Progress in TMSR Materials Research

Hefei Huang

Shanghai Institute of Applied Physics, Chinese Academy of Science (CAS)

钍基熔盐堆

中国科学院上海应用物理研究所
Shanghai Institute of Applied Physics, Chinese Academy of Sciences
SINAP

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Outline

1 TMSR Materials Introduction

2 Research Progress of the UNS N10003 alloy

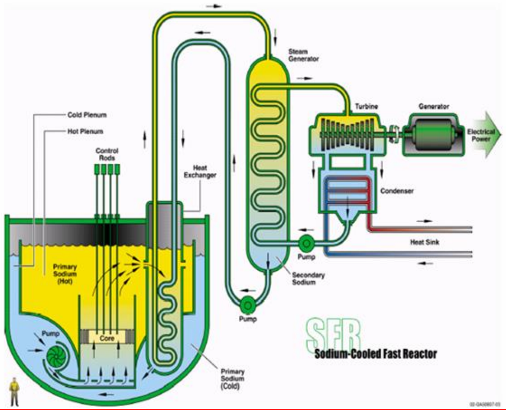
- Fabrication, Corrosion & Mechanical Property Testing
- Neutron and Ion Irradiation Activities

3 Research Progress of ultrafine-grain graphite

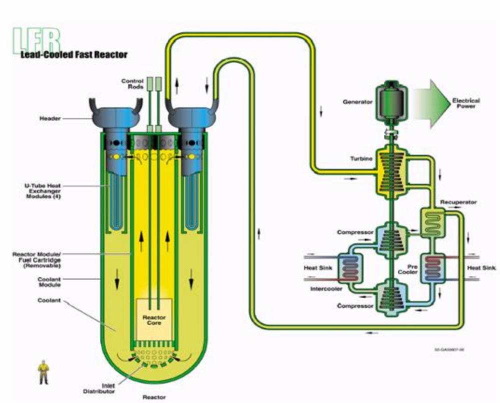
- Property of Ultrafine-grain Graphite
- Neutron and Ion Irradiation Activities

4 Next plan for TMSR materials research

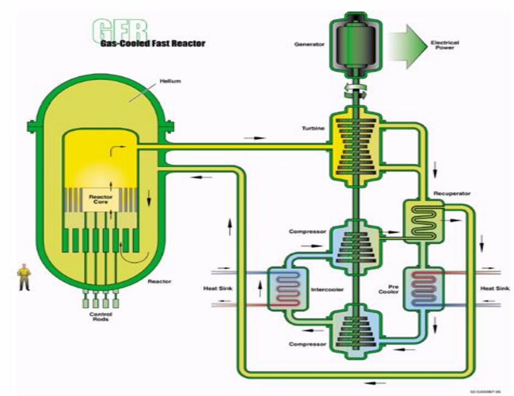
Gen IV Fission Nuclear Reactors



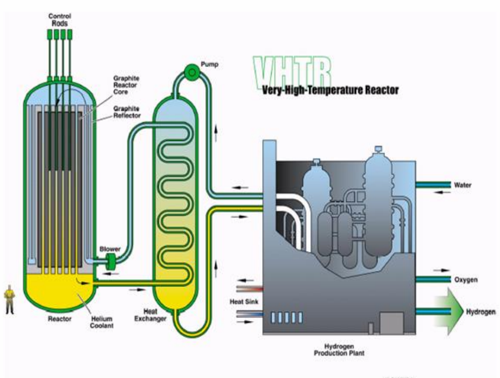
Sodium-Cooled Fast Reactor（SFR）



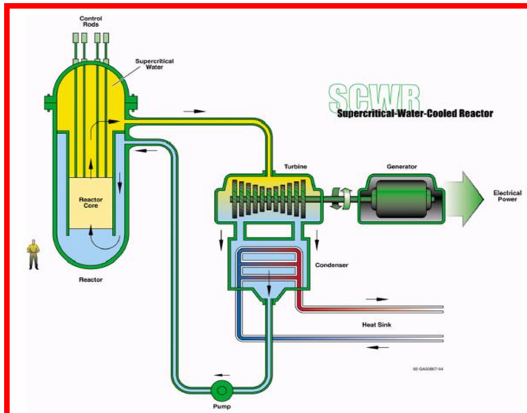
Lead-Cooled Fast Reactor（LFR）



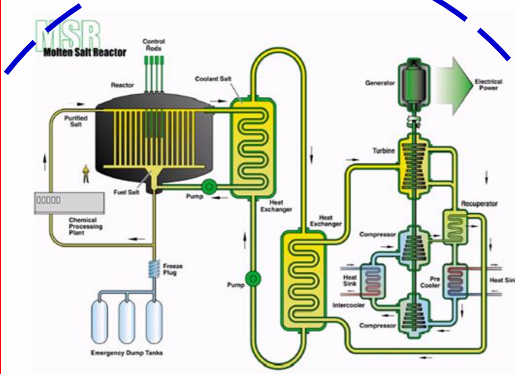
Gas-Cooled Fast Reactor （GFR）



Very-High-Temperature Reactor VHTR）



Supercritical-Water-Cooled Reactor（SCWR）



Molten Salt Reactor （MSR）

A Technology Roadmap for Generation IV Nuclear Energy Systems, Dec. 2002

Shanghai Institute of Applied Physics, Chinese Academy of Sciences

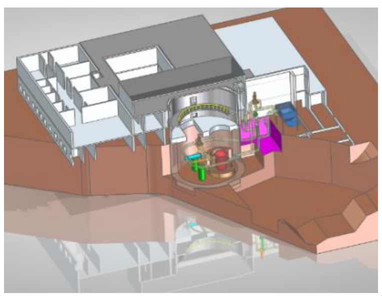
✓ CAS "Strategic Priority Research Program" by SINAP-Thorium-based Molten-Salt Reactor Nuclear Energy System (TMSR)

- Research and development of molten salt reactors for thorium utilization as nuclear fuel, aimed for self-sustained Th/U fuel cycle.
- Research on multipurpose applications of high temperature nuclear energy.

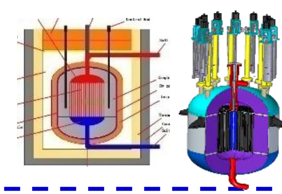
Current Status of TMSR Program

Prototype Reactor	Experimental Reactor	Demonstration Reactor

TMSR prototype reactor-SF0 (1:3)



2MW TMSR-LF1



Design of TMSR Demonstration Reactor

2019.12

2020.12

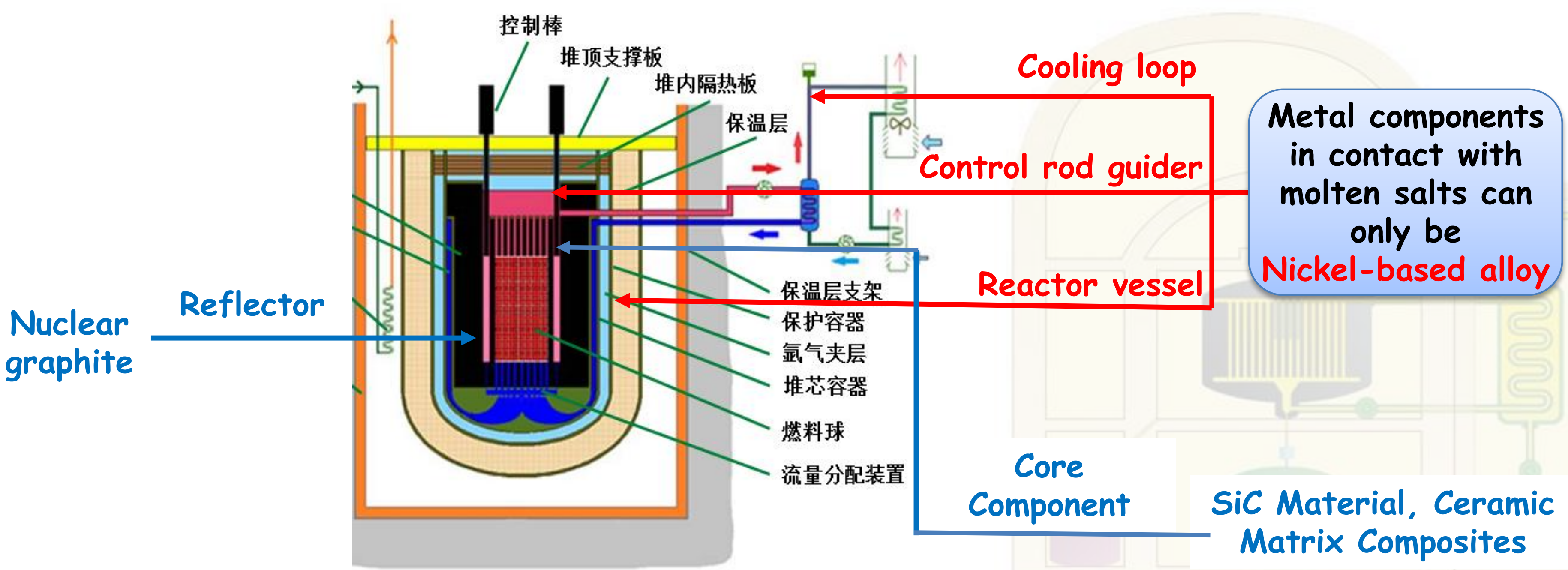
New Energy I Project	New Energy II Project	New Energy III Project

Molten Salt Reactor- the Fourth Generation Fission Reactor

Service environments

- High temperature (650°C)
- High neutron doses (> 10 dpa)
- Corrosive coolant (FLiBe)

☐ MSR material is a specially developed high temperature corrosion resistant material



UNS N10003 alloy & Nuclear graphite

□ **The most promising structural materials for MSR : Hastelloy N alloy & GH3535 alloy (UNS N10003 alloy)**

Elem.	Cr	Mo	Fe	Nb	W	Ti	Ni
Alloy	7	16	5	-	Max 0.5	-	bal.

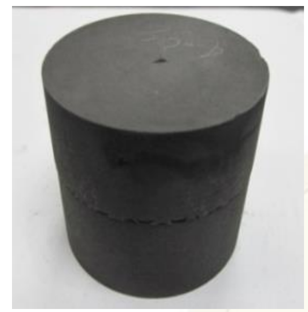
Ni: high temperature, molten salt corrosion resistance
Mo: solution strength; **Cr:** oxidation resistance
Ti: irradiation embrittlement resistance

□ **Very good corrosion resistance in molten salt**

□ **Operated successfully in MSRE for nearly five years**

□ **Still the best choice for the MSR structural material**

□ **Ultrafine-grain nuclear graphite used for MSR : NG-CT-50 & T-220**



High purity: Boron equivalent<2ppm

High density: $>1.7g/cm^3$

High Strength: Tensile > 20 MPa

Graphite properties used for MSR

- **High isotropy: < 1.1**
- **Excellent High Temperature Chemical Stability (~3000 ℃)**
- **Irradiation resistant materials (~30dpa)**
- **Micropore (<1m): Preventing molten salt infiltration**

2 Research Progress of the UNS N10003 alloy

- Fabrication, Corrosion & Mechanical Property Testing
- Neutron and Ion Irradiation Activities

Nickel-based UNS N10003 alloy

□ **Technologies for the smelting, processing, and welding of a Nickel-based alloy, UNS N10003, China standard GH3535**

GH3535 : A nickel-based alloy with an outstanding corrosion resistance in molten salts

- Technologies for smelting (10 tons / ingot), processing & welding; performance comparable to Hastelloy N
- Deformation processing technologies for nickel-based alloys with high Mo, the largest UNS N10003 seamless pipes.


hot extrusion


pipe processing


Welding

Capability	China	US Haynes
Pipe Diameter	168mm	<88.9mm

Seamless alloy pipes for the primary loop of MSR


检 测 报 告
TEST REPORT

Performance Test Report

Chinese Patent
CN103966476A


Component (head)

Alloy corrosion control

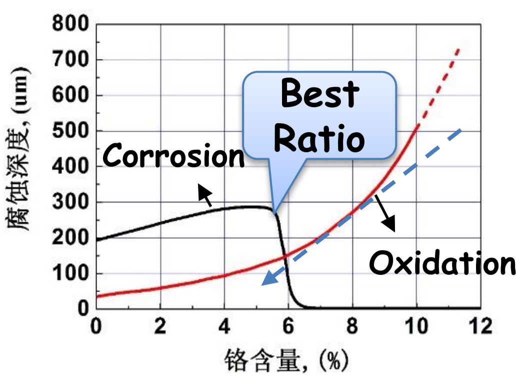
- Solving the corrosion control in fluoride salt (GH3535 static corrosion rate < 2μm/y) !

Investigating Corrosion Mechanism

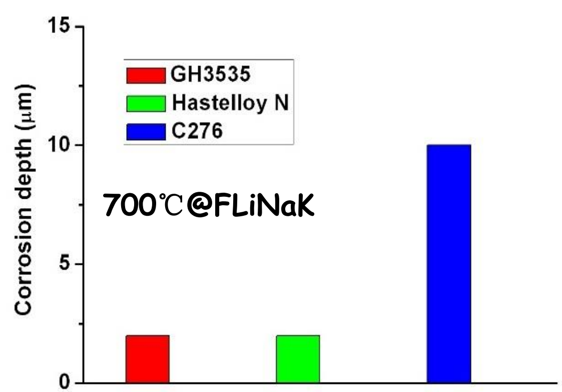
- Salt impurities;
- Elements diffusion;
- Mass transfer;

Developing Corrosion Control Technology

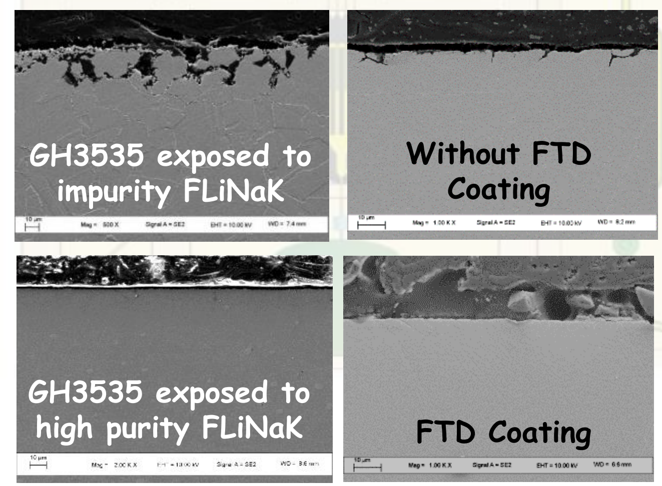
- **Design Optimization** : Optimize the composition of alloy, degrade diffusion of Cr;
- **Salt Purification:** Modify purification technology, control the impurities content;
- **Surface modification:** FTD coating, improve the corrosion resistance;



Comp. Optimization of Alloy (Cr)

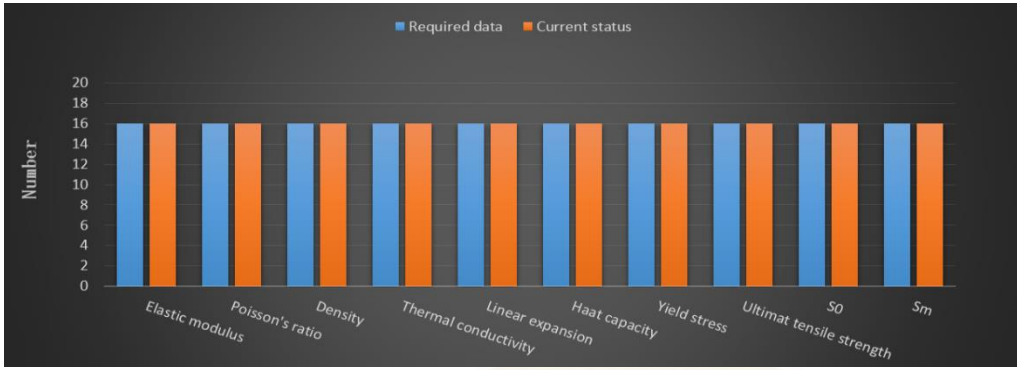


Corrosion Depth (μm/y)

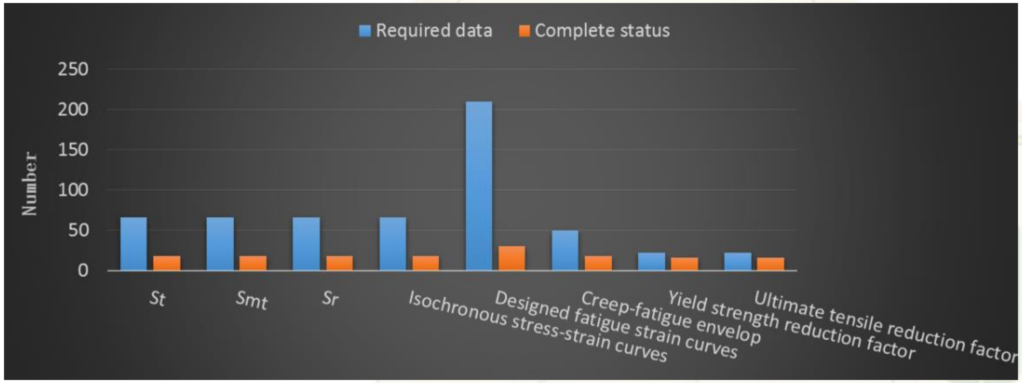


Progress in Alloy – Mechanical Evaluation

Properties	Requirements in ASME 2015	Data Completeness	Current status	Source
Elastic modulus	25-700℃,50℃interval	Complete	finished	ASMEII D,Haynes
Possion's ratio	25-700℃,50℃interval	Complete	finished	SINAP
Density	25-700℃,50℃interval	Complete	finished	SINAP
Thermal conductivity	25-700℃,50℃interval	Complete	finished	ASMEII D,SINAP
Linear expansion coefficient	25-700℃,50℃interval	Complete	finished	SINAP
Heat capacity	25-700℃,50℃interval	Complete	finished	SINAP
Base metal S_0	25-700℃,50℃interval	Complete	finished	ASMEII D
Base metal Sm	25-700℃,50℃interval	Complete	finished	ORNL, SINAP
Base metal St	450-700℃,50℃interval;Up to 300000h	Incomplete	650℃up to 30000h; 700℃up to 30000h	SINAP
Base metal Smt	450-700℃,50℃interval;Up to 300000h	Incomplete		
Weldment Smt	450-700℃，50℃interval Up to 300000h	Incomplete	650℃up to 3000h; 700℃up to 3000h	SINAP
Weldment St	450-700℃，50℃interval;Up to 300000h	Incomplete		
Weldment R	450-700℃，50℃interval;Up to 300000h	Incomplete		
Bolt S_0	25-700℃,25℃interval;	Complete	finished	ASMEII D
Bolt Smt	450-700℃，50℃interval; Up to 300000h	Incomplete	650℃up to 30000h; 700℃up to 30000h	SINAP
Isochronous stress-strain curves	450-700℃,50℃interval Up to 300000h	Incomplete	650℃up to 30000h; 700℃up to 30000h	SINAP
Designed fatigue strain curves	25℃、600℃、650℃、700℃、750℃; Fatigue rupture cycles: $10^3 \sim 10^6$	Incomplete	650℃50% confidential curve, fatigue rupture cycles up to 10^4	SINAP
Creep-fatigue envelop	No defined requirements	Incomplete	650℃, 1% strain 650℃, 0.6% strain	SINAP
Yield stress	25-700℃,50℃interval	Complete	finished	ASMEII D,SINAP
Ultimate tensile strength	25-700℃,50℃interval	Complete	finished	ASMEII D,SINAP
Yield strength reduction factor	650℃700℃; Up to 300000h	Incomplete	650℃, 700℃up to 10000h	SINAP
Ultimate tensile strength reduction factor	650℃700℃; Up to 300000h	Incomplete		SINAP



Time-independent data has been basically completed



Time-related data such as creep and fatigue are approximately 35% complete (300 000 h).

- A database of high-temp. mechanics of alloys has been established, the current data can support the operation of the experimental reactor for around 10 years.

Progress in Neutron Irradiation Test of TMSR Alloy

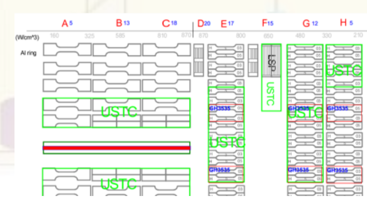
- Finish irradiation test on Hastelloy N @ T=650 °C, dose=2.5E19. PIE indicates that after irradiation the yield strength slightly increases, whereas the elongation keeps stable.

NPIC 中国核动力研究设计院
NUCLEAR POWER INSTITUTE OF CHINA

- Finish Irradiation test on Hastelloy N and GH3535 alloys (base metal & weld metal) @ T=40 °C, dose=2.5E19 & 1E20

CAEP 中国工程物理研究院
CHINA ACADEMY OF ENGINEERING PHYSICS

- High Dose (3 -15 dpa) test on GH3535 alloys to be conducted in 2019 @PSI



Irradiation damage of UNS N10003 alloy

➢ ORNL report & FHR white paper: irradiation embrittlement

Considerations of Alloy N for Fluoride Salt-Cooled High-Temperature Reactor Applications

Weiju Ren, Govindarajan Muralidharan, Dane F. Wilson and David E. Holcomb
[+] Author Affiliations

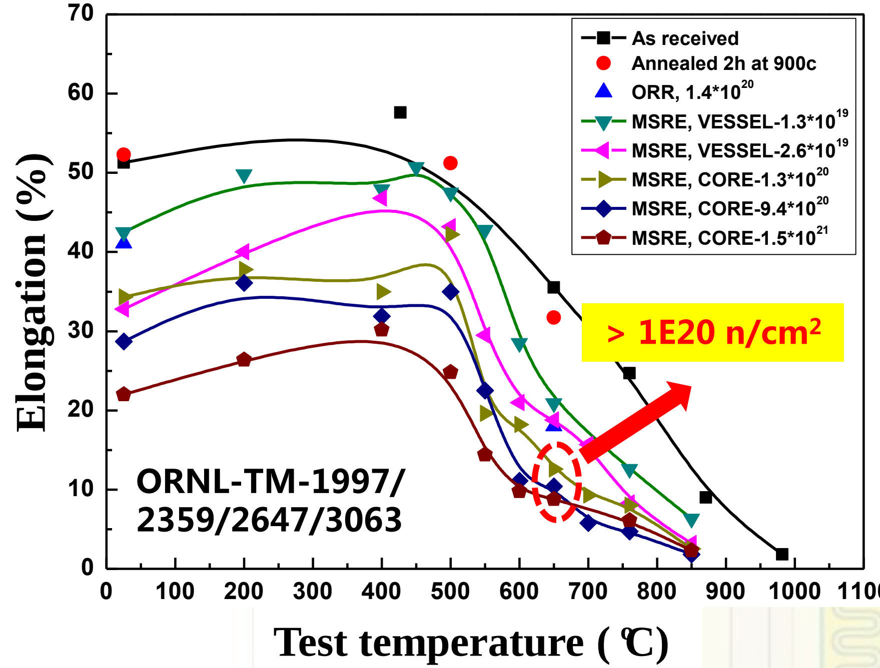
Paper No. PVP2011-57029, pp. 725-736; 12 pages
doi:10.1115/PVP2011-57029

FHR Fluoride-Salt-Cooled, High-Temperature Reactor

FHR Materials, Fuels and Components White Paper

Integrated Research Project Workshop 3

Fluoride-Salt-Cooled High Temperature Reactor (FHR) Materials, Fuels and Components White Paper

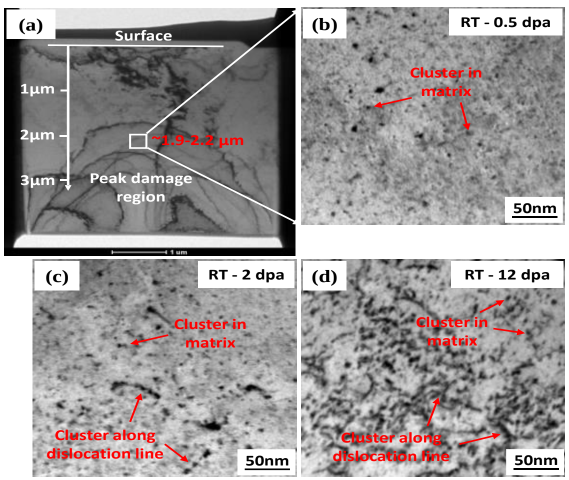


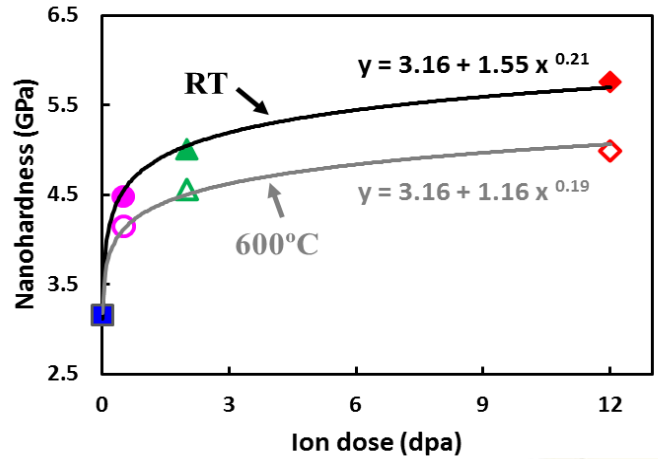
➢ Hardening embrittlement: displacement cascade damage

➢ Non-hardening embrittlement: He embrittlement (grain boundary segregation of helium bubbles)

Ion irradiation experiment (GH3535 alloy)

Materials	GH3535 Weld
Type of ions	8MeV Ni^{+}
Ion dose (ions/cm^2)	5×10^{14} , 2×10^{15} , 1.2×10^{16}
Irradiation damage (dpa)	0.5, 2, 12
Temperature	RT & 600 °C

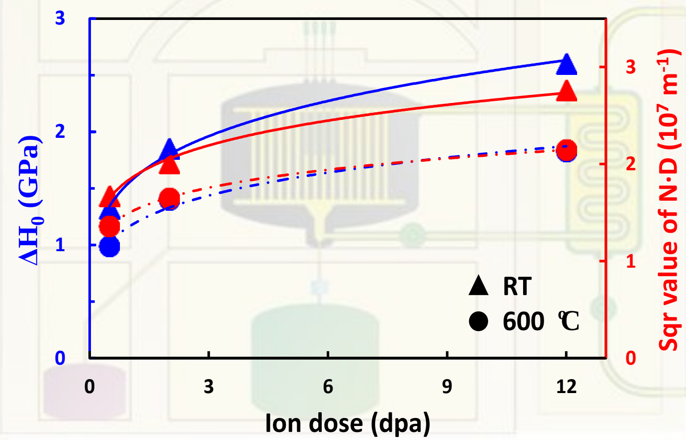




➢ An 1/5-power law dependence of the hardness increment on dpa is obtained

$$\Delta\sigma_p = \alpha \cdot M \cdot \mu \cdot b \cdot \sqrt{N \cdot D}$$

α: obstacle strength (0-1)
M: Taylor factor (3.06)
μ: shear modulus
b: Burgers vector
N: Number density of defects
D: Mean size of defects



➢ The presence of defects is the main reason for irradiation hardening

➢ Temperature effect of irradiation hardening

H.F. Huang* et al, J. Nucl. Mater 497 (2017) 108

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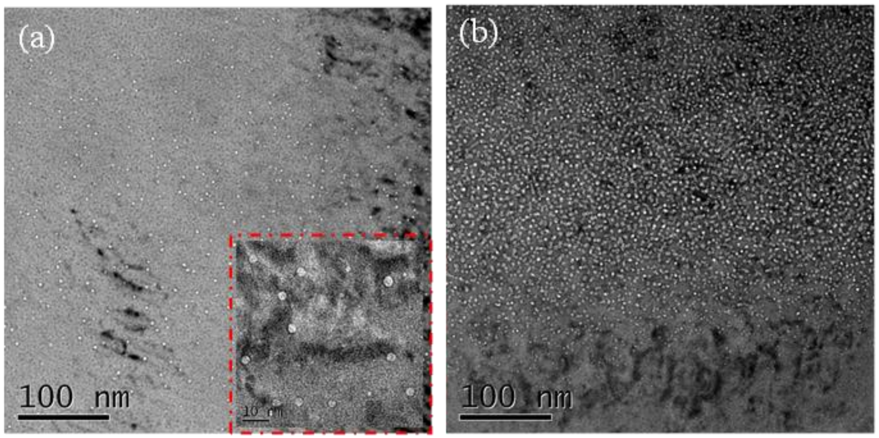
Ion irradiation experiment (Hastelloy N alloy)

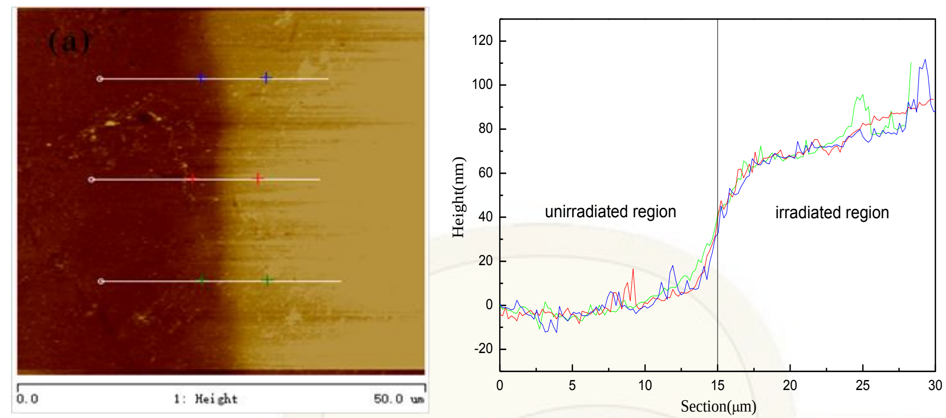
Irradiation damage peak region

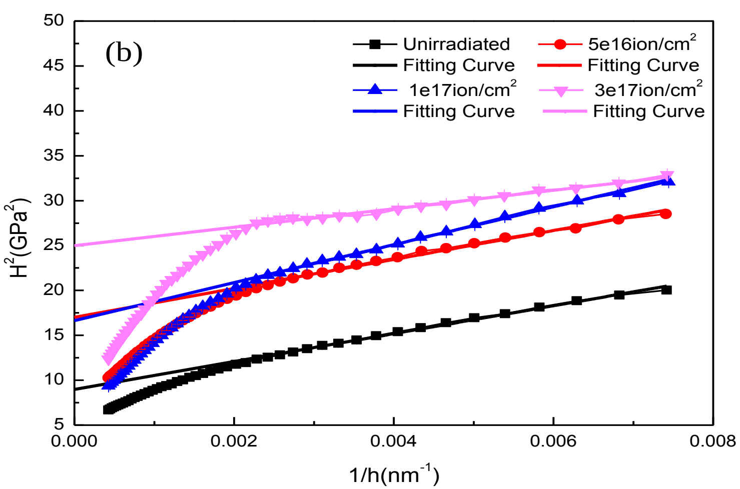
(a) 1×10^{17}ion/cm^2 (b) 3×10^{17}ion/cm^2

AFM: Irradaition swelling of 2.67%

(3×10^{17}ion/cm^2)







- ➢ **Helium bubbles formation under high temperature irradiation**
- ➢ **Helium bubbles cause the irradiation swelling and also the hardening / embrittlement**

G.H. Lei, H.F. Huang et al, J. Alloy. Comp. 746 (2018) 153

3 Research Progress of ultrafine-grain graphite

- Property of Ultrafine-grain Graphite
- Neutron and Ion Irradiation Activities

Fabrication of Ultrafine grain graphite

- Development of the ultrafine grain nuclear graphite for TMSR, involved in the establishment of ASME code of MSR nuclear graphite.

Nuclear graphite : moderator/reflector

- Industrial production technologies of Chinese ultrafine-grain nuclear graphite
- Pore diameter < 1μm, ensured better infiltration resistance than existed nuclear graphite
- Establishing database of its performance & deep involvement in Intl. Std. for MSR nuclear graphite

ASME
SETTING THE STANDARD

Two Park Avenue
New York, NY
10016-5990 U.S.A.

tel +1.212.591.8500
fax +1.212.591.8501
www.asme.org

August 21, 2014

Zeng Guang Li
SINAP
2019 Jialuo Road
Jiading District, Shanghai 37831
People's Republic of China

Dear Dr. Zeng,

The ASME BPV III Subgroup on Graphite Core Components intends to consider the improvement of the provisions for fine-grain graphite in ASME BPV Section III, Division 5. As a research organization prominent in the field of nuclear graphite material, the Shanghai Institute of Applied Physics (SINAP) is positioned to assist the Subgroup in this endeavor.

Provision for ASME code

Properties evaluation of ultrafine-grain graphite

☐ Conventional properties of graphite

- Properties of thermal, mechanical, and physical, etc. (Already completed)

☐ High-temperature properties of graphite materials

- High-temperature modulus of elasticity (In progress)
- High-temperature thermology (thermal conductivity, coefficient of thermal expansion) (Already completed)

☐ Non-conventional properties of graphite

- Fracture properties: Effect of cracks (dimension, morphology) on mechanical properties of graphite (In progress)
- Fatigue properties: (S-N curve, Goodman curve, Sinosteel AMC) (In progress)

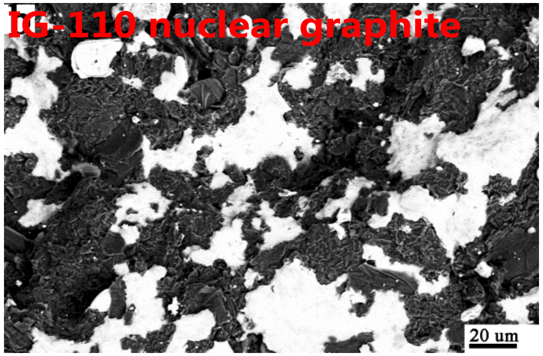
☐ Performances of graphite materials in molten Li_2BeF_4 (FLiBe) salt

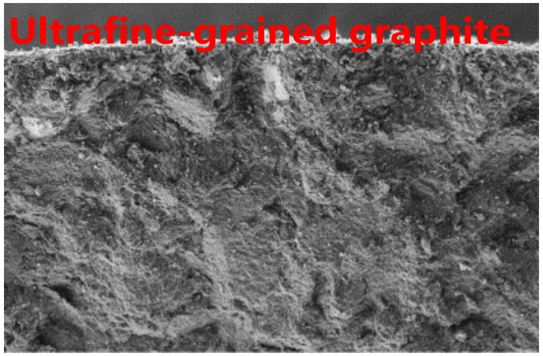
- Compatibility of molten FLiBe salt with graphite (Already completed)
- Mechanical properties for salt-impregnated graphite (tensile strength, compressive strength, flexural strength) (Already completed)

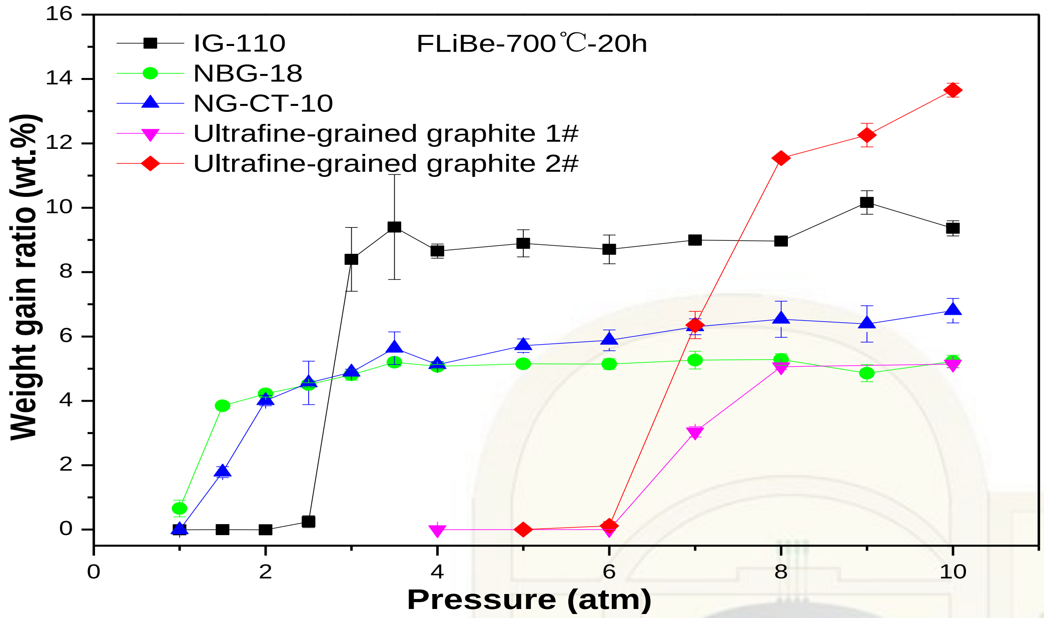
Conventional property data of ultrafine-grain graphite

Parameter	Ultrafine-grained Graphite (1#)	Data Source	Ultrafine-grained Graphite (2#)	Data Source
Bulk Density(g/cm^3)	1.87±0.01	SINAP	1.79±0.01	SINAP
Specific Heat Capacity(J/g·K)		SINAP		SINAP
Thermal Conductivity(W/m·K)		SINAP		SINAP
Open Porosity(%)		SINAP		SINAP
Expansion Coefficient		SINAP		SINAP
Boron Equivalent of Graphite Impurity(ppm)		Sinosteel AMC		Chengdu Carbon Co., Ltd
Pore Size(μm)	0.95	SINAP	0.83	SINAP
Young's modulus(GPa)		Sinosteel AMC		Chengdu Carbon Co., Ltd
Anisotropy Coefficient		SINAP		SINAP
Two-parameter Weibull Distribution for Tensile Strength (MPa)		SINAP		SINAP
Tensile Strength(MPa)		SINAP		SINAP
Flexural Strength(MPa)		SINAP		SINAP
Fracture Toughness (K_{IC}) $MPa.m^{1/2}$		SINAP		SINAP

Infiltration behavior of graphite exposed to molten FLiBe salt under different pressures







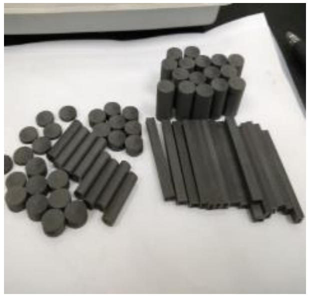
Weight gain ratios of five grades of graphite after immersion in molten FLiBe salt under different pressures

- The higher the pressure, the greater the weight gain ratio
- The threshold pressure for FLiBe salt infiltration for two grades of ultrafine-grain graphite are between 6 and 7 atm.

Neutron irradiation test of Chinese Graphite

- Over 300 samples were irradiated in HFETR at 650 °C to a dose of 0.4 dpa
- Based on primary results, Chinese ultrafine-grain graphite shows very good stability in dimension and a great enhance in strength after irradiation.

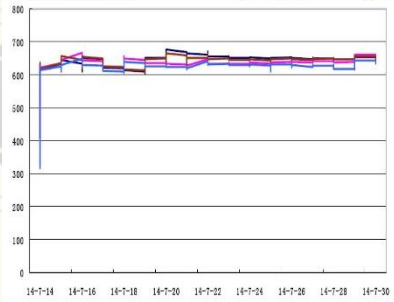
Reactor	environment	Temperature	Fluence	PIE
HFETR (NPIC)	Inert gas	650 ±50 °C	5E20 n/cm^2 (E >0.1MeV)	Dimension, weight, strength, modulus


Samples


Sample loading

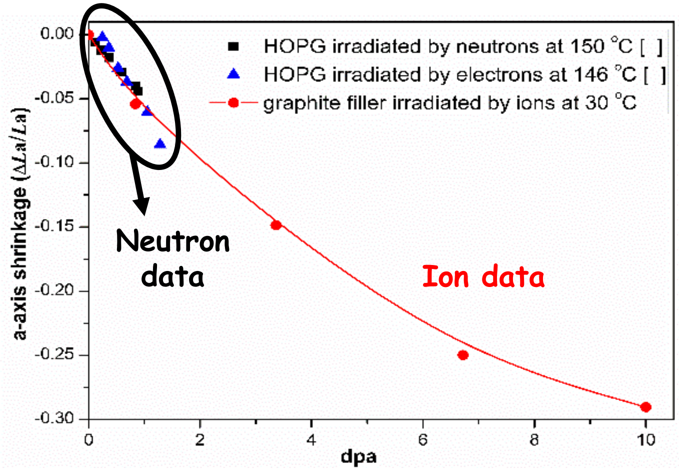

Capsule installation


PIE

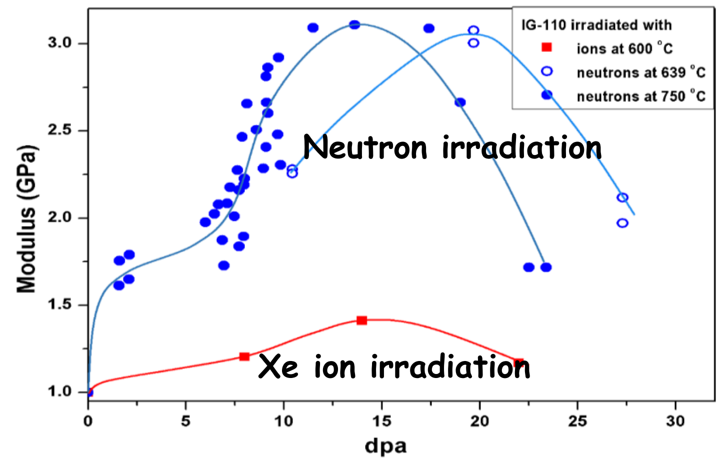

Temperature control

Equivalence of ion and neutron irradiation effects

Irradiation induced anisotropic swelling of graphite crystal

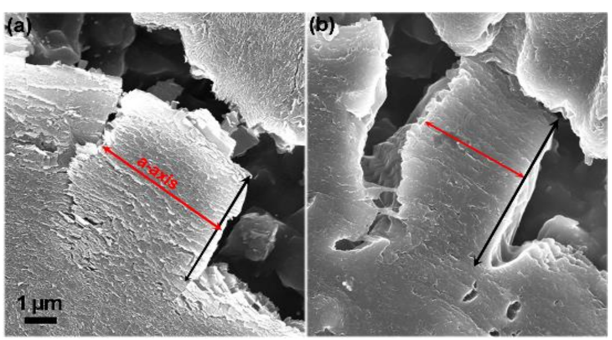


An first increase then decrease of graphite modulus induced by irradiation

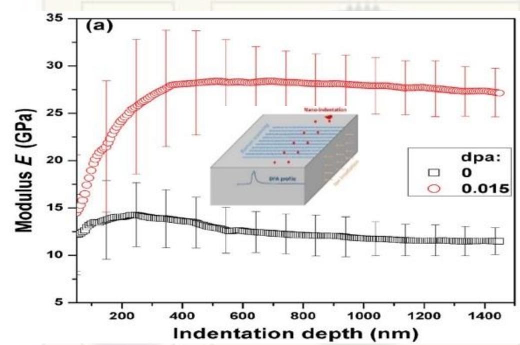


micron-scale → macro-scale

Ar ion irradiation induced anisotropic dimensional change



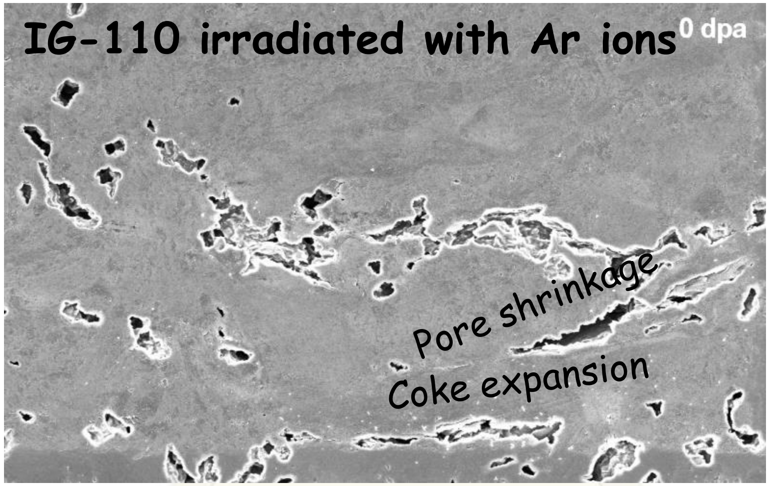
Low-dose proton-irradiation induced modulus increase

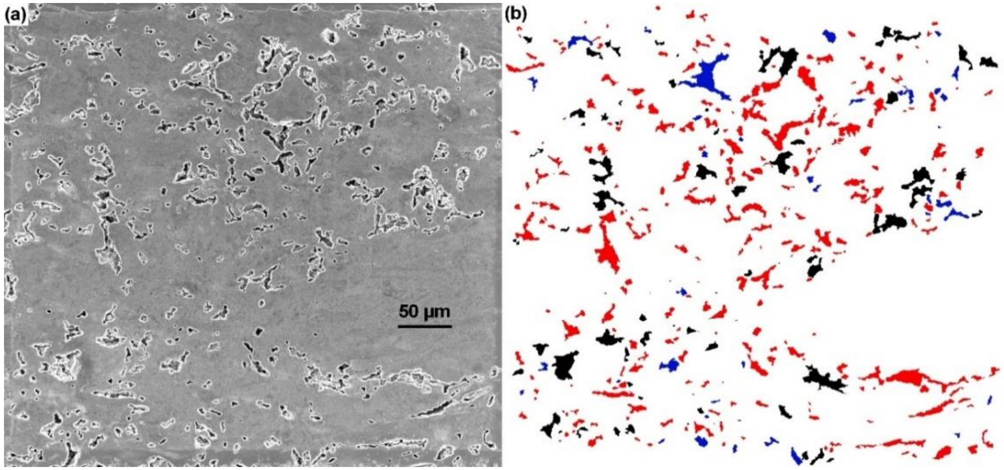


Q. Huang, et al., Nucl. Instrum. Meth. B 412 (2017) 221-226

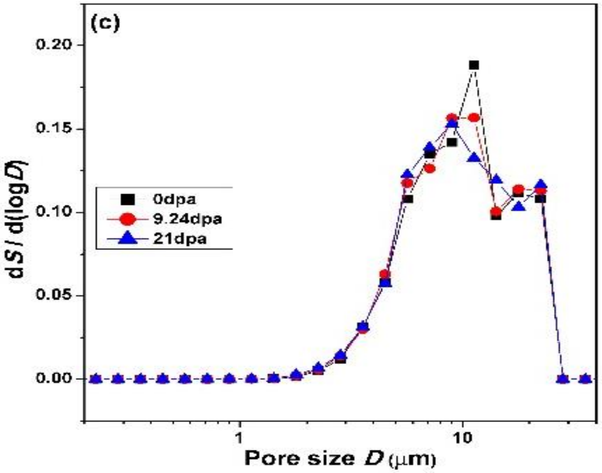
Pore structure evolution during irradiation

- After irradiation to 21dpa at 600 °C, much more contracted pores (71%) than expanded pores (12%) were found.
- Pore size distribution don't show obvious changes after irradiation, indicating that irradiation won't facilitate salt intrusion into graphite.





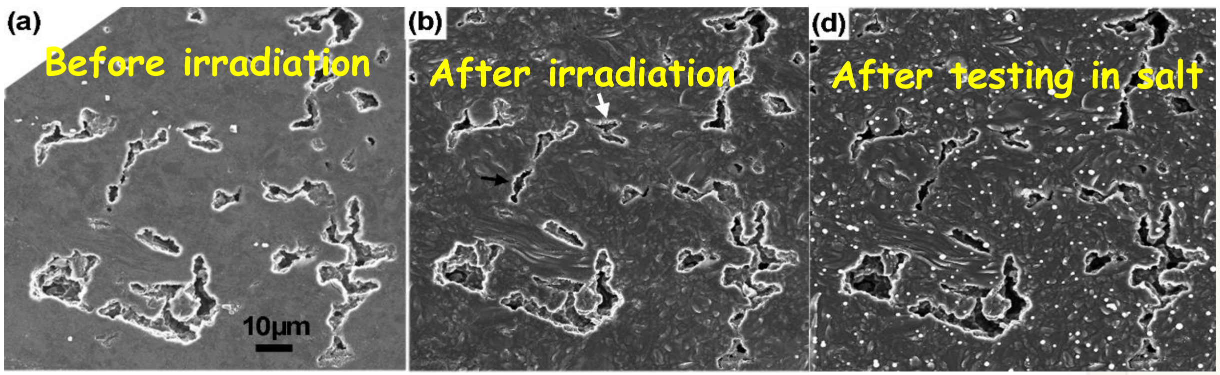
Red: shrinkage; Blue: expansion; Black: unchanged

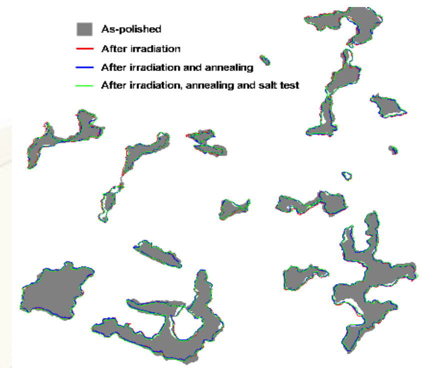


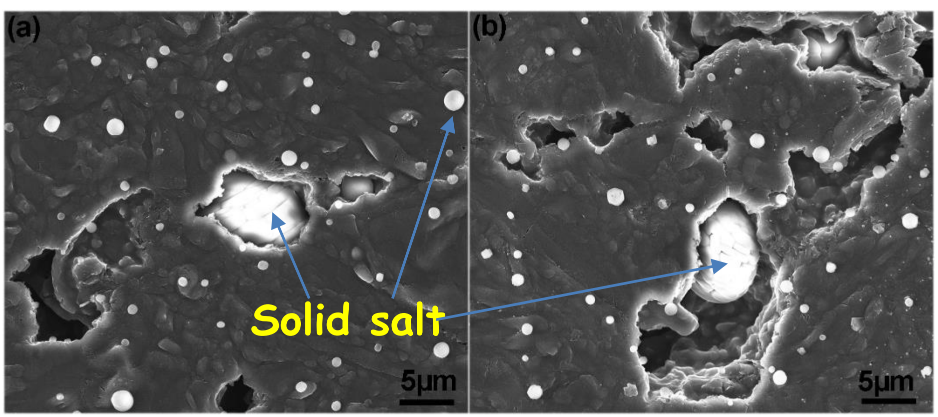
Pore size distribution during irradiation

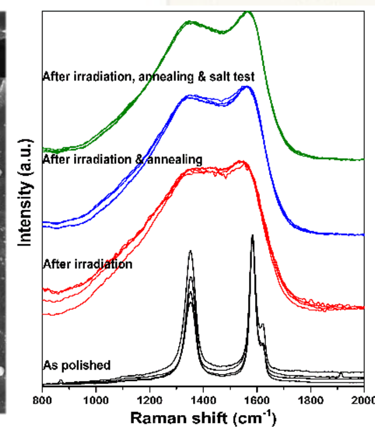
Compatibility of irradiated graphite and FLiBe salt

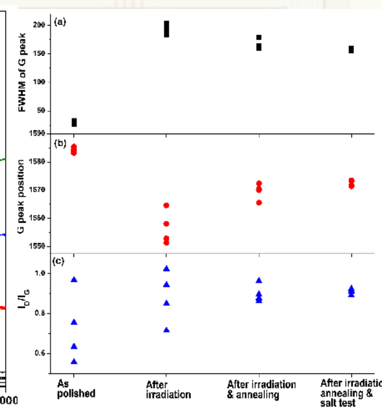
- Graphite was irradiated with Xe ions to ~4.5 dpa and then tested in molten flibe salt.
- Testing in molten flibe salt did not have obvious effects on graphite's surface morphology and Raman peaks, indicating that irradiated graphite has a great structural stability in molten flibe salt.







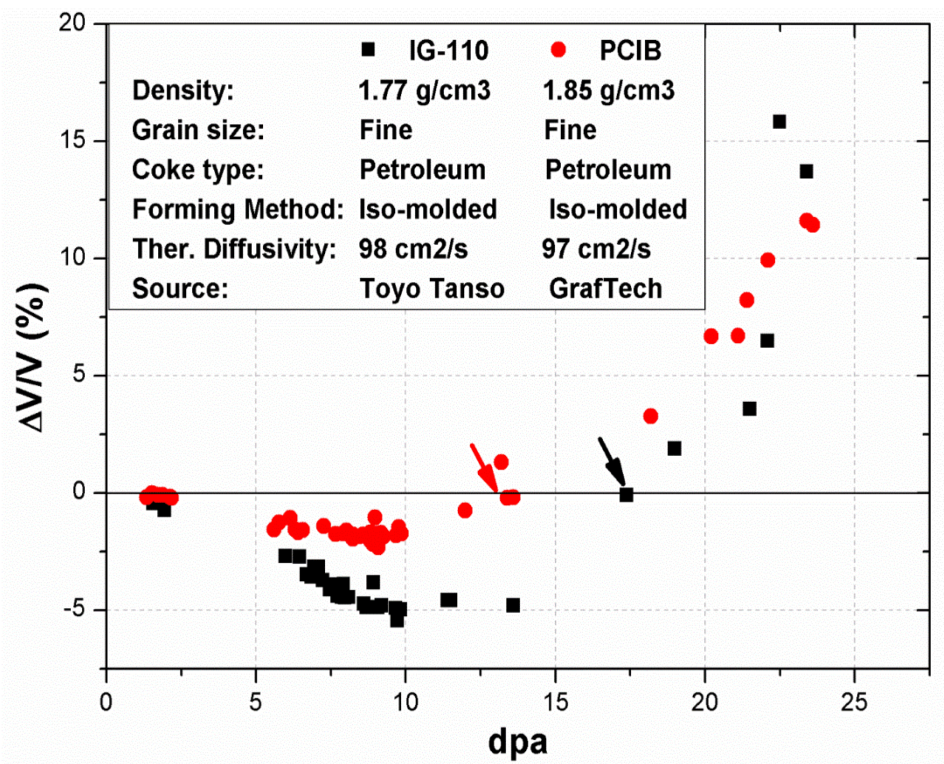


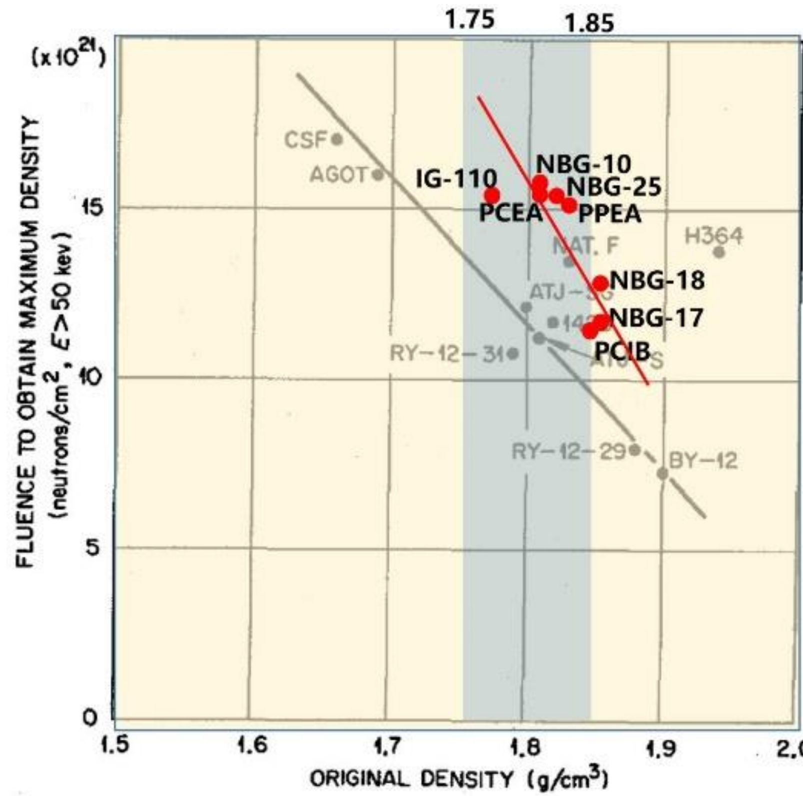


Q. Huang et al., Nucl. Instrum. Meth. B 436 (2018) 40-44

Characteristics of long-life nuclear graphite

- Neutron irradiation data of many nuclear graphites were collected and evaluated





Density's influence on irradiation life of nuclear graphite

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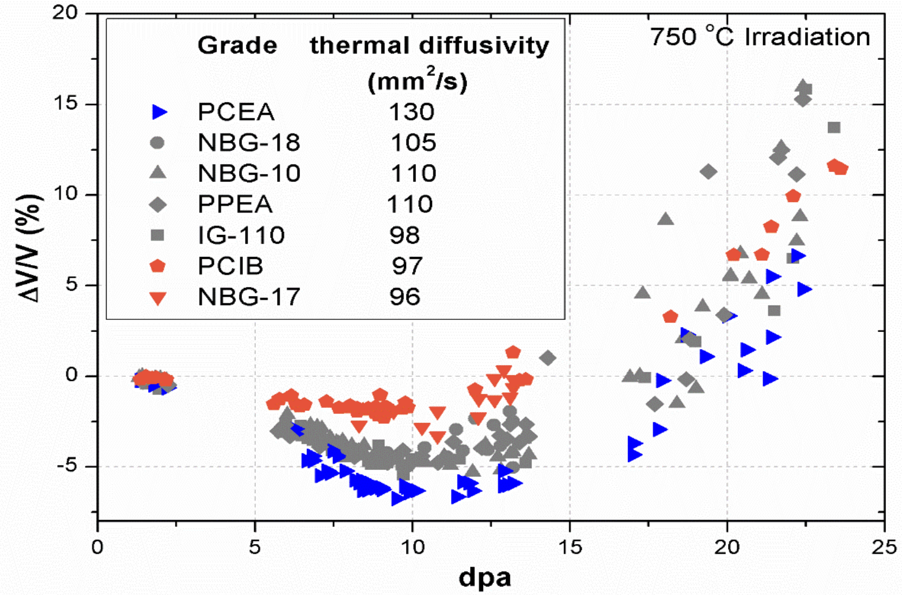
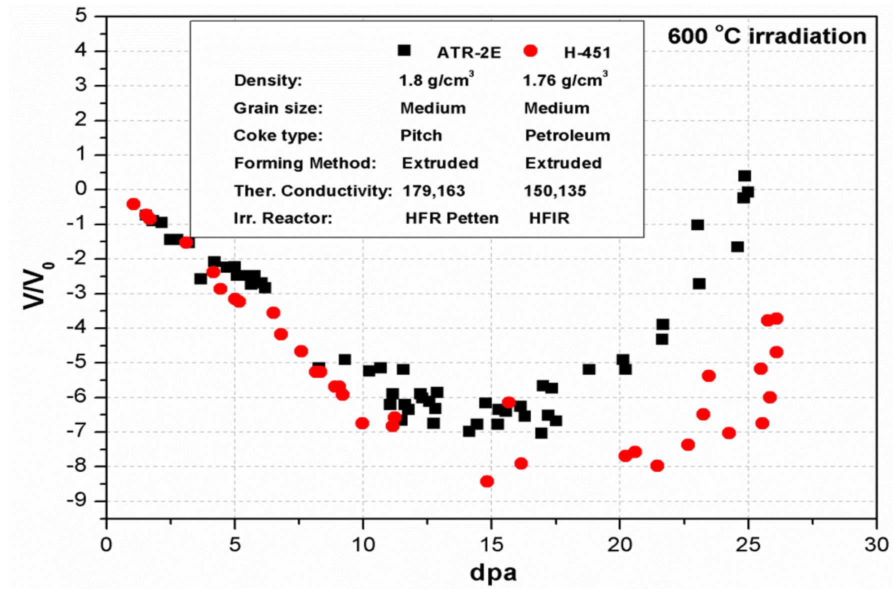
Characteristics of long-life nuclear graphite



Graphitization degree's influence on irradiation life of nuclear graphite

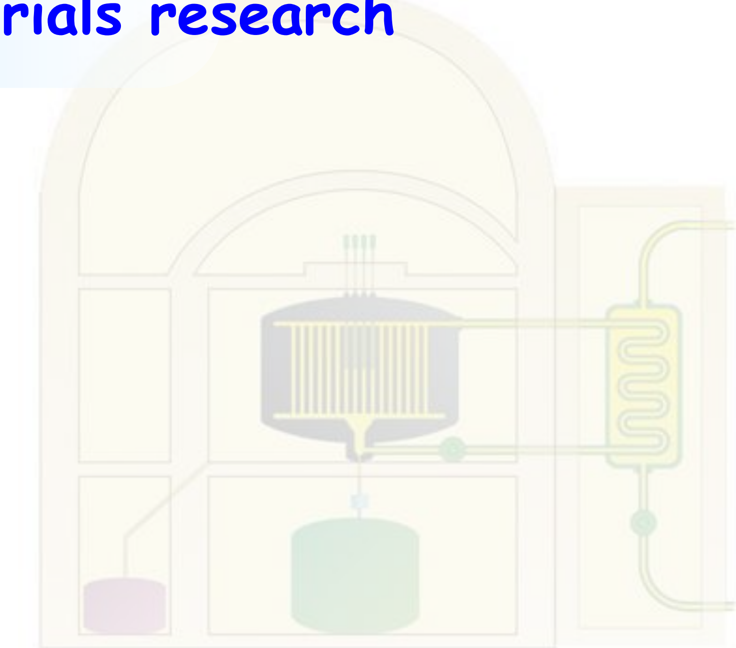


Coke type's influence on irradiation life of nuclear graphite

- ☐ Moderate density (1.75 - 1.85 g/cm^3)
- ☐ High degree of graphitization (high thermal conductivity)
- ☐ Petroleum coke seems better than pitch coke

✓ Extensive cooperation with the company to develop the new graphite, and achieve the irradiation performance modification.

4 Next plan for TMSR materials research



Main issues for the TMSR materials research

- Development of high-temperature (>800 °C) molten salt corrosion resistant Alloy;
- Te embrittlement modification of nickel-based alloys;
- Development of nuclear graphite with long irradiation life-time;
- Establishment of irradiation performance evaluation method for nuclear graphite using ion beam;
- Completion and upgrading of the current material database for molten salt reactor;

Thank you for your attention !