DOE-NE Materials Crosscut Coordination Meeting

Radiation Tolerance of Nanostructured Ceramic/Metal Composites

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University of Nebraska Lincoln | NEBRASKA CENTER FOR ENERGY SCIENCES RESEARCH

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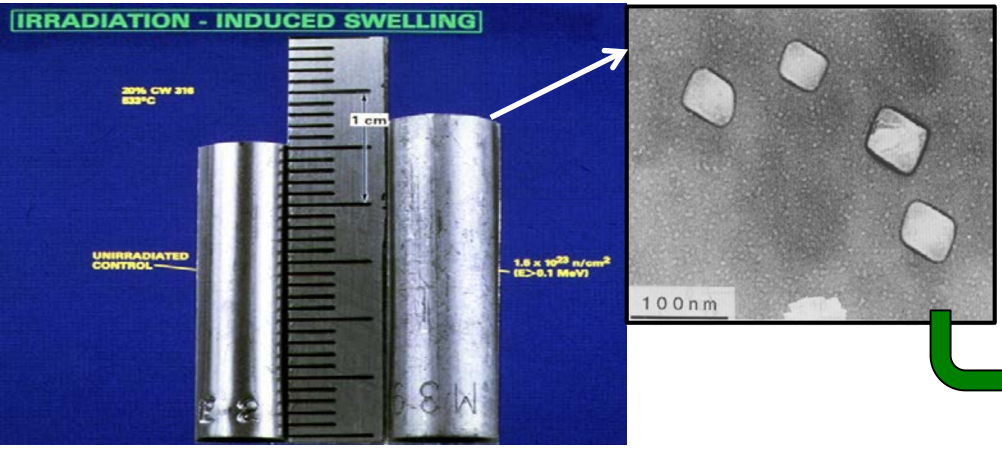
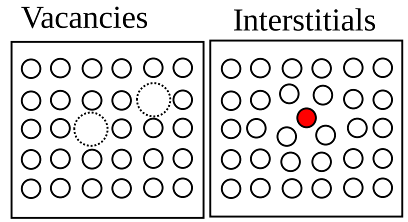
U.S. DEPARTMENT OF ENERGY

What is the problem

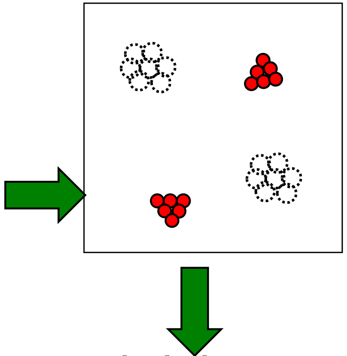
Structural materials are prone to radiation damage: *void swelling and embrittlement*



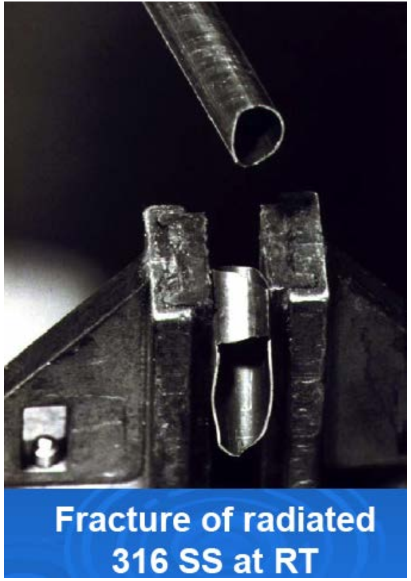
Atomic defects produced by irradiation



Defects that do NOT recombine aggregate into vacancy or interstitial clusters



Embrittlement

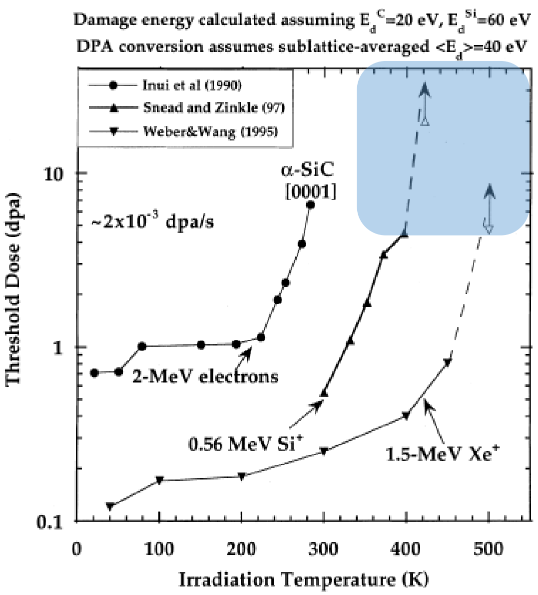


Fracture of radiated 316 SS at RT

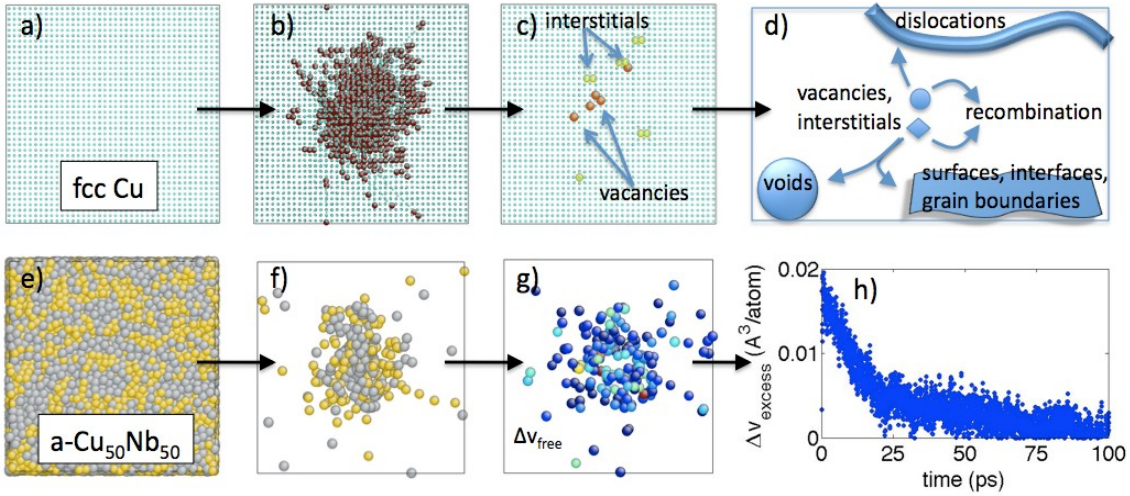
D.L. Porter and F. A. Garner, J. Nuclear Materials, **159**, p. 114 (1988)
D.J. Bacon and Y.N. Osetsky, Int. Mater. Rev., **47**, p. 233 (2002).
H. Trinkaus and B.N. Singh, J. Nuclear Materials, **323**, p. 229 (2003).

How to design radiation damage tolerant materials?

From crystalline to amorphous materials



Upper limit



Questions:

- **How do amorphous materials respond to radiation damage**
- **Are the interfaces between crystalline and amorphous materials also effective defect sinks?**

L.L. Snead *et al*., Nucl. Instr. and Meth. in Phys. Res. B 141, p. 123 (1998).
R. E. Baumer *et al*., Materials Research Letters, 2, p 221 (2014).

Team capabilities

nanostructured amorphous-ceramic/metal composites

Sample Synthesis

1. Sputtering (thin film)
2. Pyrolysis, plasma-enhanced sintering (bulk)

Ion Irradiation and He Ion Implantation

1. Si ions: 0.5-3 MeV,
2. Fe ions: 0.5-4 MeV.
3. He ions: 50-140 keV

Microstructure and Mechanical Properties Evaluation

1. TEM, SEM, XRD
2. Nanoindentation testing

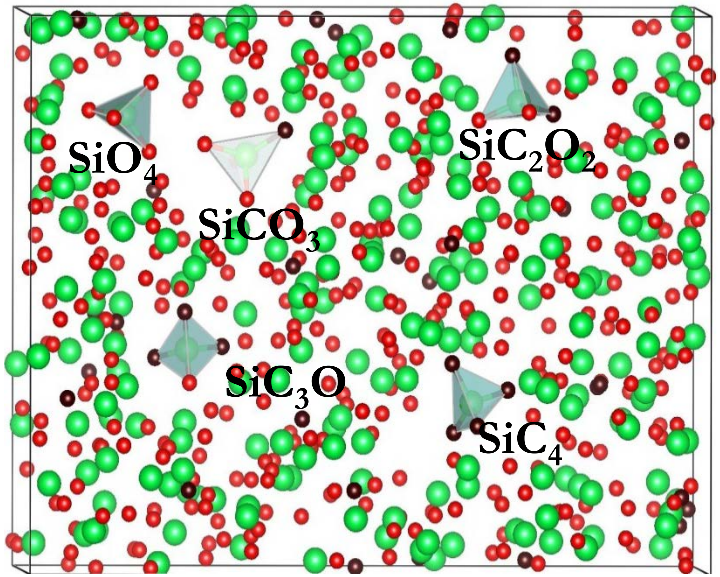
Atomistic Modeling

1. First principles density functional theory (DFT)
2. First principles molecular dynamics (MD) simulations

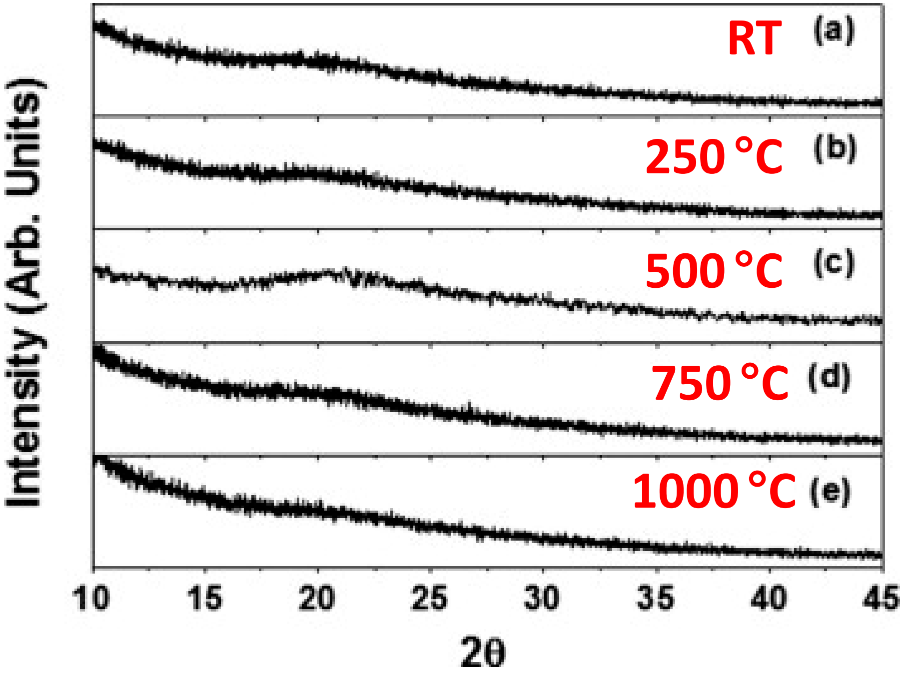
Outline

- **Radiation tolerance of amorphous SiOC**
- **Radiation tolerance of Fe/SiOC nanocomposites**
- **Modelling**
- **Summary**

Thermal stability of amorphous SiOC



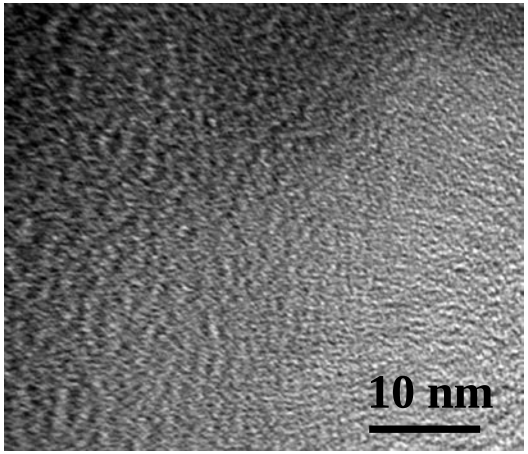
Green: Si, Red: O, and Brown: C
Five types of tetrahedra units



Amorphous SiOC is stable >1000 °C and with good oxidation and creep resistance

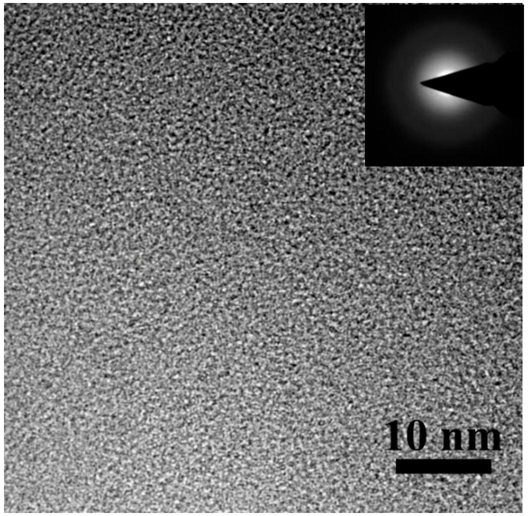
Irradiation stability of amorphous SiOC

As-prepared



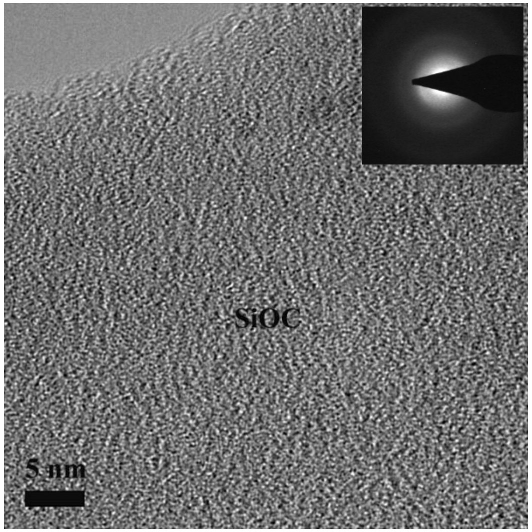
600 °C irradiation

*100 keV **He**, 20 dpa*



300 °C irradiation

*1 MeV **Kr**, 5 dpa*



SiOC remains amorphous!!!

Summary of Kr and He irradiation

Ion species	Kr	He
Acceleration voltage	1 MeV	120 keV
Cascade type	Large damage cascade zones	Scattered point defects
Irradiation temperature	RT to 300 °C	RT to 600 °C
Dose	Up to 5 dpa	Up to 20 dpa
Crystallization	No	No
Void formation	No	No

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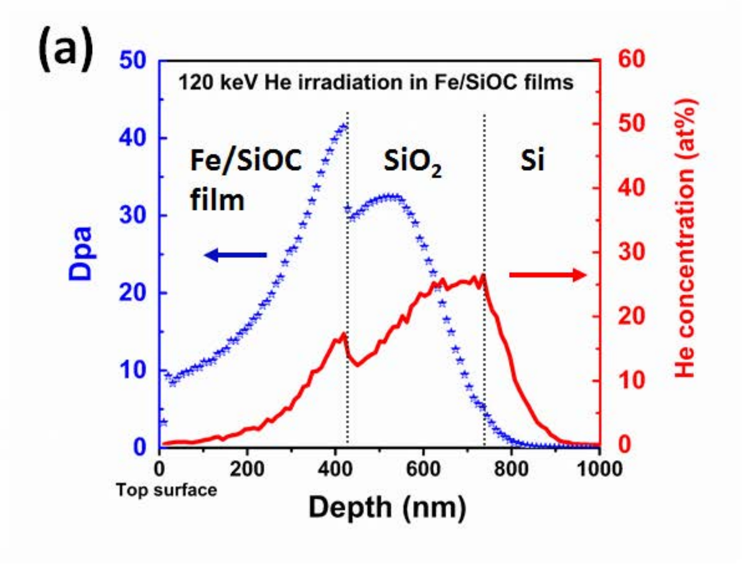
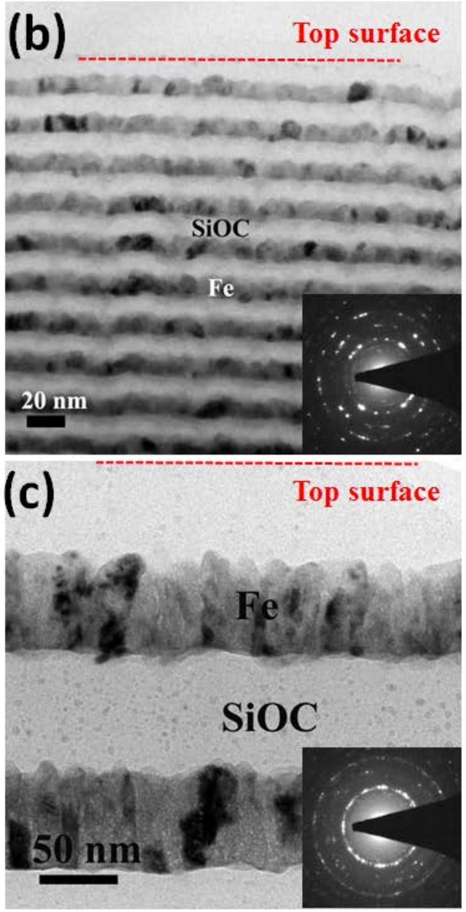
Development of Fe/SiOC composite

Goal: To possess good mechanical properties, be capable of operation at temperatures greater than 500°C, and have extreme radiation tolerance.

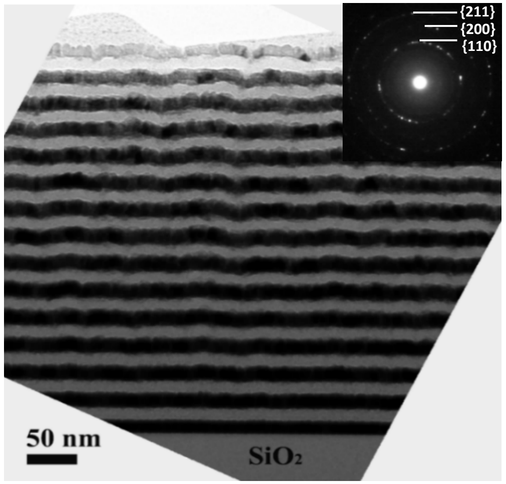




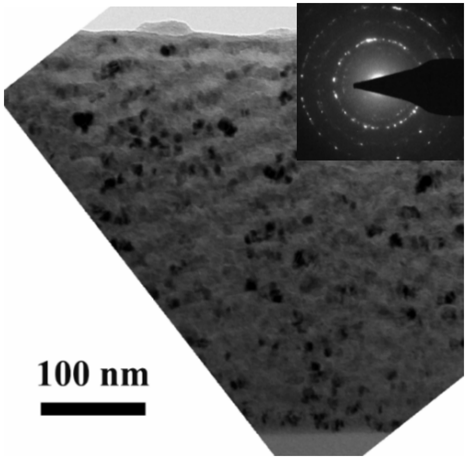
Fe/SiOC interface acts as an efficient point defects sink and results in good radiation stability of Fe/SiOC composite system.

Temperature-dependent Kr irradiation

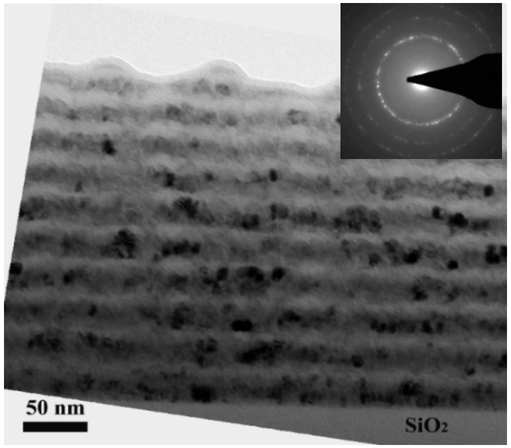
(a) Virgin



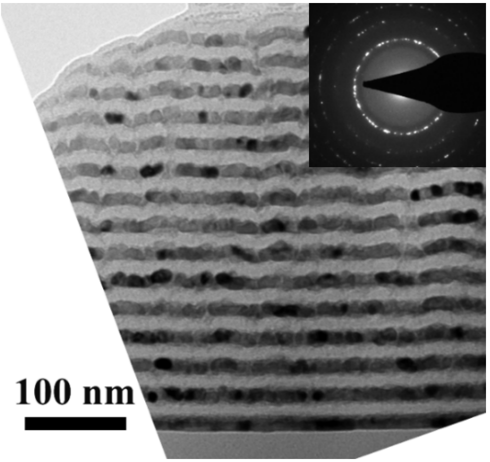
(b) 50K, 4×10^{14} ions/cm^2



(c) RT, 4×10^{14} ions/cm^2



(d) 300 °C, 8×10^{14} ions/cm^2



More radiation stability at elevated temperatures (thermodynamically stable) which benefits engineering applications.

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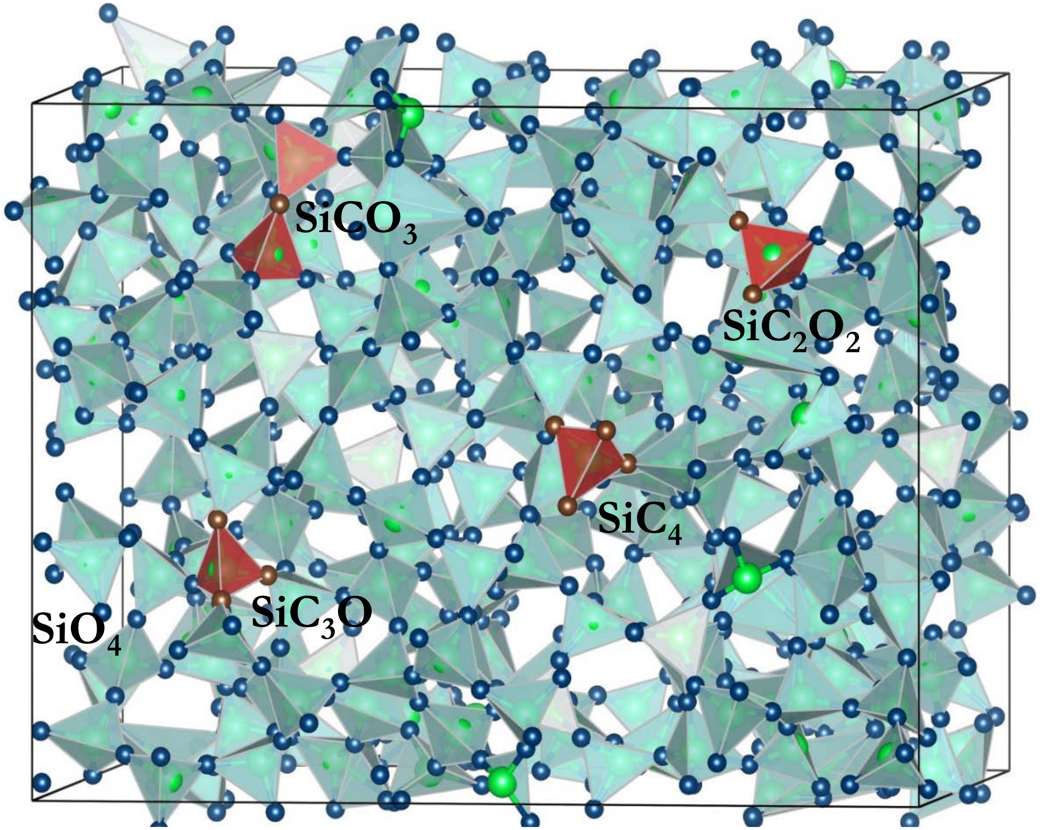
Atomic structure of SiOC

Amorphous SiOC = **continuous random network of SiOC** + free C phase + segregated SiC
Non-crystalline: disordered, but not random

- Short range order --- SiC_nO_{4-n} tetrahedra (*n* ranges from 0 to 4)
- Medium range order --- tetrahedra are corner-sharing



Si atoms in **Green**

O atoms in **Blue**

C atoms in **Brown**

How is the C distributed?

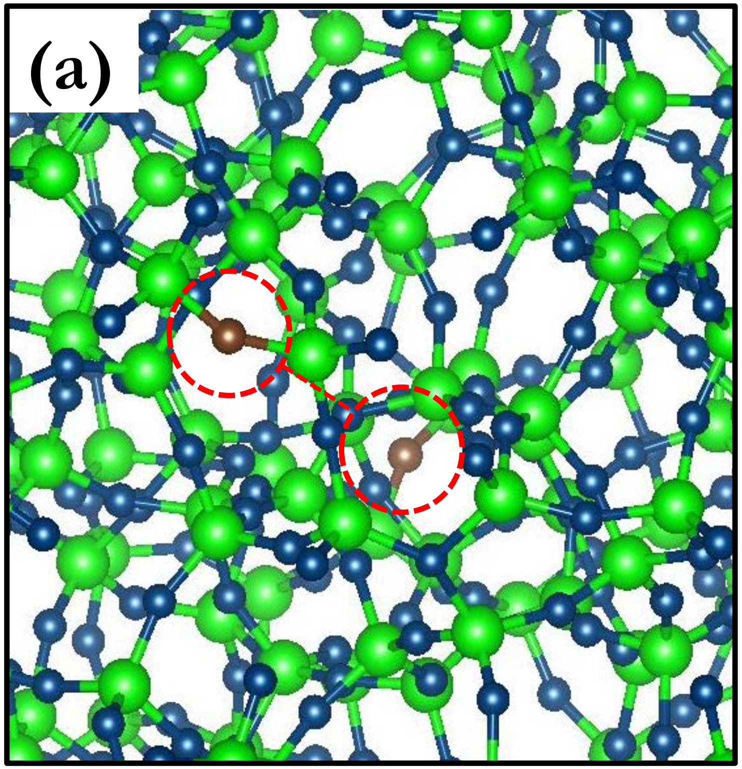
Generation of amorphous SiOC

Classical melting and quenching **fails** for SiOC because of CO/CO_2 formation

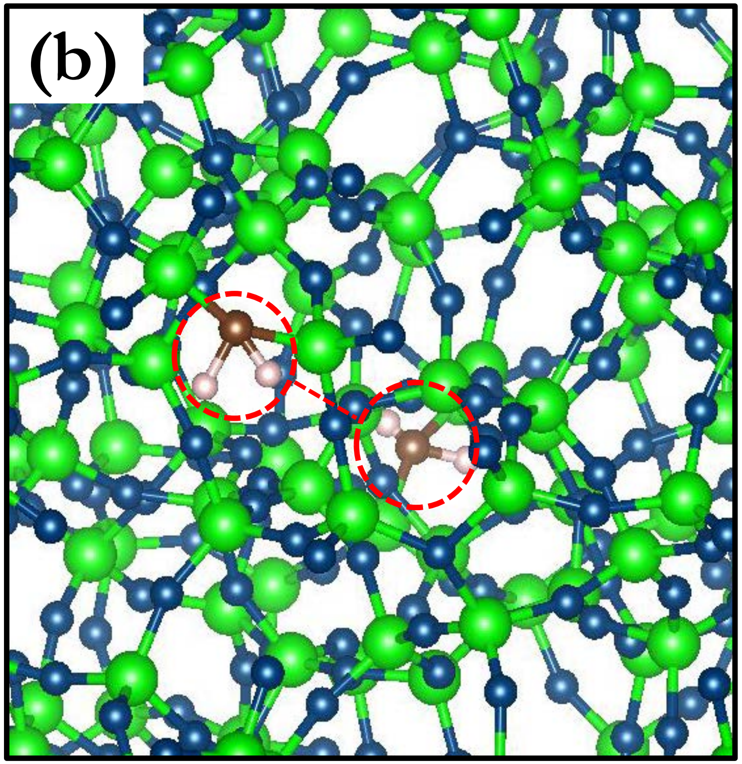
Only thermally stable below ~ 1500 K; Phase separation before melting

We start from amorphous SiO_2 (SiO_2 and SiOC share the same basic tetrahedral units)

Introduce C (a) or CH_2 (b) as dopants to replace O



(a) Replace O with C



(b) Replace O with CH_2

C-C interactions in SiOC (DFT)

(a) C replacing O

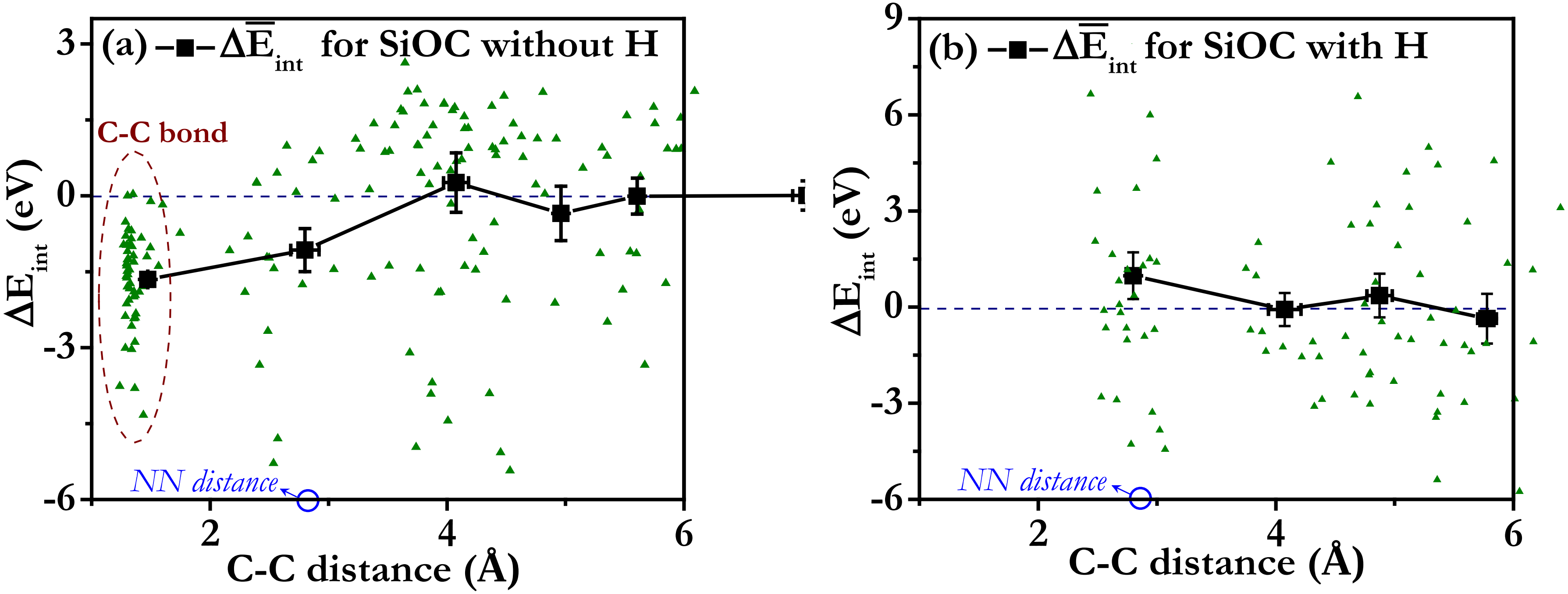
C-C interaction attractive at nearest neighbor (NN) distance

➔ Clustering of C atoms

(b) CH_2 replacing O

C-C interaction repulsive at NN distance

➔ Uniform dispersal of C atoms



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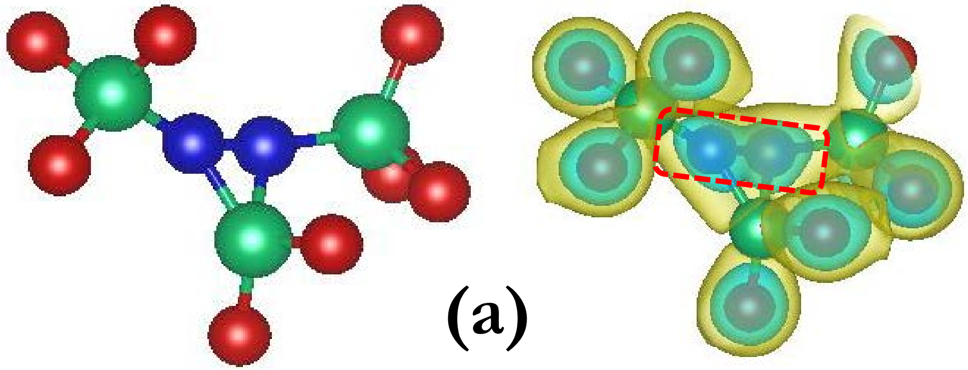
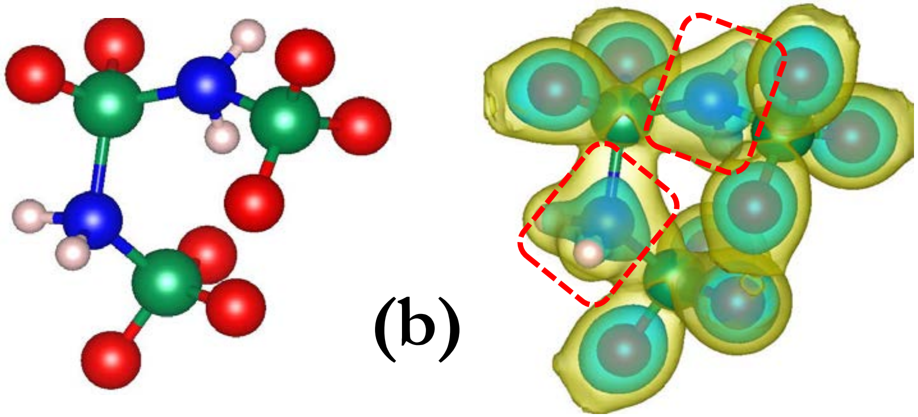
Bond configurations of C atoms

(a) Without H: Direct C-C bond formation

Initiation of phase separated C network

(b) With H: No direct C-C bonding



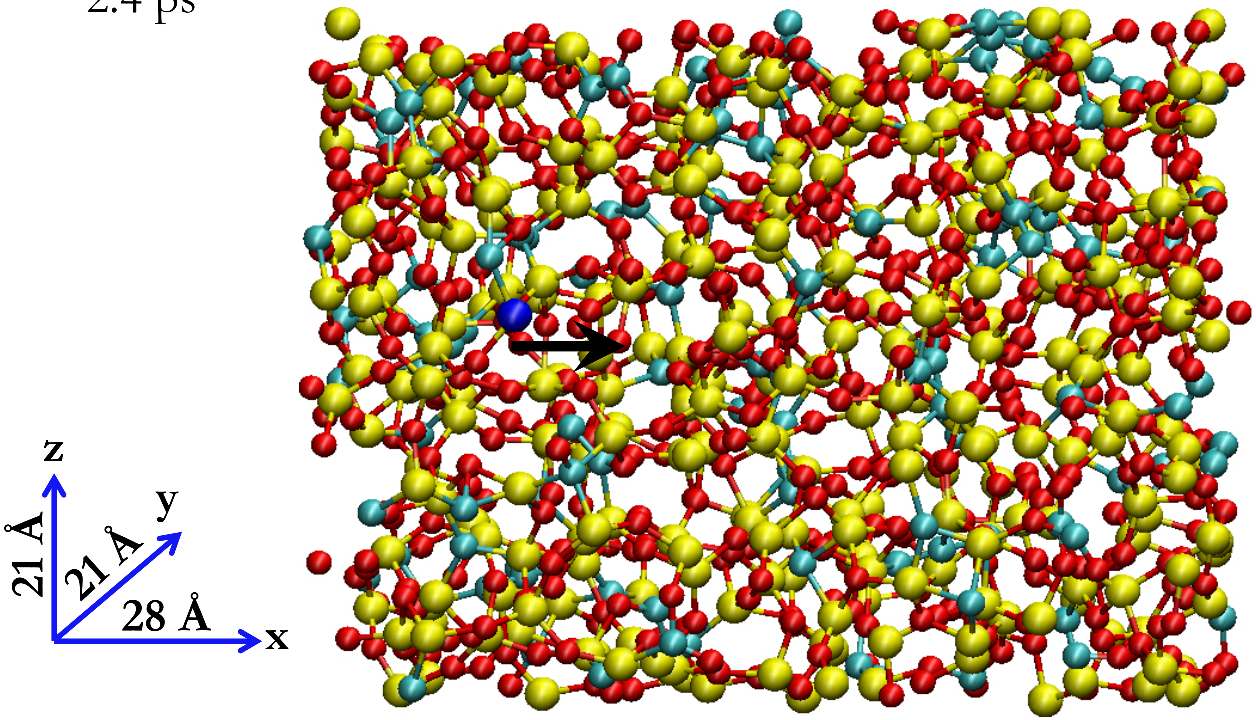


Knock-on damage in SiOC: first principles molecular dynamics (MD)

DFT MD using VASP: PAW-PBE, 500 eV, Gamma point only
Primary knock-on atom (PKA) kinetic energy: 100 eV

0 K $\xrightarrow{\text{Heating}}$ 300 K $\xrightarrow{\text{PKA}}$ ~1200 K $\xrightarrow{\text{Ion collision}}$ ~700 K $\xrightarrow{\text{Quenching}}$ 300 K

Heating	PKA	Ion collision	Quenching
NVT (Nosé)	100 eV	NVE	NVT (Nosé)
50 K increment		0.25 fs timestep	100 K increment
1 fs timestep		0.5 ps	1 fs timestep
2.4 ps			2.0 ps



Si atoms in
Yellow
O atoms in
red
C atoms in
Cyan
PKA atom in
Blue

Potential energy change due to knock-on

- SiO_2

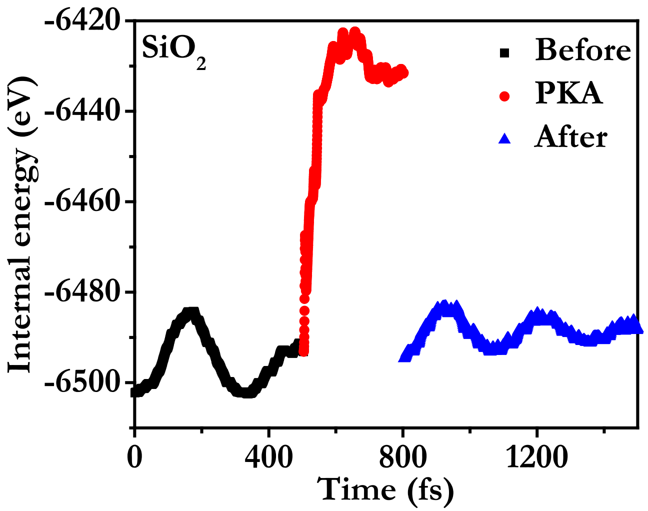
  Potential energy slightly increases

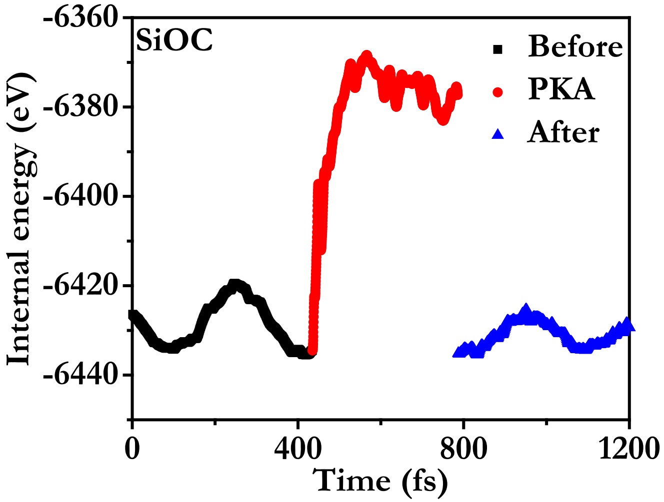
  --- Less stable after knock-on

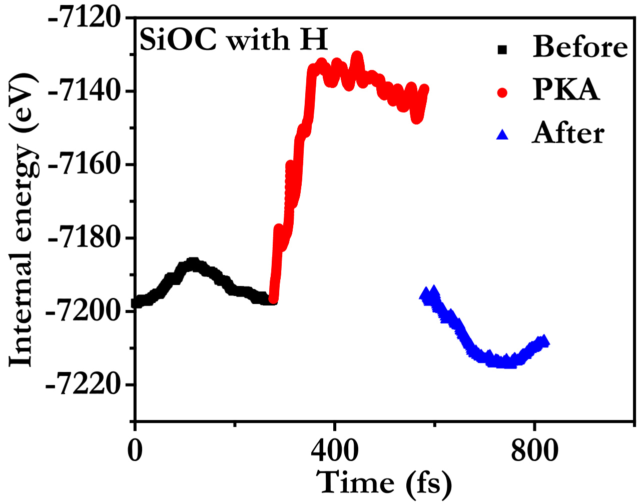
- SiOC and SiOC with H

  Potential energy the same or lower

  --- Stable upon knock-on



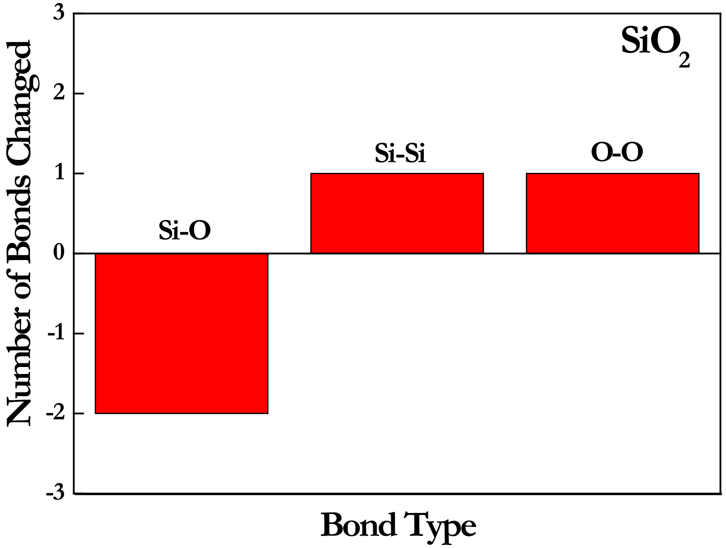


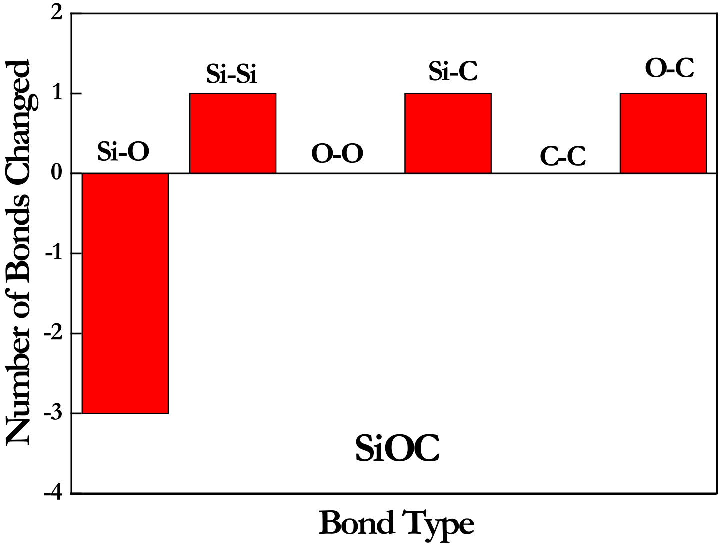


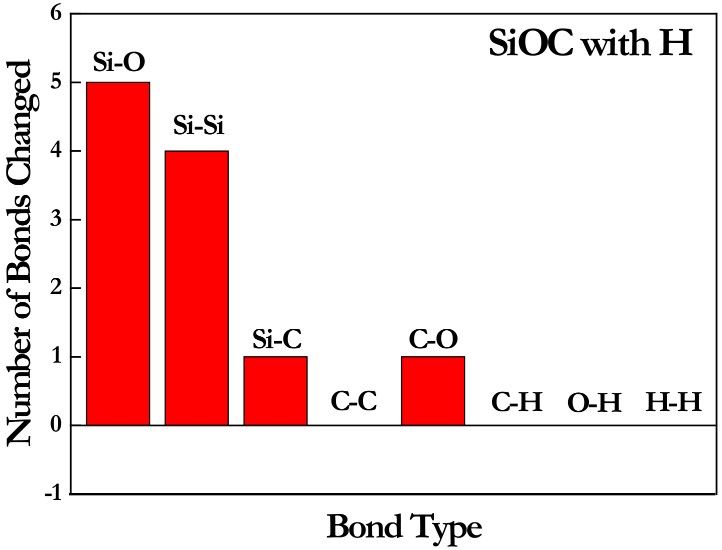
Bond breaking and reformation due to PKA

Number of bonds broken and reformed

- SiO_2
  - --- 26 broken, 26 reformed
- SiOC
  - --- 36 broken, 36 reformed
- SiOC with H
  - --- 36 broken, 48 reformed







Summary: Experimental

- Amorphous SiOC is radiation stable (He and Kr)

I. 20 dpa at 600 °C (He)

II. 5 dpa at 300 °C (Kr)

- Irradiation stability of Fe/SiOC nanocomposite

I. Room temperature stability up to ~40 dpa.

II. Amorphous SiOC/crystalline Fe interface is demonstrated as defect sinks.

III. Enhanced stability at elevated temperature.

Summary: Modelling

Amorphous SiOC

- **Without H, C-C interaction is attractive, C tends to cluster**
- **With H, C-C interaction is repulsive, C tends to disperse**

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Knock-on damage in amorphous SiO_2, SiOC, and SiOC with H:

No major structural change up to 1200 K --- thermally stable

- **SiO_2**

  Broking of Si-O bonds, formation of Si-Si and O-O bonds

- **SiOC and SiOC with H**

  No individual CO, CO_2 or H_2O molecules formed due to ion irradiation

Going Forward

- **Year 1**: Evaluation of the role of Fe/SiOC interfaces on defect mitigation out to harsher environments with >300 dpa and >500 °C. Evaluate the role of SiOC and Fe/SiOC interfaces on He incorporation. Determine mechanical properties (hardness, elastic modulus, fracture toughness and creep resistance) of SiOC and SiOC/Fe composites of various compositions, layer thicknesses, and volume fractions as a function of irradiation damage levels and irradiation temperatures. Continued development of empirical potentials and atomic structure descriptions for the amorphous alloys.
- **Year 2**: Further optimize compositions of SiOC ceramics and layered structures of Fe/SiOC to achieve the maximum radiation tolerance, and determine the roles of Fe and SiOC volume fractions on overall radiation tolerance, swelling resistance, and He solubility. Continue mechanical property evaluations. Multiscale modeling through integration of first principles calculations and molecular dynamics simulations to shed light onto the interactions of defects and gas atoms with interfaces.
- **Year 3**: Detailed experimental studies of irradiated composites using Fe(Cr) accompanied by modeling of cascade damage, defect behavior, swelling behavior, and diffusion. Mechanical property evaluations. Integration of modeling and experiments to shed light onto fundamentals and identify governing factors, which determine the maximum radiation tolerance of the composite materials.