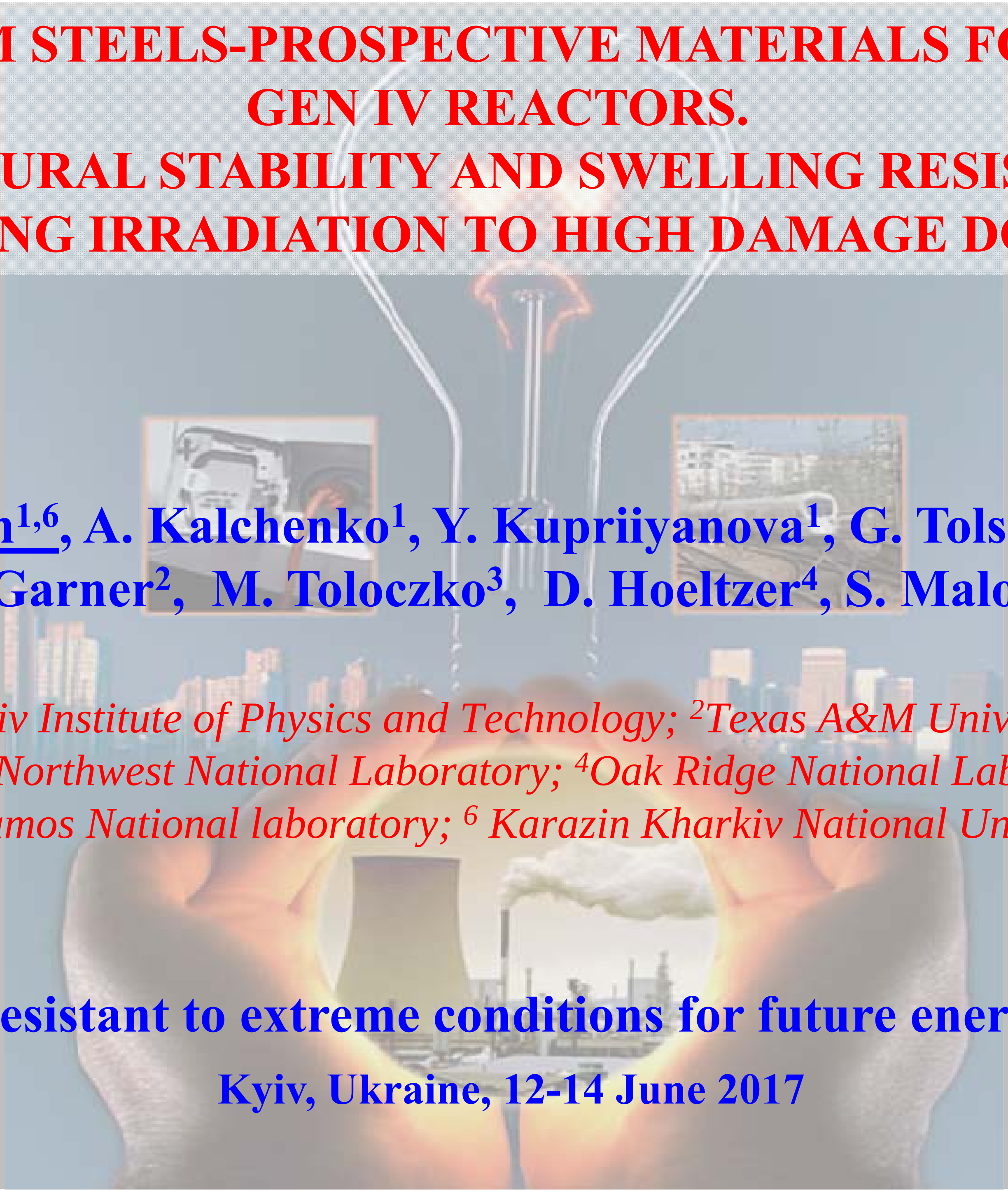

F/M STEELS-PROSPECTIVE MATERIALS FOR GEN IV REACTORS. STRUCTURAL STABILITY AND SWELLING RESISTANCE DURING IRRADIATION TO HIGH DAMAGE DOSES

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«Materials resistant to extreme conditions for future energy systems»

Kyiv, Ukraine, 12-14 June 2017

Motivation

- Realization of ambitious programs of development and construction of power plants of new generation (GEN IV, Russian BN-800, BN-1200, Terra Power Wave reactor etc.) will be possible only under solution of problems of nuclear material science.

- Just the behavior of structural materials of the cores of nuclear reactors limits the reaching of commercially necessary rate doses > 200 dpa, needed operational temperatures (500-600°C) and impedes the reaching of higher burn-up of fuel.

- For new generation of reactors , there is need for suitable materials to move from status on “paper-virtual” reactors to become operating reactors.

- The development of *radiation tolerant materials* is the big scientific/technical goal that is specific to the success of sustainable nuclear energy.

New challenges for materials of Gen IV

- Various nuclear concepts require low void swelling of structural steels at very high exposures

  Gen IV (GFR, SFR, LFR, MSR) (>200 dpa)
  Transmutation of actinides ("burners") (~400 dpa)
  Traveling wave reactors (~600 dpa)
  Fusion and ADS spallation systems (~200 dpa+gases)

- Ferritic-martensitic (F/M) steels can serve as candidates to reach high fuel burn-up levels for many type of reactors.

- Oxide dispersion-strengthened (ODS) variants of ASS and FM steels are being developed for advanced alloys.

The swelling resistance of F/M steels

Radiation damage is initiated at the atomic level, but the macroscopic effects arise from microstructural changes.

Factors, that differ the superior swelling resistance of F/M alloys(BCC) vs Austenitic alloys(FCC):

1. **The more open BCC lattice;**
2. **Differencies in relaxation volumes of interstitial and vacancies;**
3. **Differences in formation and migration energies of vacancies and interstitials;**
4. **Features of dislocation structure evolution;**
5. **Variation in minor solute concentrations.**

Features of dislocation evolution in F/M steels

- **Difference between relaxation volumes of interstitial and vacancies is higher in FCC structures than in BCC materials; this favors the decrease of bias in absorption of vacancies by voids and of interstitials by dislocation in BCC lattice.**

Syngony, Metal	**V_i , Ω**	**V_v , Ω**
FCC		
Cu	1,55 ± 0,20	–0,25 ± 0,05
Al	1,9	–0,05
Ni	1,8	–0,2
Pt	1,8	–0,2
BCC		
Mo	1,1	–0,1
Fe	1,1	–0,05

- **The BCC lattice exists at a higher homologous temperature than the face centered cubic (FCC) lattice, reducing the vacancy super saturation level that drives void nucleation.**

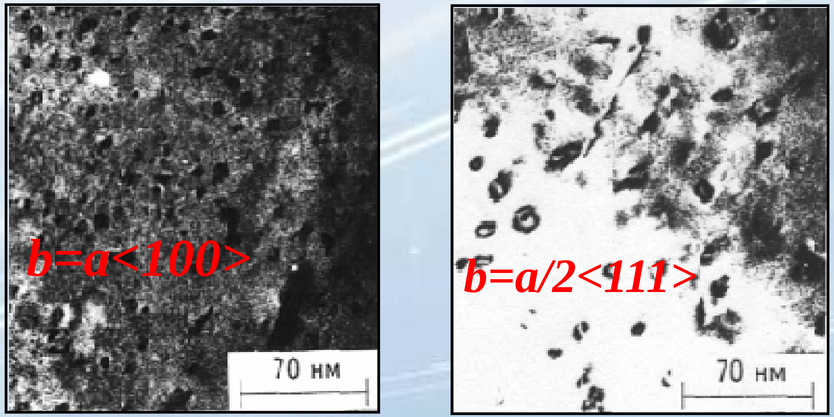
Role of dislocation loops in BCC iron systems

➢**The rates of self-diffusion in ferrite are higher than in austenitic alloys. This difference must cause the swelling suppression, especially of incubation dose, in particular, at high temperatures.**

➢**<u>Low nucleation rate</u> - more open BCC lattice results in lower interstitial bias to dislocations, leading to lower vacancy population.**

➢**<u>Low growth rate</u> – two prominent types of dislocation loops are observed in bcc iron system consisting a<100> and a/2 <111> loops. Since a<100> loops are strong preferential sinks compared to a/2 <111>, which are neutral sink that lead to the reducing of vacancy supersaturation and swelling rate.**

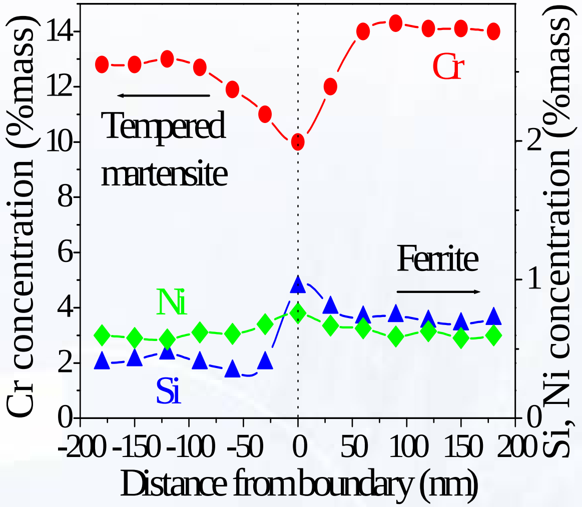
Metal	E_0^B, eV	E_M^B, eV
Ni (FCC)	1.4	1.5
γ-Fe (FCC)	1.5	1.02
α-Fe (BCC)	1.4	0.51
Cr (BCC)	1.62	1.35



a b

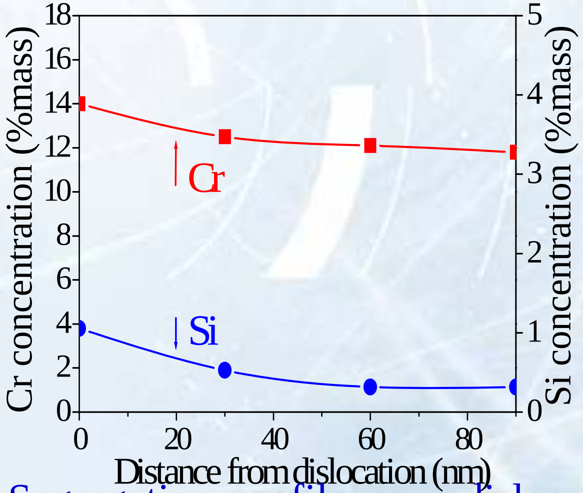
Evolution of dislocation structure in the 13Cr2MoNbVB steel (Cr^{+3}, E=3 MeV, T_{irr}=500°C)
a) D=0,5 dpa; b) D=5 dpa;

RIS features in F/M steels



Segregation profile in EP-450 steel (BOR-60, T_{irr}=500°C, D=38 dpa ,tempered martensite)

Grain boundaries ferrite-sorbite (neutral sinks) are enriched by Si and depleted by Cr, Mo, Nb.



Preferential sinks (interstitial dislocation loops with b=a <100>) enrichment of Cr and Si takes place (Stresa,1993)

Segregation profile near dislocation loop in EP-450 steel (Cr^{3+}, E=3MeV, T=550^0C, D=48dpa)

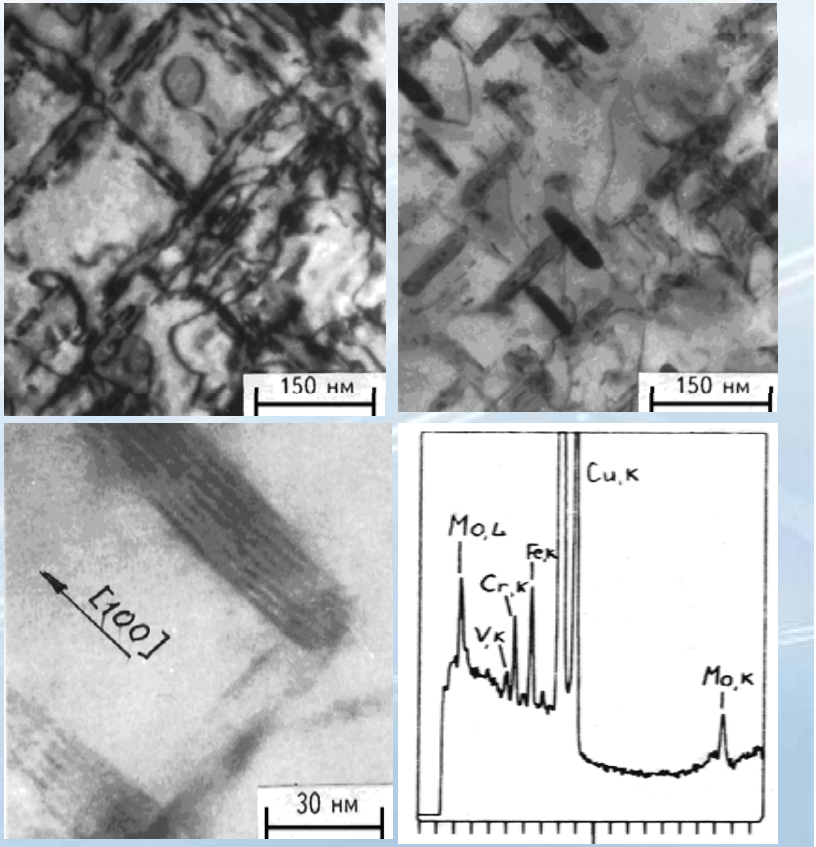
Cr increasing leads to

a)dislocation loops <100> (D= 15 dpa);

b)formation of precipitates (D=52 dpa);

c) M_2X-precipitate (big magnification);

d)X-ray spectrum from M2X (X= Cr)

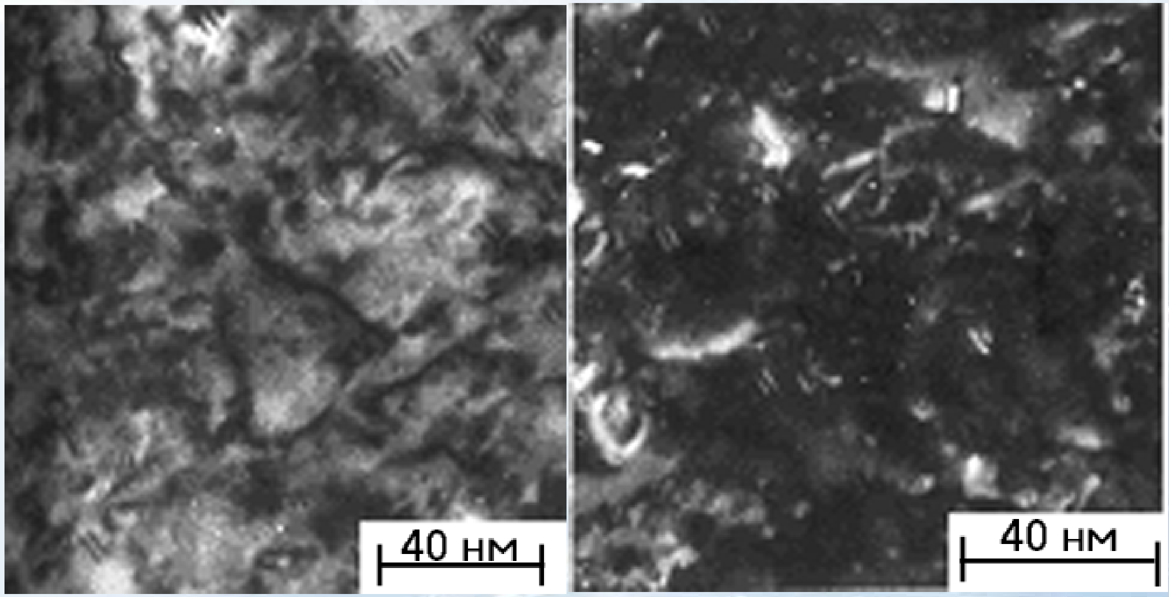


Precipitates behaviour in F/M steels

Precipitates observed in 9-12%Cr steels during irradiation include α'- phase, G-phase, M_6C and chi-phase, Laves phase.

In addition to the formation of new precipitates and their possible effect on mechanical properties, also the $M_{23}C_6$ and MX coarsen during irradiation.

- **α′-phase -predominantly Cr (up to 85–90%), are ≤10 nm in size, and are uniformly distributed through both ferrite and tempered martensite. Irradiation of lower Cr-content steels (9% to 10% Cr) can also reduce the amount of Cr sufficiently to cause the formation of the α′-phase.**



Very important that in any cases it can serve as radiation-induced phase .

Intensive radiation embrittlement results in formation of the α′-phase.

Ferritic-Martensitic (F/M) steels -main candidate of structural materials in advanced nuclear reactors

Superior Properties:

- **Thermal conductivity**
- **Thermal expansion coefficient**

Need to investigate:

- **Swelling Resistance**
- **Resistance to He/H embrittlement**
- **Resistance to irradiation creep**

Chemical composition of investigated steels:

F/M steels

EP - 450: Fe-13Cr-2Mo-Nb-V-B-0,12C (F+M)

EP - 823: Fe-12Cr-Mo-W-Si-V-Nb-B-0,16C (M+F)

HT-9: Fe-12Cr-Ni-Mo-W-V-0,20C (M+F)

EK-181: Fe-11Cr-Si-Mn-Mo-V-2W-Nb-Ni-B-0,14C (M+F)

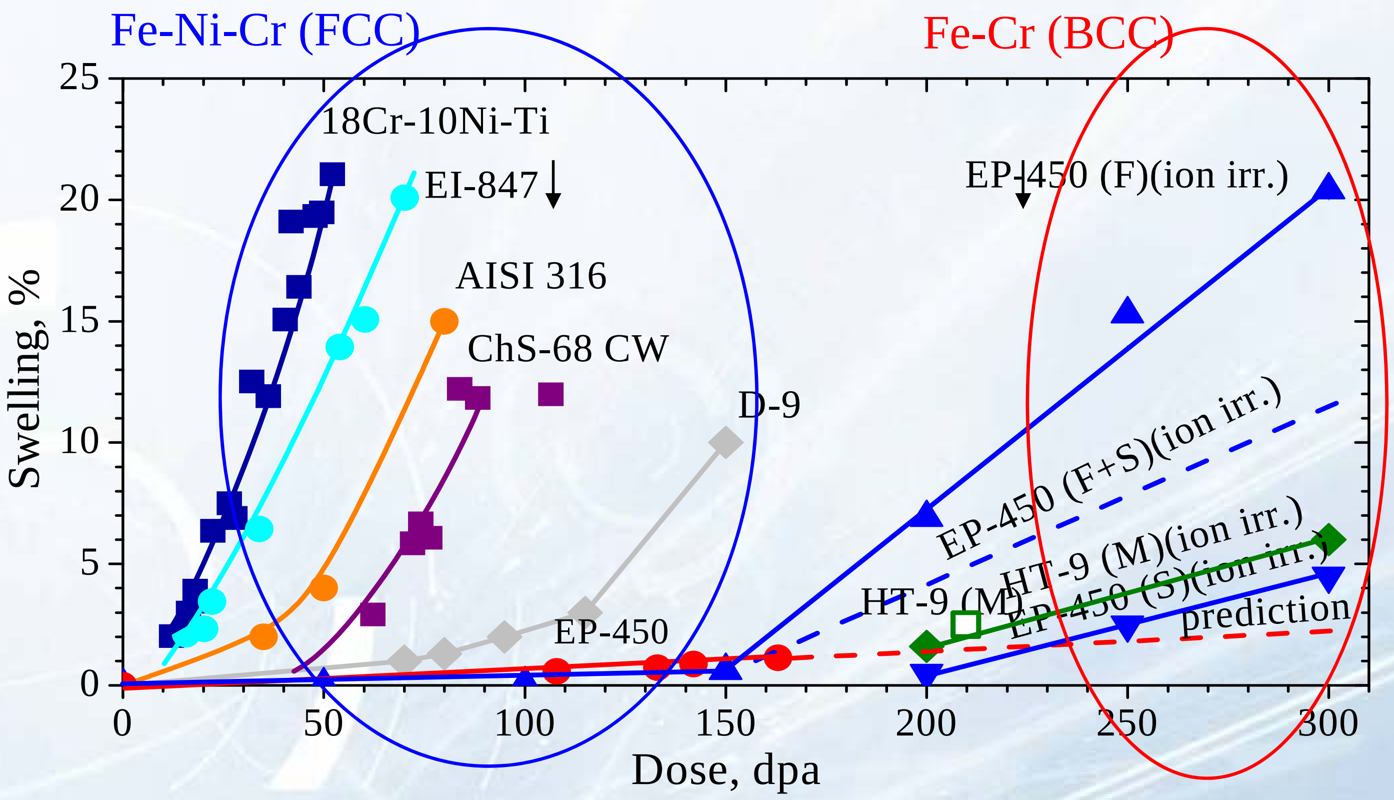
ODS alloys

MA957:Fe-14Cr-Si-Mn-Mo-Ni-B-0,01C+(1,05Ti-0,25Y_2O_3)

14YWT: Fe-14Cr-3W-Mn-0,06C+(0,4Ti-0,25Y_2O_3)

Swelling behaviour of ASS and F/M steels KIPT data (1984-2016)

Comparison of swelling data for austenitic and ferritic alloys at 0-300 dpa



(Voyevodin et.al, 12th International Workshop on Spallation Materials Technology,19-23 October 2014, Bregenz, Austria)

Bcc iron-based alloys have longer swelling incubation period and lower swelling per dpa rate (~0.2%/dpa) in steady –state void growth region than do simple fcc iron-based alloys (~1%/dpa)

High damage doses ???

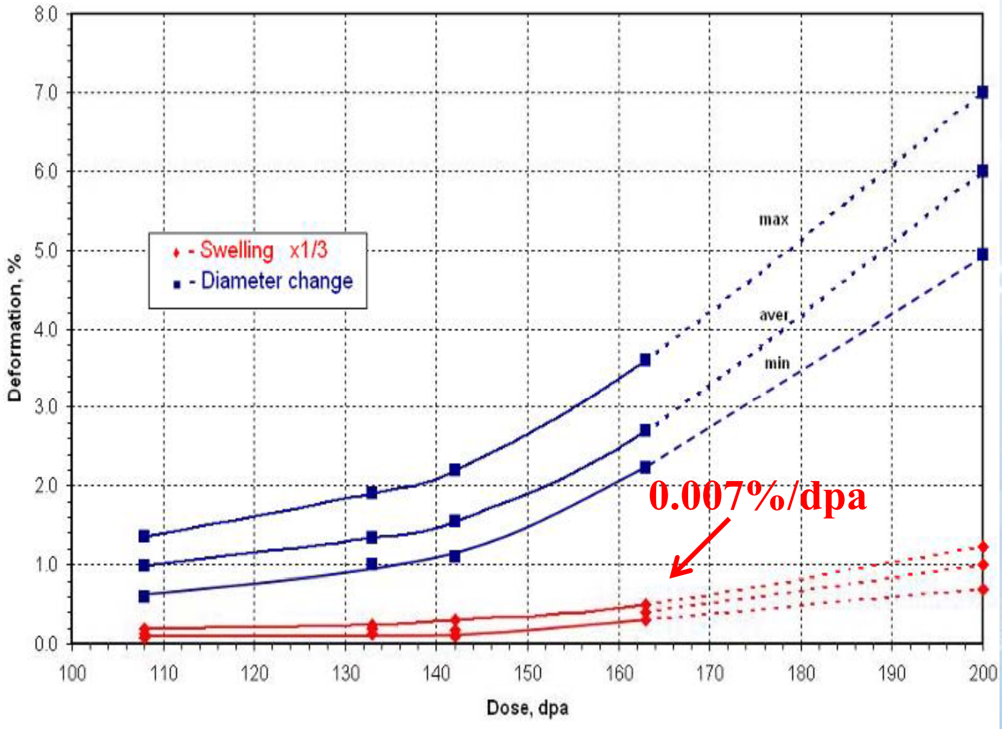
In order to explore the suitability of F/M for advanced nuclear applications, it is necessary to explore its swelling behavior to damage levels approaching 500-600 dpa.

Currently available data to ~163 dpa(RIAR, 2011) imply that void swelling rate of EP-450 is very low.

Is it reasonable to assume that the swelling rate will always be low, especially at dose levels not yet reached in reactors?

It is necessary to reach doses~ >200dpa

- **Ion-beam materials research are now only one possible unique choice in the absence of high flux neutron irradiation facility. Many nuclear facilities are shut down now (FFTF, RAPSODIE, DFR, PFR, Superphenix, Phenix, EBR-II, BR-10, Monju, JOYO, BN-350 etc).Only BOR-60 does work !**

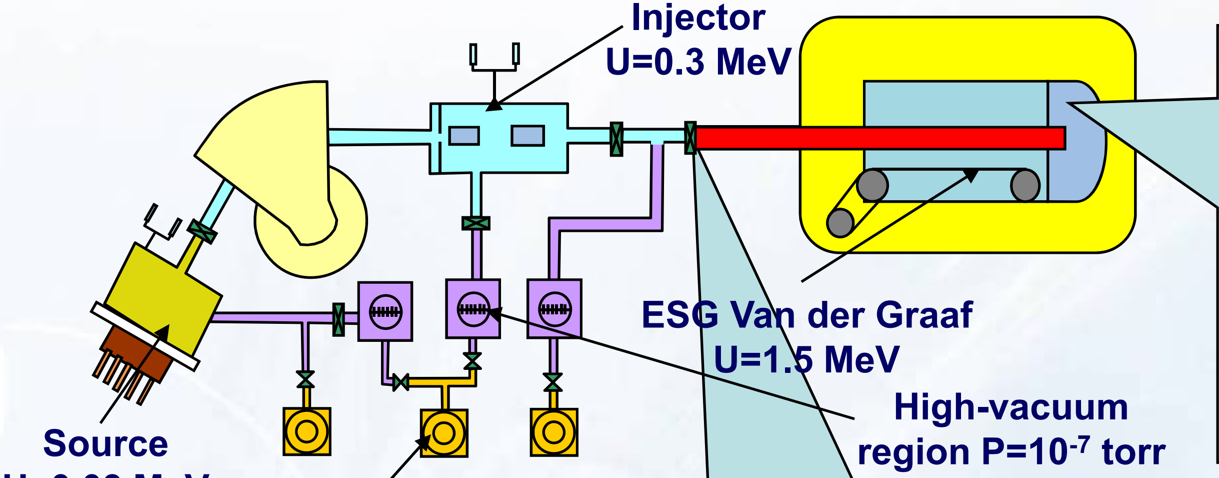


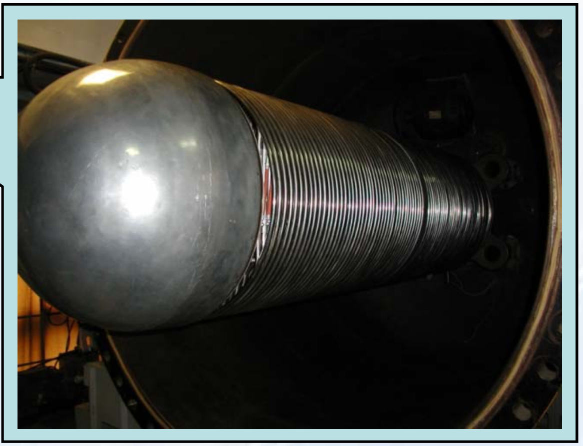
0.007%/dpa

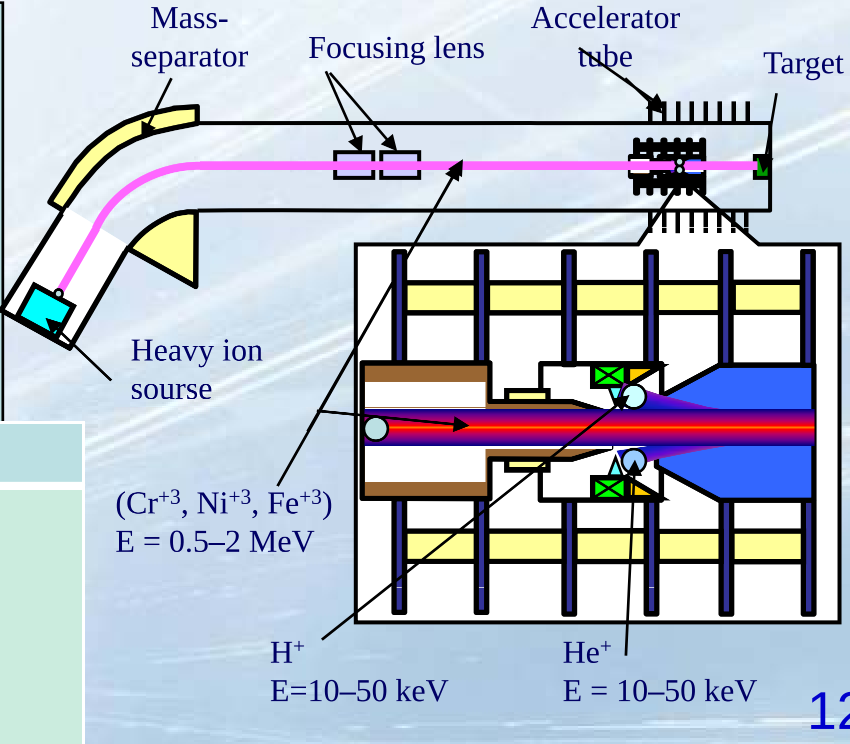
2010 ANS Winter Meeting, November 7-11, 2010, Las Vegas, Nevada, USA.

To be or not to be…?- YES!!!

Electrostatic Accelerator with External Injector (ESUVI)-KIPT

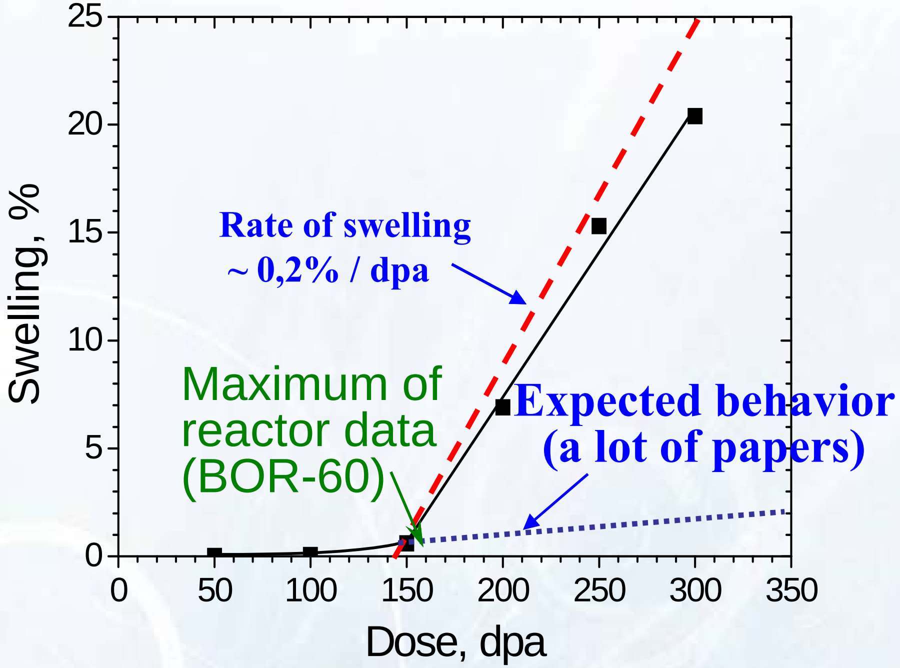


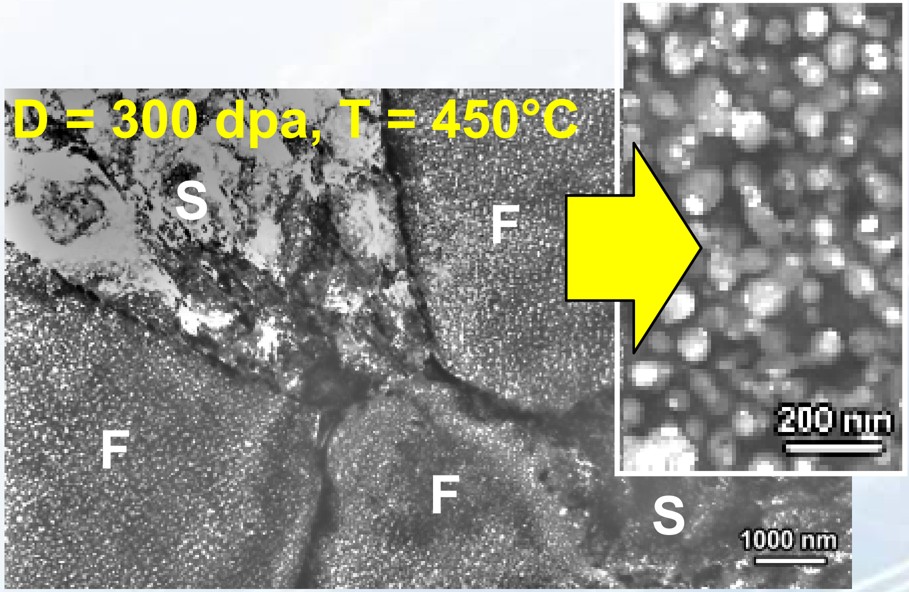




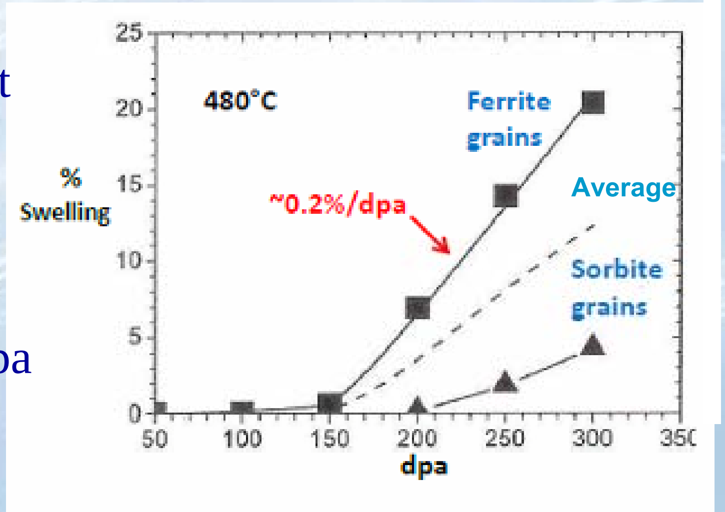
Irradiation	Parameters	
Cr Cr+He Cr+H Cr+He+H	E_{Cr}= 0.3 – 1,8 MeV j_{Cr} =1 - 35 μA/cm^2 E_{He}= 10 - 60 keV j_{He} = 1 – 500 nA /cm^2 E_H= 10 - 60 keV j_H = 1 – 500 nA /cm^2	T_{irr}= 350^0 – 800^0C D = 0 - 600 dpa k = $7\cdot10^{-5}$ – $2\cdot10^{-2}$ dpa/s 0.1 – 1.3 appmHe/s 0.1 – 1 appmH/s

Swelling of ferritic-martensitic steels EP-450 irradiated to super-high doses



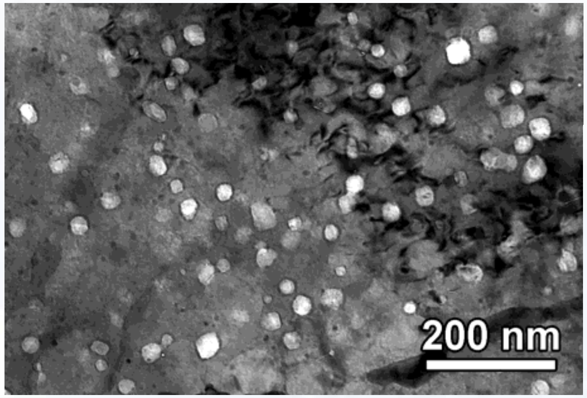


- ➢Swelling of BCC steels may reach more than 20% at super-high doses;
- ➢Ferritic grains in EP-450 begin swell early than sorbite one;
- ➢Average swelling rate depends on volume ratio of ferrite to sorbite grains;
- ➢The rate of swelling on steady-state stage is 0,2%/dpa that agreed with observed swelling of binary Fe-Cr alloys irradiated in EBR-II and FFTF.

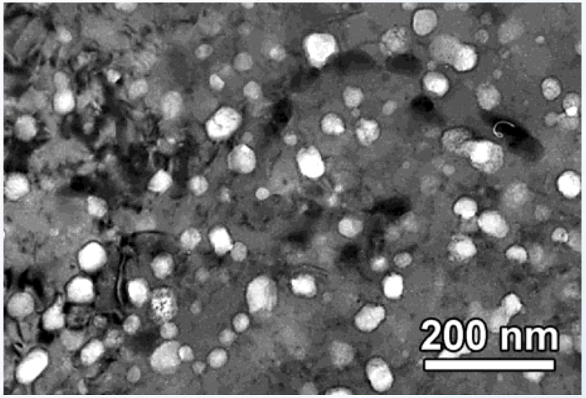


Influence of composition on swelling of F/M steels

Ion-induced swelling of cold-worked HT9 at 450°C

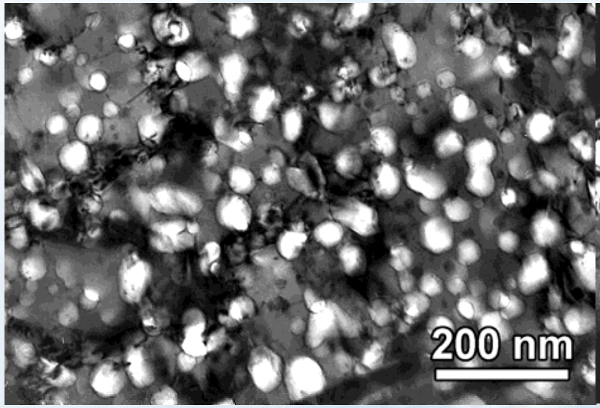


200 dpa

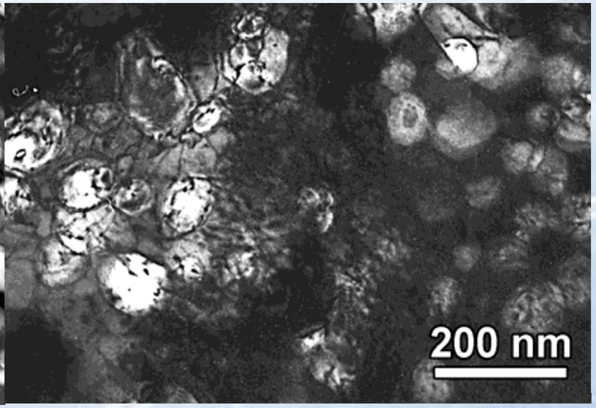


300 dpa

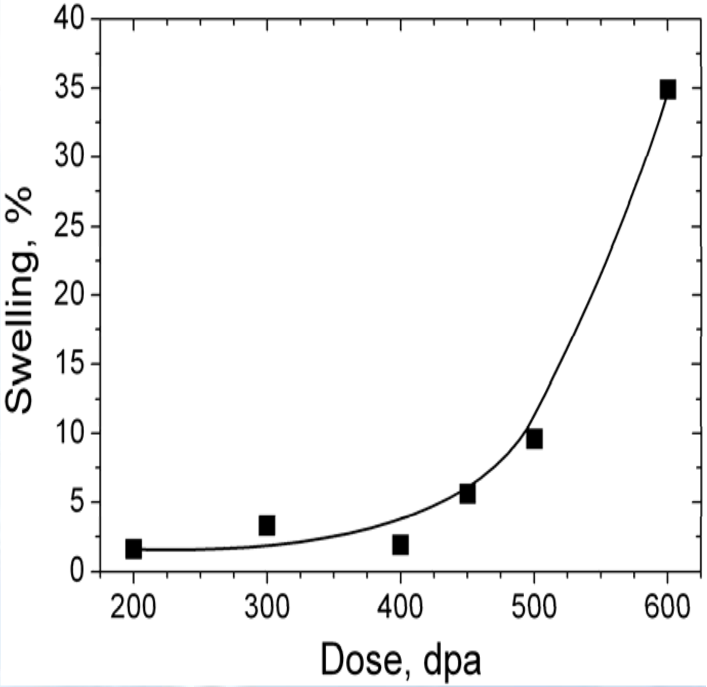
760°C/0.5h + 33% CW



500 dpa



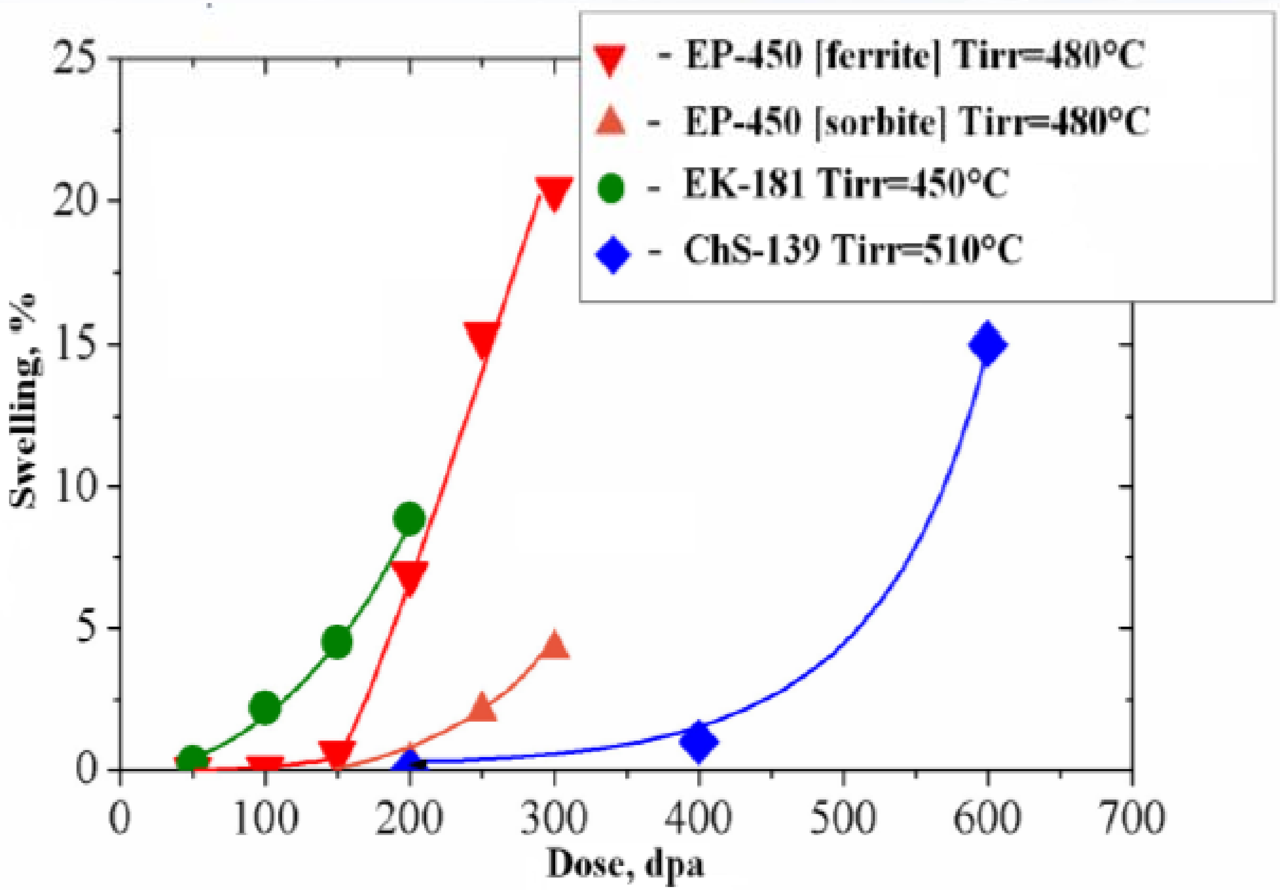
600 dpa



Decomposed martensite grains start to develop a high rate of void swelling at ~400 dpa. Pre-existing carbide precipitates within grains are missing while grain boundary carbides are still visible.

Recently released data on alloys irradiated at KIPT with 1.8 MeV Cr^+ ions *

V.N. Voyevodin

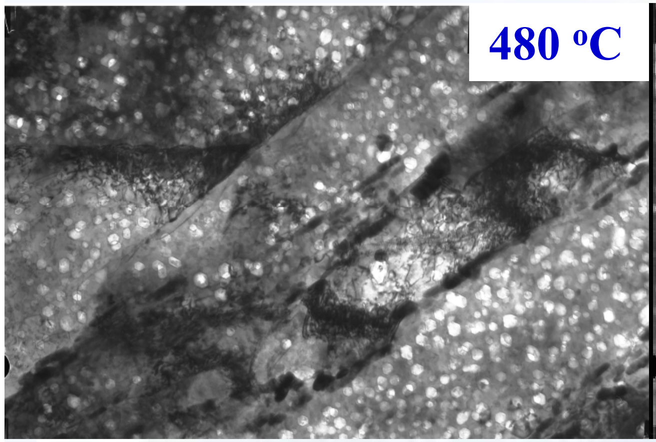


Very large difference in swelling behavior was observed in these three alloys at peak swelling temperature.

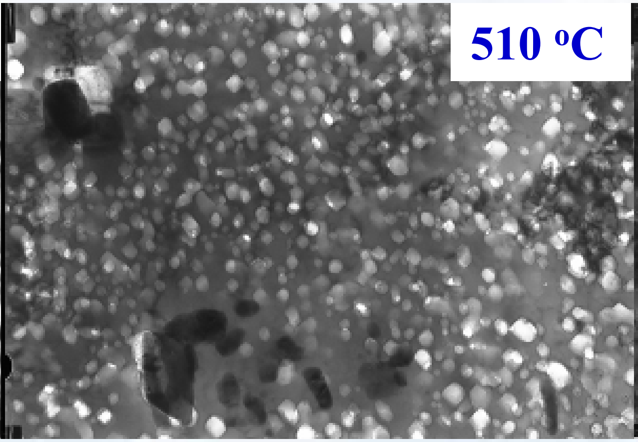
Can the differences be attributed to composition?

Influence of composition on swelling of F/M steels

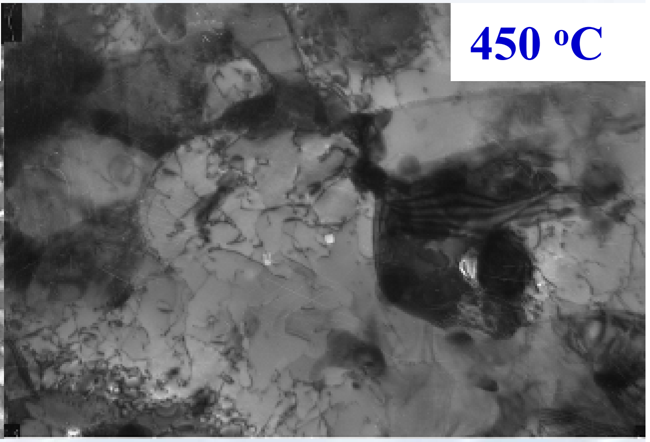
(Cr^{3+}, E=1,8MeV, D=200 dpa, T=T$_{max\ sw}$)



EP-450



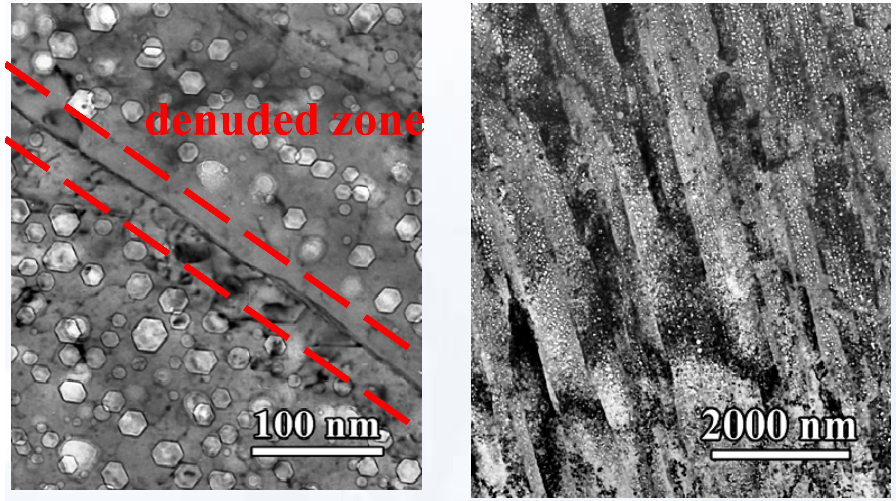
EK-181



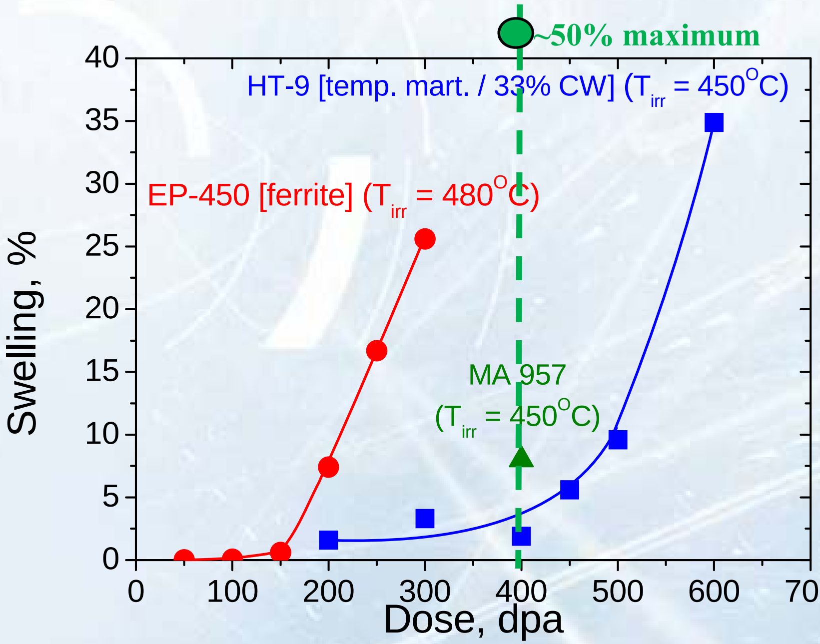
ChS-139

	C	Cr	Ni	Mo	Nb	W	V	Ta	B	Si	N	Mn
EP-450	0.11	11.2	0.08	1.33	0.5	-	0.2	-	-	0,6	-	0.6
EK-181	0,14	11,2	0,03	0,04	0,01	1,17	0,29	0,17	0,004	0,37	0,044	0,94
ChS-139	0,21	11,8	0,73	0,51	0,3	1,26	0,31	0,07	0,006	0,29	0,085	0,57

Swelling features vs structure in MA 957

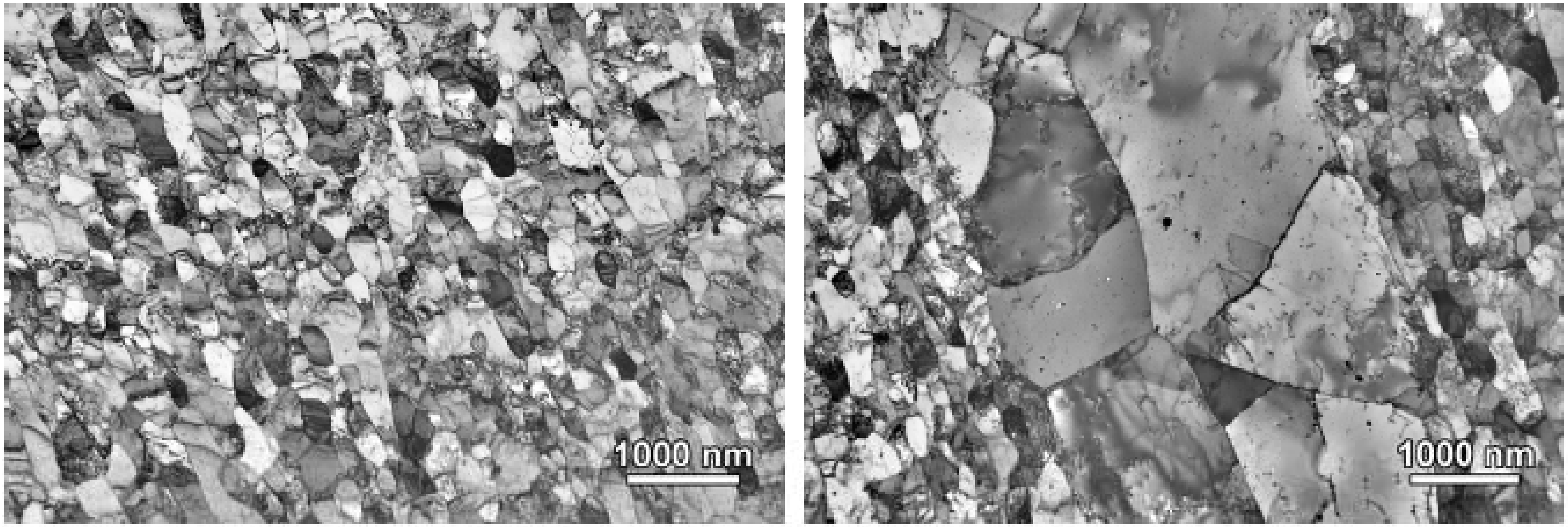


1.8 MeV Cr^{3+} , T_{irr}= 450°C, D=500 dpa



- ➢The void swelling of oxide-dispersion-strengthened (ODS) alloy MA957 under ion irradiation is very sensitive to the details of oxide dispersion.
- ➢In one heat where the dispersion is very inhomogeneous the swelling is equally inhomogeneous. At 400 dpa adjacent grains vary from 0 to~50% swelling
- ➢The better dispersion leads to lower average swelling.
- ➢Swelling within the grains reflects the influence of grain boundary denuded zones.
- ➢ODS alloy concept may extend the swelling resistance to considerably higher neutron exposures relatively HT-9 and EP-450

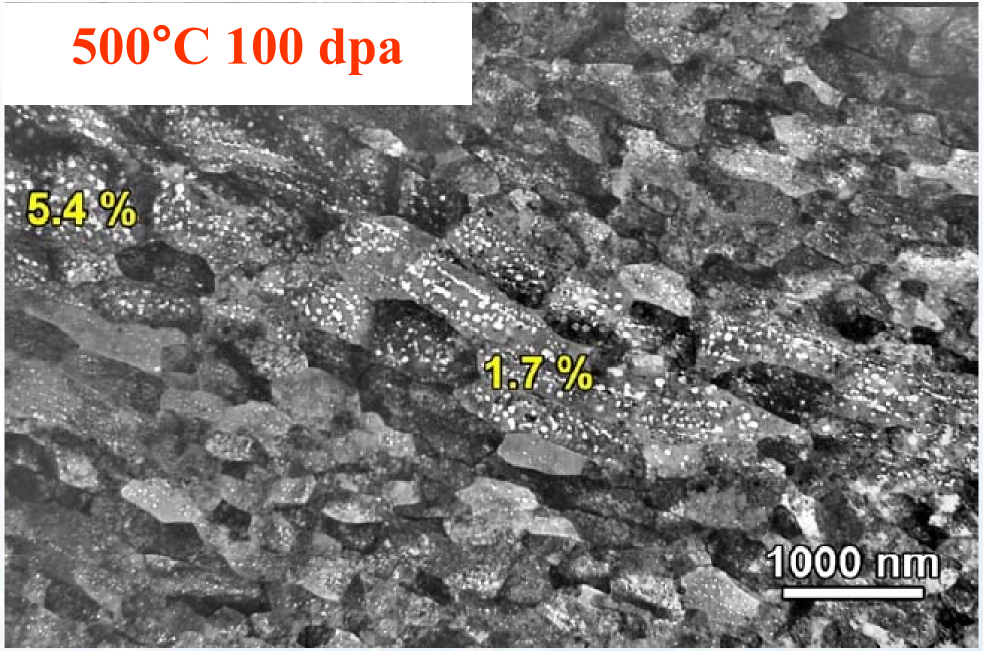
Grain structure of U.S. nano-structured dispersoid alloy 14YWT produced at Oak Ridge National Laboratory

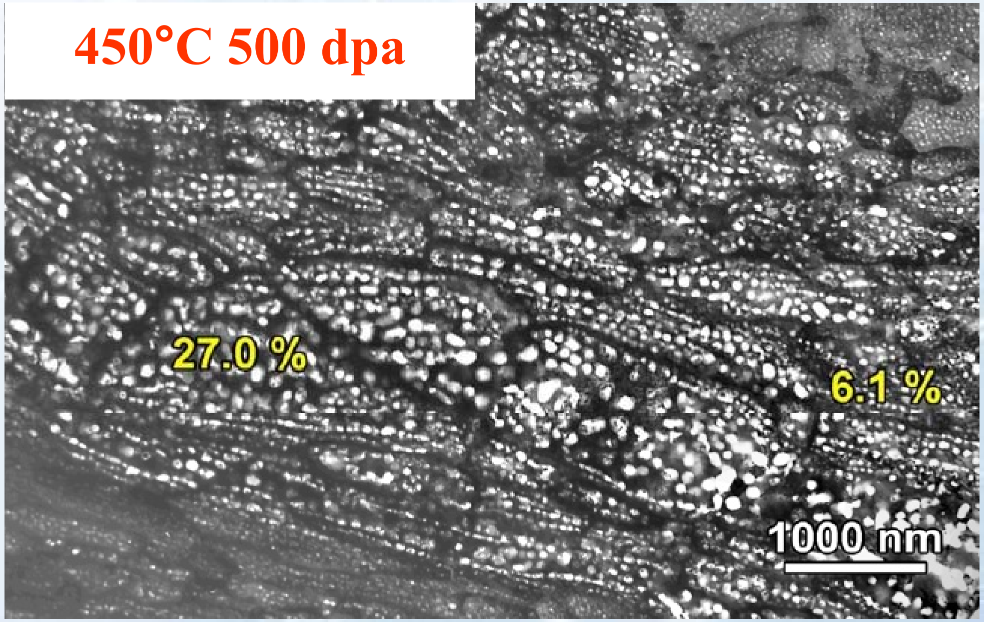


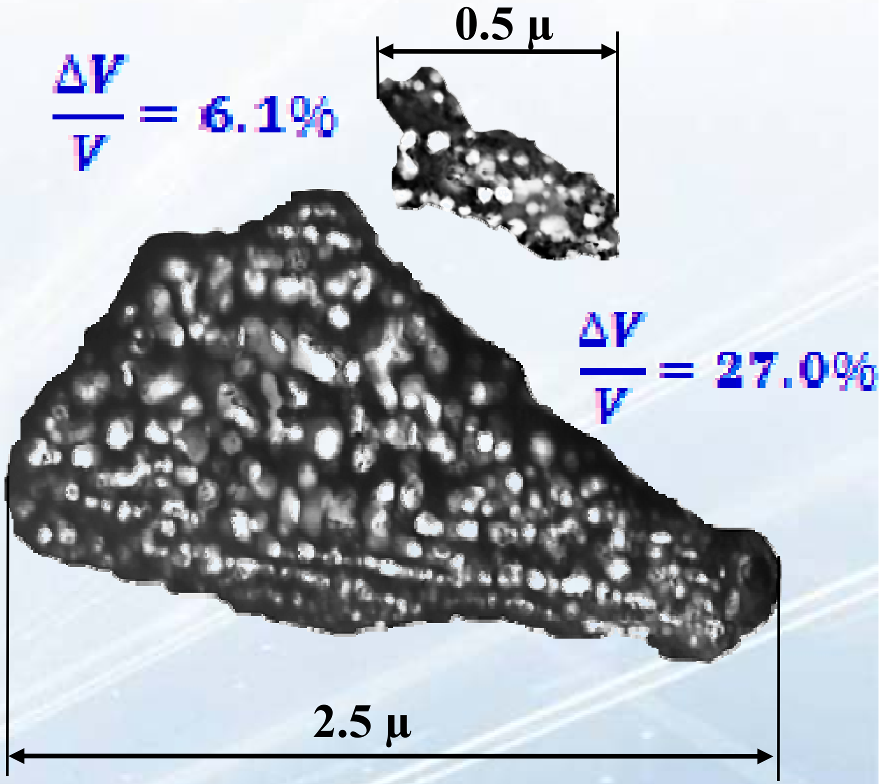
≥90% of volume is fine-grained (mean size of ~0.2 µm)

≤10% of volume is coarse-grained (mean size of 2-6 µm)

Influence of size of grain on swelling of 14YWT


500°C 100 dpa

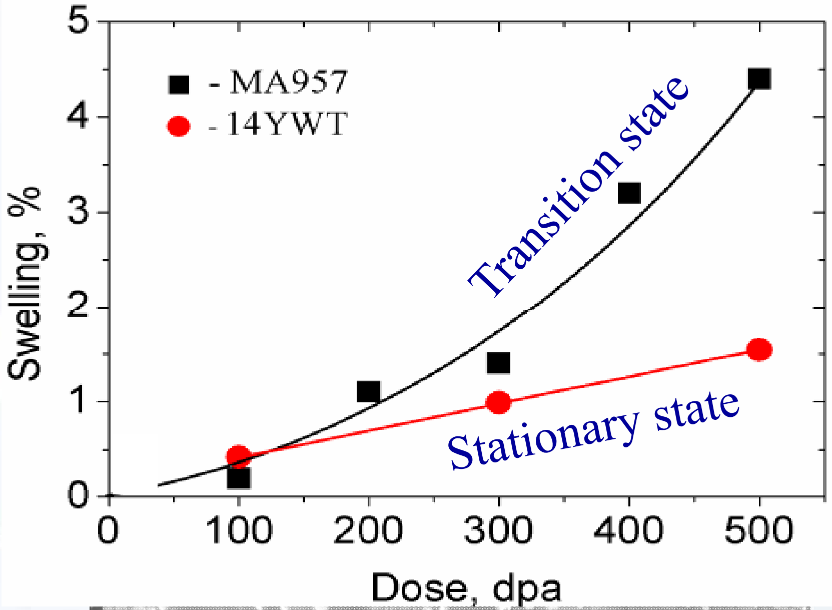

450°C 500 dpa

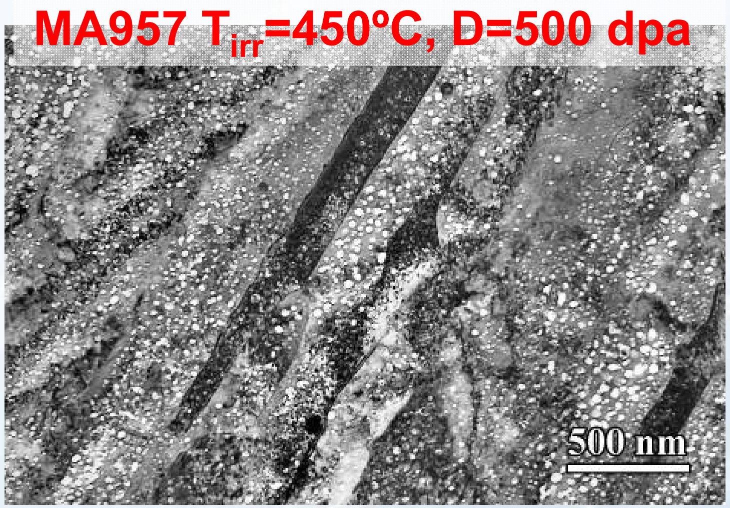


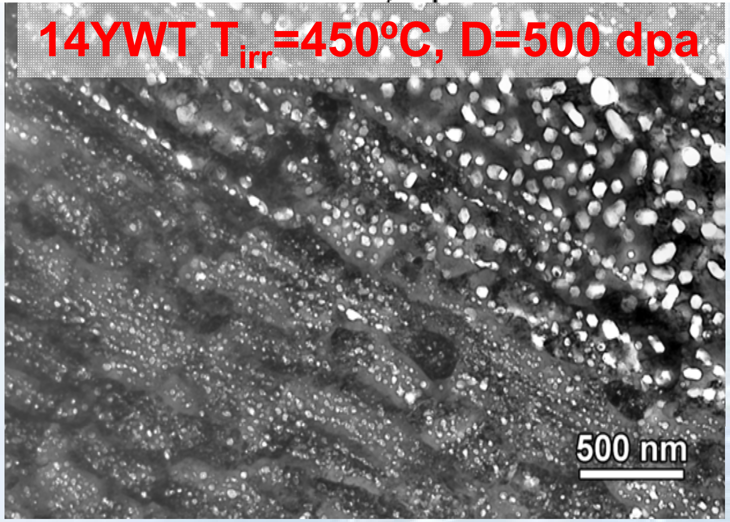
Large coarse grains in 14YWT swell much more than fine grains

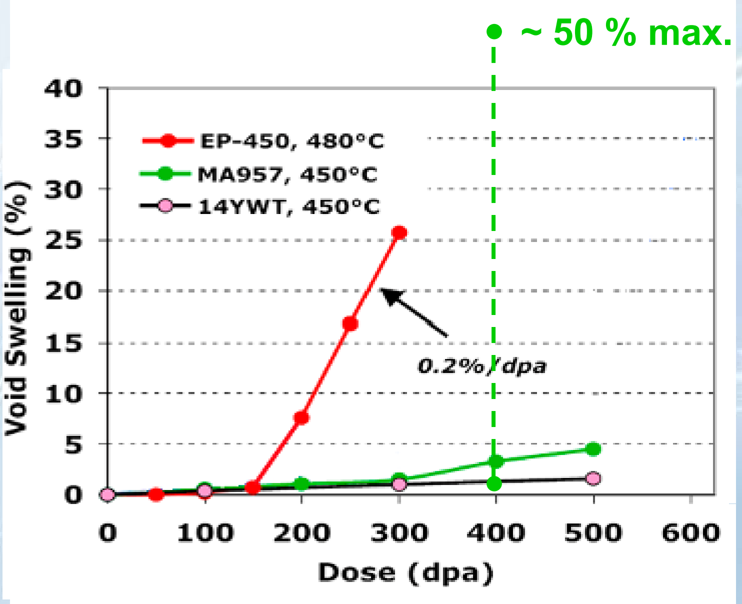
What is the better …?

MA957: Fe14Cr 1Ti 0.3Mo 0.25 wt%Y_2O_3 **14YWT**: Fe 14Cr 3W 0.4Ti 0.25 wt%Y_2O_3




MA957 T_{irr}=450°C, D=500 dpa


14YWT T_{irr}=450°C, D=500 dpa



Proposed mechanisms of swelling suppression

The void swelling of oxide-dispersion-hardened (ODS) alloy MA957 is very sensitive to the details of oxide dispersion and can changes drastically from grain to grain (from 0 till to 50% at 400dpa and average swelling near 8%). Such a long transient period for MA957 shows that more advanced ODS ferritic alloys may prolong the transient regime even to higher doses. Based on our observations, the swelling resistance appears to be associated with a high and stable density of oxide particles and high grain boundary areal density.

Steel 14YWT represents the best product of modern technologies for formation of stable elements of microstructure highly resistant to swelling. Super fine grain and high concentration of oxide nanoparticles will produce all conditions for suppression of swelling up to high doses of damaging irradiation due to increasing of recombination of point defects .

ODS problems

Despite these promising results, challenges remain.

First, steel-processing techniques for these highly-specialized alloys have not been perfected. Especially when compared to reduced-activation ferritic and martensitic steels, processes like fabrication and welding need to be perfected before reactors can be constructed.

Other problems persist. Producing of these materials in large sizes is difficult. Additionally, a lot of the metal forming processes involved such as rolling and extrusion are directional and result in elongated grain structures. This causes anisotropic behavior that can have detrimental effects such as reduced mechanical properties along certain directions in the material.

ODS problems (Cont’d)

Finally, the structures of these materials are still not completely understood. As nanocharacterization techniques improve, it is possible that our understanding can lead to further structural manipulation and even better overall properties.

As the world's energy demands increase and nuclear reactors play a larger role, higher-performing nuclear reactor materials will be required and ODS steels may be one of the prospective part of this solution.

Conclusions

1. **Ferritic-martensitic (F/M) steels** are the main candidates to reach high fuel burn-up levels for many type of reactors. Structure stability and radiation resistance of F/M alloys under high dose irradiation determine by co-evolution of all components of the irradiated microstructure and characterized by features of dislocations structure, RIS, stability of phases and their impact in the macroscopic response in terms of swelling, anisotropic growth, irradiation creep, and radiation-induced phase transformation.
2. **Charged particles irradiations** can provide a low-cost method for conducting valuable radiation effects research. Ion simulation can be used to explore the effect of various compositional, fabricational and environmental variations on void swelling. **KIPT has** irradiation facilities that provides triple ions with one accelerating tube to achieve high doses of irradiation (up to 500 dpa) with simultaneous introduction of helium and/or hydrogen in any gas/dpa ratio relatively Gen IV, Spallation, Fusion demands.
3. **The Department of Nuclear Physics and Power of NAS of Ukraine** (founded in 2004) is reliable partner for prospective development of basic and applied investigation in the areas of radiation material science, radiation technologies and new nuclear-power sources.

Thank you cordially !