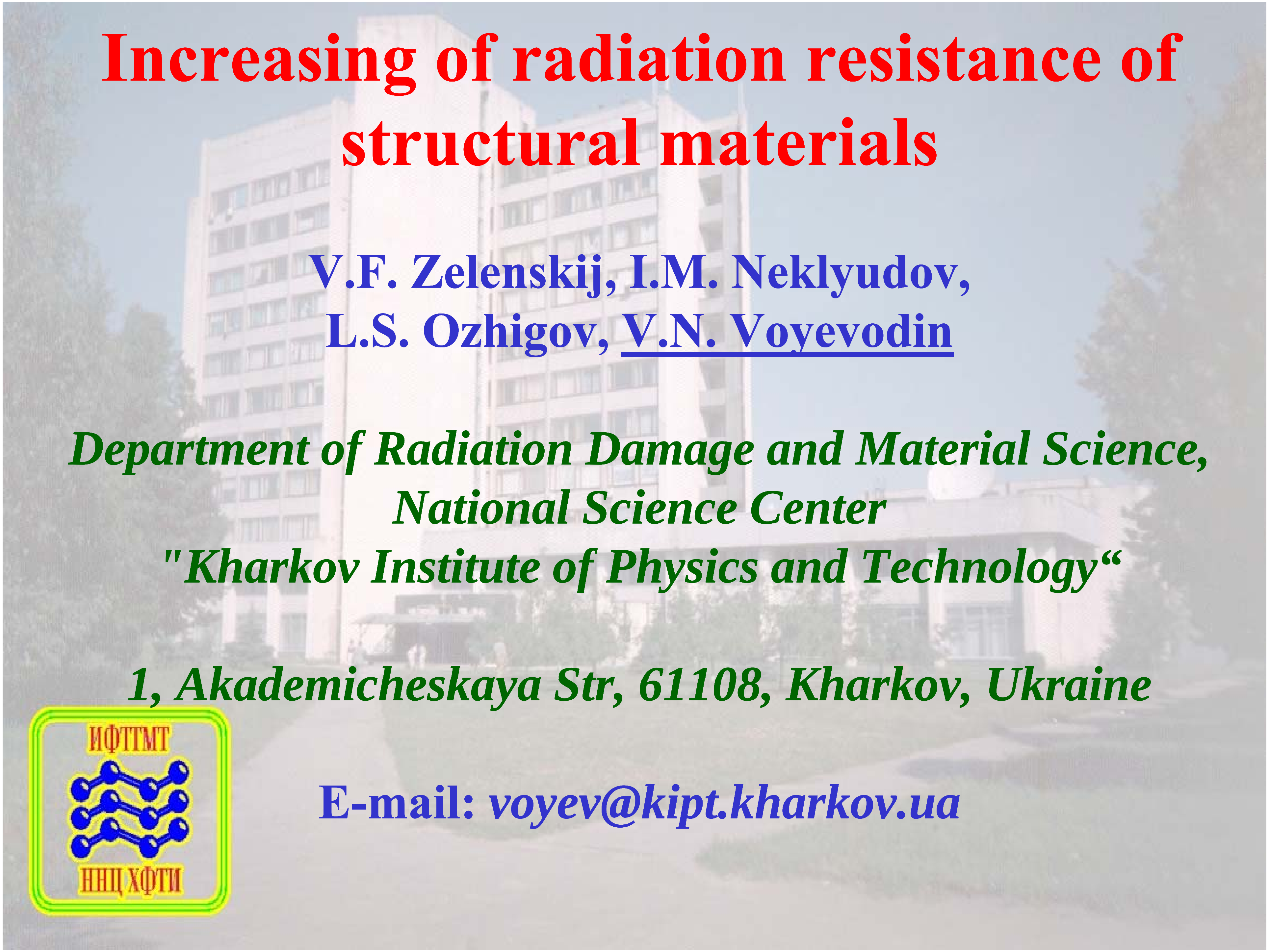


Increasing of radiation resistance of structural materials

V.F. Zelenskij, I.M. Neklyudov,
L.S. Ozhigov, V.N. Voyevodin

Department of Radiation Damage and Material Science,
National Science Center
"Kharkov Institute of Physics and Technology“

1, Akademicheskaya Str, 61108, Kharkov, Ukraine

E-mail: *voyev@kipt.kharkov.ua*

R&D of structure materials (1)

Research and development of structural material is the complex process; the important feature of this process is assigned variation of element composition, of phase state and structure in the material volume and provision of the stability of formed structure-phase state in the operational conditions.

The main factors are determined by the operational conditions of structural element of specific NPA; they also cause the main operational properties of structural material for given element.

The limiting factors determine the properties that influence on technical-economical factors of NPA but are not determining for the serviceability of the material.

Fuel burn-up and radiation stability

Now is the most effective - (real) way of improvement of technical and economical characteristics of nuclear fuel cycle – the burn-up increasing (energy, produced from unit quantity of nuclear fuel [GWdays/t]).

Modern status:

- **Light water reactors (LWR)** → 45-50 GWtd/t (~5% of heavy atoms), 8-10dpa
- **Fast reactors (FR)** → ~ 75 GWtd/t → 10-12% (h.a) , 80-90dpa

Targets:

- **Light water reactors (LWR)** → 75-80 GWtd/t (~ 8% h.a), 12-15dpa
  → 100 GWtd/t(~ 10-11% h.a), 18-20dpa
- **Fast reactors (FR)** → ~ 200 GWtd/t /т (20-25 % h.a), > 200dpa

These tasks are very complicated due to :

the insufficiency of our knowledge on nature of radiation-induced phenomena : material damage in practically not investigated range of very high irradiation doses.

Possible ways for increasing radiation stability

- There is the obvious relation between structure-phase state of irradiated material and its radiation resistance.
- The key question of evolution of radiation-induced microstructure is the difference in the absorption of interstitial atoms and vacancies on different sinks, that causes the cooperative development of all microstructure components in irradiated material.
- From the point of view of radiation damage this is precisely the structure-phase state of material under irradiation that determines the dynamic balance of point defects that were not subjected to the recombination and, accordingly, the value of swelling, distribution and parameters of porosity.

New modification of radiation resistant steels

(G.Karzov, 2006)

Steel	Mass, %									
	C	Si	Mn	S	P	Cr	Cu	Ni	Mo	V
25Cr3NiMo	0.23	0.44	0.49	0.018	0.024	3.03	0.10	1.02	0.4	-
15Cr2MoVA	0.11-0.21	0.17-0.37	0.3-0.6	0.012-0.018	0.009-0.0038	2.5-3.0	0.09-0.17	0.19-0.27	0.6-0.8	0.25-0.35
15Cr2NiMoVA	0.13-0.18	0.17-0.37	0.3-0.6	0.012-0.013	<0.035	1.8-2.3	0.07-0.08	1.0-1.05	0.5-0.7	0.10-0.12
15Cr2NiMoVAA	0.013-0.18	<1	<1	<0.035	<0.01	1.8-2.3	-	1.0-1.5	0.5-0.	0.10-0.12
15Cr3NiMoVA	0.12-0.16	<1	<1	<0.035	<0.035	2.2-2.7	-	0.8-1.3	0.5-0.8	0.08-0.15
15Cr3NiMoVAA	0.12-0.16	<1	<1	<0.035	<0.01	2.2-2.7	-	0.8-1.3	0.5-0.8	0.08-0.15
A542**	≤0.15	0.15-0.30	0.30-0.60	≤0.035	0.035	2.0-2.5	-	-	0.90-1.10	-

*** - Chemical composition of vessel steels for reactors PWR and BWR*

Ni ↓ 1,00-1,50
0,20-0,40

Cr ↑ 2,70-3,00
1,80-2,30

V ↑ 0,27-0,30
0,10-0,12

Mo ↑ 0,50-0,70
0,60-0,80

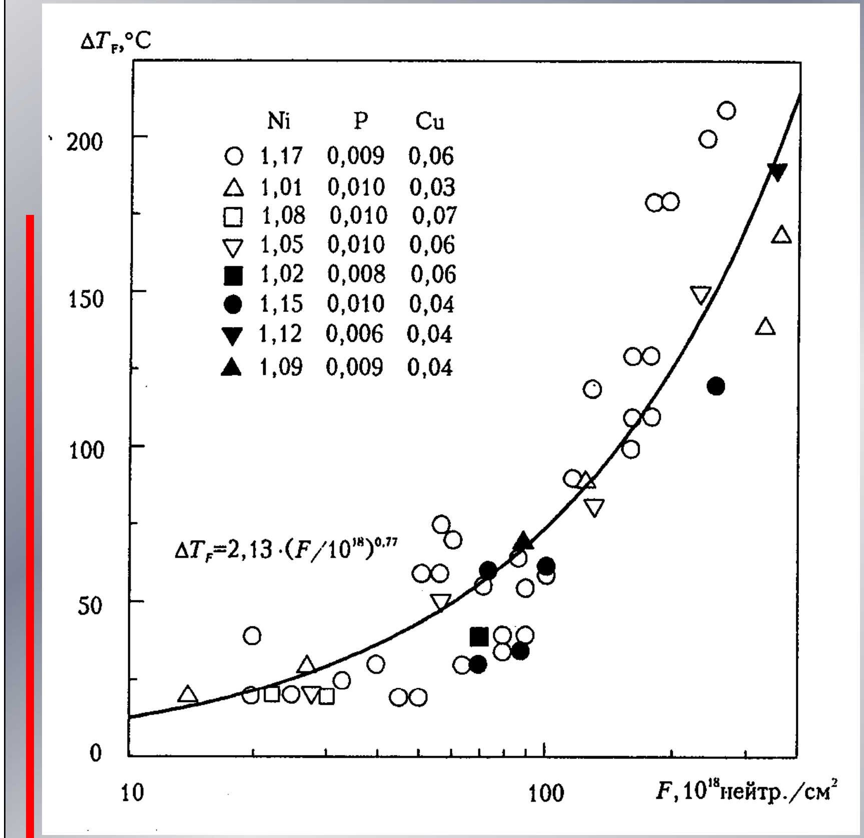
Cu ↓ 0,30
0,07

S ↓ 0,02
0,006

P ↓ 0,02
0,006

As ↓ 0,10
0,006

Influence of Ni on embrittlement of RPV (G. Karzov, 2006)



The fractional contribution of nickel into radiation embrittlement on the base of the principle of superposition at irradiation temperature 290°C gave the following dose dependence for concentration of nickel from 0 to 1,9%:

$$\Delta T_F = A_F(Cu,P)\cdot F^{1/3} + C_F(Ni)\cdot F^m =$$

$$= 685(C_P + C_{Cu})\cdot\left(\frac{F}{F_0}\right)^{1/3} + 0.38(C_{Ni} - 0.34)^{1.8}\cdot\left(\frac{F}{F_0}\right)^{1.1}$$

where $F_o = 10^{18}$n/cm^2;

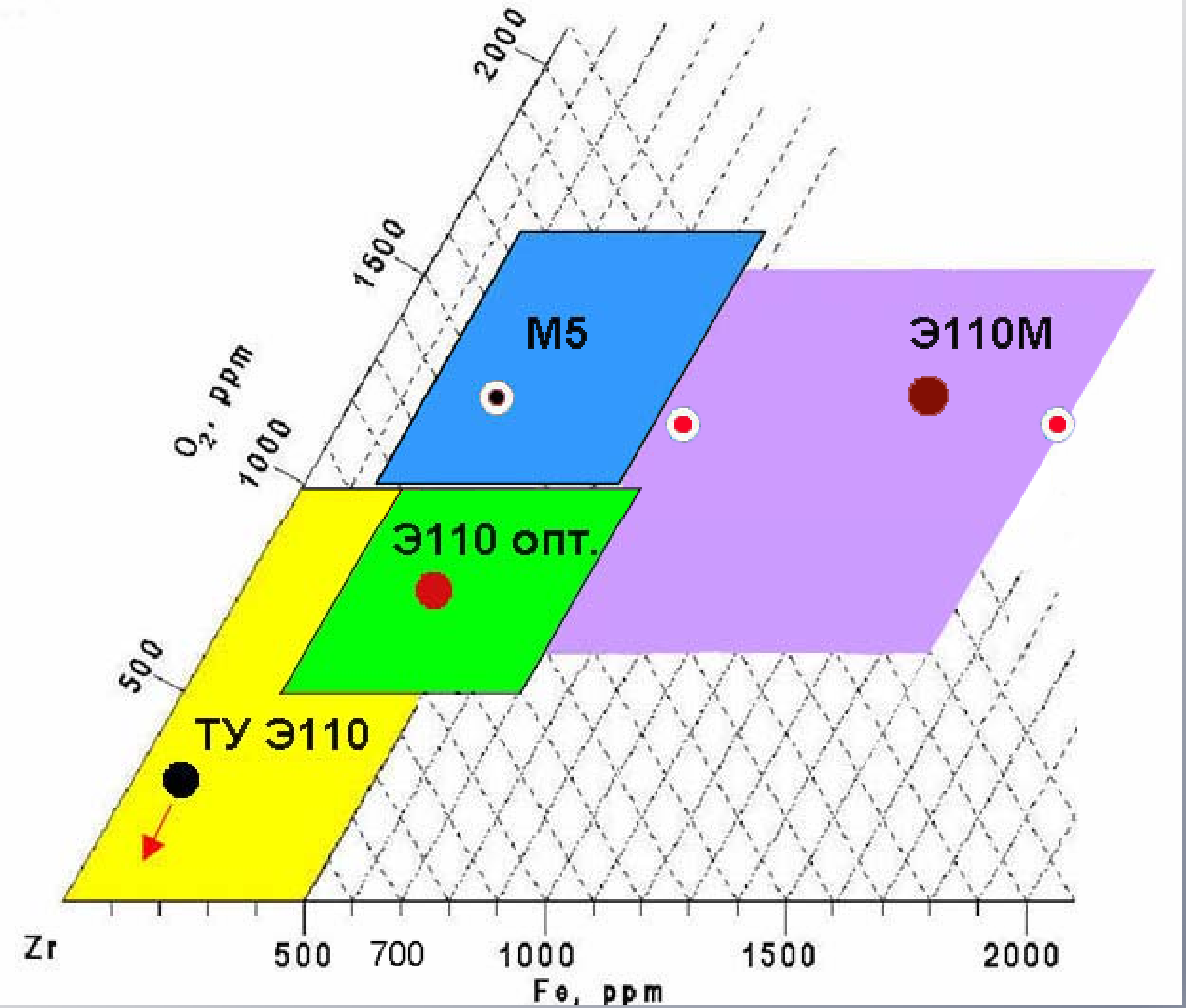
C_P, C_{Cu} and C_{Ni} – number values, mass % content of chemical elements in steel.

Influence of Ni on embrittlement of RPV (G. Karzov, 2006)

This is conditioned by the 10% increase of single-unit power of new unit in comparison with WWER-1000 and increase of the term of operation to 60 years, that is, from 300 to ~ 450 thousands hours. The designed fluence of fast neutrons on pressure vessel also increases and constitutes approximately $6.7 \cdot 10^{19} n/cm^2$.

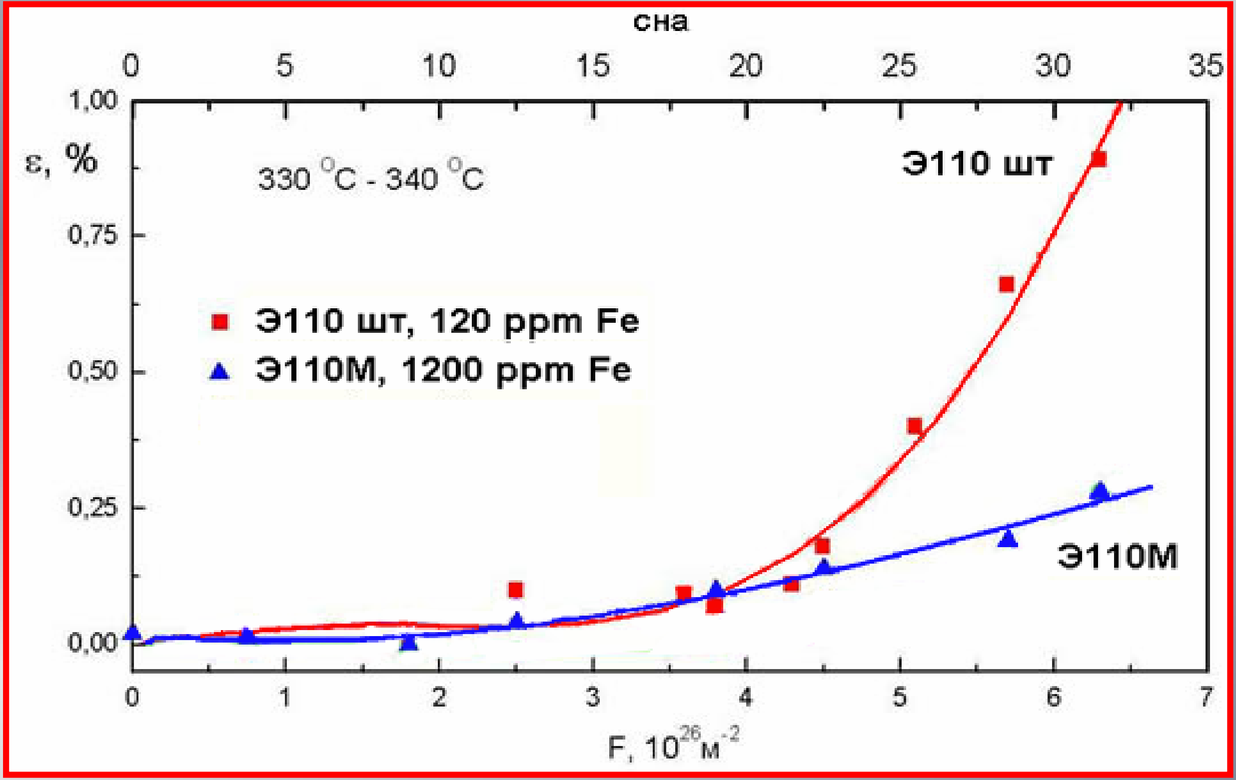
The parallel investigation of radiation embrittlement of steels 15Kh3MFA-A and 15Kh2NMFA-A performed on the metal of industrial melts had showed that steel 15Kh2NMFA-A was damaged heavily under neutron irradiation than steel without nickel. It was reflected in “Standards of strength analysis…” in the form of higher coefficient of radiation embrittlement A_F=23 at the metal operational temperature 290°C. For steel 15Kh3MFA-A at the same temperature of irradiation the value A_F is accepted to be equal to 9.

Second stage – modernization of alloy E110
Step 1 – increase of O and Fe content(V.Novikov,2008)



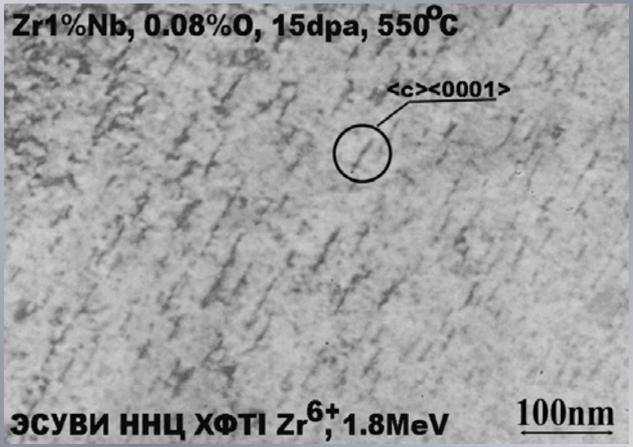
Experimental investigation of alloy E110M characteristics
(V. Novikov, 2008)

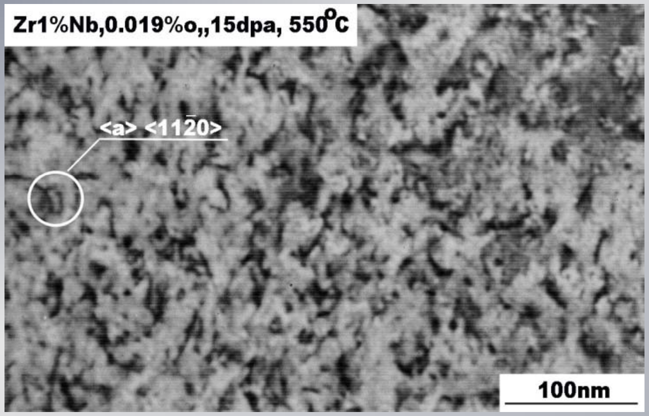
Deformation of radiation growth (irradiation in BOR-60)

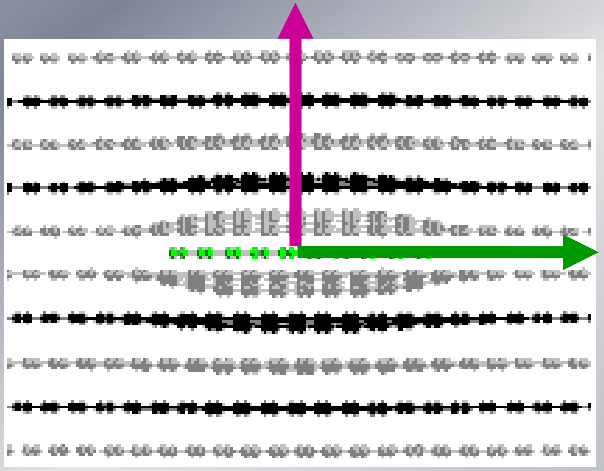


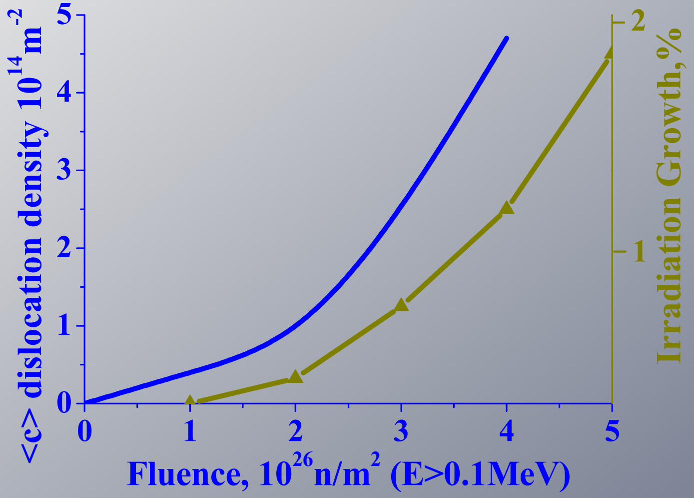
Increase of the content Fe decreases DRG under increased fluences

Oxygen influence on <c> components dislocation nucleation by ion irradiation



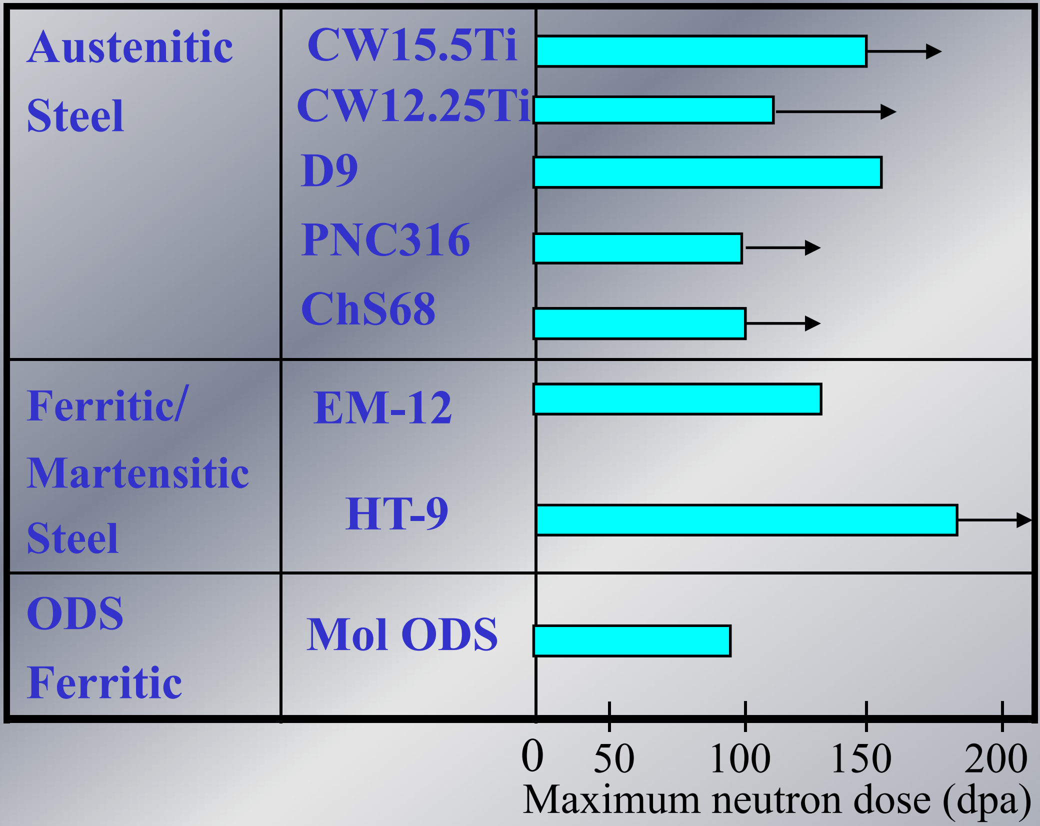




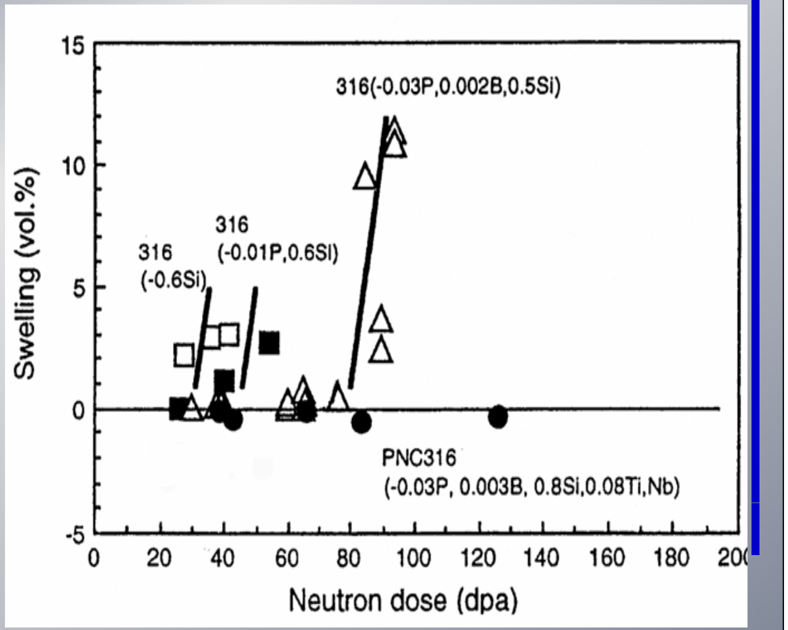


Increase of oxygen content (from 0,08 to 0,2%) in alloy Zr1% Nb causes the suppression of dislocation loops formation of <c> type <0001> being responsible for radiation growth

Materials development status



Maximum neutron dose of fuel pin cladding materials experienced in FBR fuel assemblies

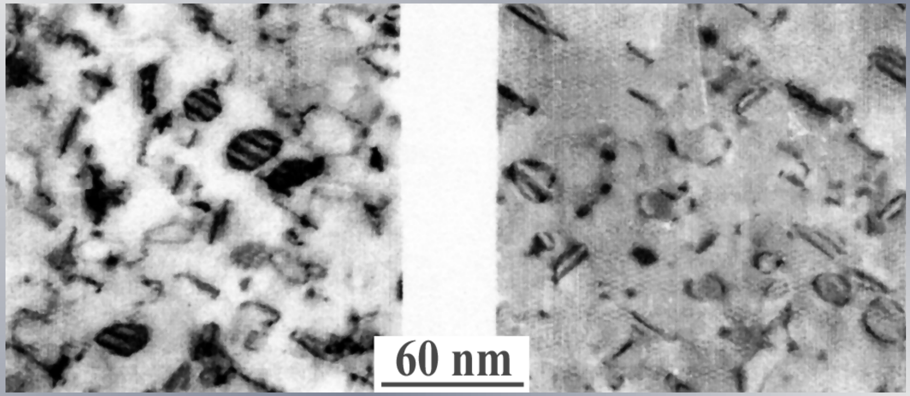


Typical swelling of few austenitic stainless steels (T_{irr} ~ $500^{O}C$)

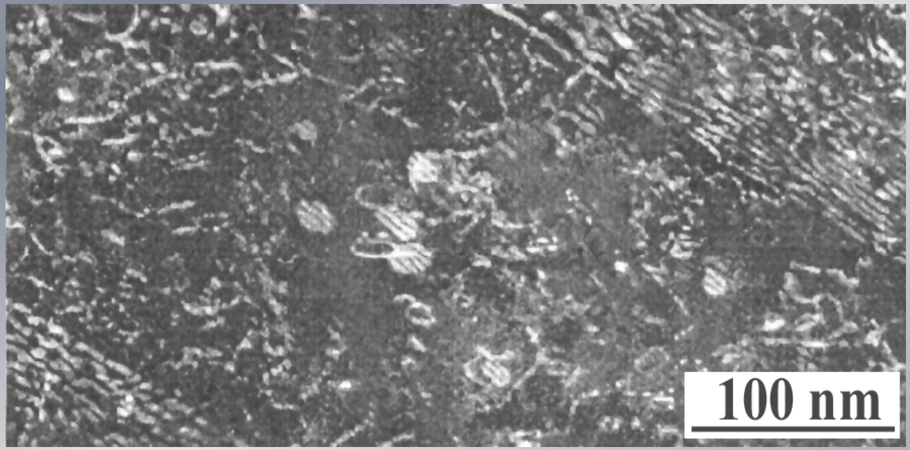
Parameters of dislocation and void structures in some austenitic stainless steels, irradiated by ions of chromium (E=3 MeV, D=2 dpa, $T_{irr.}$=600^{o}C)

Material	$T_{ir.}$ °C	Diameter of loops, nm	Density of the loops, cm	Number of interstitial atoms, cm^{-3}	Diameter of voids, nm	Density of voids, cm	Number of vacancies in voids, cm^{-3}
EI-847 (SA)	650	34.5	2.2x10	4.3x10	2.0	6x10	1.2x10
	700	81.0	1.3x10	9.2x10	-	-	-
EI-847 (SA+20%CD)	650	30.5	1.5x10	2.5x10	-	-	-
	700	69.0	1.1x10	7.2x10	-	-	-
EI-847 (SA+800^{o}C/200 h)	650	25.0	2.0x10	1.1x10	12.0	4x10	2.0x10
18Cr10NiTi (SA)	650	32.0	3.3x10	3.7x10	7.0	6x10	5.4x10
16Cr11Ni3Mo (SA)	650	41.5	1.2x10	2.4x10	-	-	-

Dislocations evolution in irradiated austenitic SS



EI - 847,Cr^{3+}, E=3MeV, D= 2dpa, T$_{irr}$=600^{O}C
1-(1050^{O}C, 30min); 2-(800^{O}C/200hours)



EI - 847, Cr^{3+}, E=3MeV, D=2dpa, Tirr=600^{O}C,
1050^{O}C, 30 min + 30%CW (dark field)

Dislocation structure in irradiated ASS follow evolution scheme which is typical for FCC materials with irradiation dose increasing:

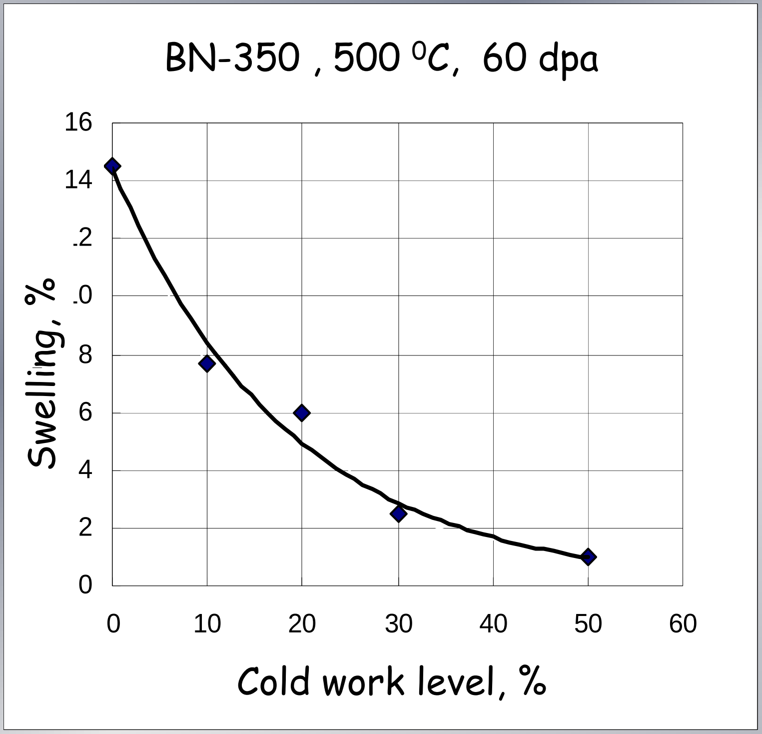
- Nucleation of interstitial clusters on (110) planes
- Frank loops formation b=a/3<111>
- Interaction of Frank loops with Shockley loops a/6<112>
- perfect loops formation b=a/2<110>
- perfect loops interaction and dislocation network formation (Neklyudov, Voyevodin, 1994)

Key and pain points for dislocation evolution are follows:

- How fast it is going? Frank loops and perfect loops have different mobility due to Burgers vectors position relatively glide plane and, as result, different absorbing possibilities for PD
- Composition can change stage of dislocation evolution and dislocation parameters. It is exists high sensitivity of transformation stage from Frank loops to perfect loops as a function of SFE
- Dislocations behaviour in CW-materials: Non uniform dislocation distribution and formation of "cell" structure can lead to non uniform recovery processes during long term thermal-radiation exposure

Structural approach – dislocation factor (A. Tselischev, 2008)

Effect of cold work level on EI847 swelling



Hyderabad, July 2-4, 2008

Progress in c.w. level of austenitic steel

ε = 15 %

ε = 18 ±2 %

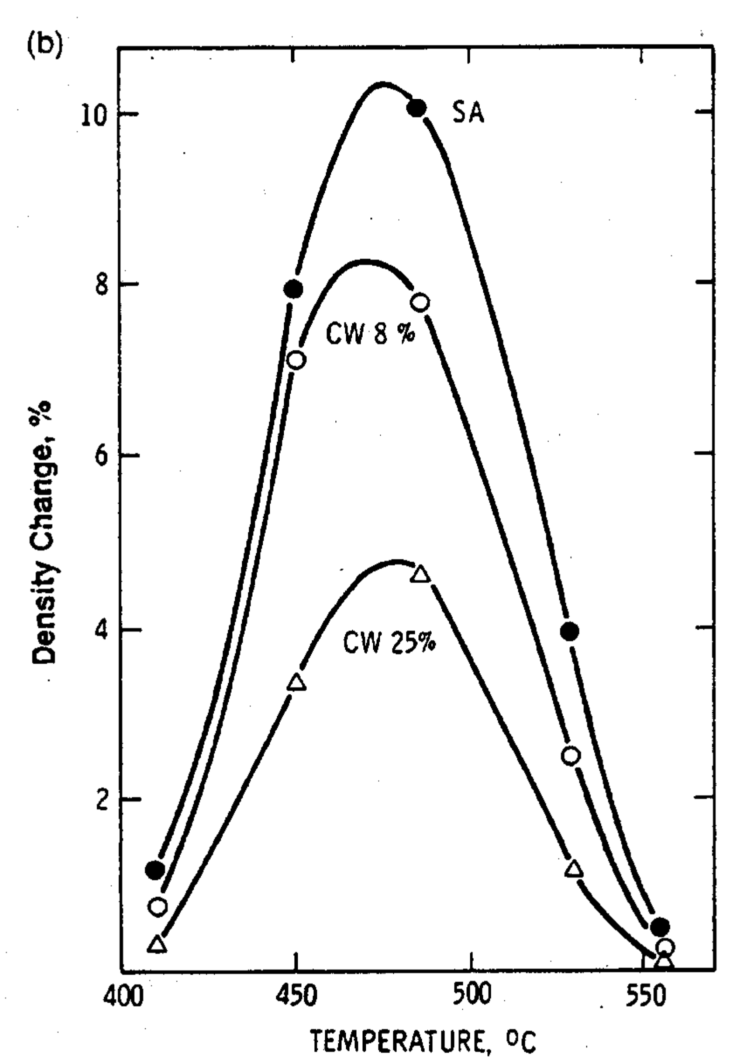
ε = 20 ±3 %

ε = 20-25 %a

In a cold worked structure, the dislocation in cell boundaries, which survived during irradiation up to doses, serve as neutral sinks.

What is the limiting dose at which the favourable effect of C.W. increase disappears?

Effect of cold work level on the swelling of AISI 316 for French steel at various temperatures in PASPSODIE for exposures of 20–61 dpaF (Dupouy et al., 1978)



Role of alloying elements-in austenitic steels composition

B plays positive role in increasing radiation resistance of ASS mainly, when it is situated in γ-solid solution. Boron reduces diffusion mobility of carbon and nitrogen and restrict formation of carbides and intermetallics. It is mean that concentration of Ni, Mo, Si, C, Nb in γ-solid solution is kept bigger in comparison with steel without boron.

Silicon has in a solid solution diffusion mobility on some orders higher in comparison with main components of austenitic steels. This acceleration in steels, alloying with silicon, reduces vacancies super saturation and, accordingly, depress rate of their nucleation.

Formation of a complex “**Ti atom** -vacancy“ (with binding energy ~ 0,3 eV) results that significant part of radiation induced vacancies is absorbed by Ti atoms. Ti successfully suppress swelling only together with silicon and phosphorus or with both of them.

As a fast and enhancer diffuser **phosphorus** in austenitic steels reduces the concentration of radiation-produced vacancies and can effectively decrease void nucleation. The phosphorus affects the microstructure via phosphorus-defect interaction at lower temperatures and via phosphides formation at higher temperatures.

Possible mechanisms of **REA** additives are-decreasing of bias factor due to formation of Cottrell atmosphere on dislocation components, trapping by impurity interstitials atoms, formation of the centers of variable polarity etc renders influence both on reduction of void number density as on void size.

THE EFFECT OF TITANIUM IN SOLUTION(B.Raj,2008)

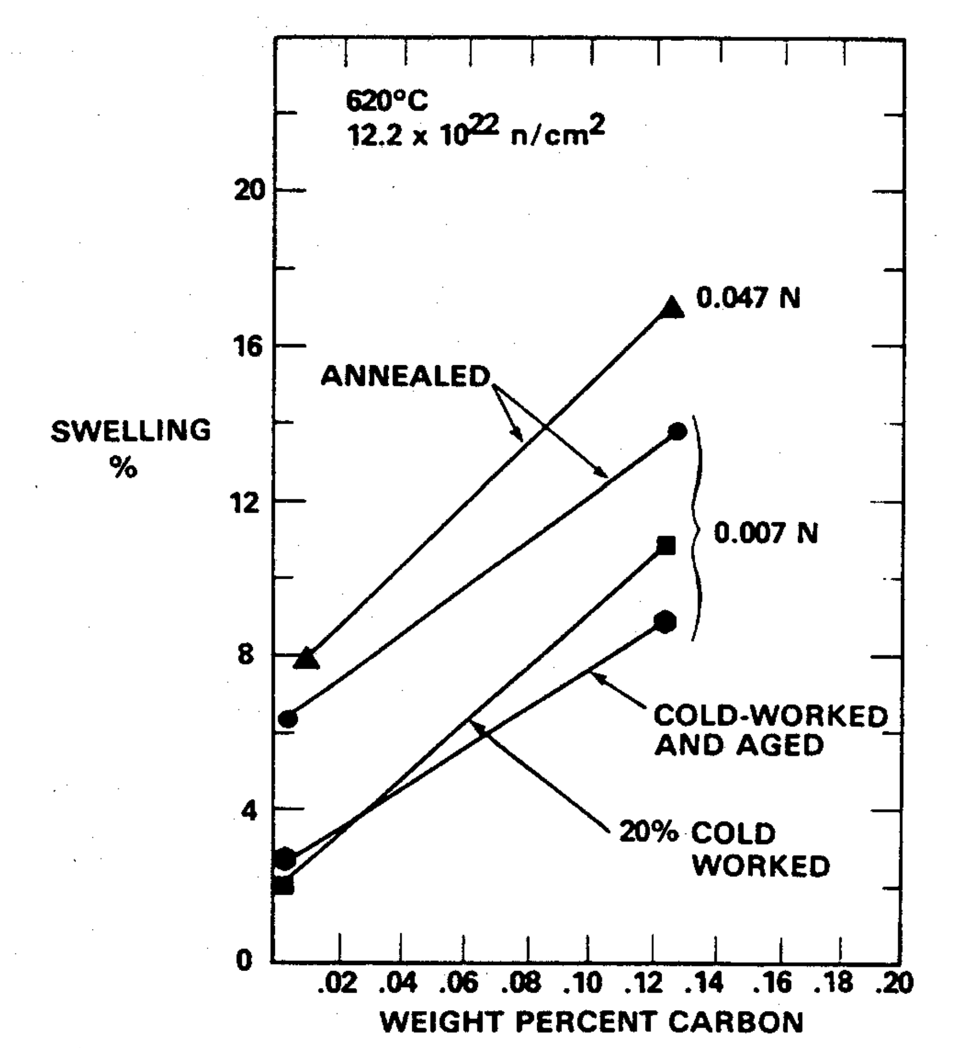
- Diffuses by vacancy migration
- The effective diffusion coefficient of vacancies is thus modified by titanium additions as

$$\boxed{D_v^{eff} = \frac{(D_v + KC_sD_s)}{(1 + KC_s)}}$$

Where, D_v is the diffusion coefficient of vacancy migration in the pure host, D_s is the diffusion coefficient of solute and K is the mass action constant for solute-vacancy dissociation in an FCC lattice

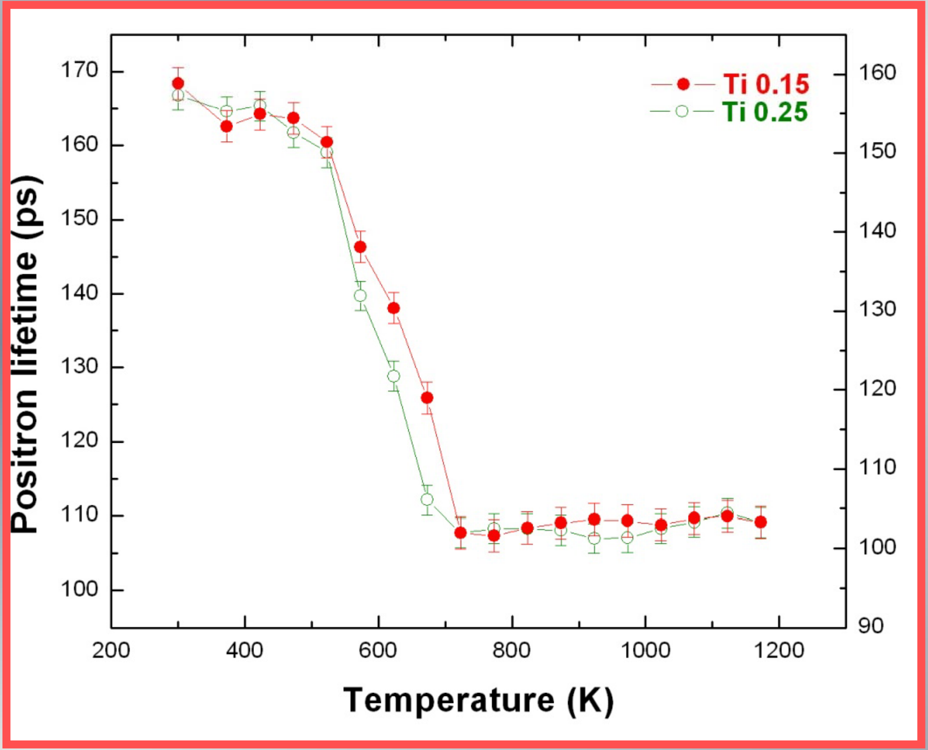
The recombination dominated regime is shortened and void growth takes place at lower temperatures.

Dependence of swelling in AISI 316 on carbon content and starting condition, indicating some possible synergism with nitrogen (after Bates et al., 1981)



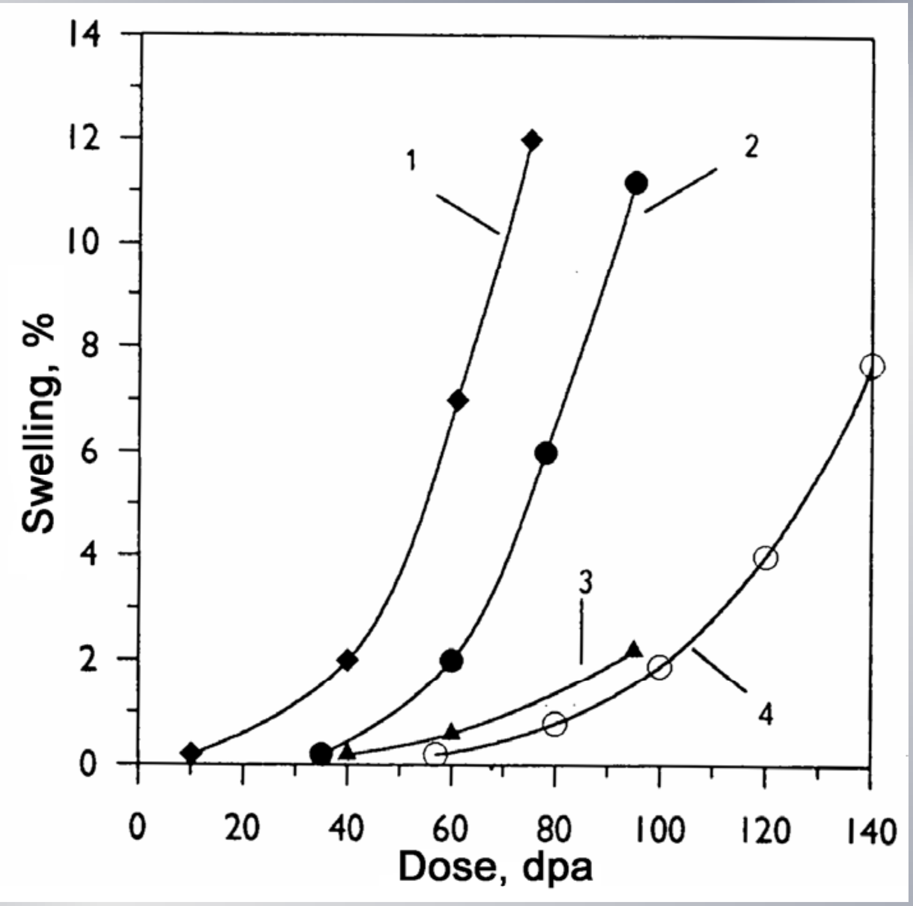
ISOCHRONAL RECOVERY CURVES FOR D9 ALLOYS WITH 0.25% AND 0.15% TI AFTER IRRADIATION WITH 3MeV PROTONS

(K.Nair, 2008)



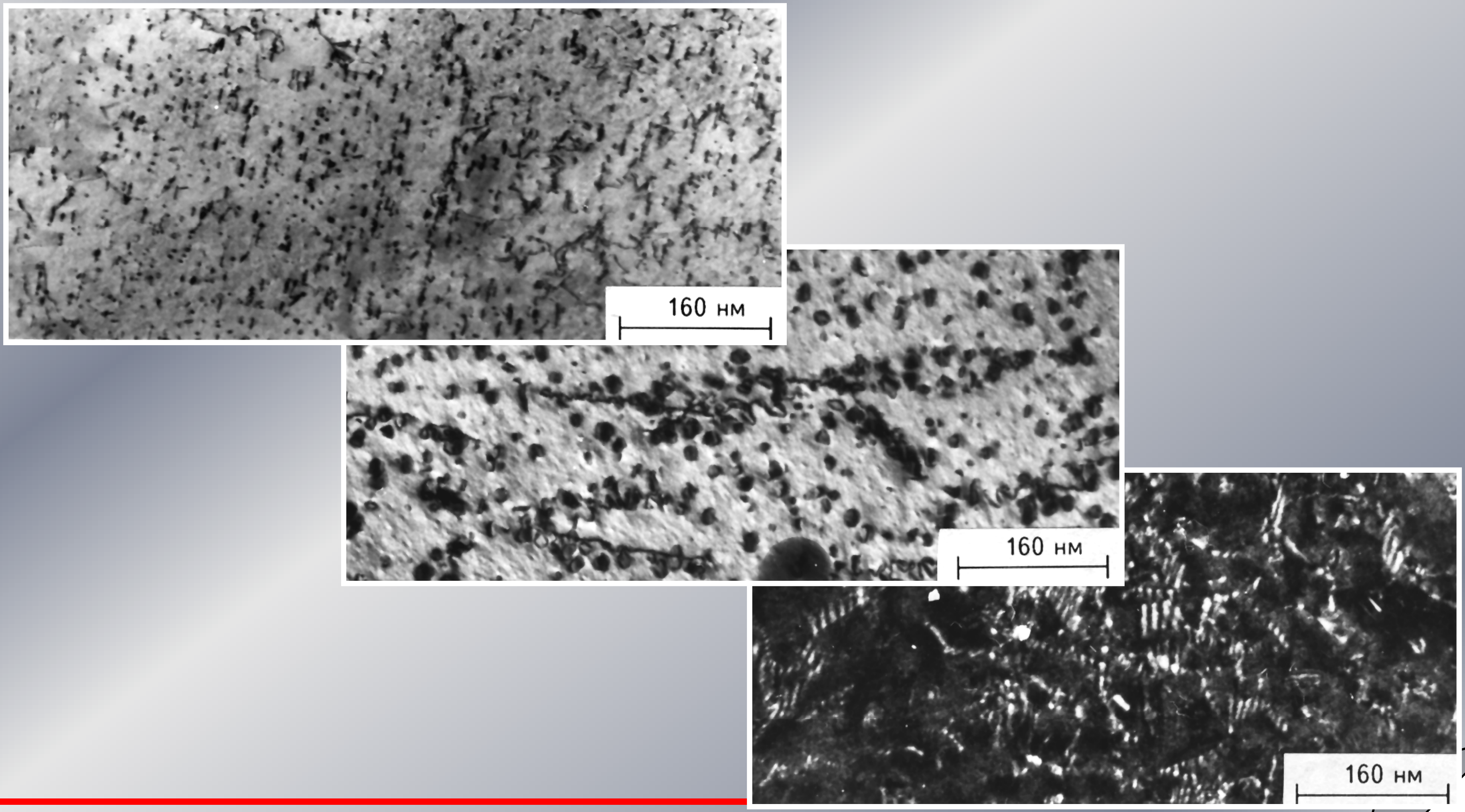
The delayed recovery in the case of alloy with lower Ti suggests slower vacancy migration

Swelling vs. dose dependence of modified steel (Cr^{3+}, E=3MeV, $T_{irr}=T_{SW\ MAX}$)



1- EI-847A (16Cr-15Ni-3Mo-Nb),
2- EP-172A (16Cr-15Ni-3Mo-Nb-B) (melt. 1, C_B=0.056%),
3- EP-172A (16Cr-15Ni-3Mo-Nb-B) (melt. 2, C_B=0.01%),
4- ChS-68 (16Cr-15Ni-2Mo-2Mn-Ti-V-B)

Singularities of behavior of dislocation loops (EP-172 SA, Cr^{3+}, $E = 3$ MeV, $T_{irr.} = 605^{o}C$), alignment of dislocations), a) D = 2 dpa, b) D = 5 dpa, c) network of split dislocations



Precipitates role in swelling suppression

The influence of precipitates on swelling behavior is classified under three effects:

□Direct, when accelerated recombination takes place

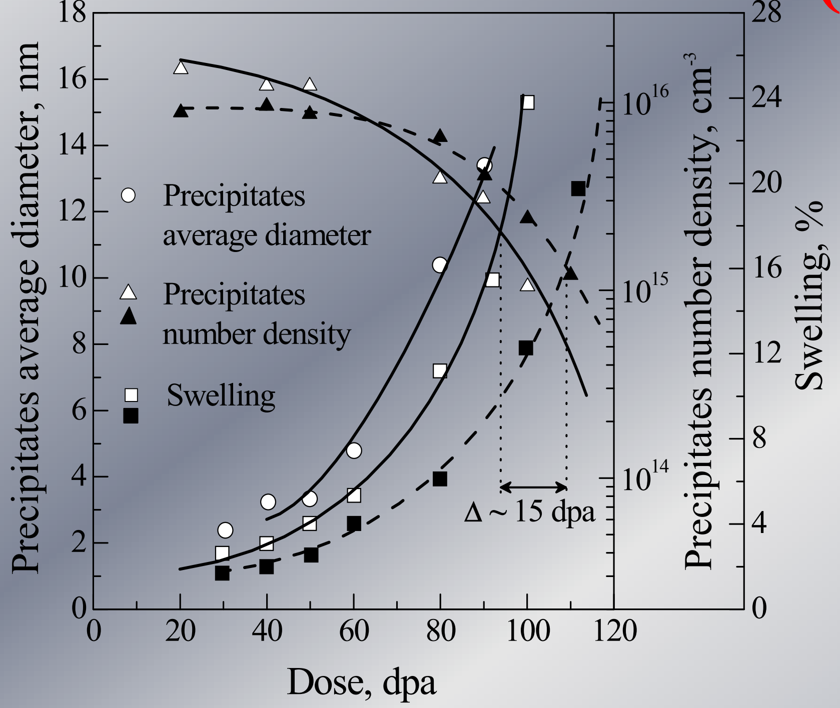
•Indirect, when the general sink capacity of the system is changed

•Intermediate, when the recombination rate of point defects changes in matrix due to concentration of impurity elements.

The existence of second phase precipitates with a positive misfit, influences the behavior of vacancies and their complex and a very close to link exists between precipitate behavior and void swelling.

MC precipitates have the biggest positive misfit (+19%) of all phases, due to lattice parameter mismatch. A large positive misfit of precipitate to matrix induces vacancies flows, which stabilize grows during irradiation of MC-precipitate-vacancy complex.

Evolution of MC precipitates and swelling in 16Cr15Ni3MoNb steel (Cr^{3+},E=3MeV,T_{irr}=600^0C)



▲■ - 16Cr15Ni3MoNbB

○ Δ □ - 16Cr15Ni3MoNb

V.Voyevodin et al JNM, 271-272, 1999

16Cr15Ni3MoNb, NbC→G-phase

15Cr15Ni2MoMnTiB, TiC→G

M.Suzuki et al, .ASTM 1046,1990

JPCA, TiC→M_6C,

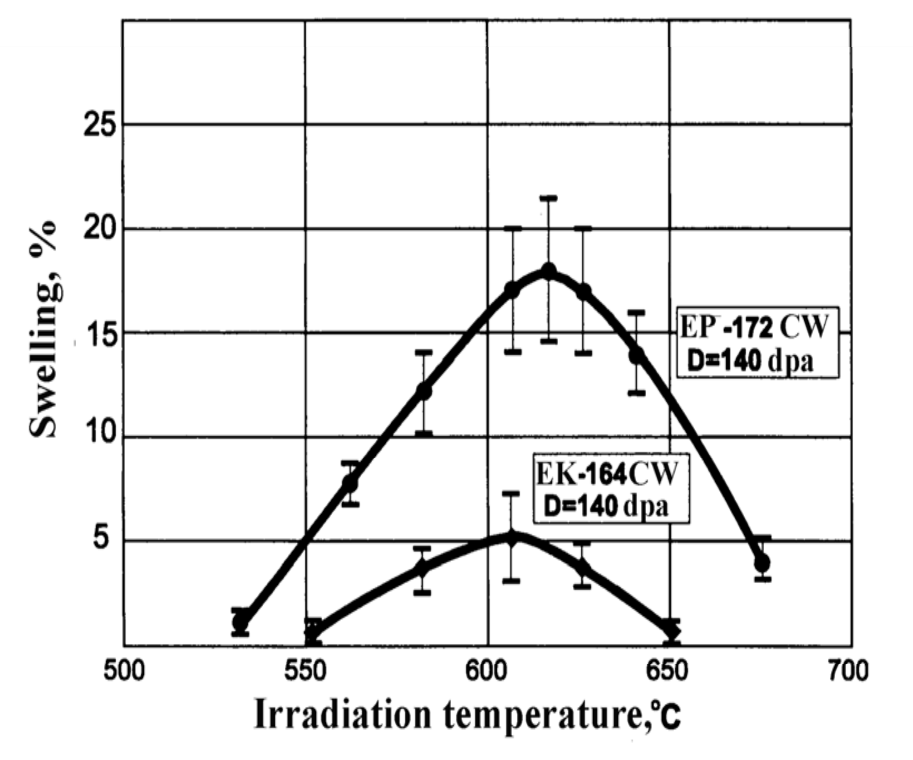
A.Rowcliffe et al, JNM, 109, 1982

USPCA, TiC→G-phase

- How long small dispersed carbides can survive? Which physical mechanisms are responsible for loss of their stability?
- Alloying elements (B, Ti, P) can shift dissolution of precipitates to area of high dose

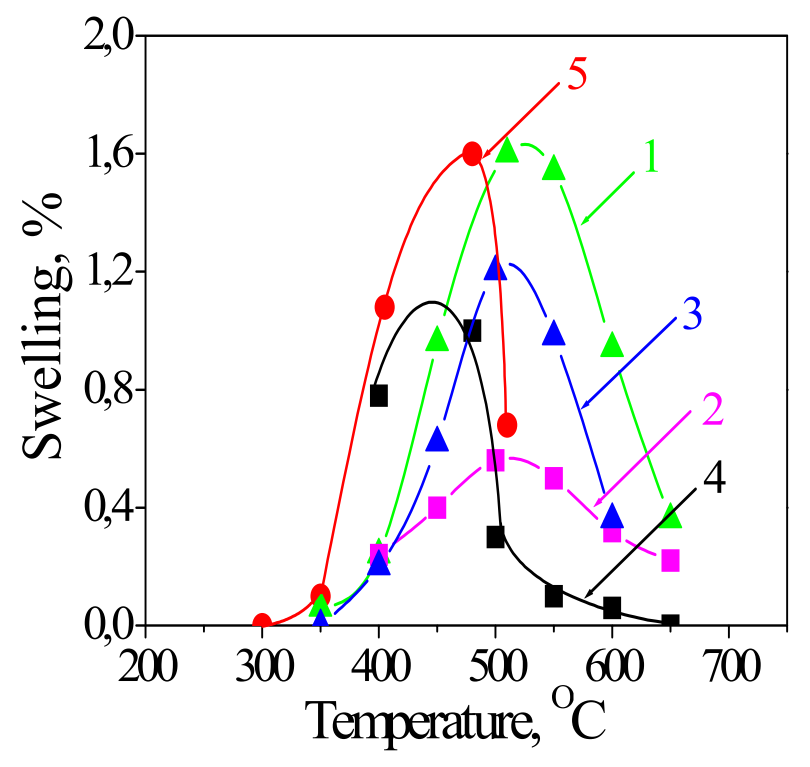
SWELLING PROCESSES

Temperature dependence of swelling for austenitic steels (EP-172, EK-164)



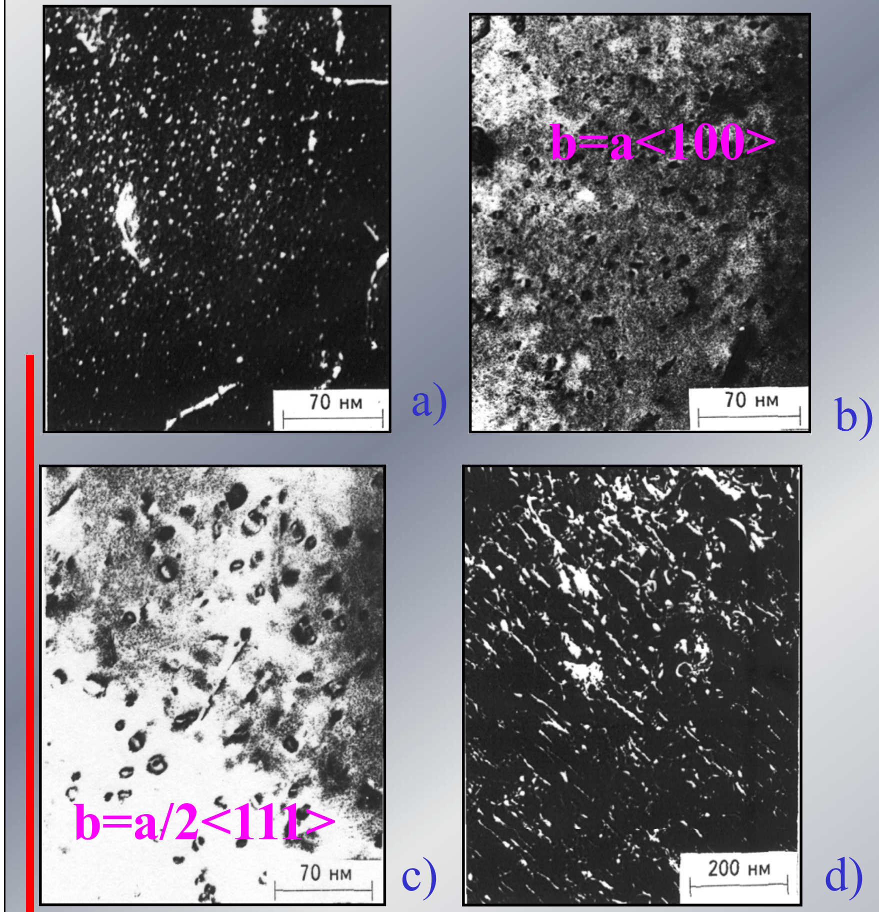
Irradiation conditions: Cr^{3+}, D=140 dpa

Temperature dependence of swelling for some iron based materials



1- α-Fe (D=100dpa)
2- EP-450 (D=150dpa)
3- Fe-12%Cr (D=100dpa)
4- 01X13M4 Cr^{3+} (D=100dpa)
5- 01X13M4 Ar^{3+} (D=100dpa)

Evolution of dislocation structures in F-M steels



**Evolution of dislocation structure in the 13Cr2MoNbVB steel (Cr^{+3}, E=3 MeV, $T_{irr}=500^{0}C$)
a) D=0,1 dpa (dark field image), b) D=0,5 dpa; c) D=5 dpa; d) D=15 dpa (dark field images)**

- The dislocation structures of irradiated α-Fe ($T_{irr}=480^{O}C$) are quite uniform and consist of dislocation segments, the majority of which having Burger vectors b=<100>, aligned on the planes (100), but some fraction of loops have Burger vectors a/2<110>.

- The formation of a dual system of dislocation loops (i.e. a<100> on (100) planes and a/2<111> on (110) planes) is the main feature of dislocation structures in irradiated α-Fe, Fe-13Cr alloy, and bi-phase steel **13Cr2MoNbVB**, but in tempered martensite loops growth in places with low initial density of original dislocations.

$$a/2\langle 110\rangle + a/2\langle 001\rangle = a/2\langle 111\rangle$$

$$a/2\langle 110\rangle + a/2\langle 110\rangle = a\langle 110\rangle$$

Possible mechanisms of swelling suppression in ferritic steels

In materials with fcc and bcc lattices the distance between adjacent atoms are different and, consequently, relaxation volume for vacancies and interstitials is different. For fcc structures relaxation volume for interstitial is lower and for vacancies is higher. As consequence, difference between relaxation volumes of interstitial and vacancies in higher in fcc structures than in bcc materials; this favors the decrease of bias in absorption of vacancies by voids and of interstitialss by dislocation in bcc lattice. The calculations showed that difference in the rate of swelling may be explained by this mechanisms.

To explain the high swelling resistance of ferritic-martensitic steels the authors of paper used the fact that 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.

Energetic parameters of vacancies

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
α-Ti (HCP)	1.55	0.50

The main input in the decrease of swelling is from so called “ trapping” mechanism: impurity and alloying elements represent the traps for vacancies decreasing considerably the degree of supersaturation by radiation-induced vacancies due to the recombination. In ferritic-martensitic steels this mechanism must operate stronger than in austenitic steels and in fcc metals in hole because the rate of trapping and of recombination on traps is determined first of all by the mobility of point defects (see Table).

Possible mechanisms of swelling suppression in ferritic steels (continued)

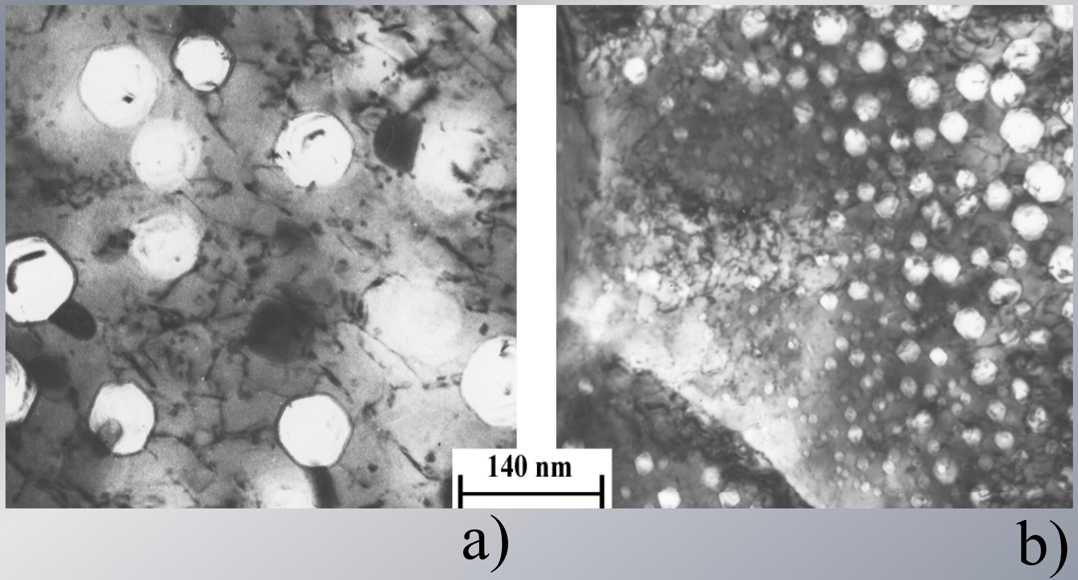
The dislocation bias for interstitials over vacancies is proportional to the magnitude of the dislocation burgers vector. Thus, the a<100> loops act as more strongly biased sinks than the (a/2 <111>) loops. In this situation of two loop types having different bias and being continuously nucleated during irradiation, there is no incentive for voids to form or grow. More specifically, a dynamic equilibrium is established where the a<100> loops preferentially attract interstitials and grow, resulting in a net flux of vacancies to the (a/2 <111>) loops causing them to shrink.

There were many attempts to use precipitates as key points in creation of steels resisted to void swelling

- Precipitates which pay influence on swelling behaviour in a matrix of irradiated ASS can be selected in two main classes :
- Precipitates which are responsible for swelling suppression mainly due to enhancing point defect recombination
- at particles-matrix interface: MC (mainly TiC,NbC,VC) Fe_2P or Ni_3Ti (in a few cases)
- Precipitates which serve as result of solid solution decay (especially due to removing of Ni and Si as RIS result) and sign as loss of radiation stability at last stages of structure evolution-M_6C and G-phases
- Formation of M_6C-$(Cr,Mo,Ni)_6C$; $(Ti,Ni)_6C$,$(Nb.Ni)_6C$ and G-phases $(Ti,V,Nb,Mn)_6(Ni,Co)_{16}$ Si_7 leads to remove from matrix such elements as Ni, Si, Ti, P and subsequent drastically swelling increasing
- Key processes leading to instability of fine MC, Fe_2P and Ni_3Ti particles appears to be dissolution in cascades and segregation mechanisms on precipitates surface

CW influence on precipitates behaviour

- The principal effect of cold working in AISI 316 and 16Cr15Ni3MoNb steels →shift the MC precipitation and displacement of the G-phase area to higher damage doses.
- Cold working provides a high density of nucleation sites for MC precipitates, beside it, the segregation solute distributed between a much higher density of sites than in the SA case.
- The better stability of the MC precipitates in CW JPCA steel in comparison with SA material could be explained that there is less flow of chromium into the MC/matrix interface. Beside it cold work will reduce the diffusion of chromium, site concentration and sink effects on the diffusion processes
- Phosphides needles in Ti+P modified steels are much finer and more stable in CW than in SA material [Watanabe, 1994]
- It was shown that cold work introduces a high dislocation density and refine phoshide particles to a great extent [Lee, 1994]



BOR-60, D=68dpa, T_{irr}=490^{O}C
a) EI-847 1050^{O}C, 30min
b) EI-847 1050^{O}C, 30min
+ 30% CW

Increasing of austenitic SS swelling resistance

- The maintenance of desirable swelling is directly coupled with maintaining a more stable microstructure during radiation exposure. Alloying influence together with treatment consists in:
- Formation of more stable dislocation structure (mainly existence of slow mobile Frank loops number density) up to higher doses .It can be achieved due to cold work or segregation processes on dislocation components, which restrict dislocation mobility;
- Save small precipitates of carbides and phosphides (prolong their life), which serve as dominant swelling suppressor in these steels, from dissolution - shift dose interval of formation for G-phases and η-carbides to region of higher doses;
- Retarding of G-phase and η-carbides formation will keep in solid solution sufficient quantities of such elements as Ni, Si and P, which mainly influence on void nucleation and growth;
- Typically for all analyzed steels stability of fine precipitates is necessary condition for preventing of high swelling.

What shall we do at high damage dose?...

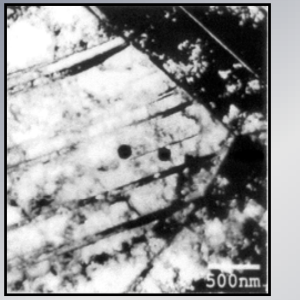
Microstructure of irradiated 316 steel

CLADDING FABRICATION DATA

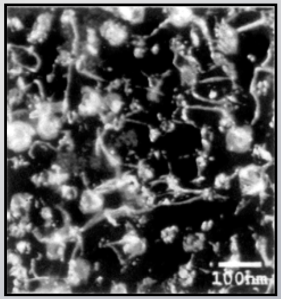
Material	Chemical composition (wt%)											Final Solution Treatment	Cold Work (%)
	C	B	Si	P	Mn	Mo	Ni	Cr	Ti	Nb+Ta	Fe		
47 MS (ordinarily 316)	0.055	0.0002	0.56	0.002	1.75	2.48	13.05	17.00	-	-	bal	1000^0C x 2min	20
S553 (PNC 316)	0.048	0.0044	0.93	0.031	1.78	2.51	13.81	16.60	0.098	0.073	bal	1085^0C x 1min	19

47 MS

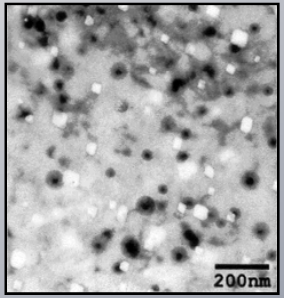
Before irradiation



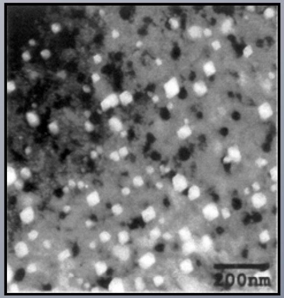
499^0C
8.4x 10^{26}n/m^2
(Rapsidie/PNC-5)



Dislocations



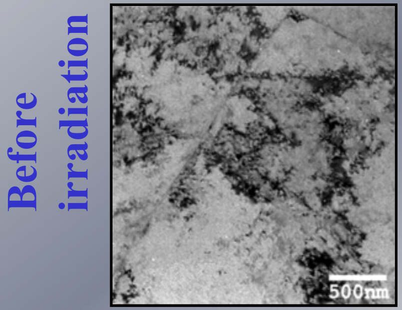
Precipitates



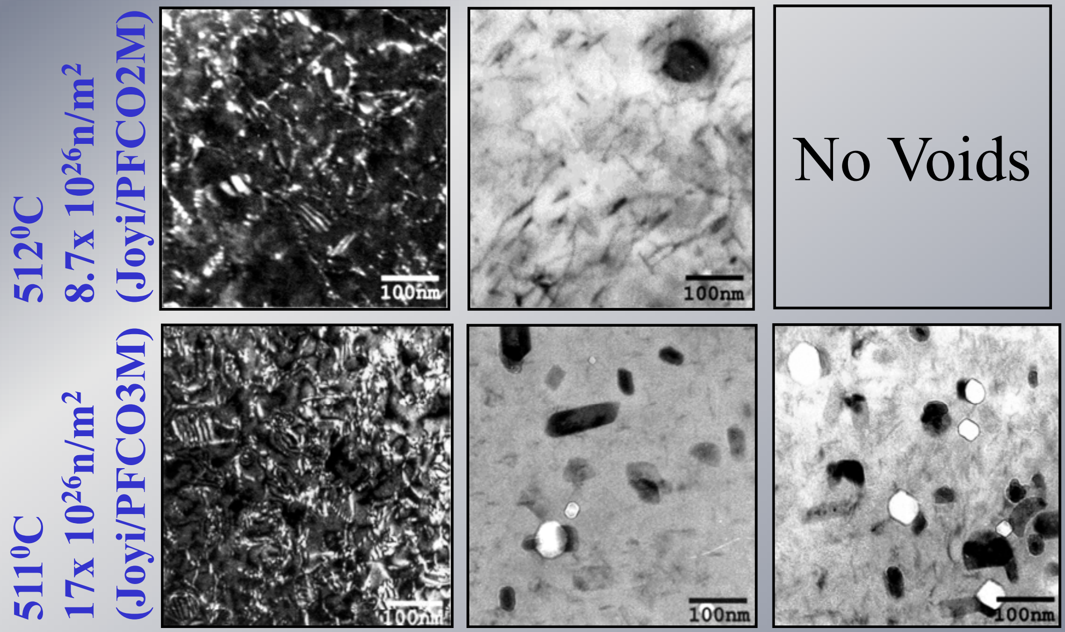
Voids

Alloying influence on microstructure evolution in modified 316 steel

PNC 316



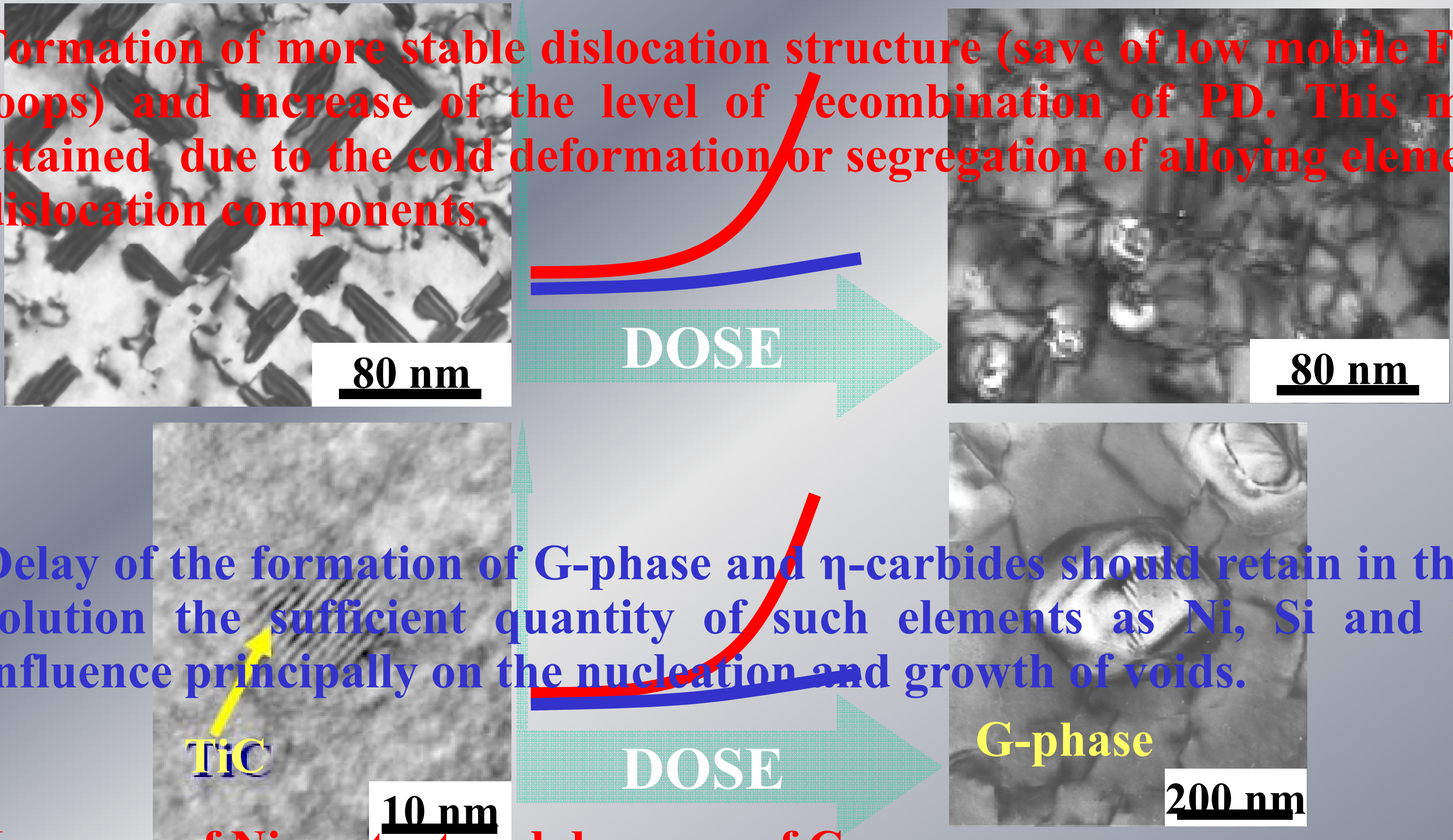
H.Watanabe et al JNM 228, 1996
Fe-Cr-Ni alloy
60.3 dpa –phoshides survive
S.Ukai et al ASTM 1325,1999
PNC 316,
80 dpa, $Fe_2P \rightarrow G$ and M_6C



No Voids

Dislocations Precipitates Voids

Philosophy of irradiation resistance of stainless steels

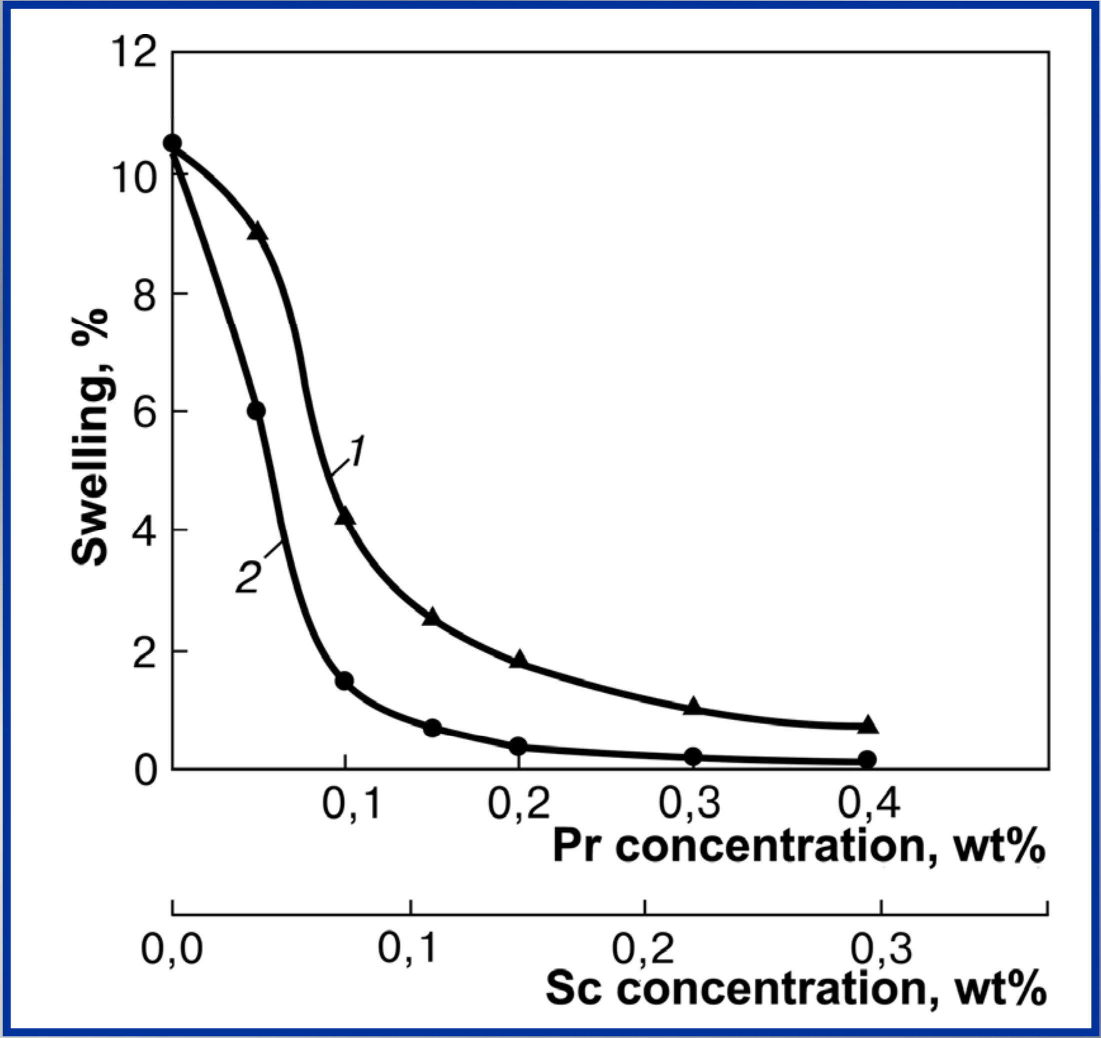


- Formation of more stable dislocation structure (save of low mobile Frankel loops) and increase of the level of recombination of PD. This may be attained due to the cold deformation or segregation of alloying elements on dislocation components.
- Delay of the formation of G-phase and η-carbides should retain in the solid solution the sufficient quantity of such elements as Ni, Si and P that influence principally on the nucleation and growth of voids.
- Increase of Ni content and decrease of Cr.
- Optimization of Ti, P, Nb, Ti/C, B, N, REM.
- Retaining of fine carbide precipitates (TiC) and phosphides (Fe_2P) (extension of their life is the main factor of the suppression of swelling in these steels and shifts the dose range of the formation of G-phases and η-carbides in the region of higher doses).

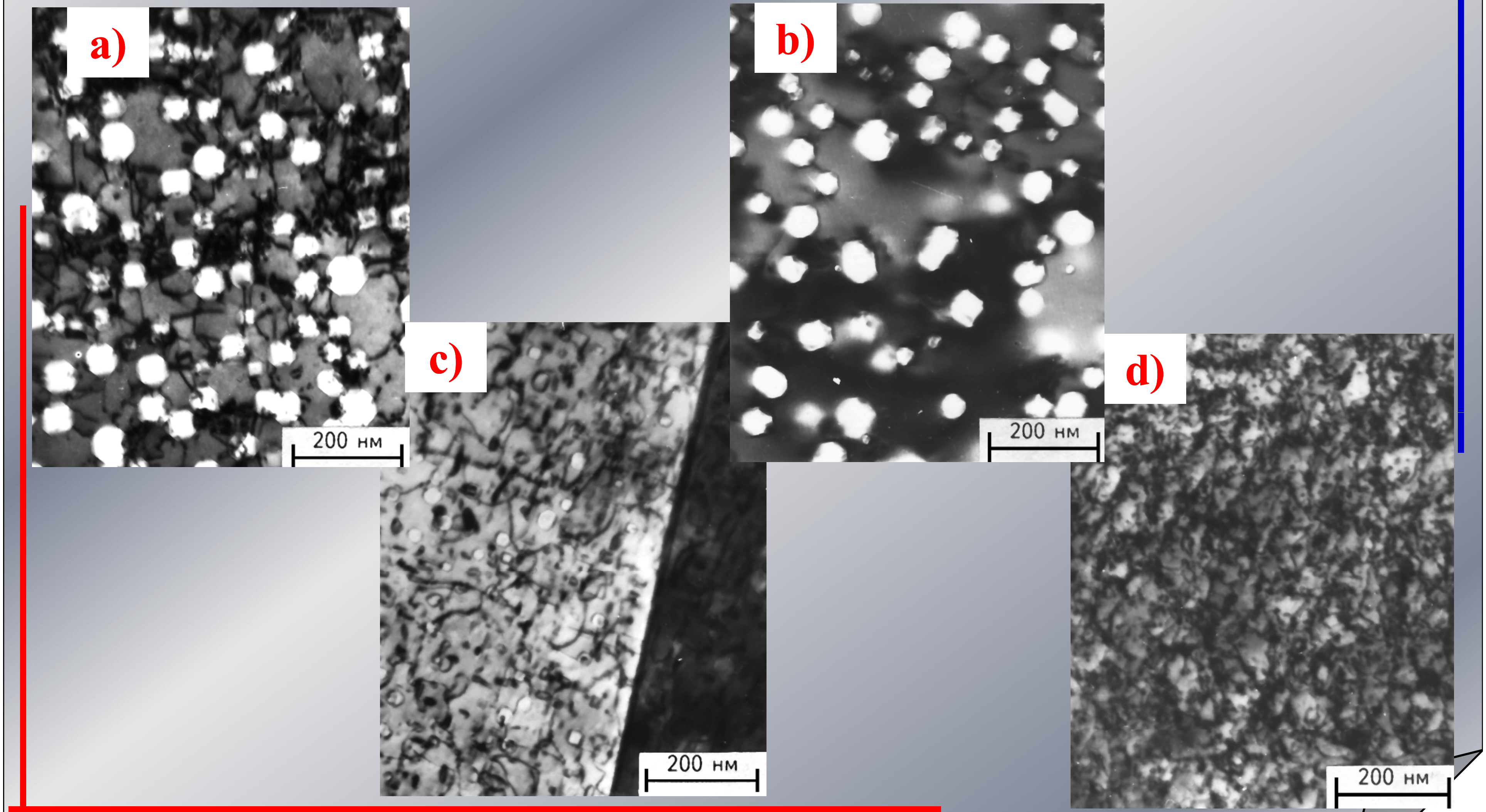
Dynamic stabilization of precipitates

- Attempts to increase up to engineering level swelling resistance of stainless steels due to positive role of small dispersed TiC carbides were not successfully.
- Creation of system with dynamic stabilization of two dispersed precipitates with different sign of misfit (TiC and Fe_2P), which can stabilize one another, may serve as "twin self-supporting buffer", preventing from G-phase formation in process of irradiation.
- Main idea-delay G-phase formation and avoid depletion of solid solution with Ni, Si, Ti and P-main swelling suppressors.
- Stability of MC precipitates during irradiation is partially controlled by the dynamic balance between displacement cascade dissolution and back flow of Ti and Cr into MC precipitates driven by chemical potential gradient. Phosphorus in solid solution increases the effective diffusion coefficient [Maziazs].
- An increased vacancy-diffused rate will increase the back flow of solution species into MC precipitate. This might have improved phase stability of MC precipitate in steels with phosphorus addition.
- Phosphorus has a big binding energy with interstitials (~0,5eV) and will go to phosphides.
- In solid solution of modified steel we have such separation: oversized Ti interact with vacancies, TiC also serve as vacancy sink but undersized P form complex with interstitials and support stability of phosphides.
- It is mean that Ti addition can stabilize phosphides and phosphorus addition can stabilize carbides.
- Beside it, rate growth of precipitates can be minimized due to distribution of fluxes of point defects between comparatively higher number density of sinks.

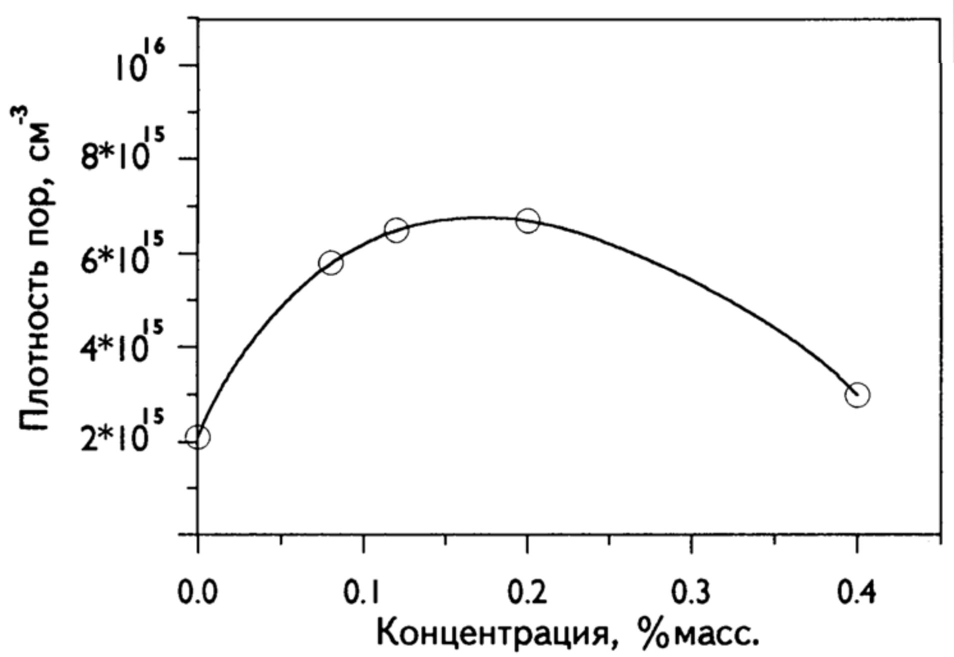
Swelling versus concentration of REE elements in Ni. T_{irr}=600°C, D=40dpa, E=2.8MeV



Microstructrure of irradiated Ni alloys (Ni^{3+}, E=3MeV, T_{irr}=600°C), a) Ni, b)Ni-0,05 %Sc, c) Ni-0,13 %Sc, d) Ni-0,3 % Sc.

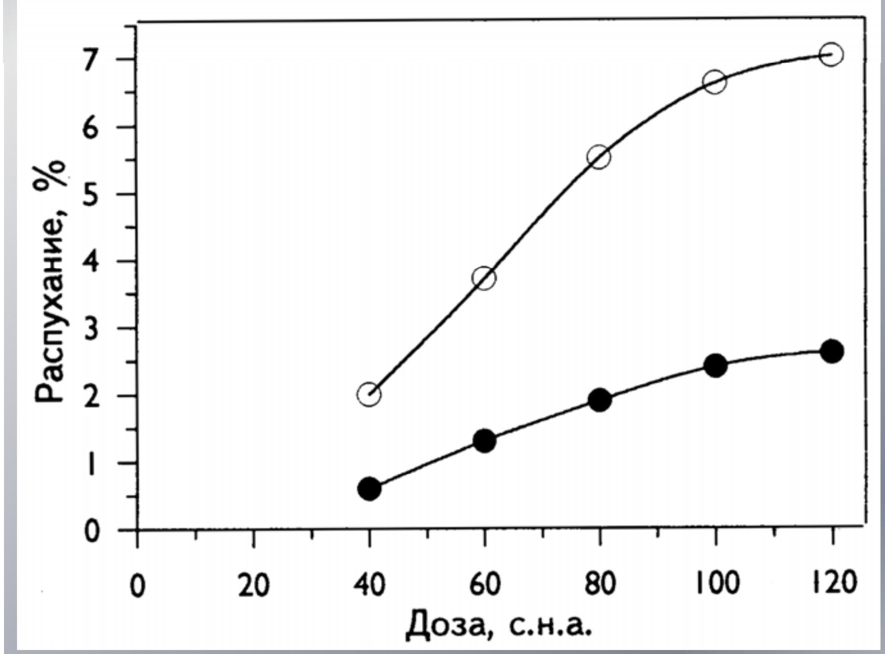


Dependence of void density on concentration of alloying addition in the alloy Ni-Pr (Ni3+, E=3MtV, D=40 dpa, Tir.=600°C

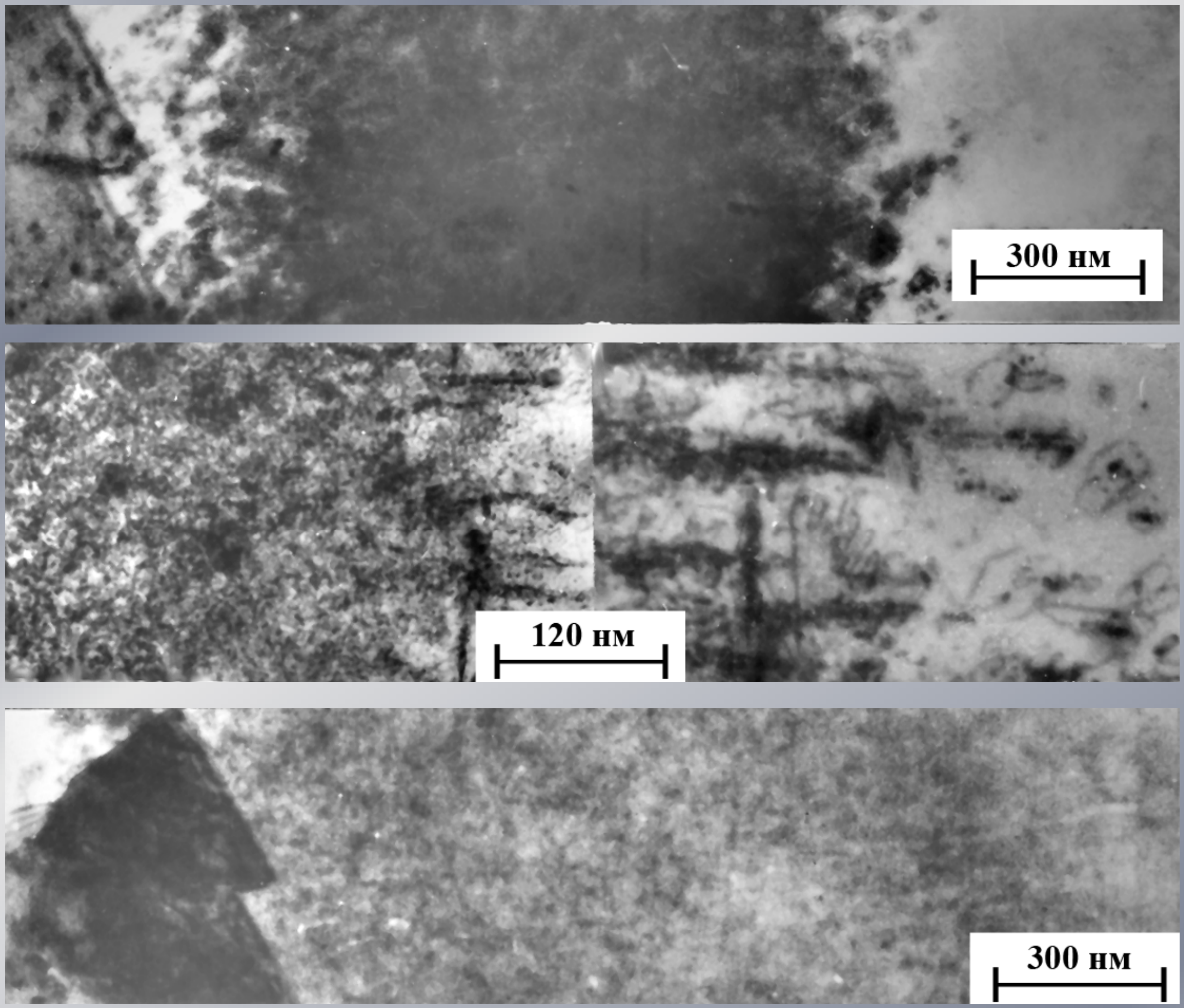


Dose dependence of alloys swelling Ni-Pr (Ni^{3+} E=3MeV, Tir.=600°C):

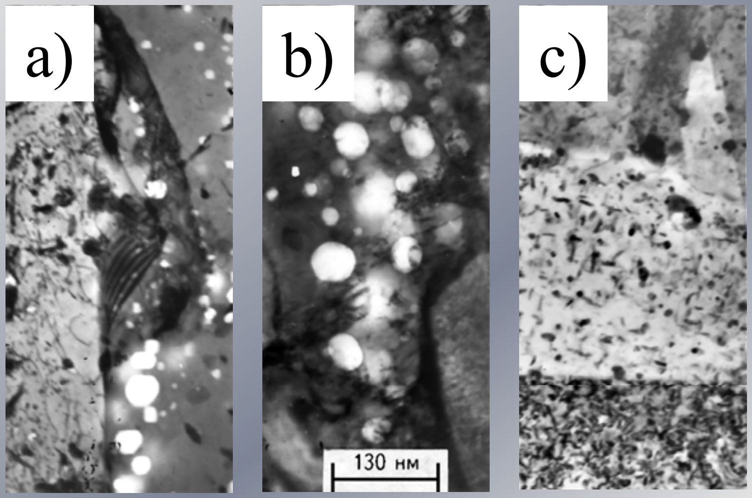
○ - Ni-0,2Pr; ● - Ni-0,4Pr.



Dislocation structure evolution in Ni-0.3% Sc alloy (e-, E=1MeV): a) D= 0,5 dpa, b) D= 5 dpa, c) D= 40 dpa.



Sc influence on radiation stability of austenitic SS



BN-600, Dose=53dpa, T_{irr}=480^{O}C
a)16Cr15Ni3MoNb + Sc
b)18Cr10NiTi + Sc
c)16Cr15Ni3MoTi + Sc

Possible mechanisms of rare earths additives (REA) are:

- decreasing of bias factor due to formation of Cottrell atmosphere on dislocation components;
- trapping by impurity interstitials atoms;
- formation of the centers of variable polarity renders influence both on reduction of void number density as on void size;
- saving important elements in solid solution

(Neklyudov, Ozhigov, Voyevodin, Bryk et al, 1996)

Steel	Sc concentration,% wt	$T_{irr,}$ ^{o}C	Sc concentration in MC	Swelling, %
16Cr15Ni3MoNb	-	475	-	12.8
16Cr15Ni3MoNb+Sc	0.135	475	4 - 20	1.7
16Cr11Ni3MoTi+Sc	0.13	475	2 - 7	0.5

Mechanism of influence of alloying elements on swelling

Few mechanisms of alloying elements influence on the process of nucleation and growth of voids may be the following:

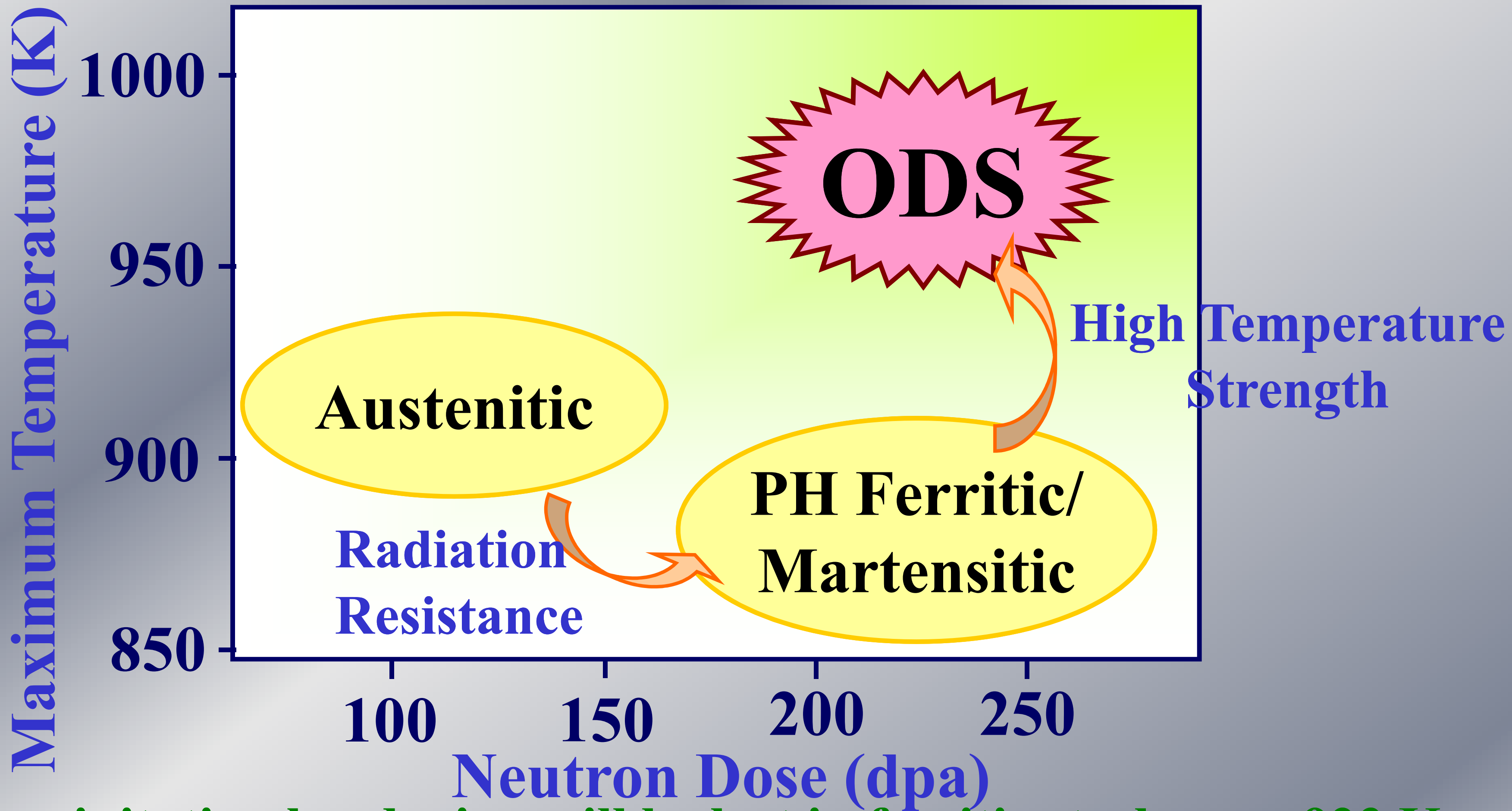
1. Formation around dislocations of Cottrell atmospheres from substitutional or interstitial atoms which have higher size than atoms of matrix; this results in the decrease of elastic field of dislocation and in the decrease of preferential absorption by dislocation of interstitials in comparison with vacancies.

2. Trapping of radiation defects by atoms of alloying elements that results in the increase of degree of point defects recombination in irradiated material. In this case concentration of free vacancies and interstitials in alloy under identical irradiation conditions must be lower in comparison with pure matrix; corresponding fluxes of point defects to the sinks, to voids and dislocation, will be also smaller.

3. Trapping of substitutional atoms by atoms of alloying additions (Sc and Pr) that can serve as the nuclei of voids will also result in the decrease of void concentration.

4. Formation of complexes “dislocation loop-precipitate” promotes the stabilization of dislocation loops and decrease the rate of their growth; in the result of this higher number of interstitials remains in matrix and recombines with vacancies that decreases respectively the swelling.

Why ODS?



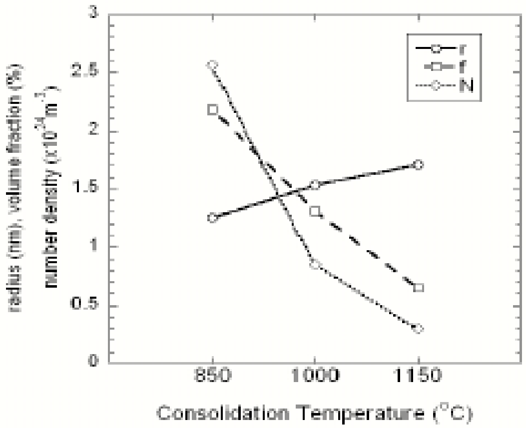
Precipitation hardening will be lost in ferritic steels over 923 K.

↓

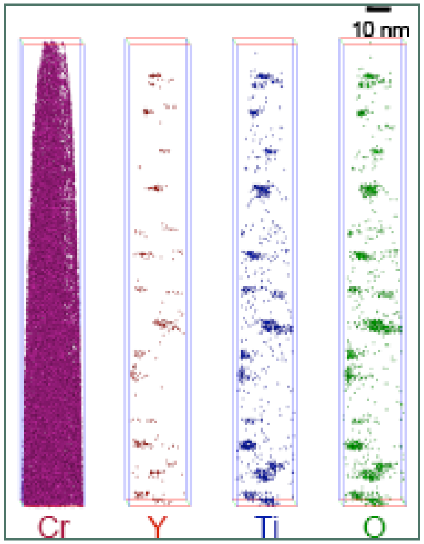
Oxide dispersion strengthening will be effective even over 973 K.

What Are NFAs?

- Atom probe (ORNL) & SANS (UCSB) -> strength result of ultra-high density (≈ $10^{24}/m^3$) nm-scale clusters of Ti-Y-O
- NF are transition phase precursors to $Ti_2Y_2O_7$ pyroclore oxides with high M/O ratios and atom densities
- Y & O dissolve during MA of Y_2O_3 and metal powders and NF precipitate during hot consolidation (HIP and extrusion) - Ti necessary at 1000 and 1150°C
- Thermo-kinetics of NF precipitation and stability characterized in extensive UCSB studies - SANS (+TEM, PAS & APT)
- NF -> $Ti_2Y_2O_7$ and Y_2O_3 oxides form at higher temperatures - consolidation (without Ti) & annealing



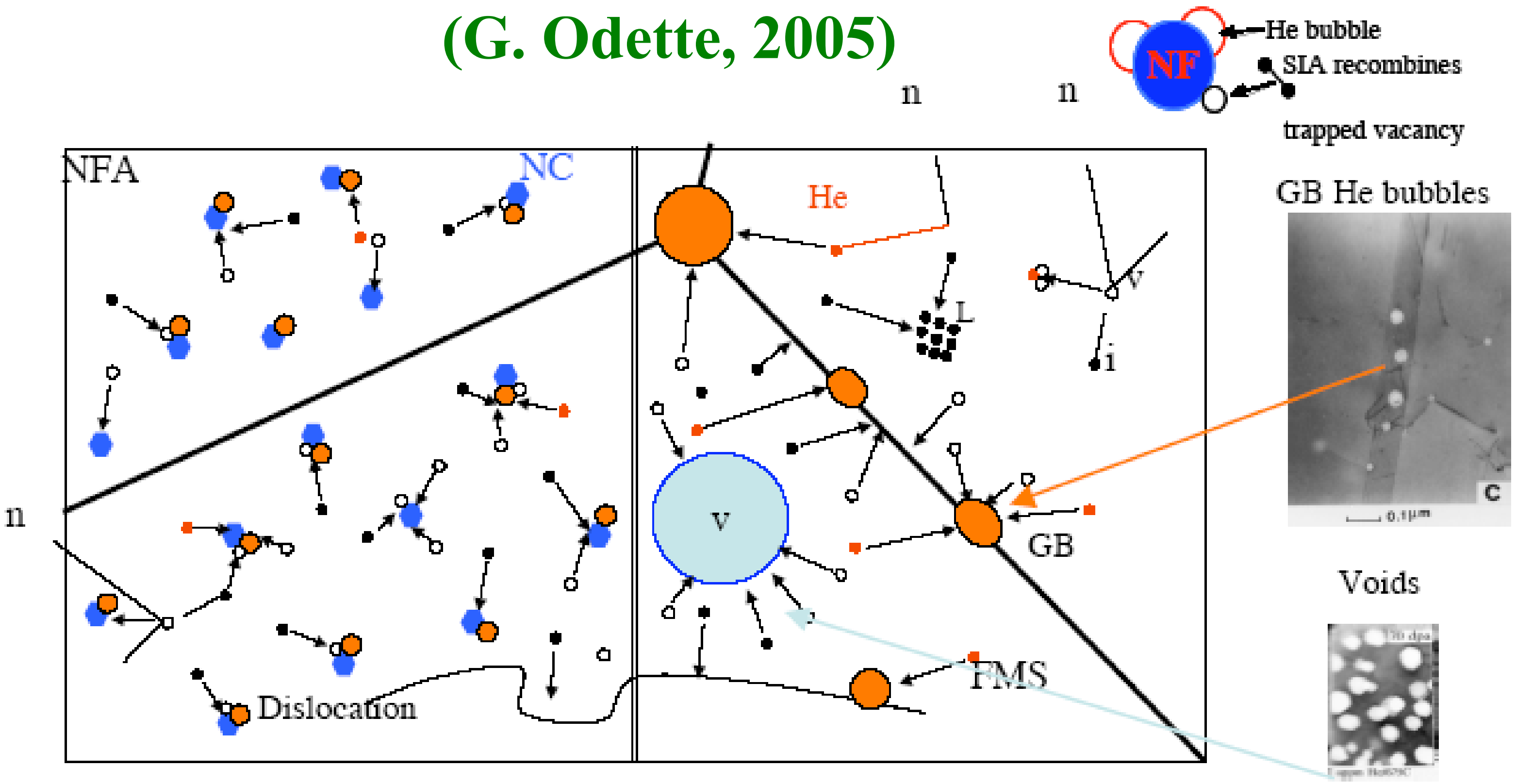
3-D APT Atom Map of 12YWT



M. K. Miller *et al* (2003)

Managing Radiation Effects

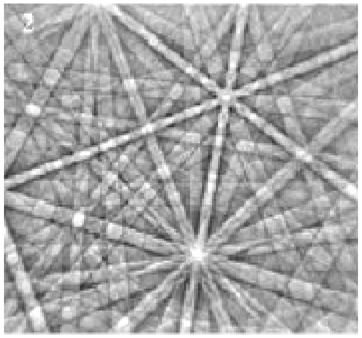
(G. Odette, 2005)



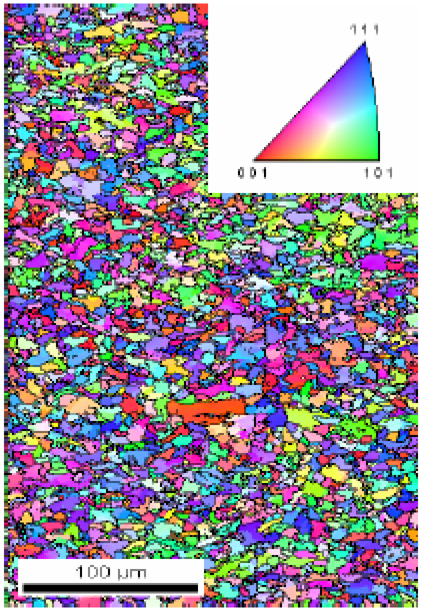
- Use high sink strength of nanofeatures to trap (getter) both He (in fine bubbles) and vacancies (to enhance self-healing of damage by recombination with SIA)

Grain Boundary Engineering (GBE) - To Overcome Embrittlement

Steel: Mod. 9Cr1Mo steel -
Normalised, Tempered (760°C / 1hr)
& Aged (550°C / 8400 hrs)



Typical Input
Data in
Orientation
Imaging
Microscopy



FERRITICS

FAVOURABLE BOUNDARIES

ROGUE BOUNDARIES

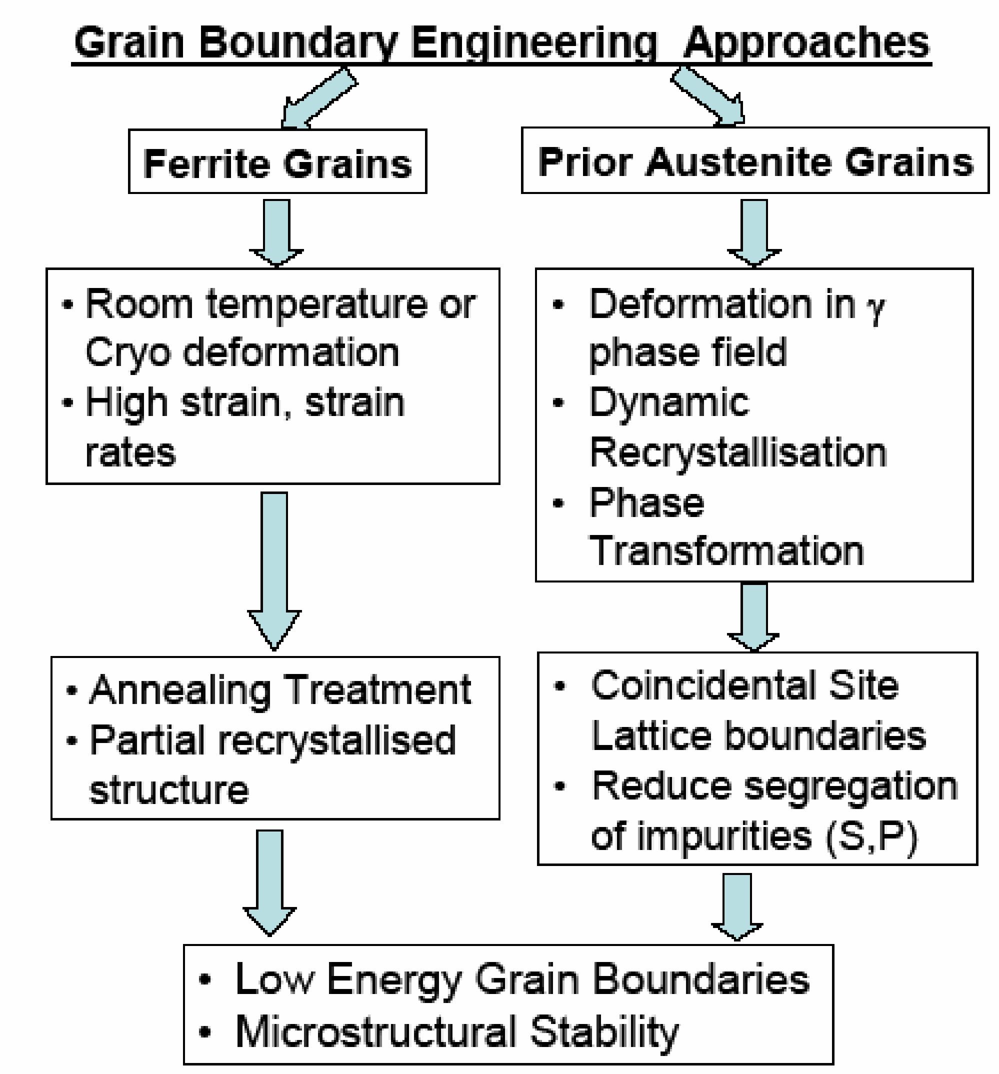
Low misorientation angle
inhibits segregation
of metalloids

Promotes
segregation
of P, S, Sb

**REDUCE NUMBER OF
UNFAVOURABLE BOUNDARIES**

**USE ORIENTATION IMAGING MICROSCOPY
To IDENTIFY THESE BOUNDARIES BY
ANGLE OF MISORIENTATION**

Rational for selection of Thermomechanical treatment towards grain boundary engineering in Ferritic steels (B. Raj, 2008)



Grain Boundary Engineering Approaches

Ferrite Grains

- Room temperature or Cryo deformation
- High strain, strain rates

- Annealing Treatment
- Partial recrystallised structure

Prior Austenite Grains

- Deformation in γ phase field
- Dynamic Recrystallisation
- Phase Transformation

- Coincidental Site Lattice boundaries
- Reduce segregation of impurities (S,P)

- Low Energy Grain Boundaries
- Microstructural Stability

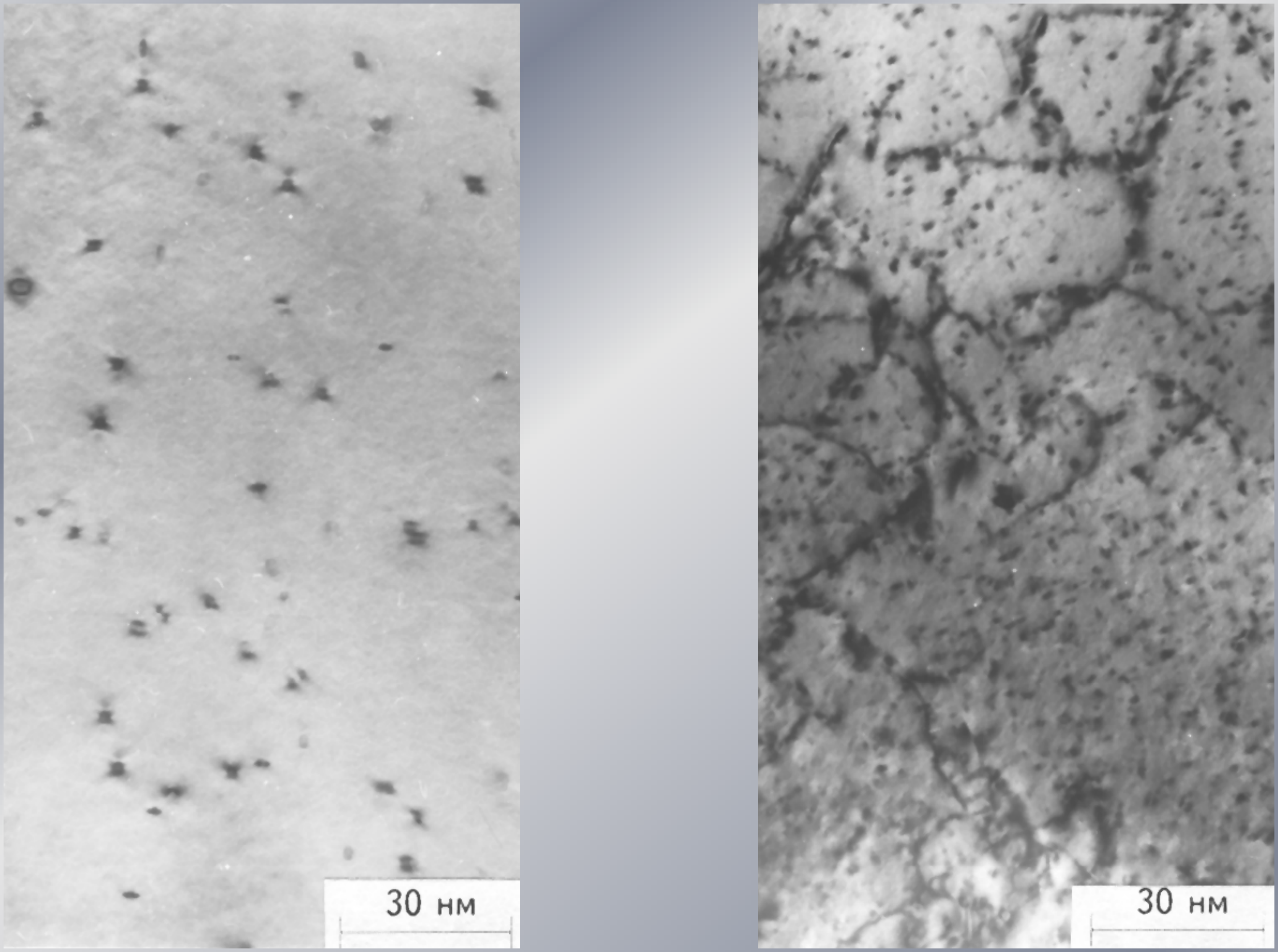
Enhanced radiation damage resistance via manipulation of nanoscale properties (M. Fluss, 2008)

Substantial improvements in radiation damage resistance can be realized through manipulation of nanostructure and chemical composition to:

Increasing time scale

- influence cascade dynamics so as to reduce the number of defects produced in the cascade,
- enhance the efficiency of sinks (such as interfaces) to trap and effectively recombine defects retained after the cascade, and
- use a combination of nanostructuring and alloying to enhance microstructural stability under extreme conditions of irradiation and temperature.

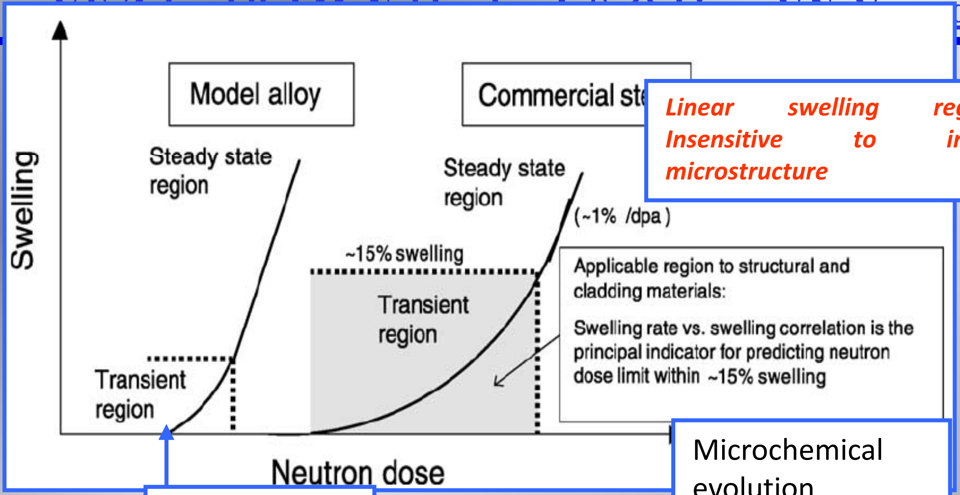
Microstructure of EI-847 steel (a) and Ni (b), irradiated Ni ions at room temperature: a) D=40 dpa; b) D=20 dpa.



Road Map of materials for Indian FBR programme

Material for Present core of PFBR - Target 100 GWd/t (85 dpa).

Clad and wrapper 20% CW D9 Alloy: Ti ,Si



Linear swelling regime Insensitive to initial microstructure

Microchemical evolution

(Incubation dose)

Materials for future core of PFBR :

Target 150 GWd/t (130 dpa)

Clad D9I – P,Si ,Ti

Wrapper- Ferritic-martensitic steels

Fe-9Cr-1 Mo-0.1C-0.5 Si

↔

Incubation dose for Void swelling depends on Stability of TiC, Fe-Ti-P and Ni_3(SiTi) precipitates

Target 200 GWd/t (170 dpa)
Clad ODS Ferritic-martensitic steels
Fe-9Cr-0.1C-1W-0.2Ti-0.4Y2O3
Fe-12Cr-1W-0.015C-0.2Ti-0.4Y2O3

↔

Stability of nano oxide dispersion at high dpa

Summary to lecture 4

- The paused aim – participation in “nuclear renaissance” and achievement of commercially necessary levels of burn-up of nuclear fuel may be achieved only on the base of contemporary interpretation of the role of physical mechanisms of microstructure evolution associated with the change of initial physical-mechanical properties under irradiation.
- Major approaches in decreasing harmful radiation effects are based on selection of initial chemical and phase compositions, optimal modifications of microstructures (texture and grain size) and aimed at increasing recombination of point defects (that will leave fewer defects for creation of non-desirable secondary agglomerates like voids ,precipitates dislocation loops) and maximal stabilization of all structural components of theirs (dislocation structure, solid solution, precipitates system etc.) during irradiation.