Experimental studies of irradiated and hydrogen implantation damaged reactor steels

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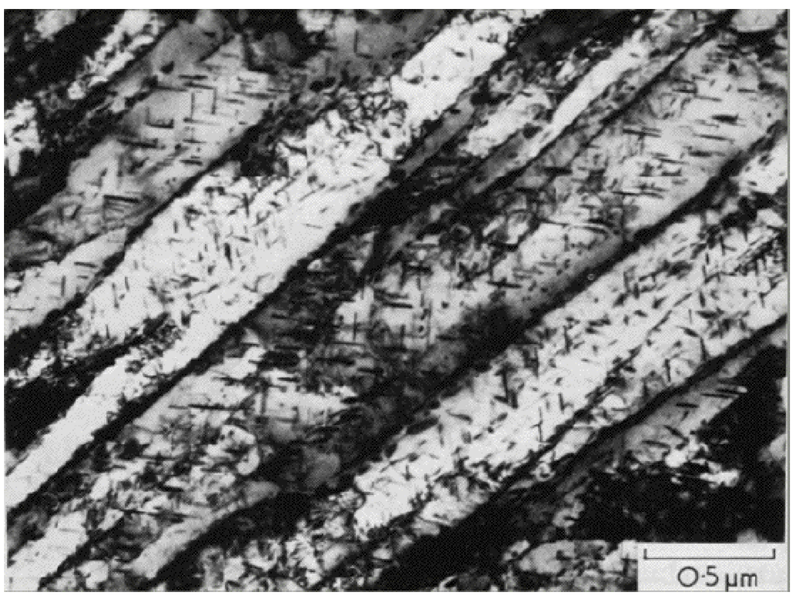
The EPR pressure vessel in Olkiluoto 3 (Finland) – 2009

VVER-440
annealing facility

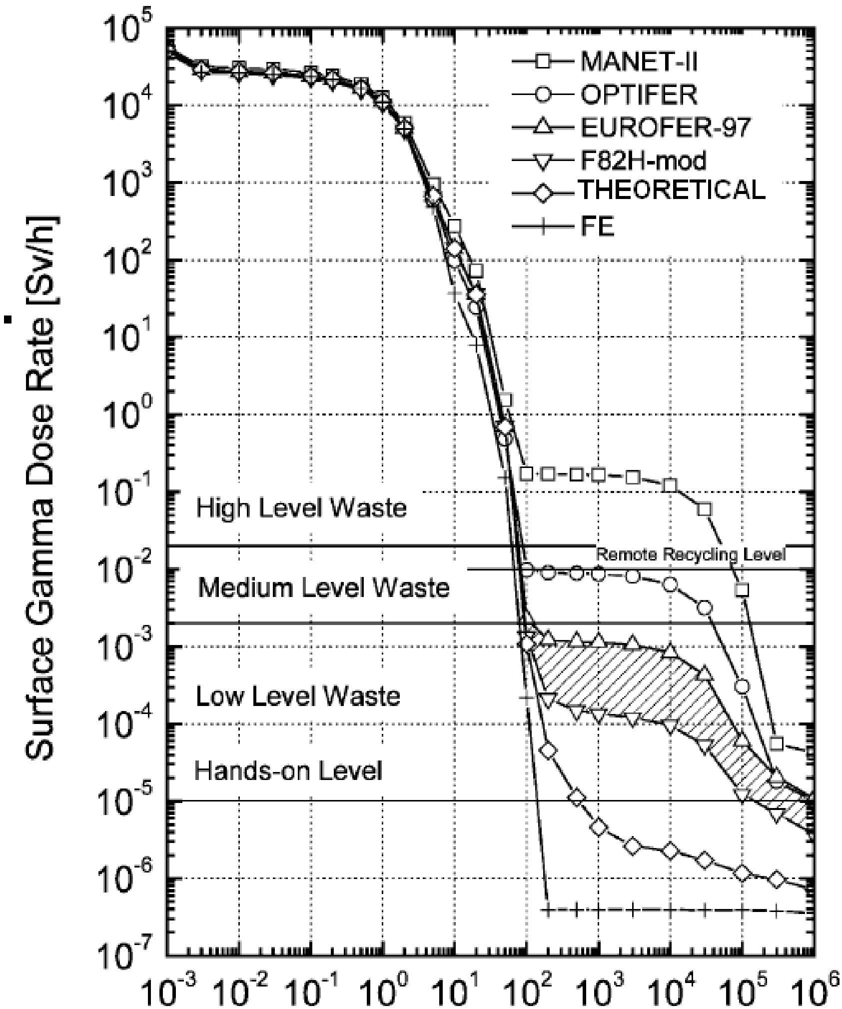
VVER-440 V-213
Pressure vessel

Feritic/martensitic (FM) steels

- Temperature limit - 650°C (ductility loss),
- Appropriate values of strength (martensite) and ductility (ferrite),
- Lower content of nickel and cobalt – reduced activated FM steels (RAFM).



FM steel – martensite looks like needles.



Overview

Techniques

TEM Transmission electron microscopy

XRD X-Ray Difraction

SEM Scanning electron microscopy

APFIM Atom Probe Field Ion Microscopy

OM Optical Microscopy

SANS Small Angle Neutron Scattering

PAS Positron annihilation spectroscopy

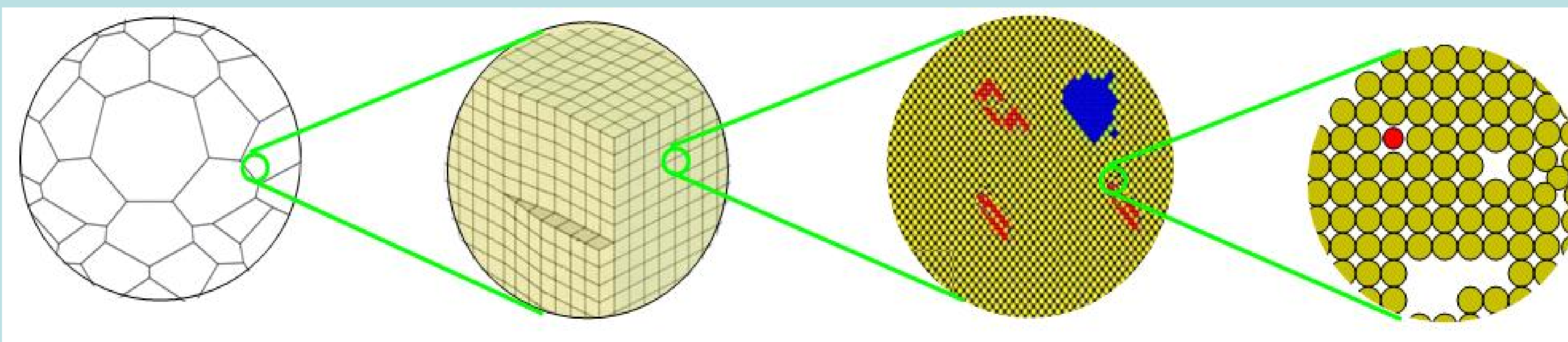
Defects

Grain boundary

Dislocations

Dislocation loops, precipitations

Frenkel Defects, Small Vacancy clusters



Dimensions

~10mm	~100 nm	~10 nm	~1 nm
~10^{-5} m	~10^{-7} m	~10^{-8} m	~10^{-9} m
~10^{5} Å	~1000 Å	~100 Å	~10 Å

Available techniques for material studies:

Positron Annihilation Spectroscopy: Conventional PALS 2-det. or 3-det. Set-ups (for irradiated materials), digital Doppler Broadening set-up, *experiences with PLEPS measurements at FRM-II in Garching from past*

Moessbauer spectroscopy,

Atomic force microscopy,

X-ray diffraction, Barkhausen Noises measurements,

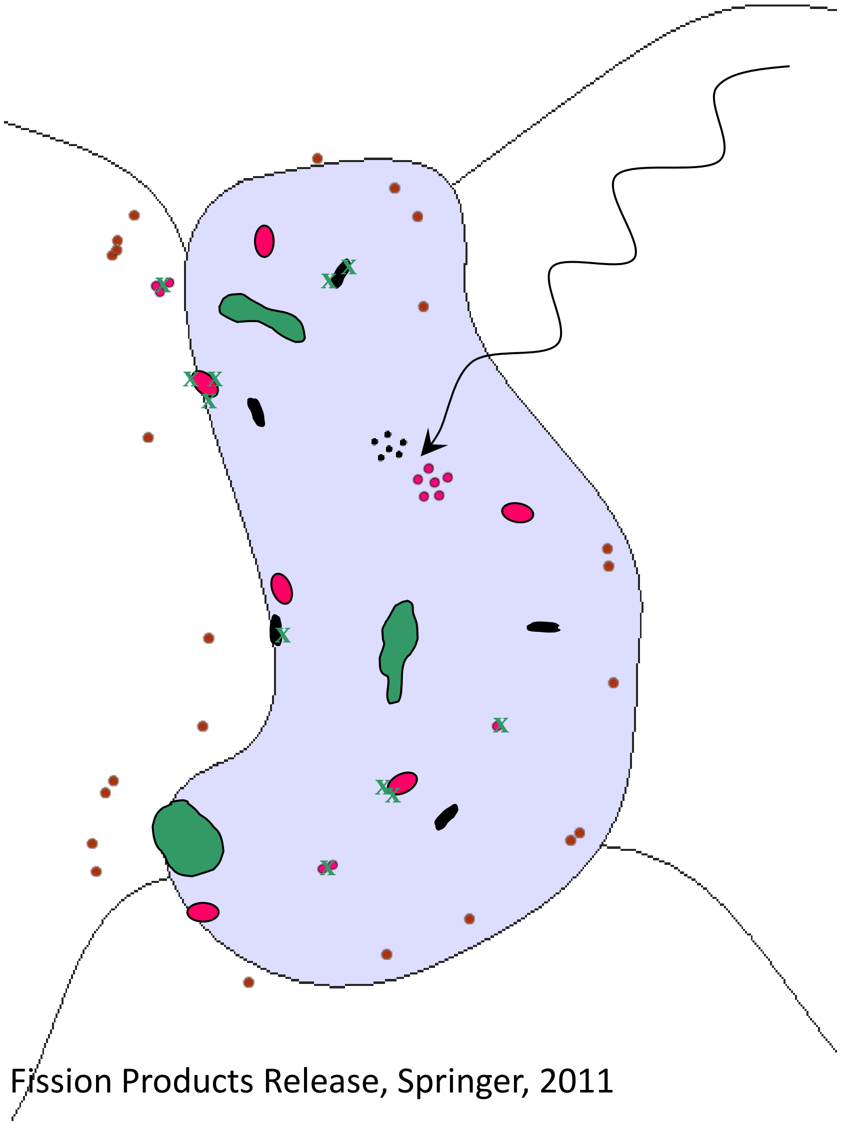
Alfa, beta, gamma spectroscopy including low/background chamber,

In collaboration with other institutes:

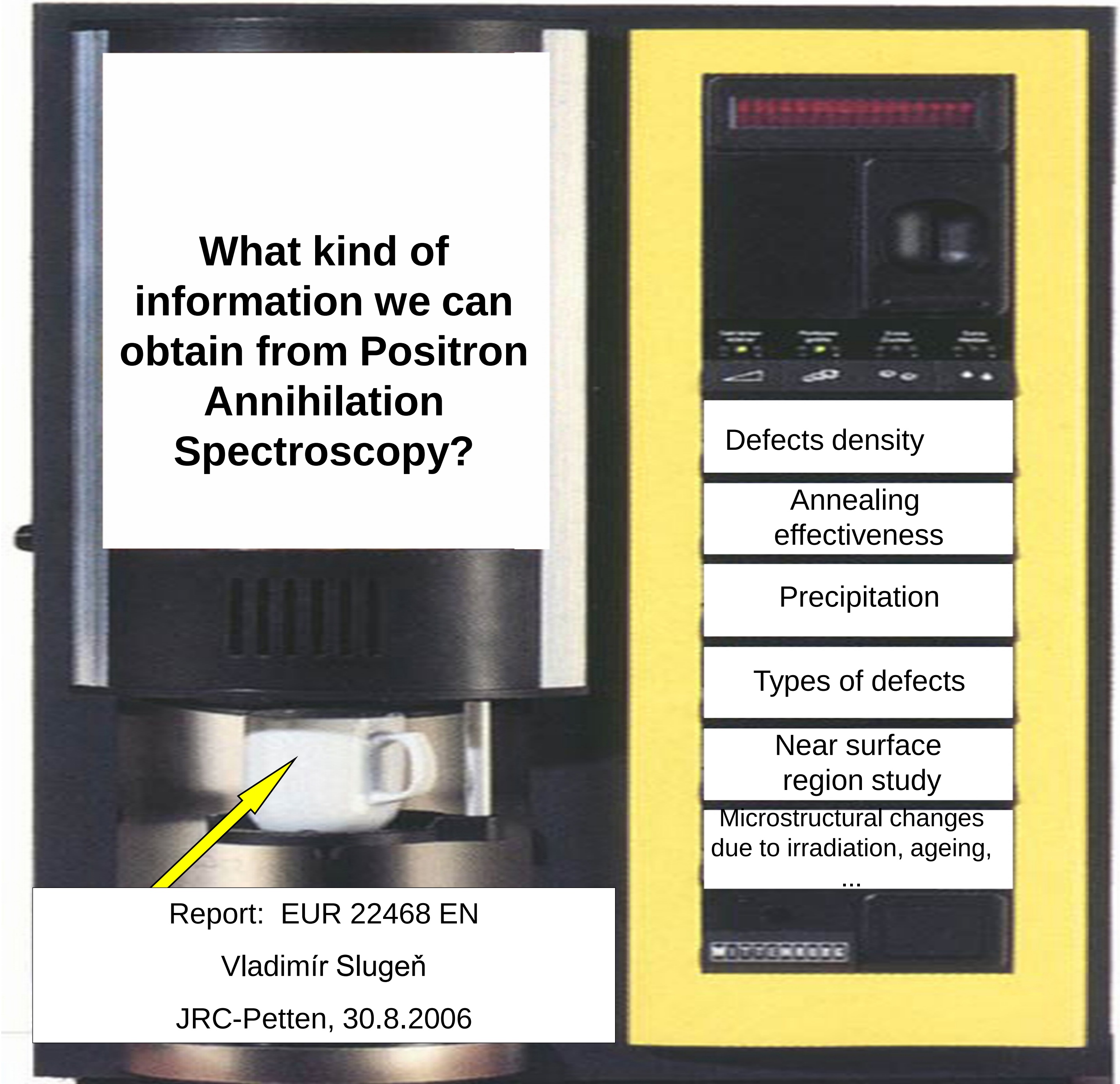
TEM, SEM and Auger spectroscopy

Irradiation-induced changes

- ✓ Neutron-irradiation
  - Defect production
    - Self-interstitial atom (SIA) & vacancy (V) rich regions
  - Matrix damage
    - SIA-clusters, SIA-loops
    - Micro voids
  - Solute atom diffusion
    - Precipitates
    - Complex defect-solute configurations
    - GB segregation



Slugeň, V., Safety of VVER-440 Reactors – Barriers Against Fission Products Release, Springer, 2011



What kind of information we can obtain from Positron Annihilation Spectroscopy?

- Defects density
- Annealing effectiveness
- Precipitation
- Types of defects
- Near surface region study
- Microstructural changes due to irradiation, ageing, ...

Report: EUR 22468 EN

Vladimír Slugeň

JRC-Petten, 30.8.2006

Reasons for application of PAS

- Mechanical tests give not enough information about changes in material microstructure. Therefore, additional methods should be applied.

- PAS technique is a well-established method for studying open-volume type atomic defects and defect's interactions in metals

- Ability of PAS to detect very small defects as well as very low defects concentration

- PAS can give additional information about
  - radiation induced defects,
  - thermal annealing of these defects.

-

Difficulties with irradiated RPV steels and advantages for implantation

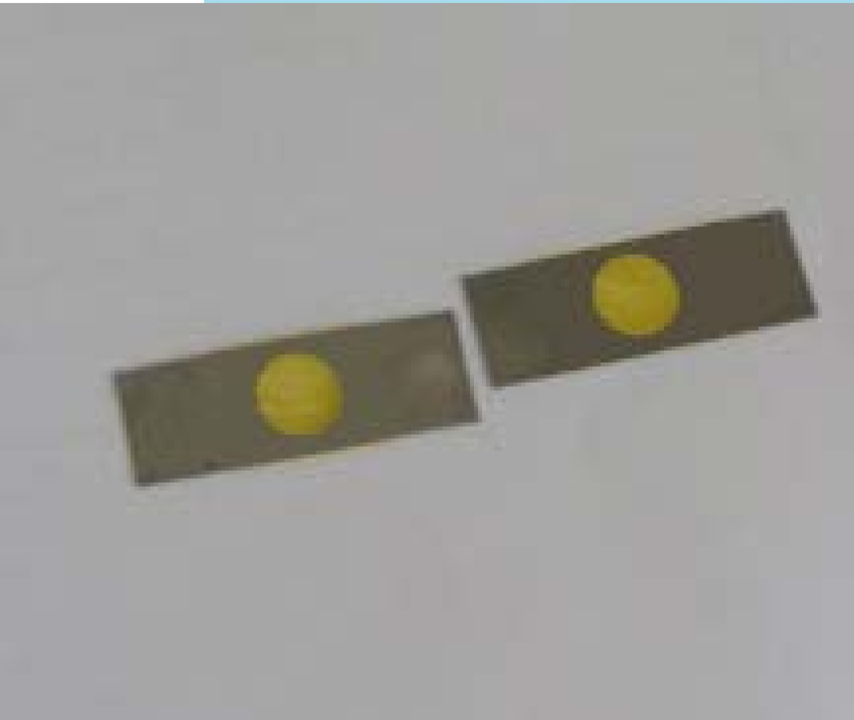
- Radioactivity —> special rules for handling, transport, polishing, storage... (PROBLEMS),
  - Reducing of volume,
  - Reducing of number of samples,
  - Application of other techniques if possible.

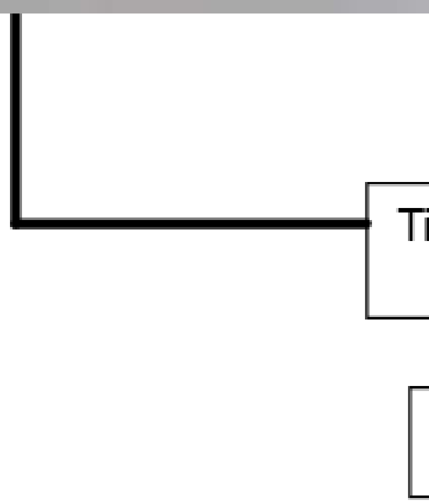
- PAS disturbing ^{60}Co contribution (photopiks 1.17 and 1.33 MeV)
  - 1. Measurement using PLEPS (very thin samples of about 20 μm are necessary),
  - 2. Measurement using 3 detector set-up in coincidence mode (takes about 2 weeks),
  - 3. To wait ... ($T_{1/2}$(Co-60)=5.27 a).

- <u>Ion implantation</u> – none transmutations = none ^{60}Co, very short half-time of decay for radionuclides, only 2 detectors measurement equipment for PAS

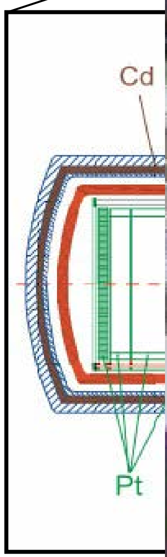
In ODS steels – 0 Co content (theory)

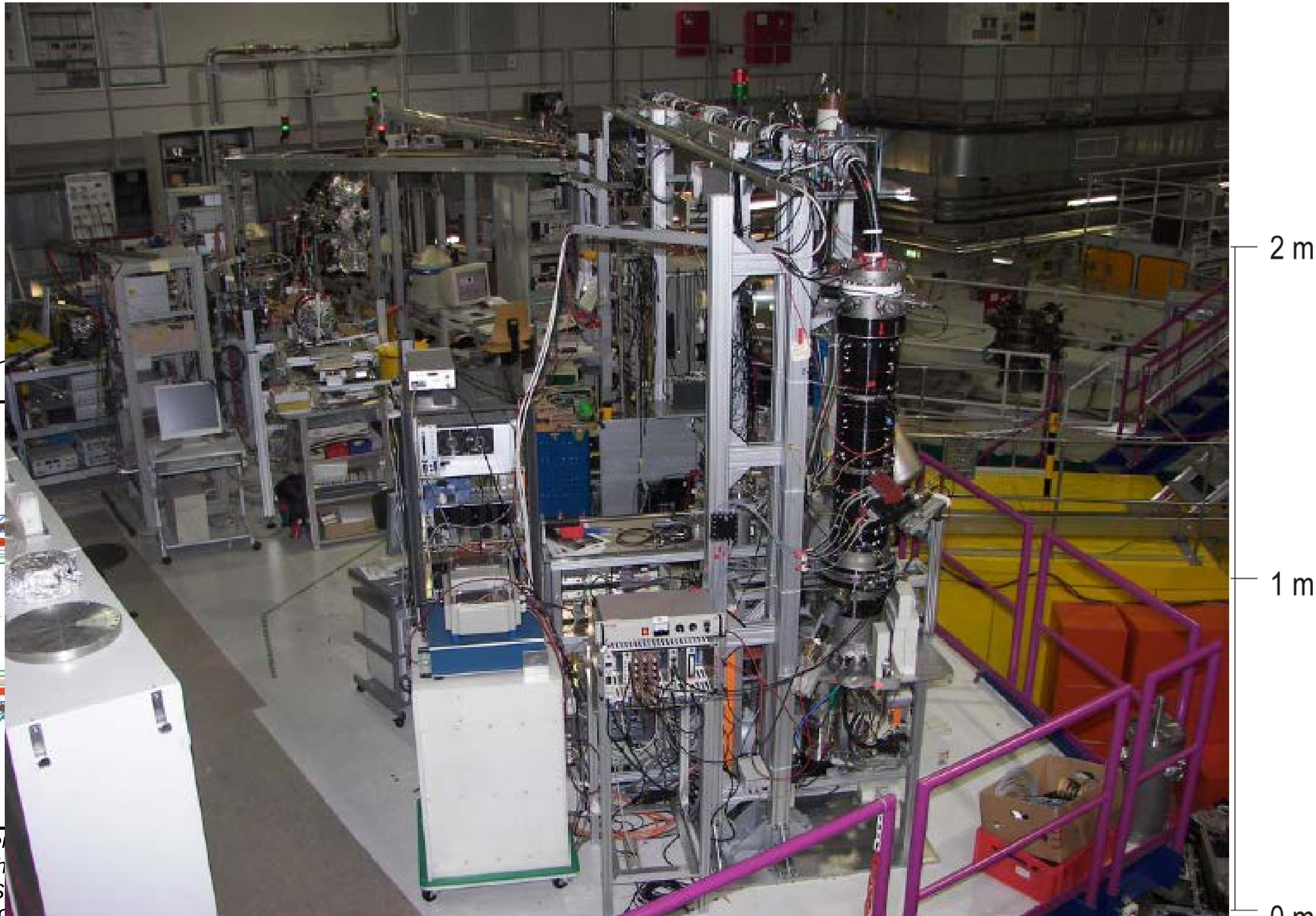
PALS equipment





Pulsed low energy positron system (PLEPS)





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[2] Hugensch
Repper R., S
Issue 1, p. 29

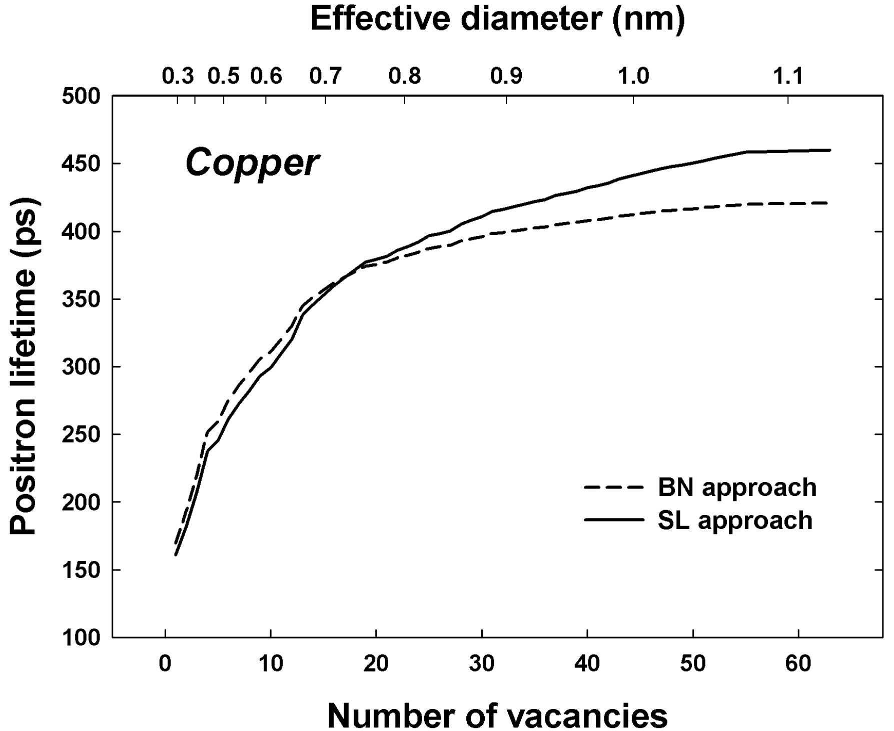
PAS effective applications (contribution) in RPV steels studies

- *A) Comparison of calculated and measured positron lifetimes.*
- *B) Differences in RPV according to chemical composition.*
- *C) Differences in the same type of steels according to different thermal treatment.*
- *D) Irradiation effect study (neutron embrittlement)*
- *E) PAS parameters in comparison to results from other techniques (TEM, SEM, HV10, MS, XRD).*
- *F) Defects depth profiling study and studies of near-surface region.*
- ***G) Evaluation of high implanted (irradiated) regions in nuclear materials.***
- *H) Evaluation of role of Cr, Ni, Mn, Cu… in reactor steels.*

Comparison of calculated and measured positron lifetimes

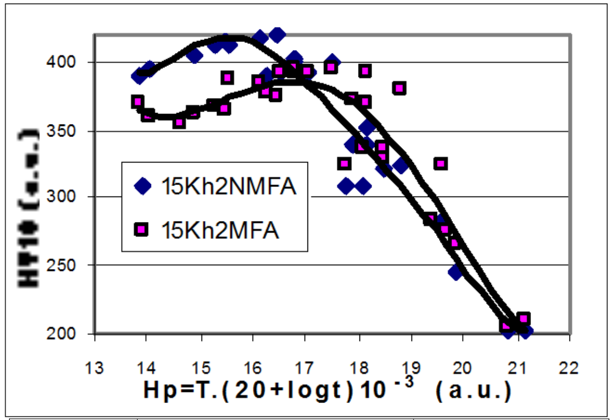
Table 4 – Theoretical calculated lifetimes in selected materials

Material	Positron lifetime (ps)
Fe-bulk	110
Fe-dislocations	165
Fe-monovacancy	175
Fe-divacancy	197
Fe-3 vacancy cluster	232
Fe-4 vacancy cluster	262
Fe-6 vacancy cluster	304
VC	99
$V_{0.86}Cr_{0.09}Mo_{0.04}Fe_{0.01}C$	105
Mo_2C	112
$Mo_{1.4}Cr_{0.6}C$	116
Cr_7C_3	107
$Cr_{23}C_6$	112
$Mn_{26}C_6$	99
Fe_3C	101

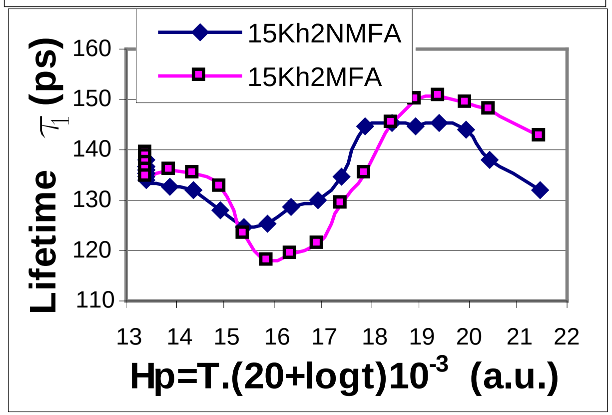


Calc. dependence of the pos. lifetime on the size of the vacancy cluster in Cu.
Slugen, Kuriplach, Ballo, Domonkoš, Nuclear Fusion 44, 2004

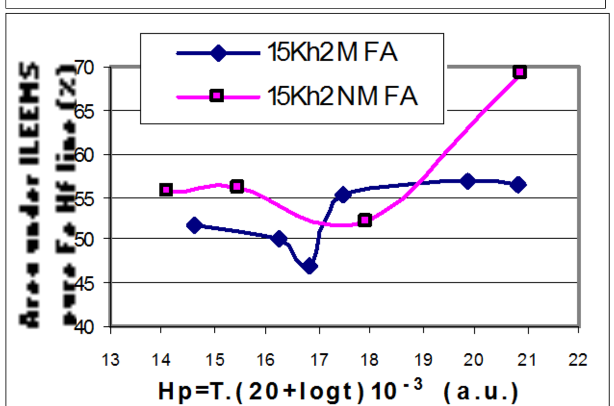
HV10



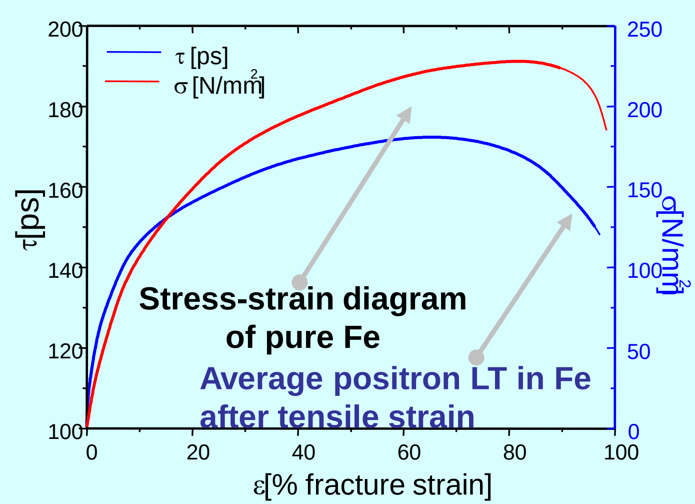
PAS,



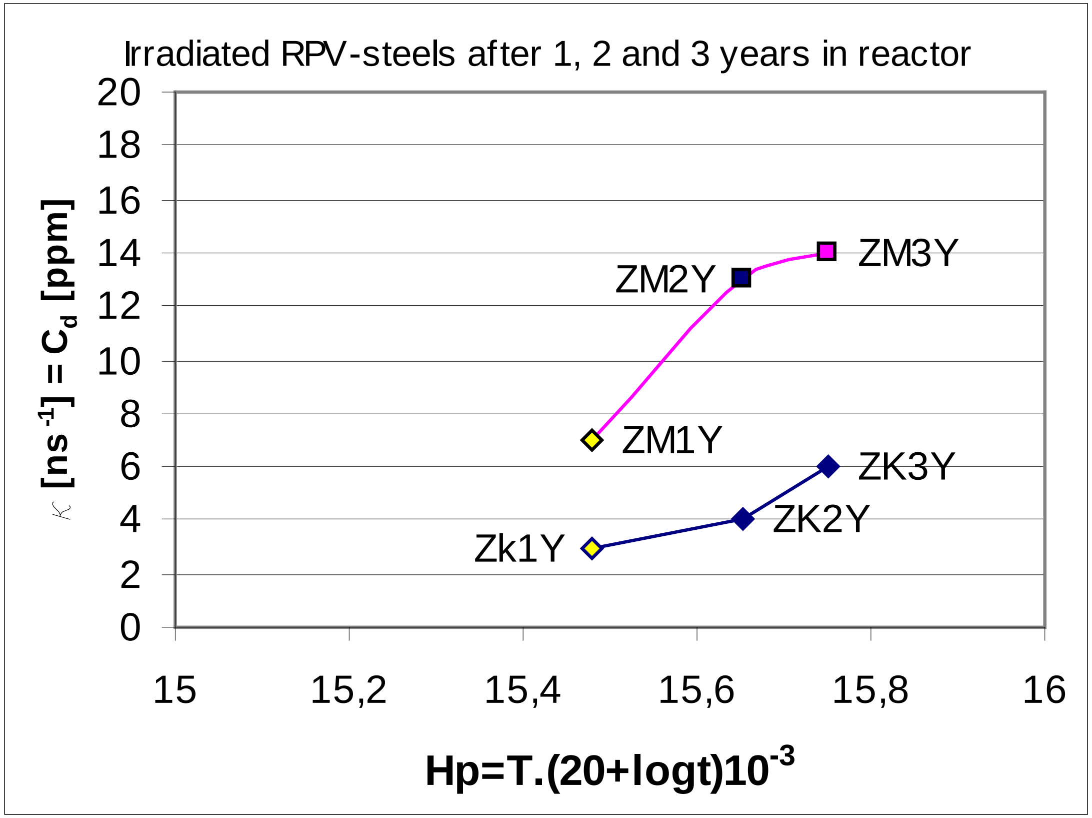
MS



- Stress-strain experiments on Fe
- Distinct positron trapping after 80% Hooks range (fully elastic region)
- Early stage of fatigue



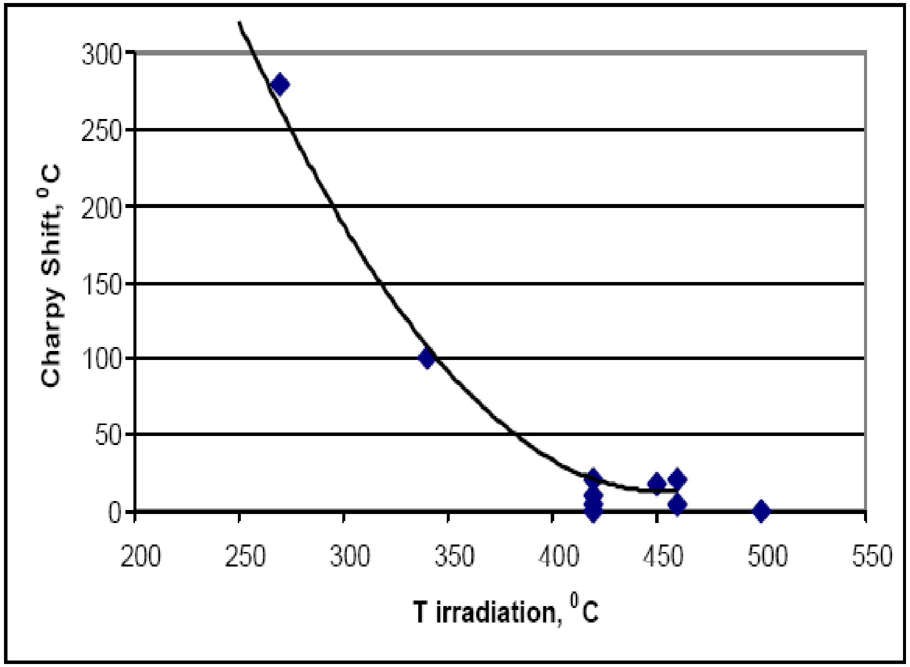
SLUGEŇ, MAGULA, V.: Nuclear engineering and design 186/3, 1998

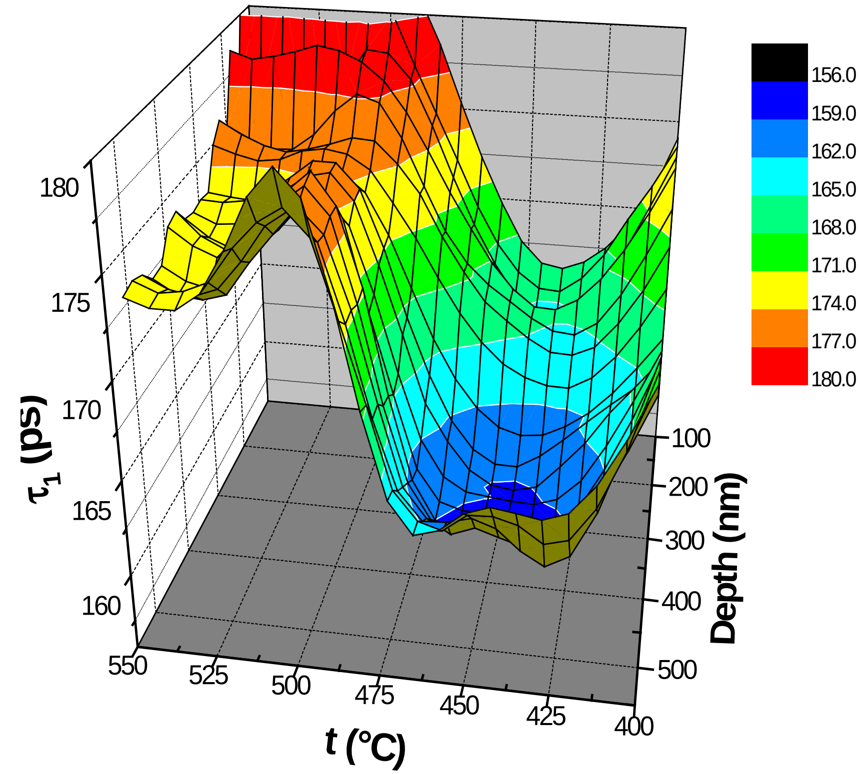


The total trapping rate κ versus Hollomon-Jaffe´s parameter at RPV specimens from WWR-440 base (ZM) and weld (ZK) alloys after 1, 2 and 3 years residence in reactor irradiation chambers (neutron fluency in the range from 7.8 10^{23} m^{-2} to 2.5 10^{24} m^{-2}). The lower limits for κ, as derived from saturation trapping according to the Standard trapping model [26] is 10 ns^{-1} total,

Trapping rate κ as well as the total defect concentration cd (the same values but in ppm) increase slightly for both base and weld materials as a function of the irradiation dose.

PAS Results - Annealing temperature for WWER-steels at 475 °C is acceptable, but PAS gives more information.





The 3D presentation of PLEPS results (Tau1) of irradiated ($1.25x10E24m^{-2}$) and annealed Sv-10KhMFT steel (WWER-440 weld).

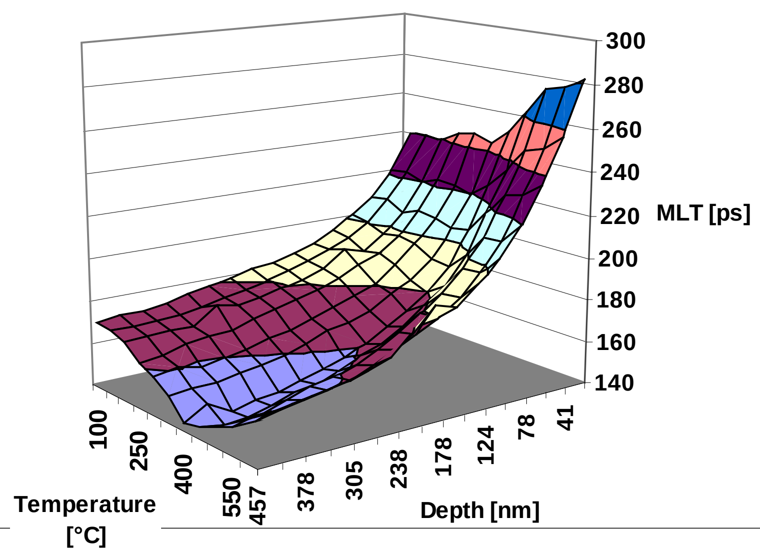
The effectiveness of the annealing process to removing of small defects (mono/di-vacancies or Frenkel pairs) can be followed via significant decrease of parameter tau1. This figure also shows rapid increase of mentioned small defects in WWER type of RPV steels after about 480 ºC.

Slugen et al: NTD&E Int. 37 (2004) 651

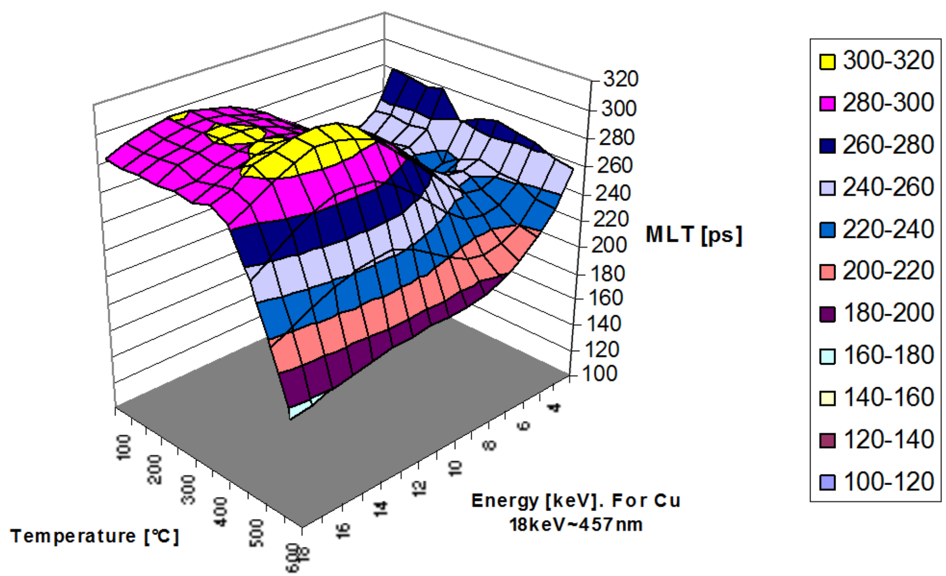
Defects depth profiling study and studies of near-surface region.

PAS and TEM results are useable for microstructural evaluation of new materials

SS non-irradiated sample



SM sample



Long-term challenge: Comparison of as received, irradiated and annealed RPV specimens to H+ ions implanted annealed for typical Russian (VVER) and German RPV steels from PAS point of view

Polished specimens used for measurement.

Evaluation of role of Cr, Ni, Cu… in RPV steels.

1. **Chromium plays an important role in the formation of small vacancy clusters and also the size of these defects depends on the chromium content.**

KRŠJAK et al: Applied Surface Science, 2008.

- **2. The formation of solute clusters during irradiation of RPV steels resulted in depletion of Cu and P in the matrix, but Ni retards this depletion. Ni may segregate to microvoids and stabilise them and/or it can be control their formation through its influence on the microstructure.**

SLUGEŇ et al: NTD&E international 37, 2004, 651-662.

Chemical composition of German CARINA/CARISMA steels.

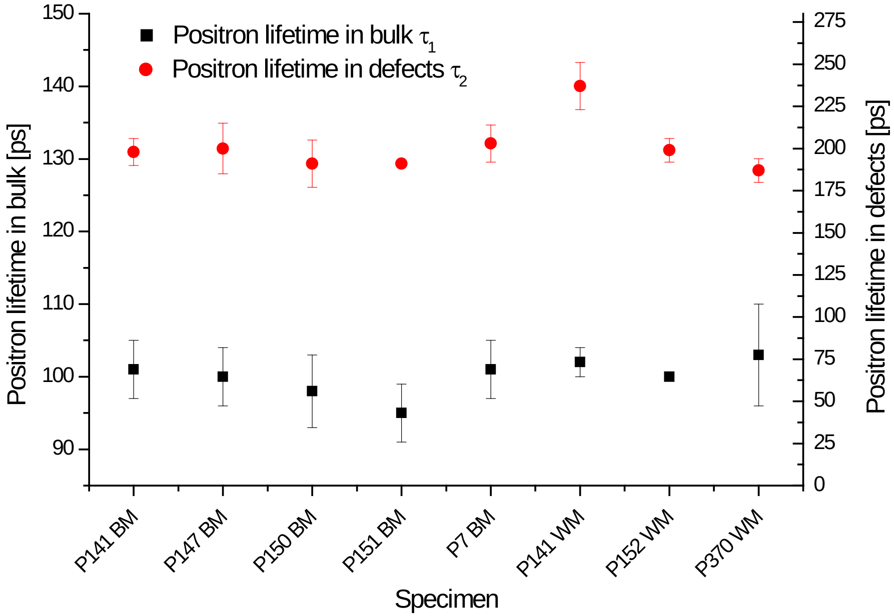
Material	Project	German PWR Generation	Project Code	Cu [wt.%]	P [wt.%]	Ni [wt.%]
20MnMoNi5-5 JSW	CARISMA	4 (Konvoi)	P141 BM	0.05	0.01	0.79
22NiMoCr3-7 Klöckner	CARISMA	1-2	P7 BM	0.12	0.02	0.97
22NiMoCr3-7 JSW	CARISMA	3-4	P147 BM	0.05	0.01	0.84
S3NiMo1/OP 41 TT UP, GHH	CARISMA	4 (Konvoi)	P141 WM	0.03	0.02	1.01
NiCrMo1 UP(modified)/ LW320, LW330	CARISMA /CARINA	1	P370 WM	0.22	0.02	1.11
22NiMoCr3-7 JSW	CARINA	3	P150 BM	0.05	0.008	0.83
22NiMoCr3-7 Klöckner	CARINA	1-2	P151 BM	0.09	0.007	0.97
Molytherme Electrode Sulzer	CARINA	1	P152 WM	0.03	0.015	0.08

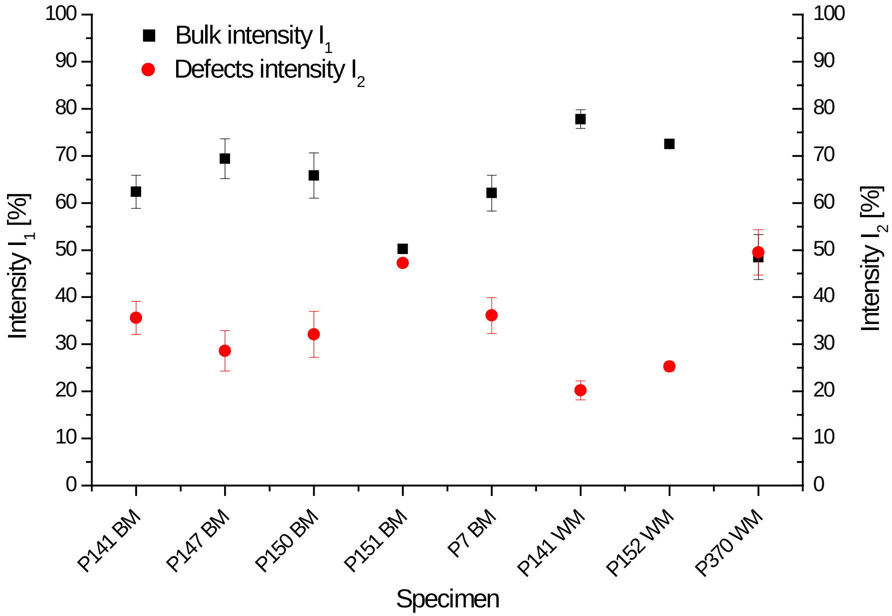
BM – base metal
WM – weld metal

Positron parameters in studied CARINA/CARISMA steels.

Bulk and defects positron lifetimes.

Bulk and defects intensities.





Conclusions 1

- In comparison German reactor RPV steels, it seems that Russian RPV steels contain more defects in “as received” stage (delivered from higher MLT).

- If we focus our attention on so called “small-defect component” – $\tau 2$ value, its intensity is higher in case of Russian-RPV steels (67% in case of base metal and 57% in case of weld) in comparison to German steels, were these intensities are significant lower (maximal value 49% in case of weld P370WM.

- On the other hand, these defects are a little bid larger (about 200 ps) which implies higher concentration of di-vacancies in German steels. In case of Russian steels we register higher concentration of dislocations an mono-vacancies.

Conclusions 2

- *According to the results from our comprehensive positron annihilation lifetime measurements performed between 2000-2010 on different irradiated Russian RPV-steels, the total trapping rate κ in ns^{-1} as well as the total defect concentration cd (the same values but in ppm) increases slightly for both base and weld materials as a function of the irradiation dose.*

Neutron irradiated steels

CARINA/CARISMA steels studied in frame of LONGLIFE
Next step: PAS studies of irradiated samples

Their activities are

Ni-63	**1,20E8 Bq**
Co-60	**8,47E7 Bq**
Fe-55	**4,66E7 Bq**
Nb-93m	**3,04E5 Bq**
Nb-94	**1,77E4 Bq**
Cs-137	**3,82E3 Bq**

Neutron irradiated steels

- Activity of radioisotope ^{60}Co in irradiated specimens to the date 24.01.2013 was measured

Specimen	P370WM-D77 (fluence 2.21E19 cm^{-2} E> 1MeV)	P370WM-D161 (fluence 2.23E19 cm^{-2} E> 1MeV)	P16WM-S103 (fluence 1.16E19 cm^{-2} E> 1MeV)	P16WM-GS67 (fluence 4.81E19 cm^{-2} E> 1MeV)
Activity [kBq]	12.85	97.31	40.09	161.46

- Specimens P370 SG (two irradiated: D-77 and D-161, as well as one non-irradiated CD159) are from the same bulk, cut at different positions. The same is valid also for both P16 SG specimens (S103 and GS67) but there was no specimen from non-irradiated P16 SG material.
- In case of irradiated steels τ_{AVG} was calculated, considering only annihilation in bulk structure and annihilation in defects

Neutron irradiated steels: PAS results

- In case of both P370SG specimens, the increase of τ_{AVG} parameter was from 142 ps to 147ps and 157 ps, respectively. Results achieved for the P16SG specimens were at level of about 172 ps.
- Therefore the general defects structures can be concluded as dislocations and some small defects as mono/di-vacancies
- According to the lifetimes values from our measurements performed on CARINA/CARISMA RPV-steels we calculated total defect concentration (the same values but in ppm).

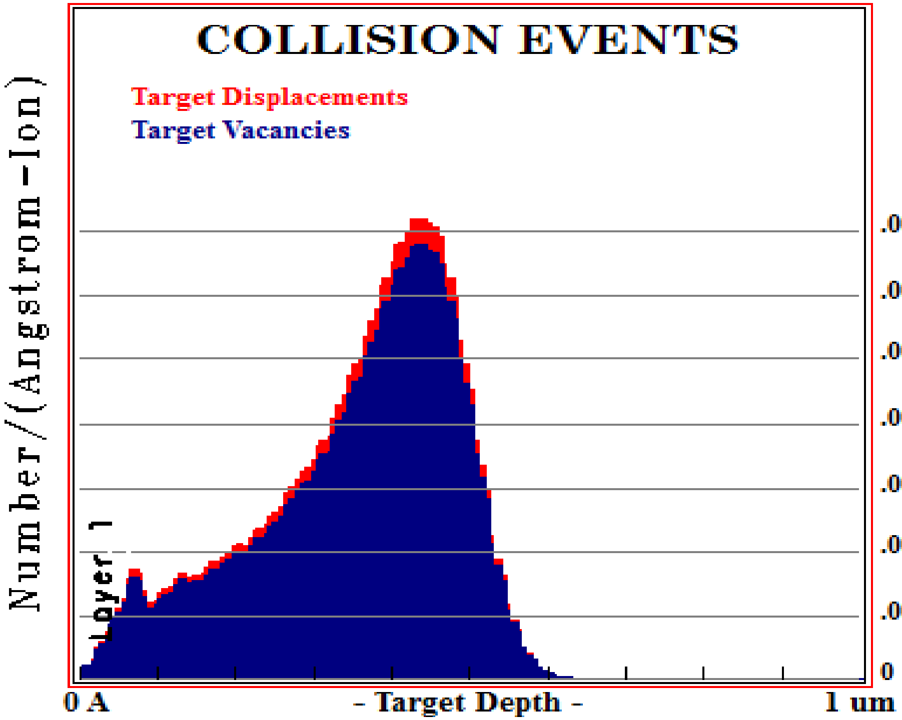
Specimen	**P370 SG-CD159 Not irradiated**	**P370SG-D77 (fluence 2.21E19 cm^{-2} E> 1MeV)**	**P370SG-D161 (fluence 2.23E19 cm^{-2} E> 1MeV)**	**P16SG-S103 (fluence 1.16E19 cm^{-2} E> 1MeV)**	**P16SG-GS67 (fluence 4.81E19 cm^{-2} E> 1MeV)**
Vacancy concentration [ppm]	**1.35**	**3.09**	**2.38**	**12.3**	**11.2**

- Slight increase of the concentration of vacancies due to irradiation was registered in case of P370 SG. Higher concentration of vacancies were observed in case of P16SG. Unfortunately, this concentration can be not compared with not irradiated material.
- There can not be stated that the small differences in neutron fluencies caused the higher concentrations of defects in studied materials.

SUMMARY

- In comparison to non-irradiated steels there was observed some increase in the defects size due to performed neutron treatment.
- Based on our PAS results there were no large voids or vacancy clusters formed due to irradiation in German RPV steels.
- This fact can be interpreted in the conclusion that vacancy type defects bear hardly any responsibility for radiation-induced hardening and embrittlement. This mechanism at studied level of neutron fluences does not limit lifetime of reactor pressure vessel and does not affect significantly the long-term operation of nuclear power plants from safety point of view.

Hydrogen Ion Implantation
vs.
neutron irradiation



Specimens – RPV Steels

- German and Russian RPV PWR steels
- German – 2 steels from CARINA/CARISMA program
  - Irradiated in experimental reactor VAK Kahl (Φ ~$2x10^{19}$ cm^{-2})
- Russian – commercial steels from VVER-440/230
  - Irradiated as Surveillance specimen program in NPP Jaslovske Bohunice (Φ ~$1.25x10^{20}$ cm^{-2})

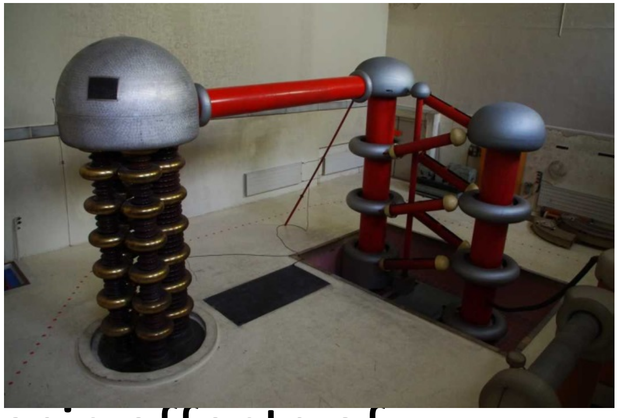
Russian steels

Type	Code	C	Si	Mn	Mo	Ni	Cr	Cu	P	S	V	Co	Total
Base metal	**15Kh2MFA**	0.14	0.31	0.37	0.58	0.20	2.64	0.08	0.011	0.017	0.27	0.019	4.651
Weld metal	**Sv10KhMFT**	0.048	0.37	1.11	0.39	0.12	1.00	0.104	0.01	0.013	0.13	0.020	3.347

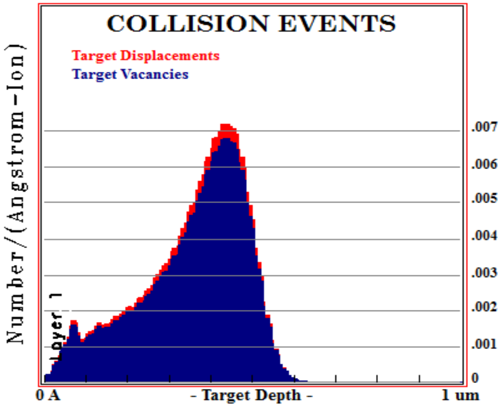
German steels

Specimen	German PWR Generation	C [%]	Si [%]	Mn [%]	P [%]	S [%]	Cr [%]	Mo [%]	Ni [%]	Cu [%]
P370 WM	1	0.08	0.15	1.14	0.015	0.013	0.74	0.60	1.11	0.22
P16 WM	3	0.05	0.15	1.14	0.012	0.007	0.07	0.46	1.69	0.08

Ion Implantation



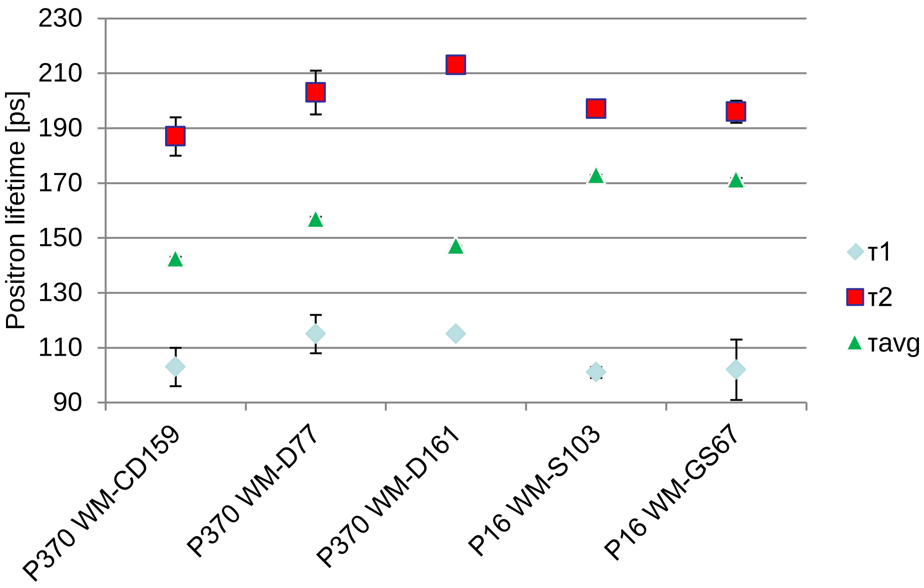
- **Advantages:** no transmutation –
  - minimal activity of material
  - short time
- **effective method** for the study of the basic effects of irradiation on the material
- Implantation of hydrogen ions **(protons)**
- Energy of implantation – **100 keV**

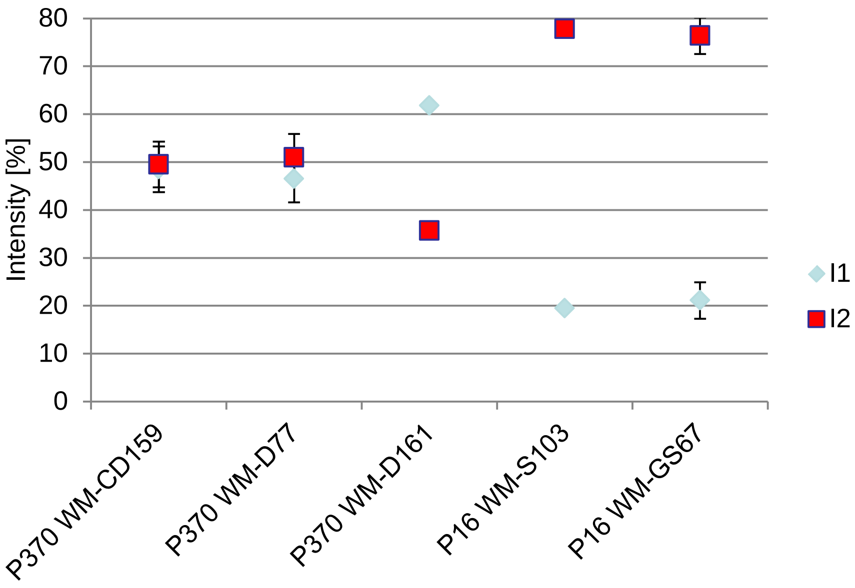


H implantation	Implanted dose [C/cm^2]	Number of implanted ions [cm^{-2}]	Dose in implanted region [dpa]
1. level	0.10	6.24×10^{17}	1.980
2. level	0.82	5.12×10^{18}	16.235
3. level	3.20	2.00×10^{19}	63.354

Experimental results

- Neutron Irradiated German Specimens

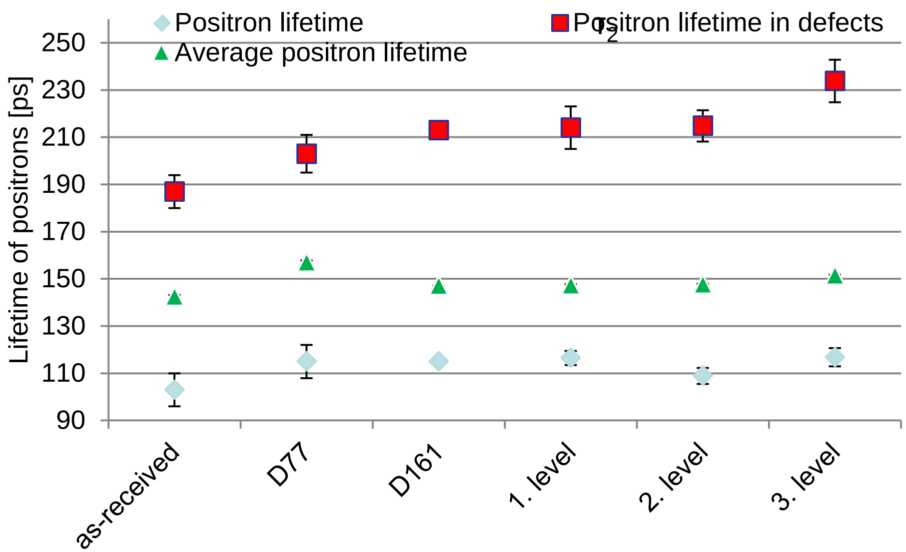


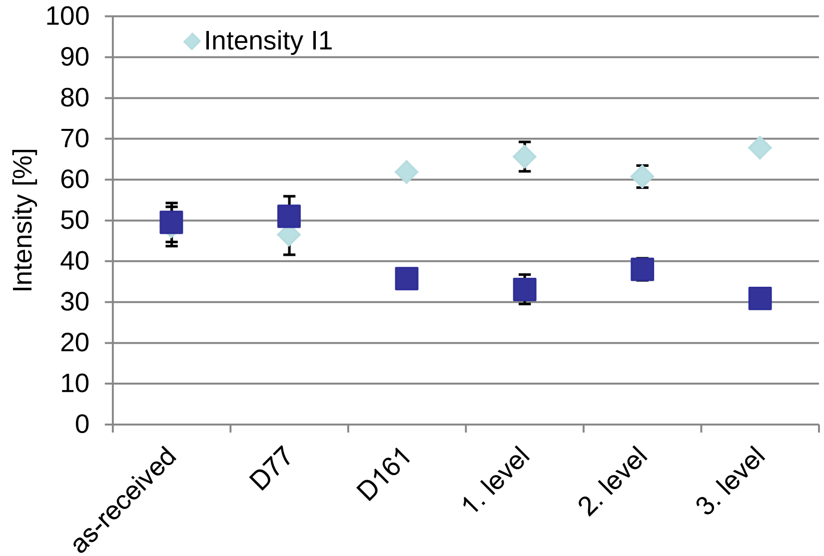


- Lifetime of positrons in defect increased due to irradiation in P370 WM specimen from 187 ps to 203-213 ps (defect size of about 1-2 vacancies increased to 2-3 vacancies)
- Defect size in P16 WM is about 2 vacancies
  - P16 WM – smaller defects in relatively high amount – more homogeneously distributed
  - P370 WM – bigger defects in relatively less amount – not so homogeneously distributed

Experimental results

- Hydrogen implantated German Specimens





- During implantation the defect size increased predictably to similar values as in the neutron irradiated specimens (to 2-3 vacancies)
- 1. and 2. level of implantation – similar defect size
- 3. level of implantation – equal fluence of impacted particles as in neutron irr. Specimens
  - defect size increased up to 3 vacancies

Conlusions

- Russian steels contain more defects in „as-received“ state but are smaller than in German steels
- No large voids or vacancy cluster were formed due to irradiation in investigated German or Russian RPV steels which could cause dangerous embrittlement of RPV and limit operation of NPPs
- Due to hydrogen implantation increased defect size to similar values as in neutron irradiated specimens and defects agglomerated to the bigger clusters – it is possible way to simulate neutron irradiation under certain circumstances

Relevant literature

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Thank you!

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