Wir schaffen Wissen – heute für morgen

Microstructural changes in ferritic-martensitic steels under mixed proton-neutron irradiation

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1. *Materials and backgrounds.*

2. *Proton irradiation experiments (intragranular microstructure):*

   - *solid spallation products;*

   - *spatial distribution of chemical species;*

   - *comparison with TEM data.*

3. *Conclusions and perspectives*

chemical composition, at %

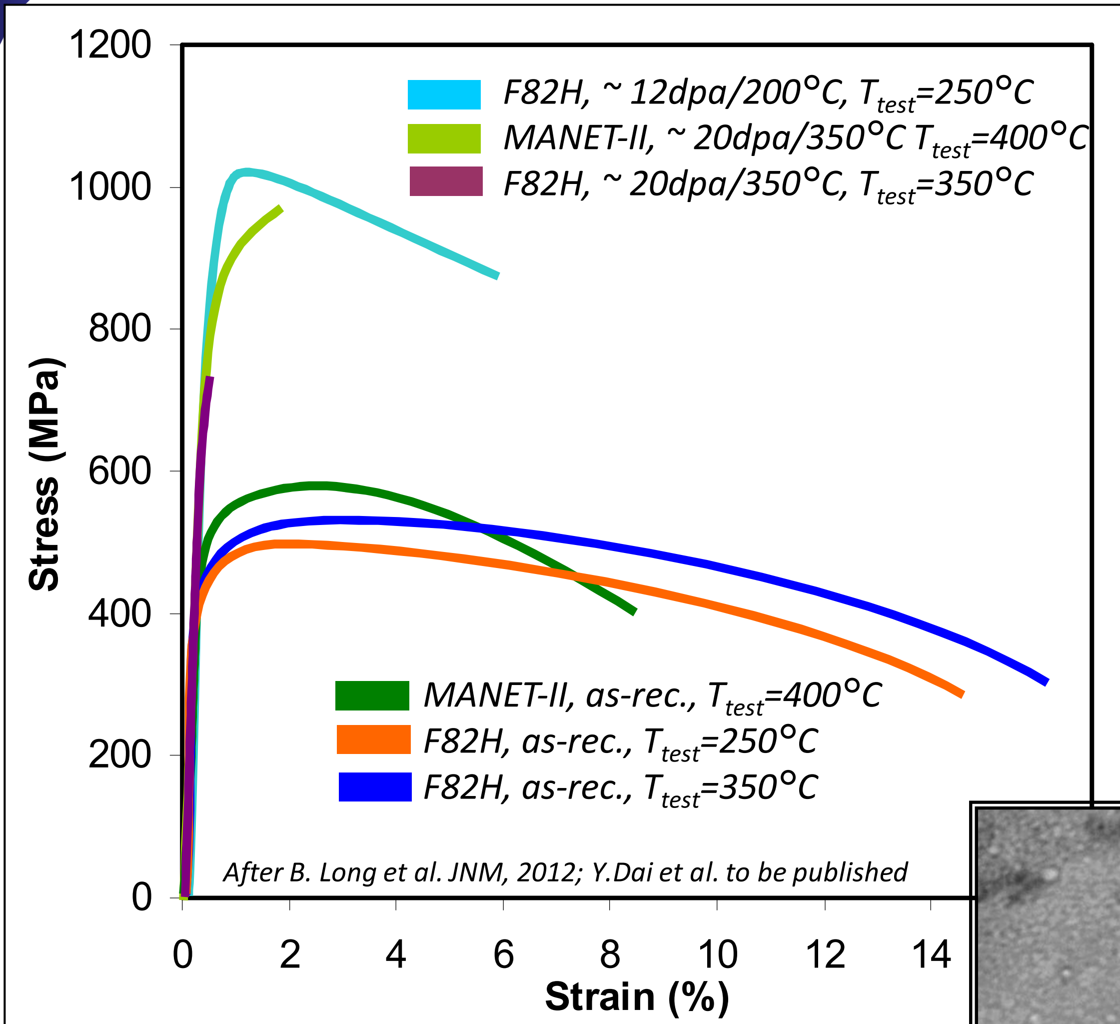
Materials	Cr	Si	Mn	V	C	W	Ta	Ni	Mo	Nb	P	N	S	B	Fe
F82H	8.25	0.22	0.16	0.17	0.4	0.61	0.006	-	-	-	-	-	-	-	balance
MANET II	10.92	0.35	0.85	0.21	0.51	-	-	0.61	0.33	0.08	0.009	0.12	0.007	0.15	balance

irradiation conditions, SINQ, STIP-II, $E_{protons} \approx 500 MeV$

	F82H		MANET II	
T, °C	192	345	196	357
Irradiation dose, dpa	11.8	20.3	12.4	20.4

characterisation of materials response to irradiation:

- tensile tests → changes of mechanical properties
- TEM → defect clusters and He bubbles
- APT → chemical elements distribution



mechanical tests (B. Long et al. JNM, 2012):

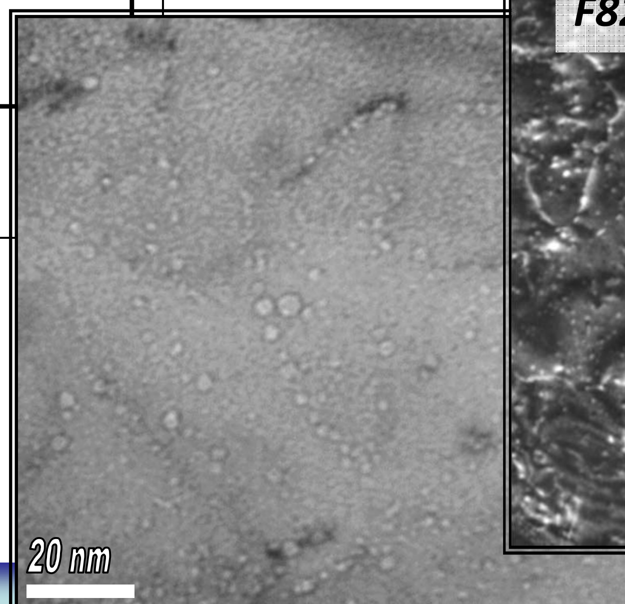
- *radiation induced hardening ($\Delta\sigma_y$);*
- *loss of ductility.*

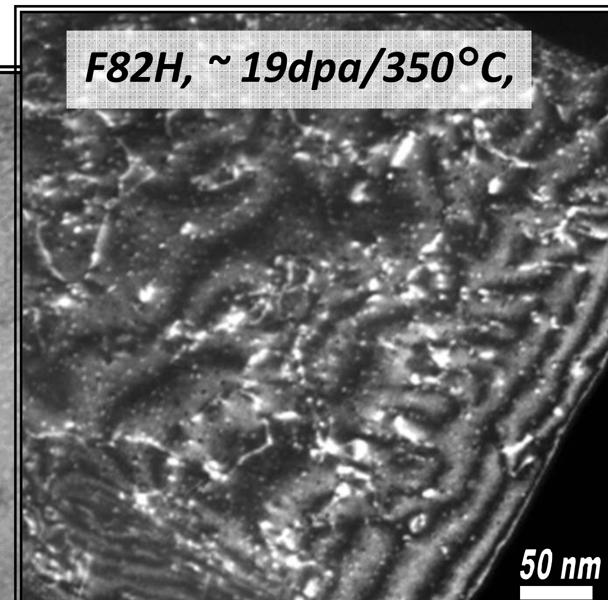
microstructure:

TEM (Jia and Dai, JNM, 2006):

- *"black dots";*
- *dislocation loops;*
- *He bubbles*

APT: stability of phases?

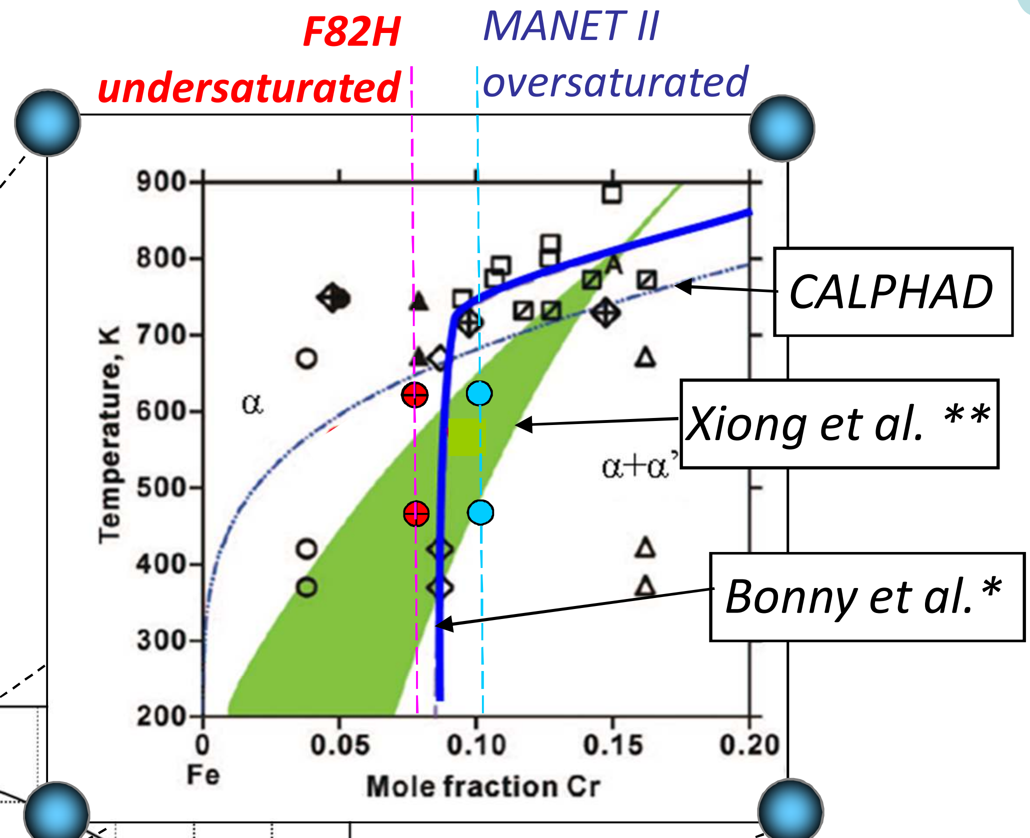


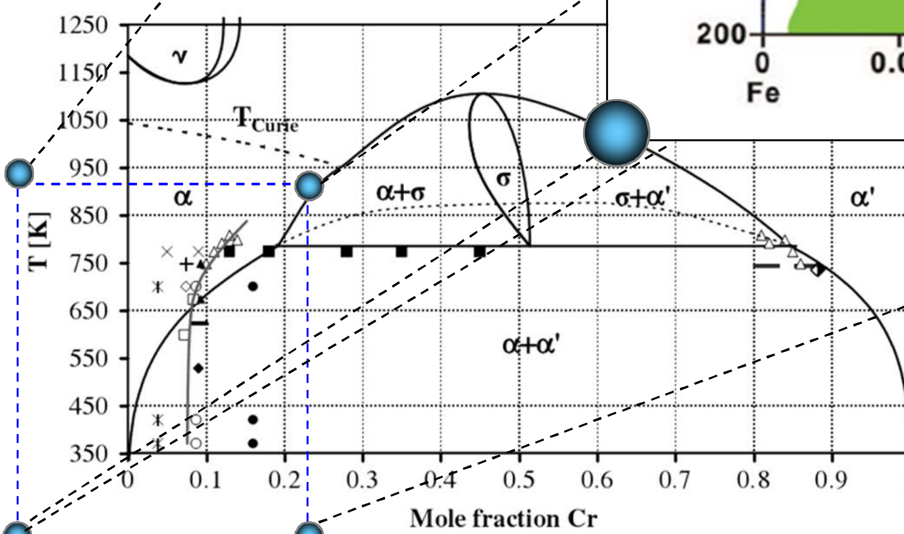


irradiation of FM steels: what we can expect?

Wide variety of phases:

- *Cr-enriched α' particles;*
- *Cr, Si and Ni enriched M_6X precipitates;*
- *Cr and V enriched M_2X precipitates;*
- *Ni and Si enriched G- , χ (Chi)- and σ (sigma)- phases;*
- *MP and M_3P type phosphides;*
- *Mo-rich or W-rich Laves phases.*





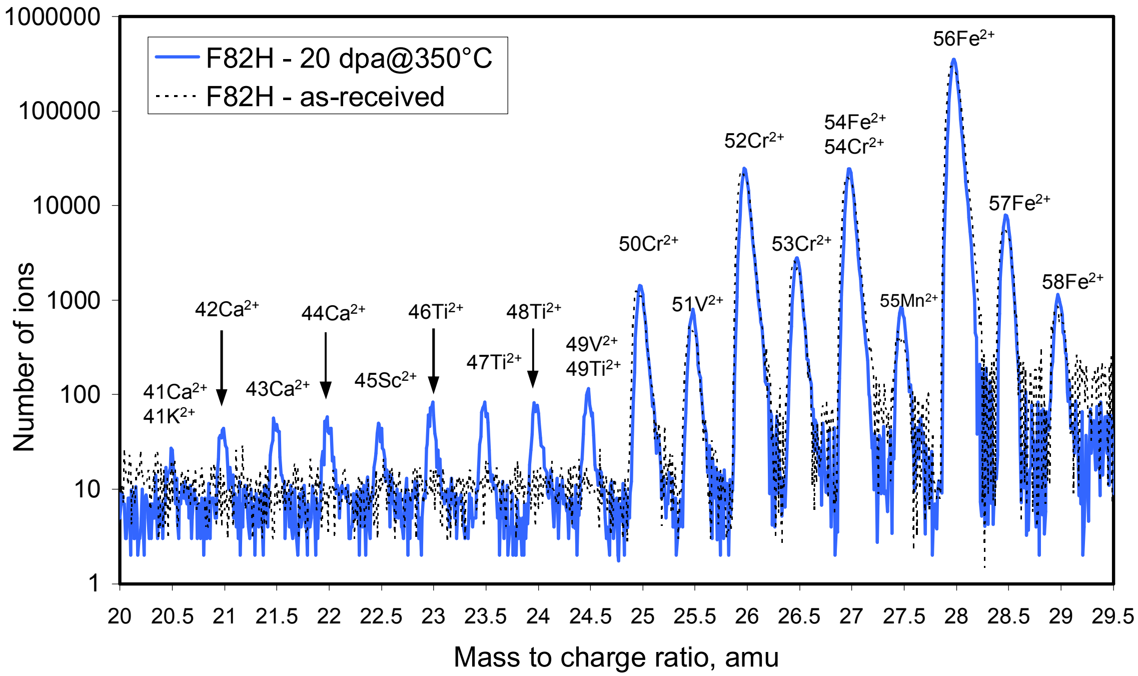
α' phase

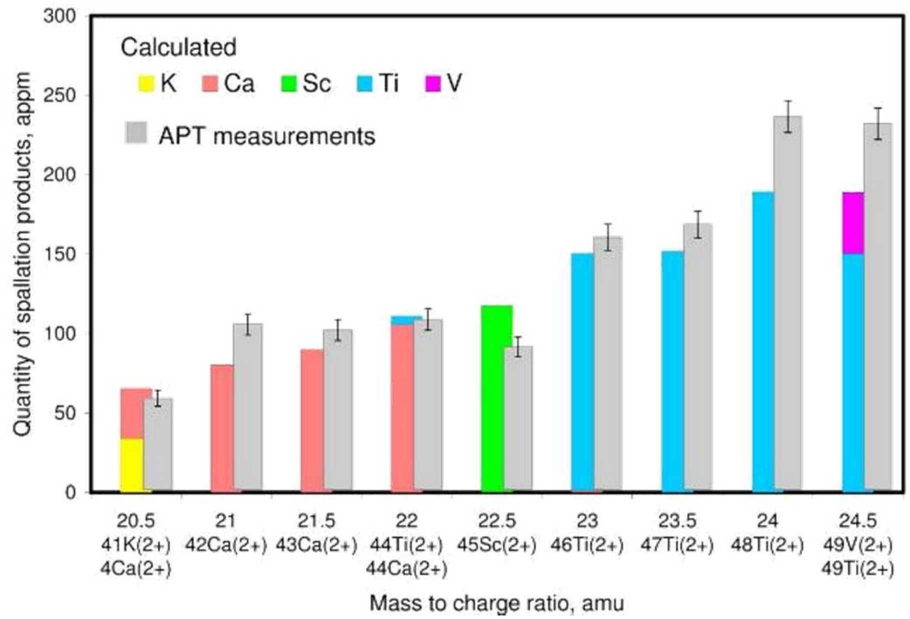
***F82H** – induced ?*

***MANET II** - enhanced?*

**G. Bonny et al. Scripta Materialia 59 (2008) 1193-1196.*

** * W. Xiong et al. Solid State and Materials Sciences Volume 35 (2010) 125 - 152.*

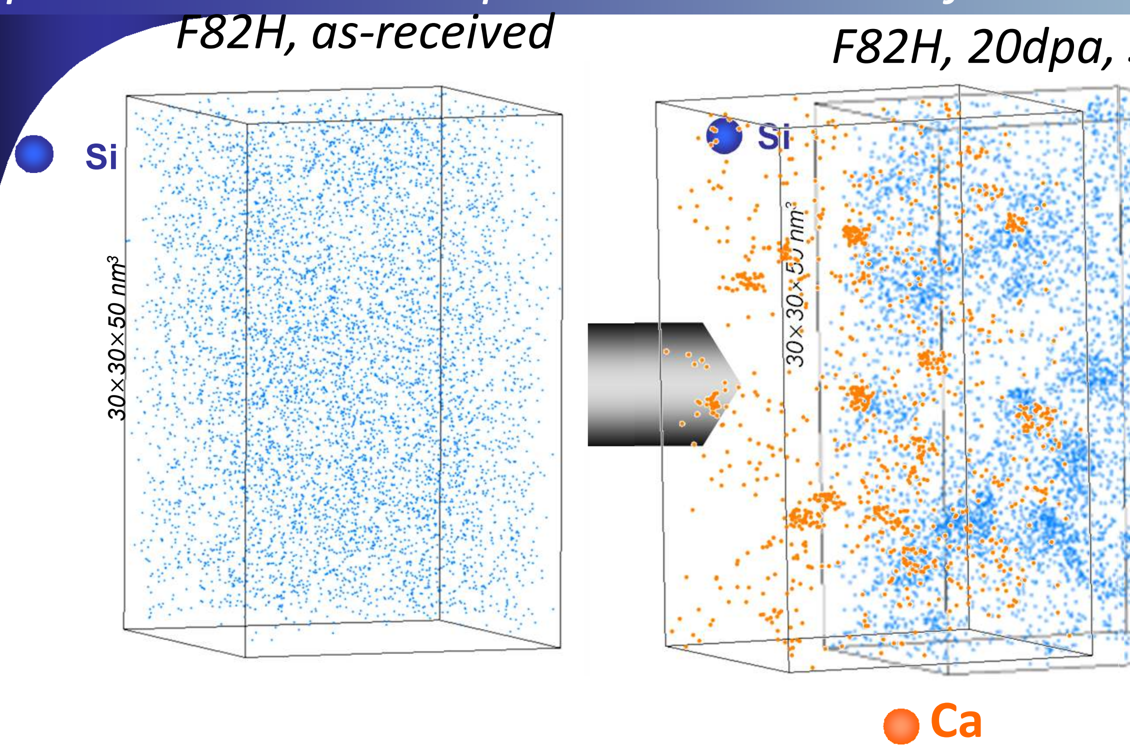


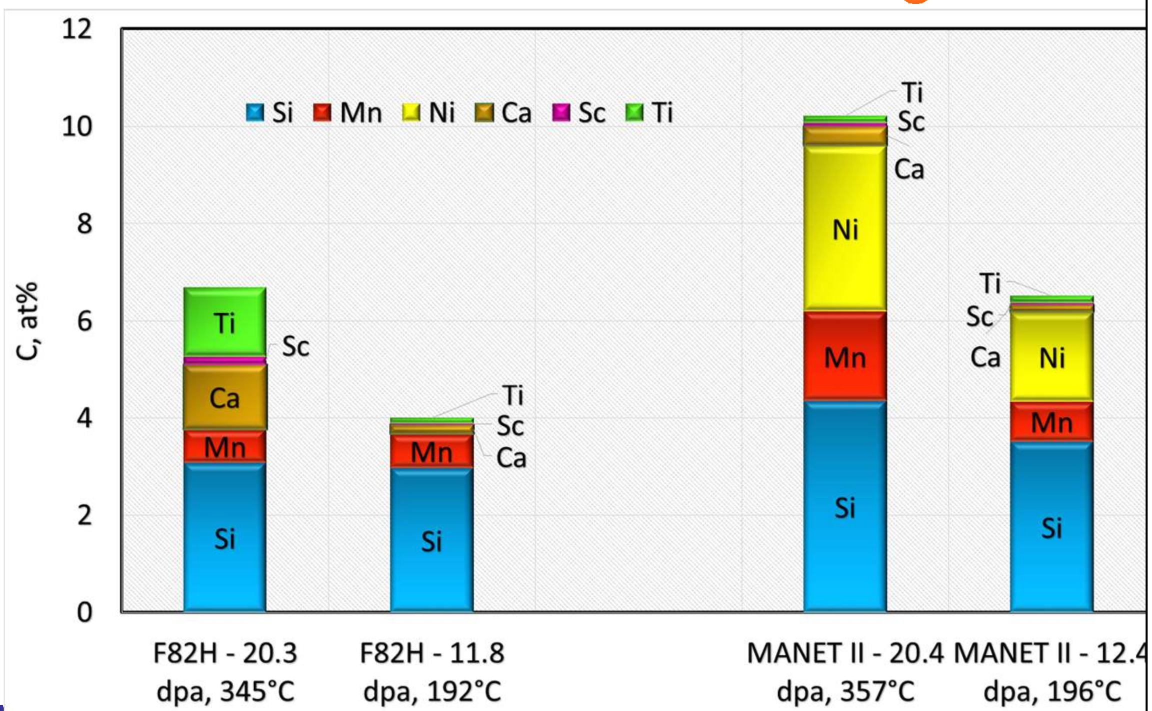


the abundance of spallation elements is not natural → *calculations of isotope production* → *Ti, Sc and Ca are the main solid spallation products*

Solid spallation products content, APT result

	F82H		MANET II	
Dose	11.0 dpa	20.3 dpa	12.9 dpa	20.4 dpa
Ti, appm	570±30	800±10	570±30	760±10
Sc, appm	50±30	90±20	50±30	90±10
Ca, appm	240±40	370±10	200±40	400±10





Si-enriched clusters:

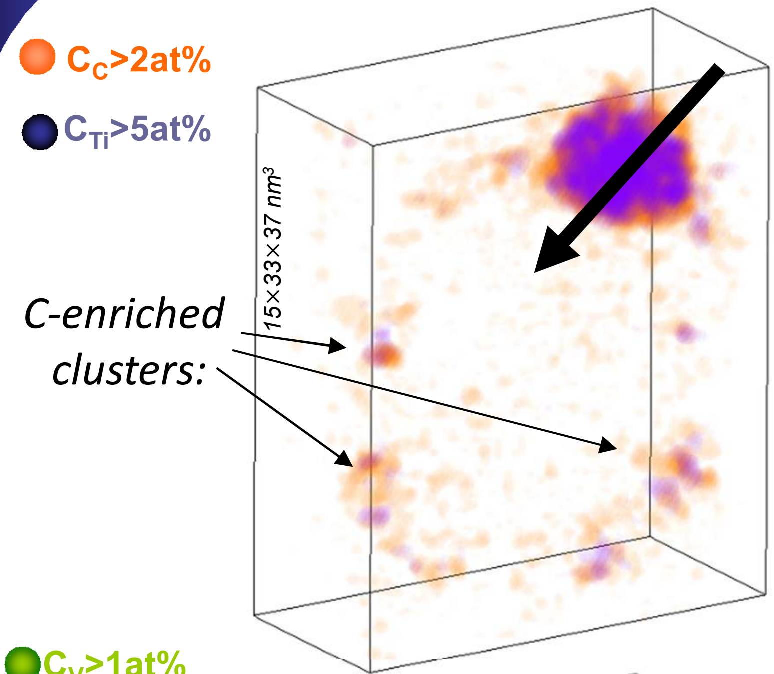
- *in all samples (F82H and MANET-II);*
- *homogeneously distributed in the matrix;*
- *size D ~ 2.5 to 4 nm and number density ~ 3…11 × 10^{23} m^{-3};*
- *contain Si, Mn, Ni (only in MANET-II) and spallation Ca (the highest enrichment factor up to ~ 70), Ti and Sc;*
- *no thermodynamic driving force for precipitation;*
- *often reported in irradiated FM-steels , Fe-Cr model alloys and bainitic steels, never without irradiation;*

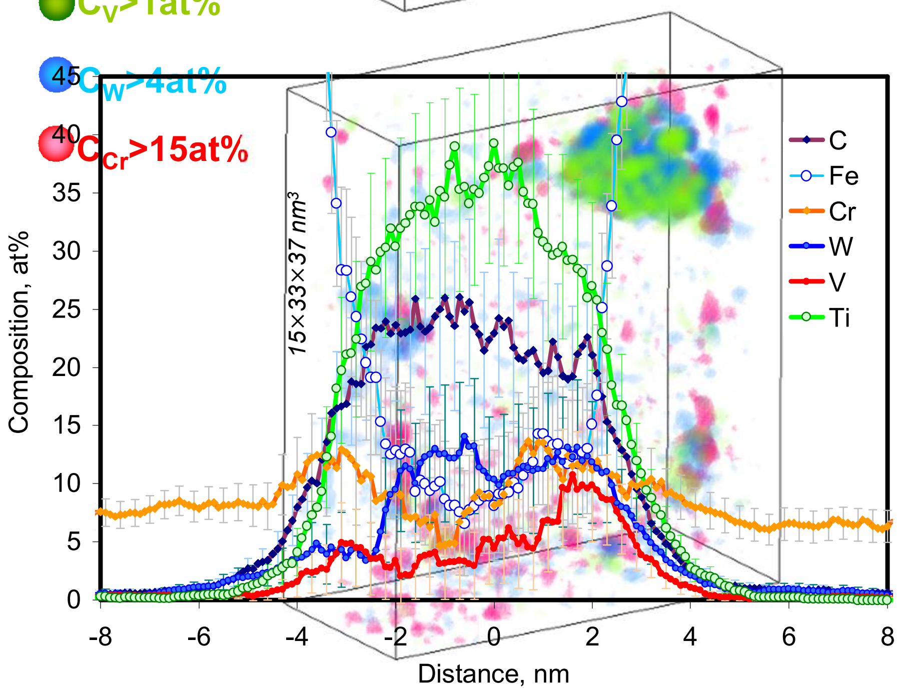
Radiation induced

- *can be related to radiation induced Si- and Ni-rich phases such as G-, χ- or σ-phase?*

But: *no data about such phases in the studied steels*

F82H, 20dpa, 350°C





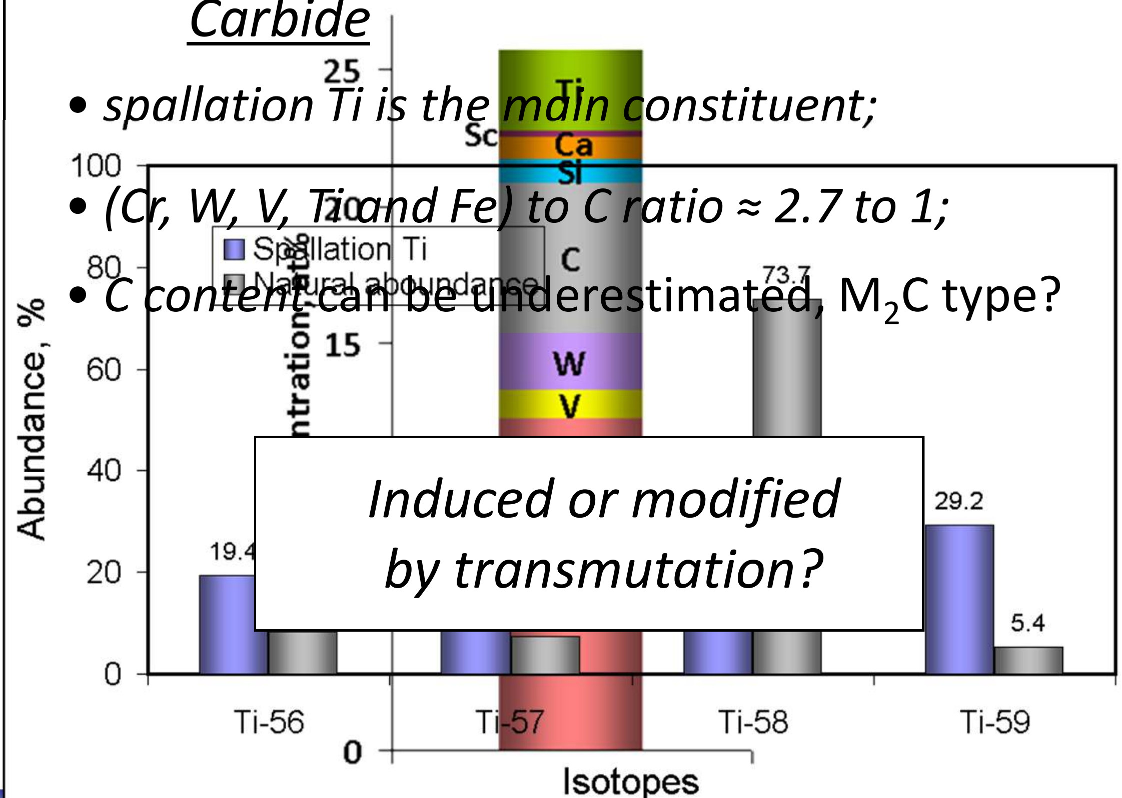
C-enriched clusters:

- on the loops or in its neighborhood;

Radiation induced

- contain spallation elements (mainly Ti);
- (Cr, W, V, Ti and Fe) to C ratio ≈ 17 to 1, $M_{18}C$ carbide Chi (χ) -phase?
- But: no data about such phases in F82H

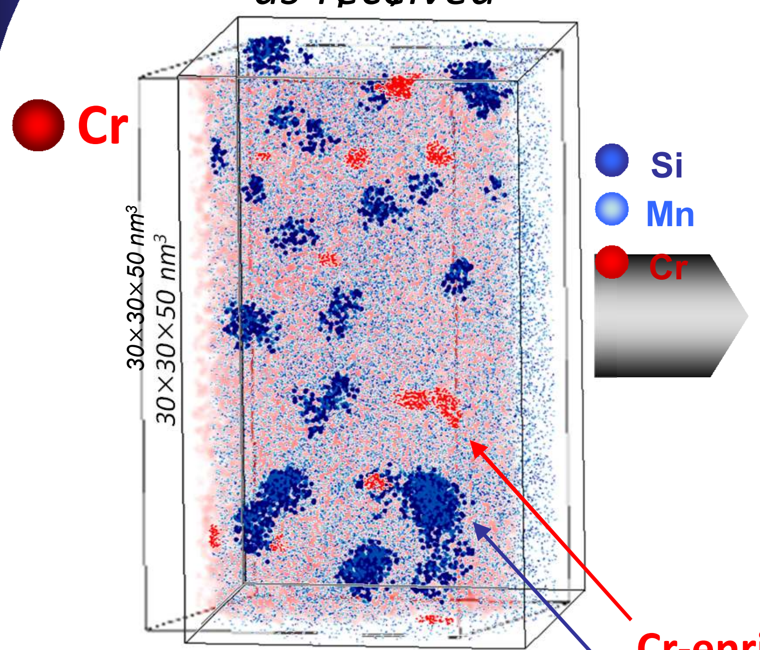
Carbide



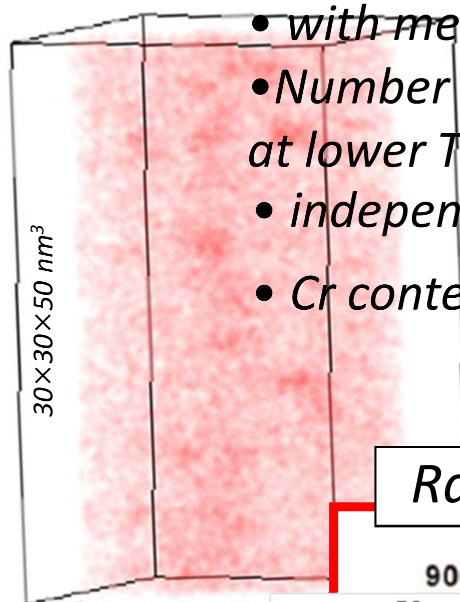
- spallation Ti is the main constituent;
- (Cr, W, V, Ti and Fe) to C ratio ≈ 2.7 to 1;
- C content can be underestimated, M_2C type?

Induced or modified by transmutation?

MANET-II,
as-received



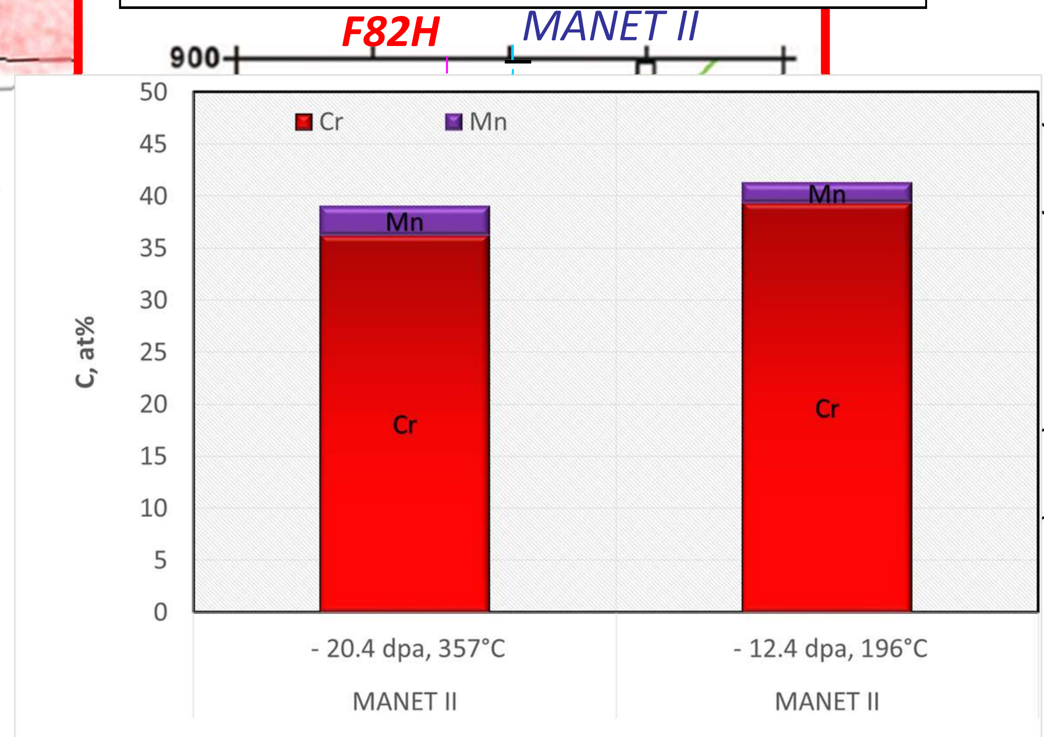
MANET-II,
20.4dpa, 354°C



Cr-enriched clusters:

- *presence just in supersaturated MANET-II steel;*
- *with mean diameter of about 2 to 3 nm;*
- *Number dencity is one order of magnitude lower at lower T_{irr};*
- *independent from Si clusters;*
- *Cr content is similar at different T_{irr};*

Radiation enhanced α' clusters



*G. Bonny et al. Scripta Materialia 59 (2008) 1193-1196.
* * W. Xiong et al. Solid State and Materials Sciences Volume 35 (2010) 125 - 152.

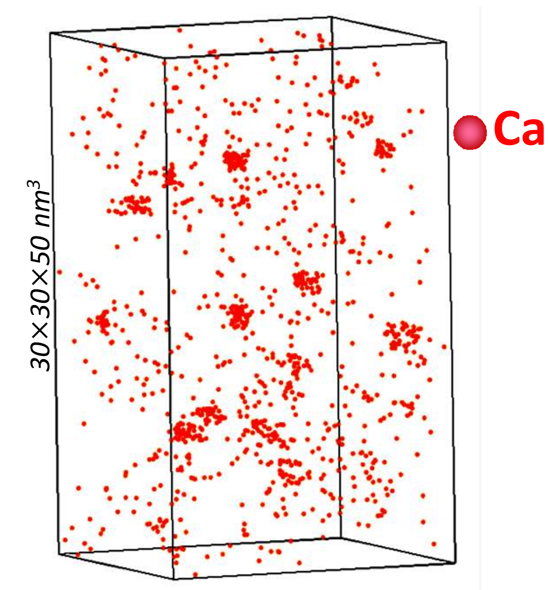
proton irradiation: APT vs TEM

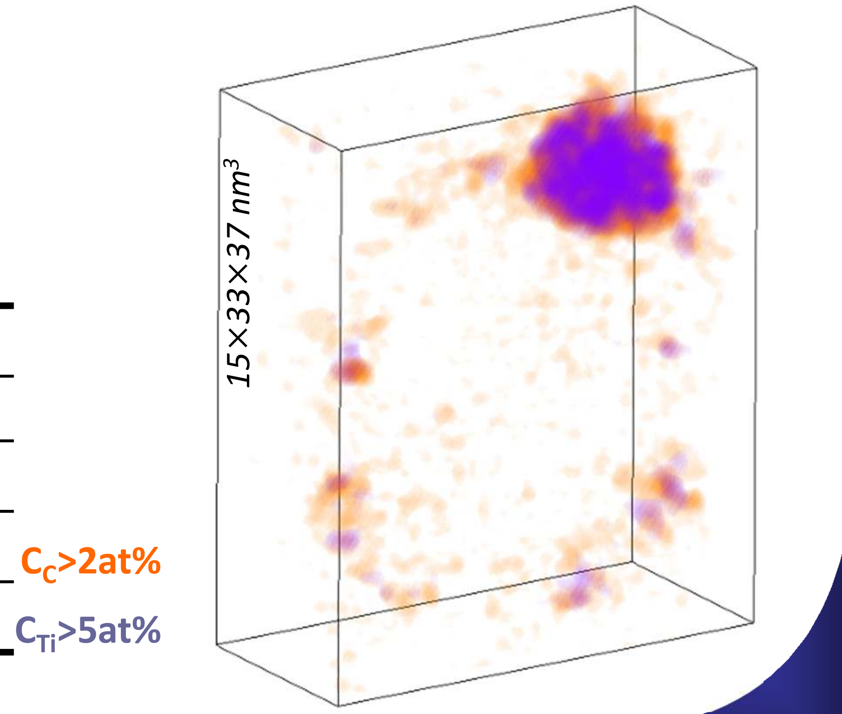
	F82H		MANET II	
dpa	11.8	20.3	12.4	20.4
T, °C	192	345	196	357
Si enriched cluster (radiation induced)				
Number density, m^{-3}	4.0×10^{23}	1.6×10^{23}	7.4×10^{23}	5.5×10^{23}
Diameter, nm	5.0 ± 0.6	3.8 ± 0.4	2.52 ± 0.6	4.05 ± 0.5
Other clusters				
Type	-	**C-cluster (radiation induced)**	α' clusters **(radiation enhanced)**	α' clusters **(radiation enhanced)**
Number density, m^{-3}		8×10^{22}	5.4×10^{22}	1.44×10^{23}
Diameter, nm		5.0 ± 0.6	1.9 ± 0.5	2.8 ± 0.6
TEM for similar irradiation conditions	Jia and Dai, JNM, 2006 (10dpa@185°C)	Jia and Dai, JNM, 2006		Shen, Li and Dai, to be published
SIA clusters density (m^{-3})	4.0×10^{22}	2.9×10^{22}		2.5×10^{22}
SIA clusters size (nm)	4.2	8.5		5
Bubbles density (m^{-3})	3.8×10^{23}	2.5×10^{23}		3.6×10^{23}
Bubbles size (nm)	1	5		2

APT: Ti, Sc, Ca are the main solid spallation products

- Ti, Sc and, especially, Ca participates in forming of Si-enriched clusters;
- Ti participates in forming of C-enriched clusters;
- Ti segregates on dislocation loops;
- Ti alters the microchemistry of carbides
- Ca and Sc can affect the SIA and dislocation mobility due to a large misfit with matrix Fe atoms (~ 28.5% for Ca and ~ 14% for Sc).

F82H, 20dpa, 350°C

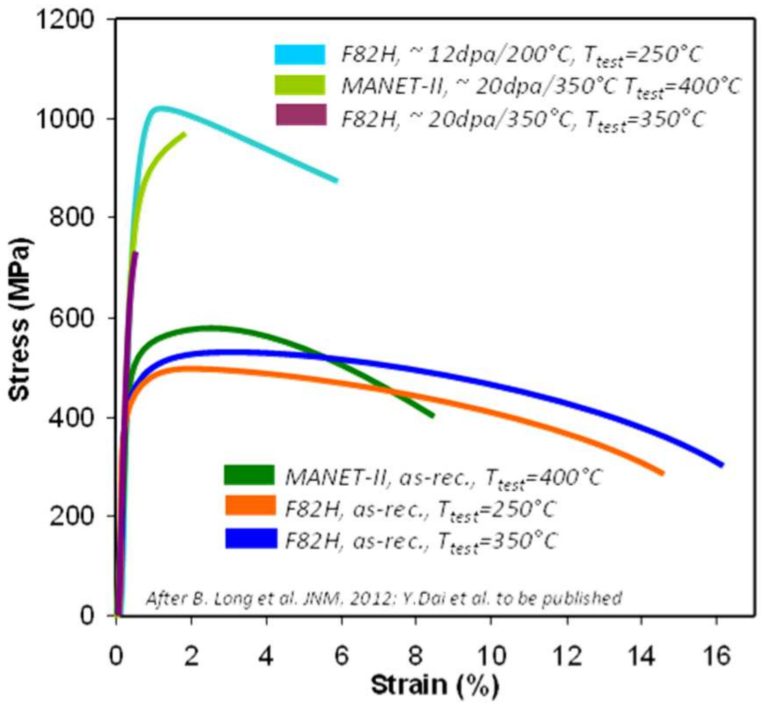




Solid spallation products content in the matrix

	F82H		MANET II	
Dose	11.8 dpa	20.3 dpa	12.4 dpa	20.4 dpa
Ti, appm	~ 470	~ 440	~ 580	~ 590
Sc, appm	~ 40	~ 40	~ 80	~ 40
Ca, appm	~ 150	~ 190	~ 170	~ 170

What can contribute to the irradiation induced hardening and loss of ductility?



Radiation induced clusters:

- ***homogeneously distributed Si-enriched clusters;***
- ***C-enriched clusters on the dislocation loops (in F82H).***

Radiation enhanced precipitation:

Cr-enriched α' clusters in supersaturated MANET II.

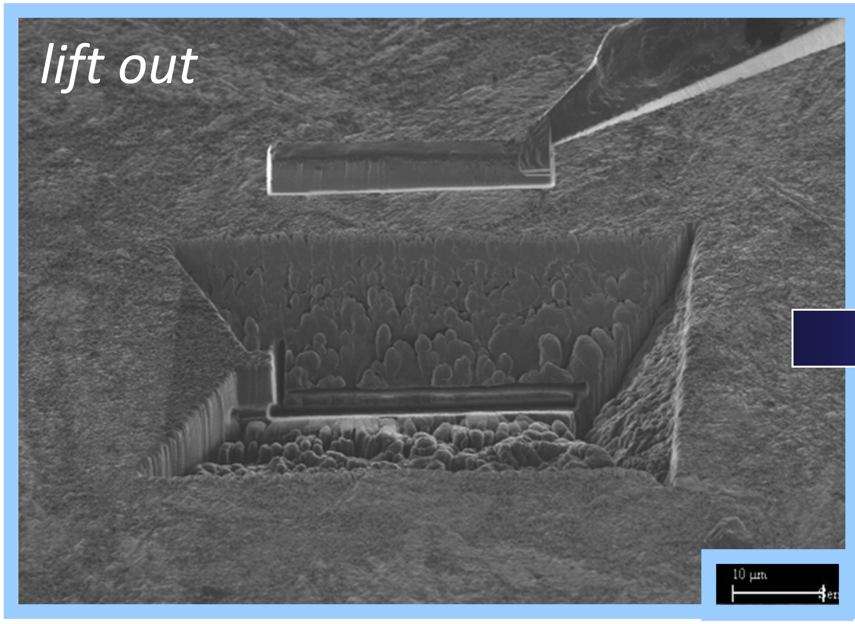
Segregations of Cr, C, V, W and spallation Ti atoms on dislocation loops in F82H;

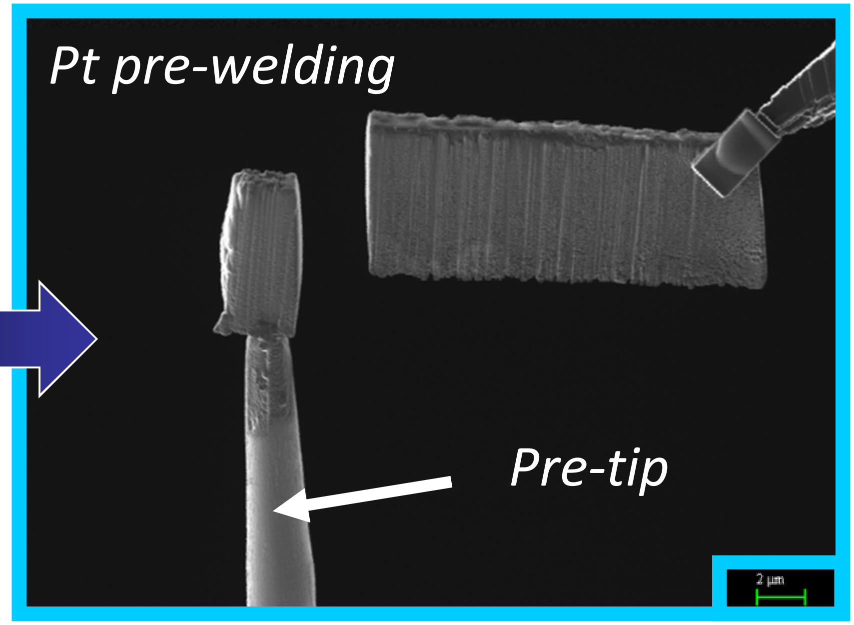
Creation and redistribution of solid spallation products

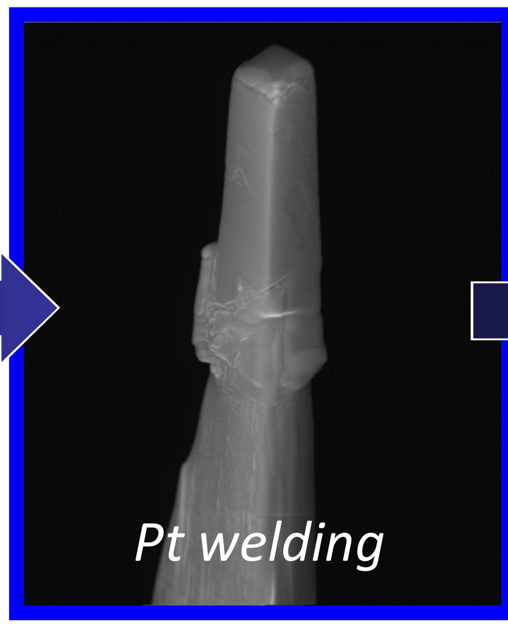
Thank you for your attention!

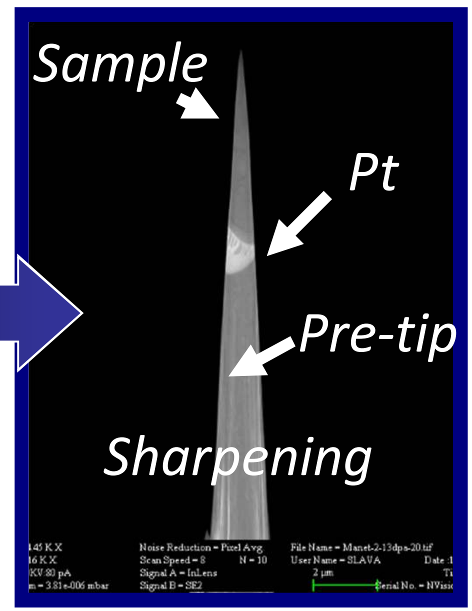
Back-up slides

Activity for a half of a tensile sample: $5.18 \cdot 10^{6}$ Bq







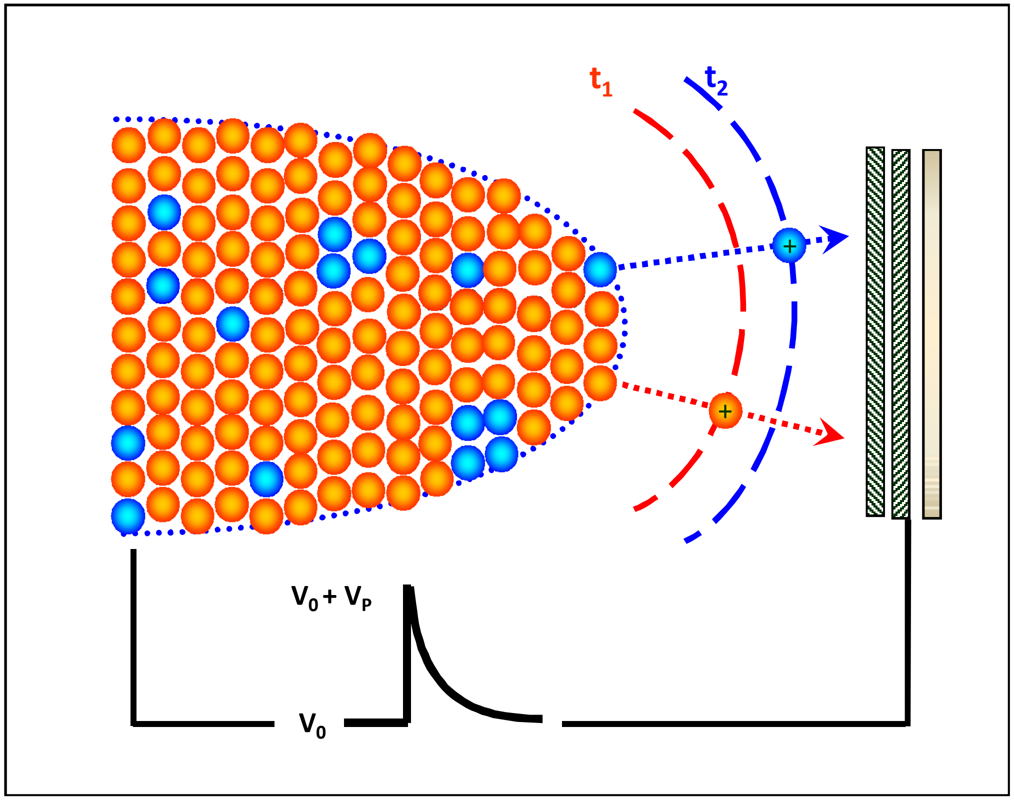


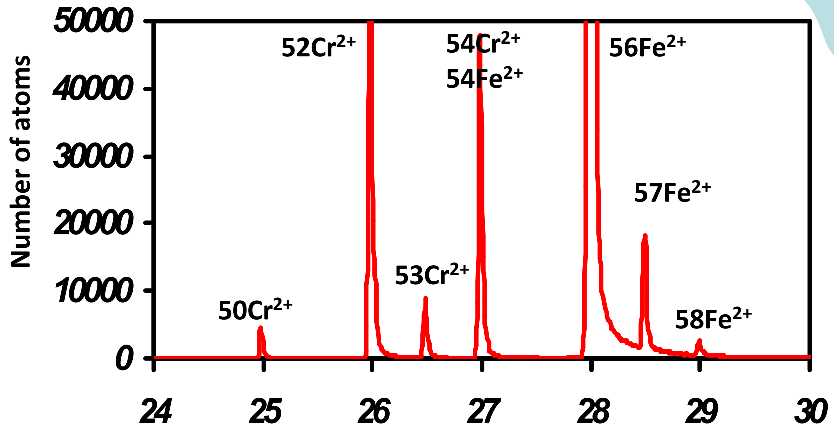
Activity for an APT sample: $1.36 \cdot 10^{-3}$ Bq *electric field is induced at the apex of a tip*

$$E = \frac{V}{\beta R} \approx 10 \ldots 30 \frac{V}{nm}$$

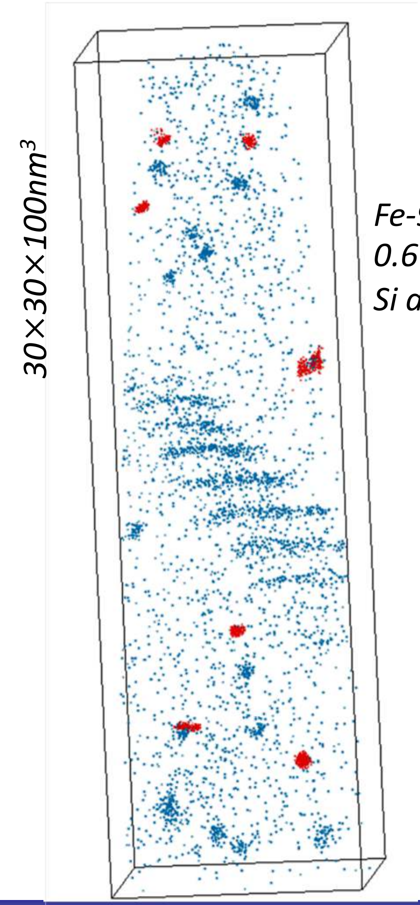
mass to charge ratio of the ions allows to determine their chemical nature

$$\frac{m}{n} = 2 \cdot e(V_O + V_P)\left(\frac{t}{L}\right)^2$$





Mass spectrum of Fe-Cr alloy

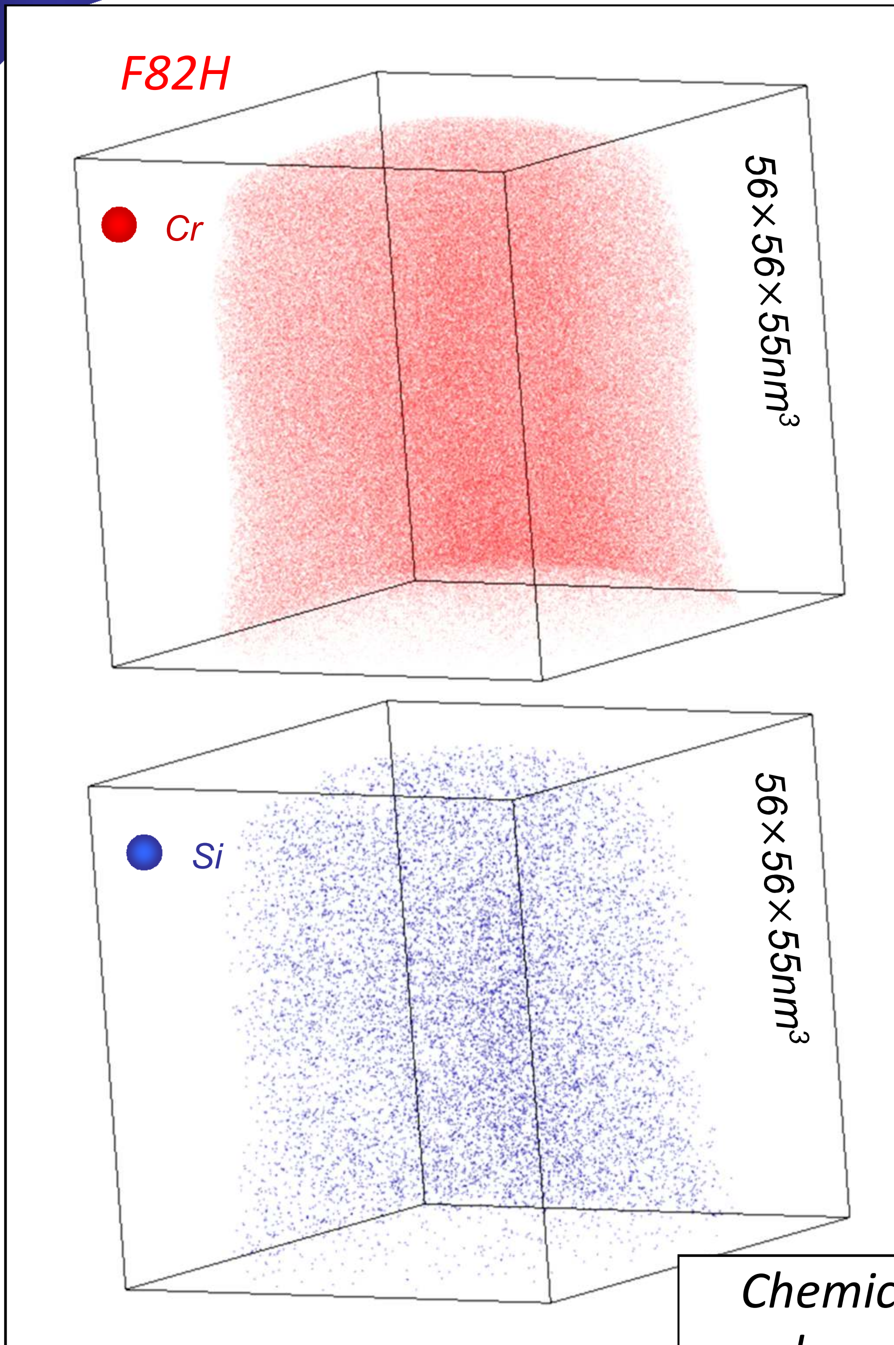


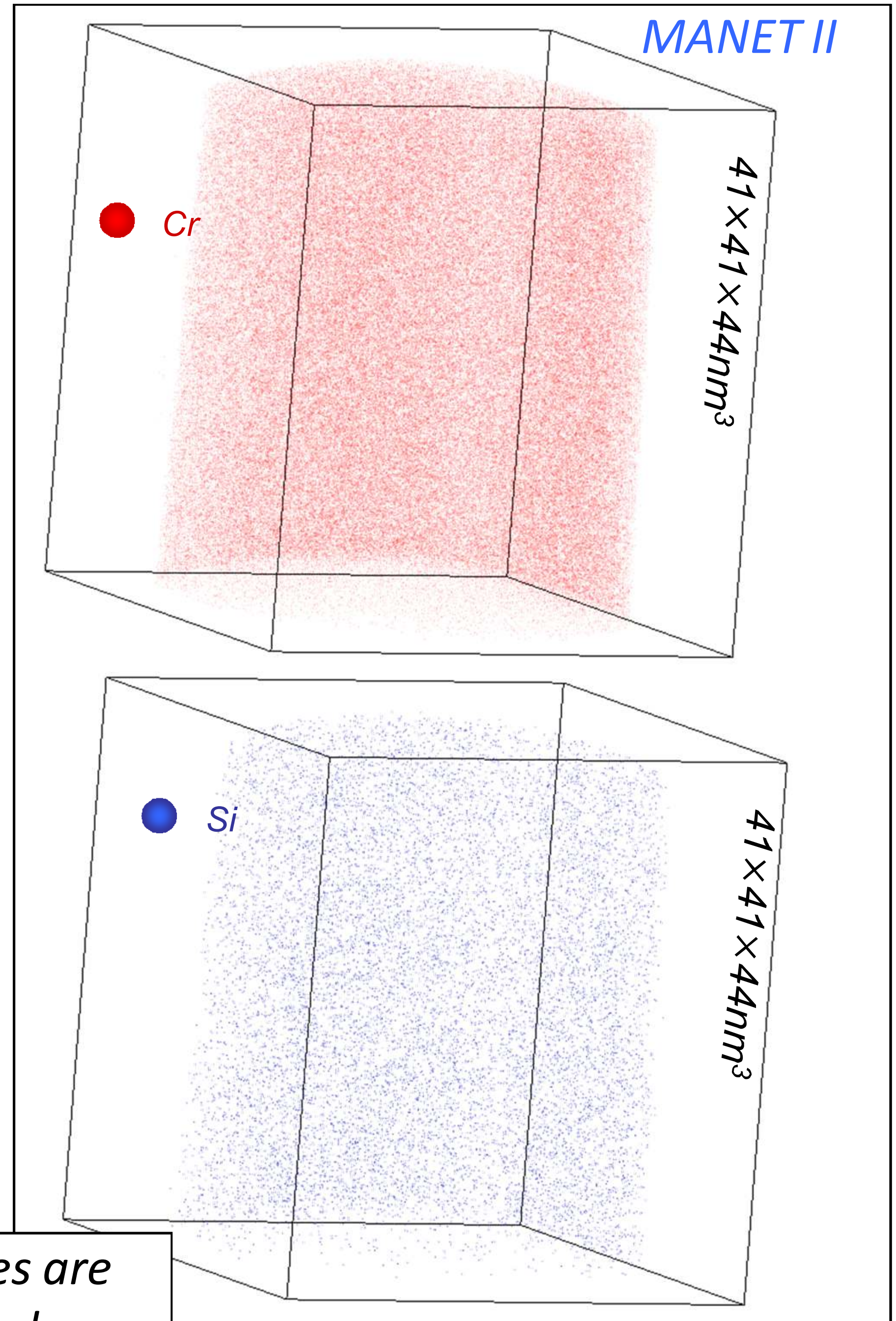
Fe-9%Cr alloy, 0.6 dpa, 300°C Si atoms

conditions:

cryogenic temperatures T=40…45K

Ultra high vacuum ~ 10^{-10}bar

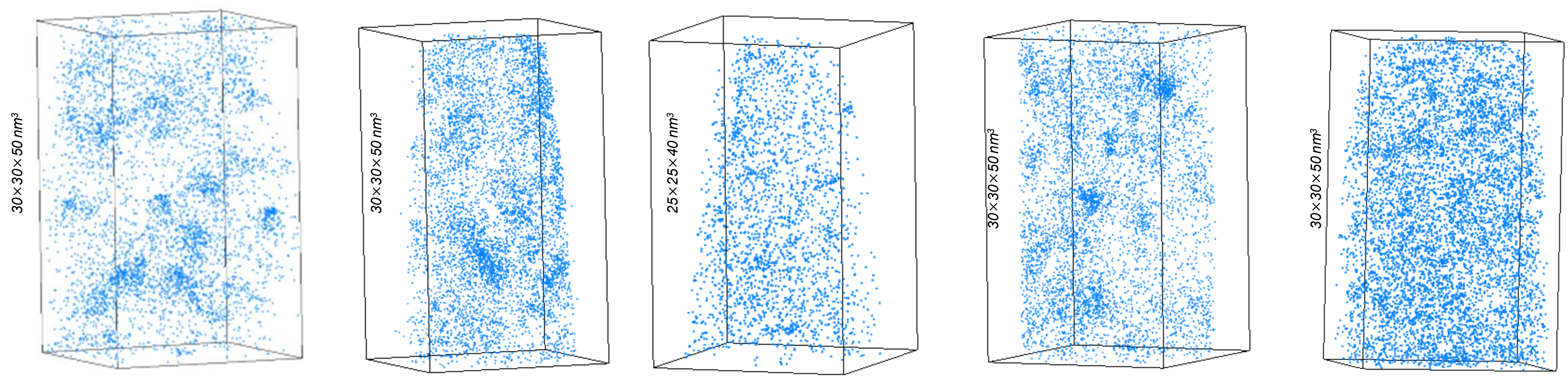




Chemical species are homogeneously distributed

Si clusters

	F82H	F82H	F82H	MANET II	MANET II
	- 20.3 dpa, 345°C	- 11.8 dpa, 192°C	- 20.3 dpa, 345°C + 600°C 1h	- 20.4 dpa, 357°C	- 12.4 dpa, 196°C
dpa	20.3	11.8	20.3	20.4	12.4
T	345	192	345	357	196

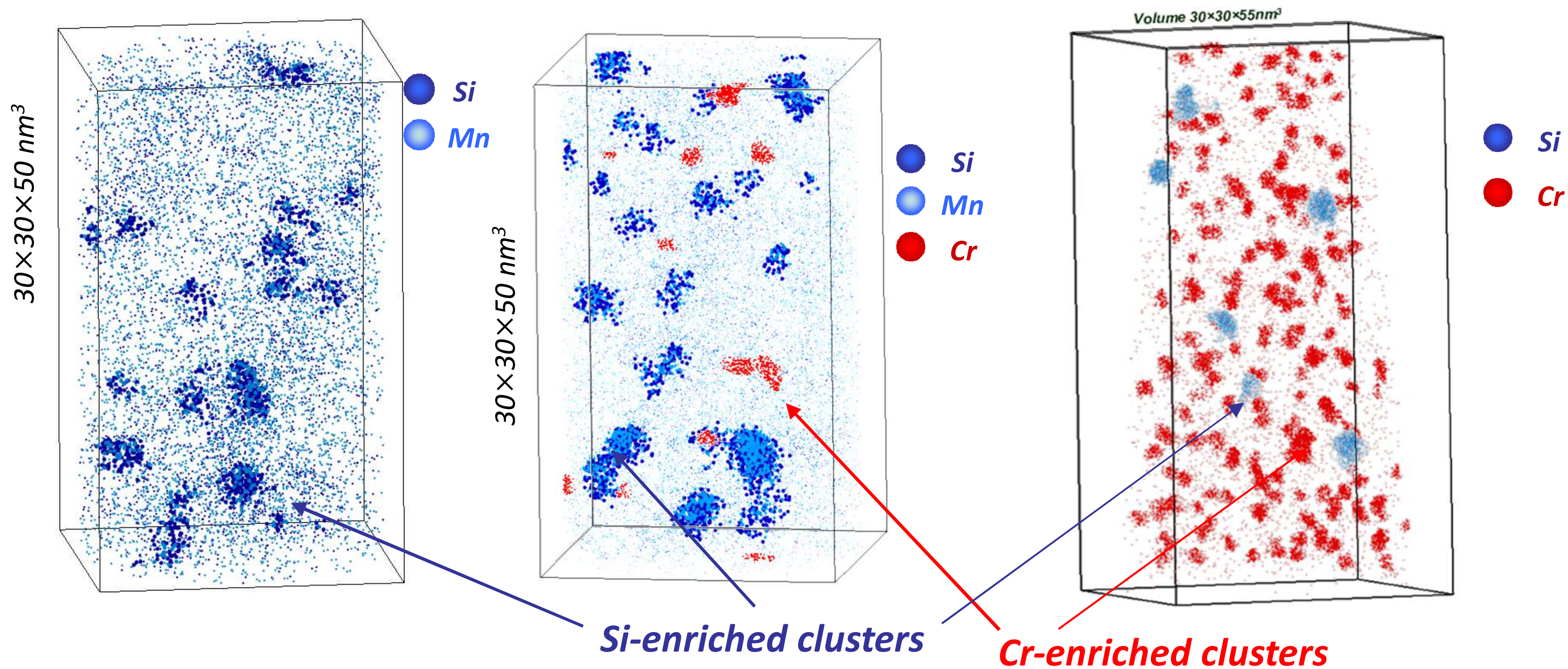


ND m-3	2.70E+23	no dislo		4.03E+23			6.47E+23			5.15E+23			1.12E+24		
	1.60E+23	+dislo													
Diameter, nm	3.8	±	0.4	3.7	±	0.8	1.82	±	0.47	4.05	±	1.42	2.52	±	0.58

F82H (8.25at%), SINQ-20.3dpa, 350°C	MANET-II (10.7at%), SINQ-20.4dpa, 354°C	Fe – 12Cr (industrial purity) BR-2 irr, 0.6 dpa, 300°C

V. Kuksenko et al. IWSMT-12, 2014

V. Kuksenko et al. JNM, 2011,



Compositions of Si-enriched clusters, measured by APT (at%)

	SINQ F82H, 20 dpa	SINQ MANET-2, 20.4 dpa	BR-2 Fe-12Cr, 0.6 dpa
Cr	8.14±0.26	8.45±0.22	12.5±3.0
Si	3.08±0.16	4.36±0.16	5.2±2.0
Ni	0.69±0.08	3.41±0.14	1.6±1.1
P	-	-	1.2±1.0
Ca+Sc+Ti	~2.92	~ 0.39	-
Fe	Balance	Balance	Balance