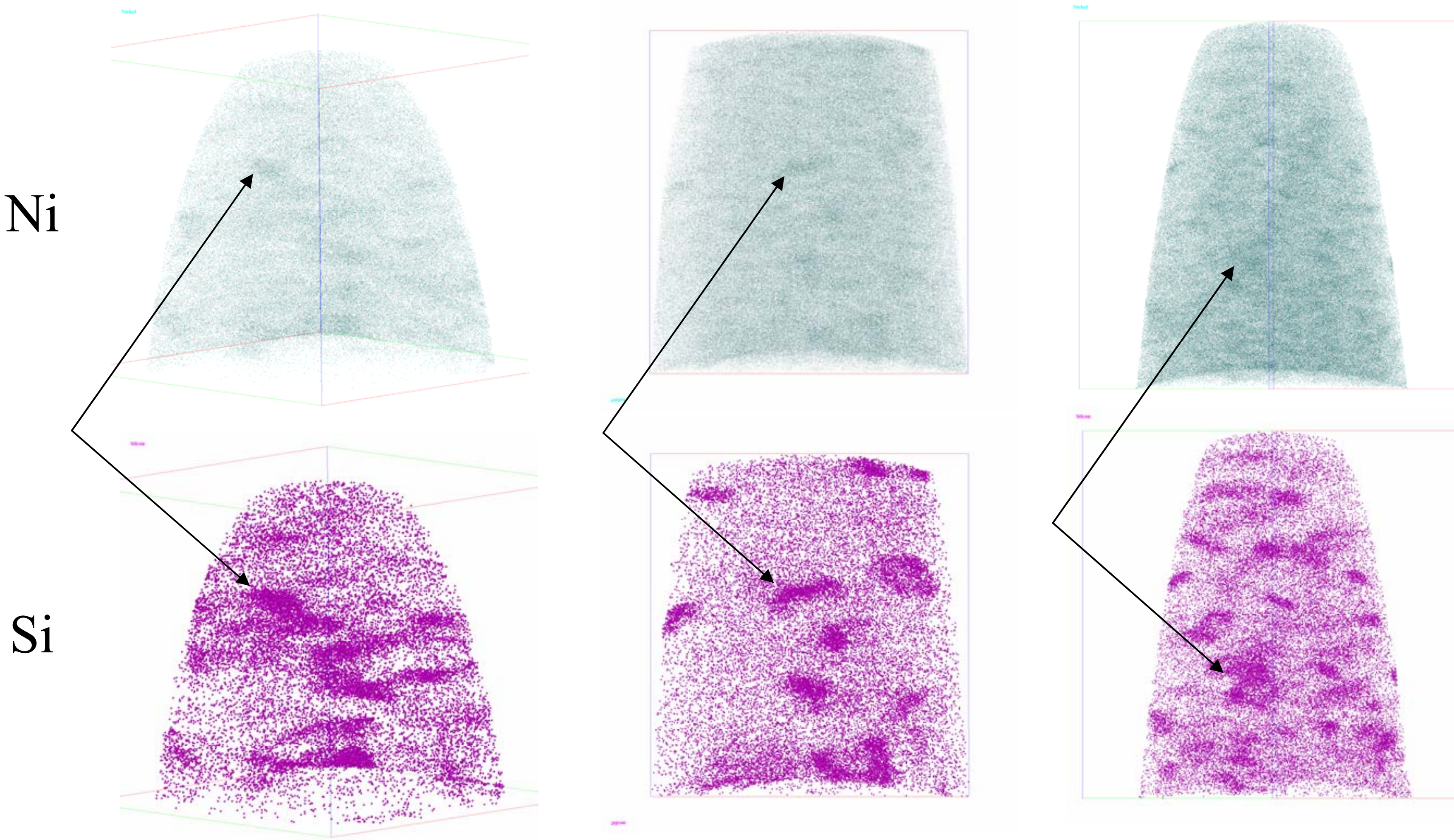
Unirradiated Specimen



Si Ni

No apparent precipitation of Ni or Si has formed prior to irradiation

Precipitation of Ni and Si



Evidence of small, radiation-induced NiSi phases not observed in TEM

Summary

- Through STEM-EDS, oversized solute additions show decreases in RIS
- Zr shows less RIS than Hf at 3 dpa due to increase in binding energy for vacancy trapping
- Presence of Zr and Hf in the matrix can be verified through FIM using FIB and LEAP^{TM}

Acknowledgments

- I would like to thank my collaborators at ORNL, Jeremy Busby and Mike Miller
- I would also like to thank Jim Bentley, Ed Kenik and Neal Evans at ORNL who have provided me with tremendous support in the SHaRE program