JRC Scientific and Technical Reports

Proceedings of the PRIMAVERA International Workshop on Re-embrittlement after Annealing of Reactor Pressure Vessel Steels

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Abstract

The International PRIMAVERA Workshop on "Re-embrittlement after Annealing of Reactor Pressure Vessel Steels" took place at JRC-IE Petten, Netherlands, in March 2011, and was organized together by the POS and MATTINO Actions of the SPNR and SFNR Units of JRC-IE. The main purpose of the workshop was to present the results of the PRIMAVERA project, which is currently in its final phase, to identify and discuss open issues in the topics covered by the project (annealing and re-embrittlement after annealing), and to propose additional investigations to address the identified open questions. A second objective of the workshop was to explore the possibilities of cooperation among the IAEA, JRC and the rest of the PRIMAVERA partners on research in advance materials and their behaviour under neutron irradiation, as materials from future reactors (e.g., Gen IV reactors) will be exposed to high neutron fluence and high temperature.

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1 Introduction

The International PRIMAVERA Workshop on “Re-embrittlement after Annealing of Reactor Pressure Vessel Steels” took place at JRC-IE Petten, NL, on March 14th – 15th, 2011, and was organized together by the POS and MATTINO Actions of the SPNR and SFNR Units of JRC-IE, respectively. The workshop programme is given in the Annex 1, and the list of participants in the Annex 2.

2 Objective of the workshop

The main purpose of the workshop was to present the results of the PRIMAVERA project, which is currently in its final phase, to identify and discuss open issues in the topics covered by the project (annealing and re-embrittlement after annealing), and to propose additional investigations to address the identified open questions.

A second objective of the workshop was to explore the possibilities of cooperation among the IAEA, JRC and the rest of the PRIMAVERA partners on research in advance materials and their behaviour under neutron irradiation, as materials from future reactors (e.g., Gen IV reactors) will be exposed to high neutron fluence and high temperature.

3 The PRIMAVERA Project

The PRIMAVERA project is a cooperation project on re-embrittlement assessment of VVER-440 welds. The project is coordinated by the RRC Kurchatov Institute (Russia) with the participation as partners of VTT (Finland) and JRC-IE. Sponsors of the project for the Russian and Finnish contributions are Rosenergoatom and Fortum, respectively. The objectives of the project are the following:

- To study of re-embrittlement after annealing of VVER-440 vessel materials
- Validation of re-embritlement kinetics models
- Understanding the role of P and Cu in embrittlement kinetics
- Validation of innovative ageing monitoring methods
- Validation of possible re-embrittlement monitor/reference materials
- Development of guidelines

The scope of the PRIMAVERA project is summarized below:

1. Selection of VVER relevant material and samples provision.

2. Irradiation in Rovno NPP surveillance channels:

    - in Unit 2 to accumulate fluence in one operational year, and
    - in Unit 1 at lower fluence rate (important facing possible flux effects)

3. Annealing of irradiated samples.

4. Re-irradiation of annealed samples.

5. Extraction and testing of sample sets at different re-embrittlement stages.

A detailed description of the technical programme of the project can be found in the document of the Ref. 1.

4 Workshop content

The first part of the workshop was dedicated to put the project in context and to present the PRIMAVERA results. Special emphasis was given to the results of the work performed by ITEPh (Institute of Theoretical and Experimental Physic in Moscow), that was contracted by JRC for this project. Two types of experimental techniques were used by ITEPh in PRIMAVERA. Namely, the positron annihilation technique and atom probe tomography. These experimental techniques are needed for a fully understanding of the annealing and re-embrittlement process occurring in the material. These techniques complement the usual mechanical testing with Charpy and tensile specimens.

The second part of the workshop was focussed on embrittlement issues in advance materials with presentations from IAEA, ITEPh and JRC. An extensive overview of materials for innovative reactors was given by the IAEA representative, followed by a presentation of the research conducted by ITEPh on ODF Eurofer material, and a research proposal from JRC on the use of V alloys in future reactors.

Appropriate time was allocated to the discussion and to draft future lines of collaboration.

5 Summary of the presentations

All the presentations performed in the workshop are attached to the proceedings. Below is a short summary.

Part 1: PRIMAVERA Results

L. Debarberis introduced the PRIMAVERA project. He outlined the scope of the project and presented its objectives. He described how the project was born and was based on the successful research conducted by the AMES European Network. The PRIMAVERA project is an outstanding collaboration project among EU and Russian organizations.

A. Ballesteros gave an overview of the annealing techniques (dry and wet annealings) and existing models for re-embrittlement. Only dry annealing can be effectively applied for substantial recovery of RPV material properties. He reviewed the basic models (conservative, lateral and vertical models) and presented several semi-mechanistic models.

A. Chernobaeva summarized the PRIMAVERA results, with emphasis in the mechanical testing results. She concluded that the use of annealing allows approximately twice irradiation dose extension for reaching some fixed value, as compared to irradiation without annealing. In general, rates of hardening and embrittlement under re-irradiation are lower than under primary irradiation.

S. Rogozkin presented the results of the tomographic atom probe (APT) investigations conducted in PRIMAVERA (Ref. 2). The study focused on the weld metal with high concentration of phosphorus in different states (irradiated, annealed and re-irradiated). As a relevant observation, a new generation of Cu-P-enriched clusters was found under re-irradiation after annealing.

A. Zeman presented published data on microstuctural research for comparison with PRIMAVERA results. Strengthening of multi-tools approach is needed for a complete understanding of the hardening and embrittlement mechanisms. The best approach is using a combination of various techniques and computer simulation (ATP, TEM, PAS, SANS, etc.).

V. Krsjak reported about the positron annihilation spectroscopy (PAS) studies carried out in the frame of the PRIMAVERA project, Ref. 3. He also gave an extensive overview about the different PAS techniques (angular correlation, positron annihilation lifetime, etc.). The PRIMAVERA results presented demonstrate the potential of the positron annihilation spectroscopy method as a unique and complementary tool to mechanical testing, APT, TEM and other microstructural techniques.

A. Kryukov discussed the basic results of PRIMAVERA and the open issues identified. His presentation addressed the question of the validation of re-embritlement kinetic models. There is a good agreement between the microstructural and mechanical testing results of the PRIMAVERA project. The results are also consistent with other relevant works and modelling developments.

Part 2: Future Reactors

S. Rogozkin presented the works being performed by the Institute for Theoretical and Experimental Physics in Moscow on atom probe characterization of nano-scaled features in unirradiated and irradiated ODS Eurofer steel. He stated that further investigations are necessary to understand the development of the nano-structure during the different production steps, and their influence on the material properties.

A. Zeman gave an overview on materials for innovative reactors. An IAEA Coordinated Research Programme CRP on accelerator simulation and theoretical modelling of radiation effects is ongoing. He presented also the new IAEA CRP on benchmarking of advanced materials pre-selected for innovative nuclear reactors.

A. Kryukov reported about the vanadium alloyed low nickel steel that have being used in VVER-440 reactors due to its high radiation stability. This steel presents acceptable radiation stability at least up to a neutron dose of 2 dpa at irradiation temperature 270 ºC. At irradiation temperatures above 400 ºC the T_k shift is very small. He made a comparison between the 2CrMoV and ferritic-martensitic steels. Further studies are required to qualify the material for Gen IV applications.

6 Workshop conclusions

The following are some important general results of the PRIMAVERA project presented in the workshop:

- The absolute values of strength properties and absolute values of T_K are lower at re-irradiation than at primary irradiation under comparable dose conditions.

- Use of annealing allows approximately twice irradiation dose extension for reaching some fixed value as compared to irradiation without annealing

- The lateral shift model is over-conservative for description of re-irradiation embrittlement of the welds with 0.027% phosphorus and with 20-60 ºC higher than the experimental values. Embrittlement under re-irradiation of the welds with 0.031-0.038% phosphorus is described adequately by the lateral shift model.

- Study of fine structure of weld with phosphorus content 0.038 wt% has revealed high heterogeneity of phosphorus and copper distribution in all investigated states. Annealing leads to some redistribution of alloying elements and admixtures in the material caused by dissolution of fine structure elements. But high heterogeneity of phosphorus distribution remains intact.

- High phosphorous concentration in the investigated material (0.038 wt%) led not only to copper enriched cluster formation but also to segregation of phosphorous into relatively small clusters. Such behaviour had not been observed in specimens cut from the templets, where P content was less (0.029 wt%).

- Re-irradiation after recovery annealing leads to formation of a new population of P-enriched clusters, which apparently are responsible for high level of embrittlement of this high phosphorus material. Formation of a new population of Cu-enriched clusters is not detected.

- Experimental investigation of the PRIMAVERA steel samples was carried out using positron annihilation spectroscopy. By evaluating the experimental results and correlating them with published data it was possible to identify radiation- induced defects and to estimate their size and concentration.

Regarding the use of materials in future reactors the following is concluded from the presentations:

- The major part of the next generation nuclear systems call for use of fast and epithermal neutron spectra, which will challenge materials performance with increased radiation damage. In addition, these systems will operate at higher temperatures and higher radiation doses than in current reactors. Irradiation hardening and embrittlement will be of relevance for the candidate materials used in future reactors.

- The evolution of the nano-structure of the steel under irradiation can be studied using ATP. This technique allows to optimize the micro/nano structure, in order to further improve the material properties.

- The IAEA Coordinated Research Programmes on advanced materials for innovative nuclear reactors address critical review of structural materials pre-selected for innovative reactor systems, and is stimulating further technological improvements in area of advanced structural materials.

- The VVER steel with low nickel and low level of detrimental impurities presents acceptable radiation stability at least up to neutron dose 2 dpa at nominal operational temperature. At higher temperatures, up to 500 °C, VVER steels embrittlement is very small even at higher doses.

- Preliminary comparison between VVER and some representative ferritic-martensitic was presented. For the neutron dose 1.5-2 dpa and irradiation temperature of 300 °C the transition temperature shifts for VVER steel and Eurofer welds are comparable. In the temperature range

350-500 °C the radiation embrittlement level of both VVER and ferritic-martensitic steel is low.

7 Open issues and recommendations for future works

The following relevant open issues were identified on the basis of the PRIMAVERA results:

- There is some evidence of flux effect. Testing of PRIMAVERA Set N. 6 with low flux and high fluence should help to clarify this issue.

- More comprehensive microstuctural studies should be carried out on re-irradiated material and focused on metal with high phosphorus content. Results of other research programmes should be taken into account.

- A better integration of the positron annihilation technique results in the whole picture is desirable.

- A more general analysis of RPV material annealing and re-embrittlement problem should be undertaken.

- Re-embritllement Guidelines for practical use should be developed in cooperation with IAEA, VTT, Gidropress and Prometey.

- A further elaboration of re-embrittlement kinetic model is possible on the basis of the PRIMAVERA results and using data from other investigations.

During the workshop discussions the following complementary PRIMAVERA testing/activities were proposed:

- Positron annihilation measurements on re-irradiated samples: 12 samples, 3 P steels, 4 states of re-irradiation. Using both, lifetime and angular correlation AC methods.

- The results of the PRIMAVERA works show that it is necessary to continue the microstructure study (APT and TEM) of high and low phosphorus welds re-irradiated in Rovno-1 until fluences equal to the maximum fluence for primary irradiation ($\sim 6\times10^{19}$ cm^{-2}, E>0.5 MeV).

- For comparison, it is recommended to perform APT on material with low Cu content.

- It is also recommended to perform some positron annihilation spectroscopy in JRC for benchmarking purposes.

- To perform complete investigation of the last set of re-irradiated specimens (which are now in Kurchatov Institute hot cells without testing). It is of high interest to clarify the flux effect issue.

- Further analysis of the PRIMAVERA results is recommended (joint effort IAEA-JRC). For instance, comparison of measured values with the predictions according to different semi-mechanisms models.

- Integration of the VTT results is needed.

- It is recommended to prepare an inventory of available surveillance material for research, in particular for highly irradiated material. Key organizations for this activity are: RRC-KI, NRI Rez and Vuje.

8 References

[1] A. Chernobaeva et al. “The results of reconstituted specimens testing of VVER-440 welds with different phosphorus content after irradiation, annealing and re-irradiation during 2 and 3 campaigns in the surveillance channels of Rovno-1. Analysis of the atomic probe tomography results”. RRC Kurchatov Institute. Report N. 180-16/10. February 2009.

[2] S. S. Rogozkin et al. “The Effects of Post-Irradiation Annealing on VVER-440 RPV Materials Mechanolocal Properties and Nano-Structure under Irradiation”. Proceedings of the ASME 2009 Pressure Vessels and Piping Division Conference PVP2009. Prague, July 2009.

[3] V. I. Grafutin, E.P. Prokopev, V. Krsjak, R. Burcl, P. Haehner, A. Zeman, O.V. Ilyukhina, D. Erak, M. A. Mogilevskyi, G. G. Myasischeva, and Yu. V. Funtikov. “Positron Annihilation Spectroscopy Study of Materials for Reactor Vessels”. Physics of Atomic Nuclei Vol.74 No.2, 2011.

Attachments:

Annex 1: Workshop Agenda
Annex 2: List of Workshop Participants
Annex 3: Debarberis’ presentation on PRIMAVERA
Annex 4: Ballesteros’ presentation on Annealing and Re-Irradiation
Annex 5: Chernobaeva’s presentation on PRIMAVERA Results
Annex 6: Rogozkin’s presentation on APT results
Annex 7: Zeman’s presentation on Microstructural Investigation

Annex 8: Krsjak's presentation on Positron Annihilation Results
Annex 9: Kryukov's presentation on PRIMAVERA Results and Open Issues
Annex 10: Rogozkin's presentation on EDS Eurofer Steel
Annex 11: Zeman's presentation on Materials for Innovative Reactors
Annex 12: Kryukov's presentation on Vanadium Alloyed Low Nickel Steel

Annex 1: Workshop Agenda

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Safety of Present Nuclear Reactors

PRIMAVERA Seminar

organized by POS and MATTINO Actions

AGENDA (final version)

March 14th and 15th, 2010

JRC-IE Petten, Building 312, Meeting Room in 1st floor

March 14th	Topic/Activity	Presenter
9:15-9:30	Opening of the Seminar	A. Ballesteros
9:30-09:45	The PRIMAVERA Project (objective, programme, etc.)	A. Kryukov / L. Debarberis
09:45- 10:30	Annealing and Re-Embrittlement of RPV Materials	A. Ballesteros
10:30-11:00	**Coffee Break**	
11:00-11:45	Results of the PRIMAVERA Project	A. Chernobaeva
11:45-12:15	Results of the PRIMAVERA Project Microstructural Investigations	S. Rogozkin & A. Zeman
12:15-13:30	**Lunch Break (in Building 325)**	
13:30-14:00	Continuation Results of the PRIMAVERA Project Microstructural Investigations	S. Rogozkin & A. Zeman
14:00-15:00	Results of the PRIMAVERA Project Positron Annihilation Results	V. Krsjak & V. Grafutin, R. Burcl

15:00-15:30	PRIMAVERA Basic Results and Open Issues	A. Kryukov
15:30-16:00	**Coffee Break**	
16:00-17:00	Discussion and conclusions	All

March 15th	**Topic/Activity**	**Presenter**
9:15-10:45	Discussion: 1) Proposal of additional PRIMAVERA testing 2) Possible use of Rovno irradiated material for GEN IV investigations 3) Advance materials for nuclear applications	All
10:45-11:15	**Coffee Break**	
11:15-12:15	Collaboration plan and Conclusion	All
12:15-13:30	**Lunch (in FORUM)**	

Annex 2: List of Workshop Participants

PRIMAVERA Workshop

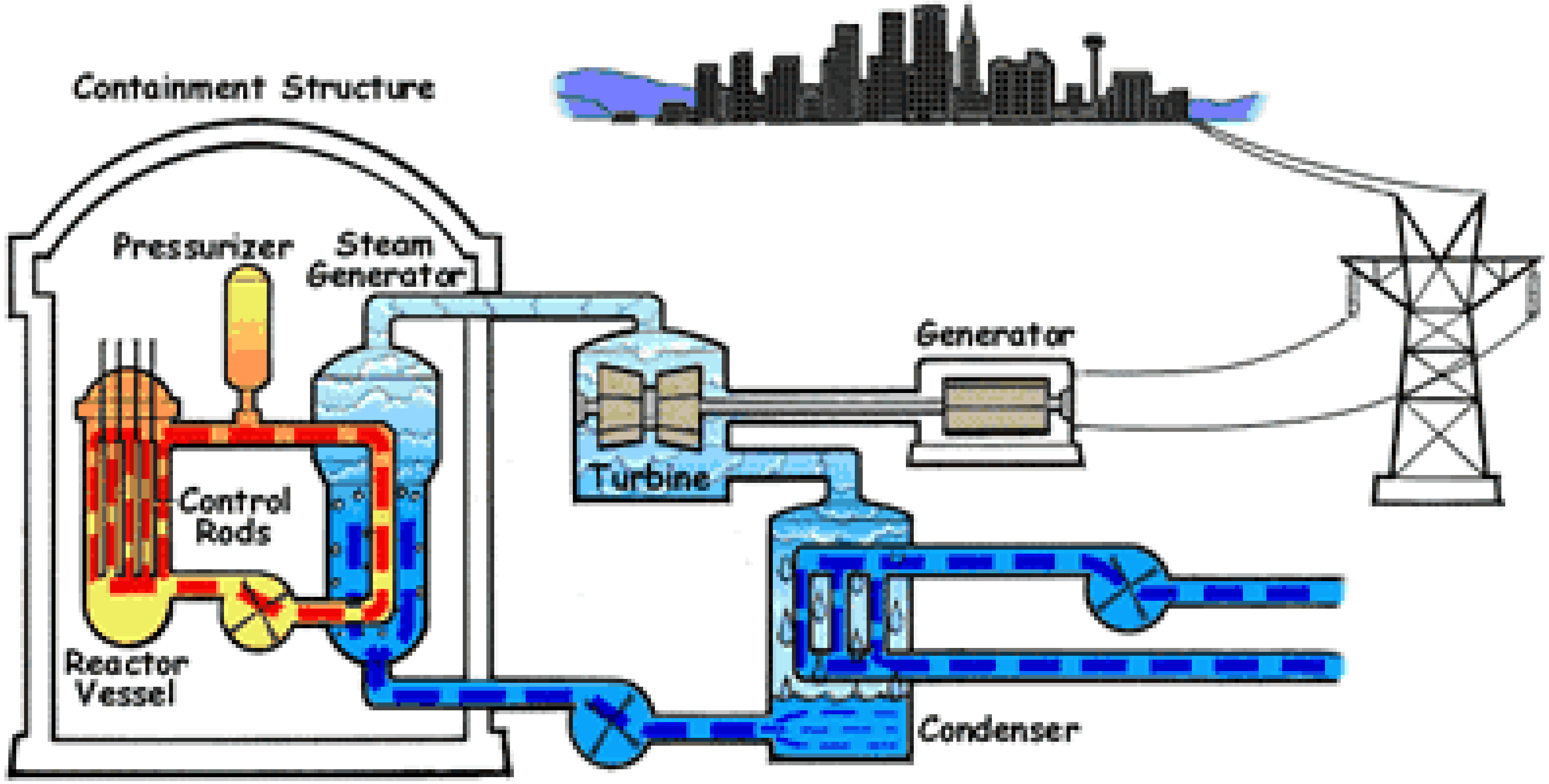
Participants list

- Luigi Debarberis (JRC)
- Peter Haehner (JRC)
- Vladimir Krsjak (JRC)
- Alexander Kryukov (JRC)
- Ralf Ahlstrand (JRC)
- Antonio Ballesteros (JRC)
- Rudolf Burcl (Consultant)
- Anna Chernobaeva (Kurchatov Institute)
- Victor Grafutin (ITEPh)
- Sergey Rogozkin (ITEPh)
- Olga Ilyukhina (ITEPh)
- Andrej Zeman (IAEA)
- Darina Blagoeva (NRG)
- Milos Kytka (NRI Rez)

Annex 3: Debarberis' presentation on PRIMAVERA

Petten, 14-15 March, 2011

PrimaVERA Co-operation



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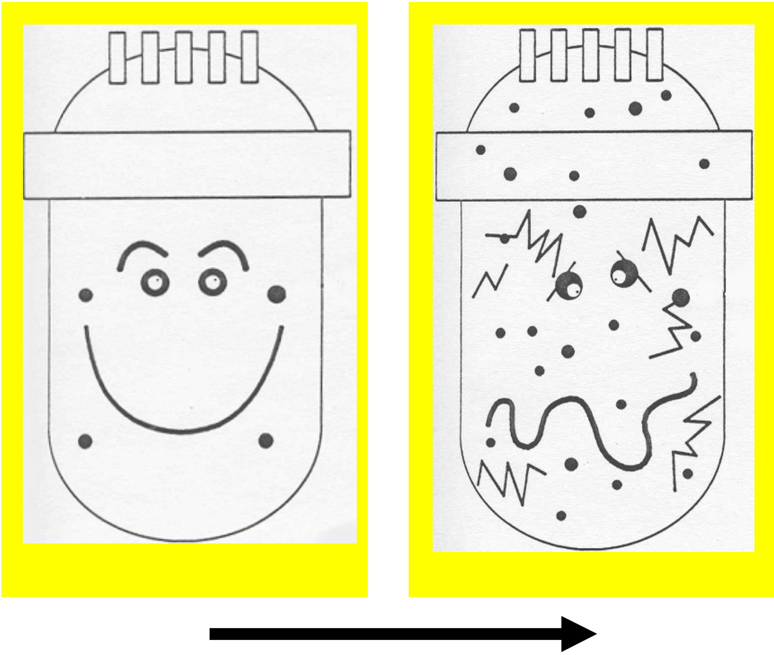
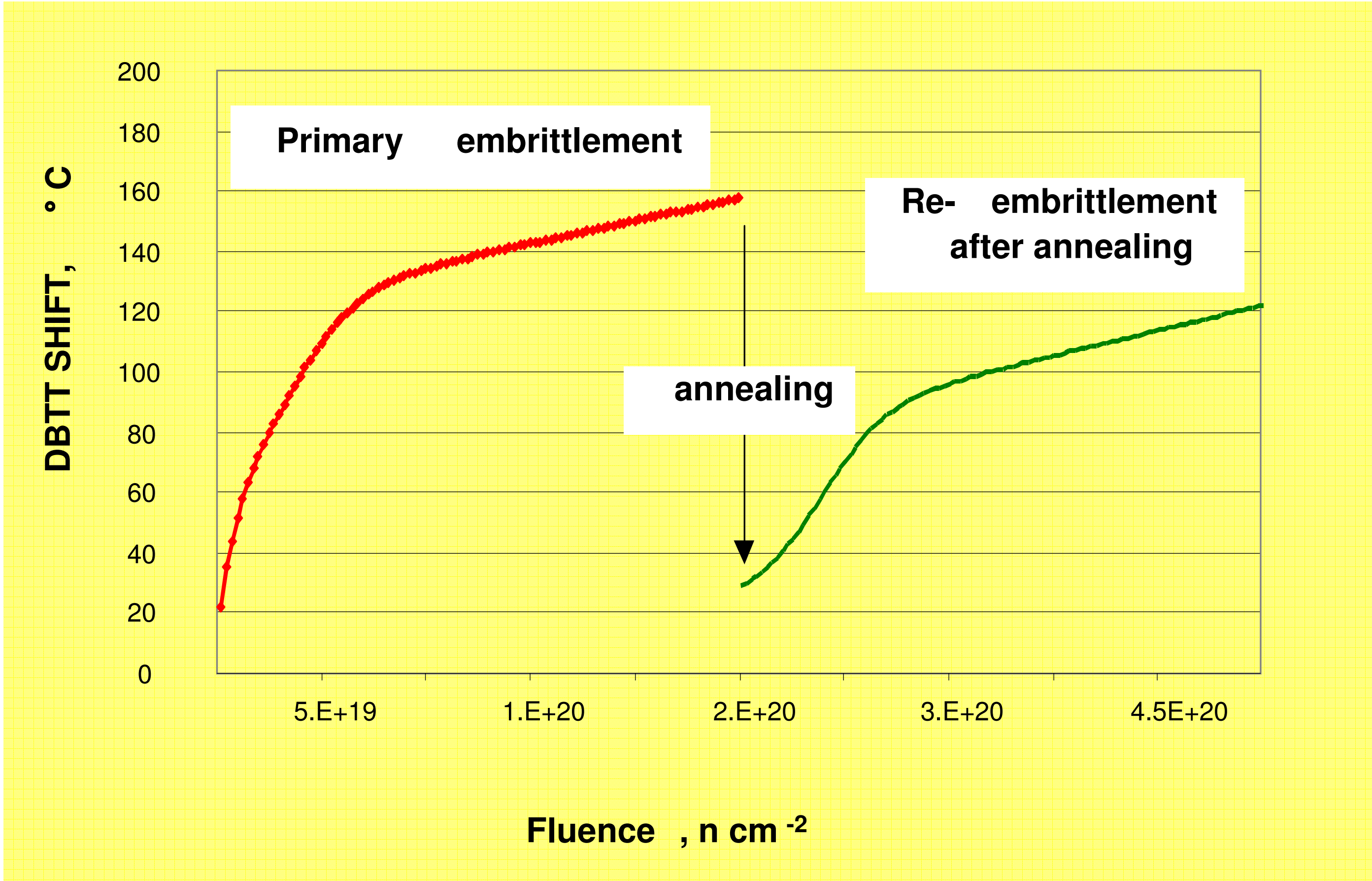
Radiation Embrittlement Understanding





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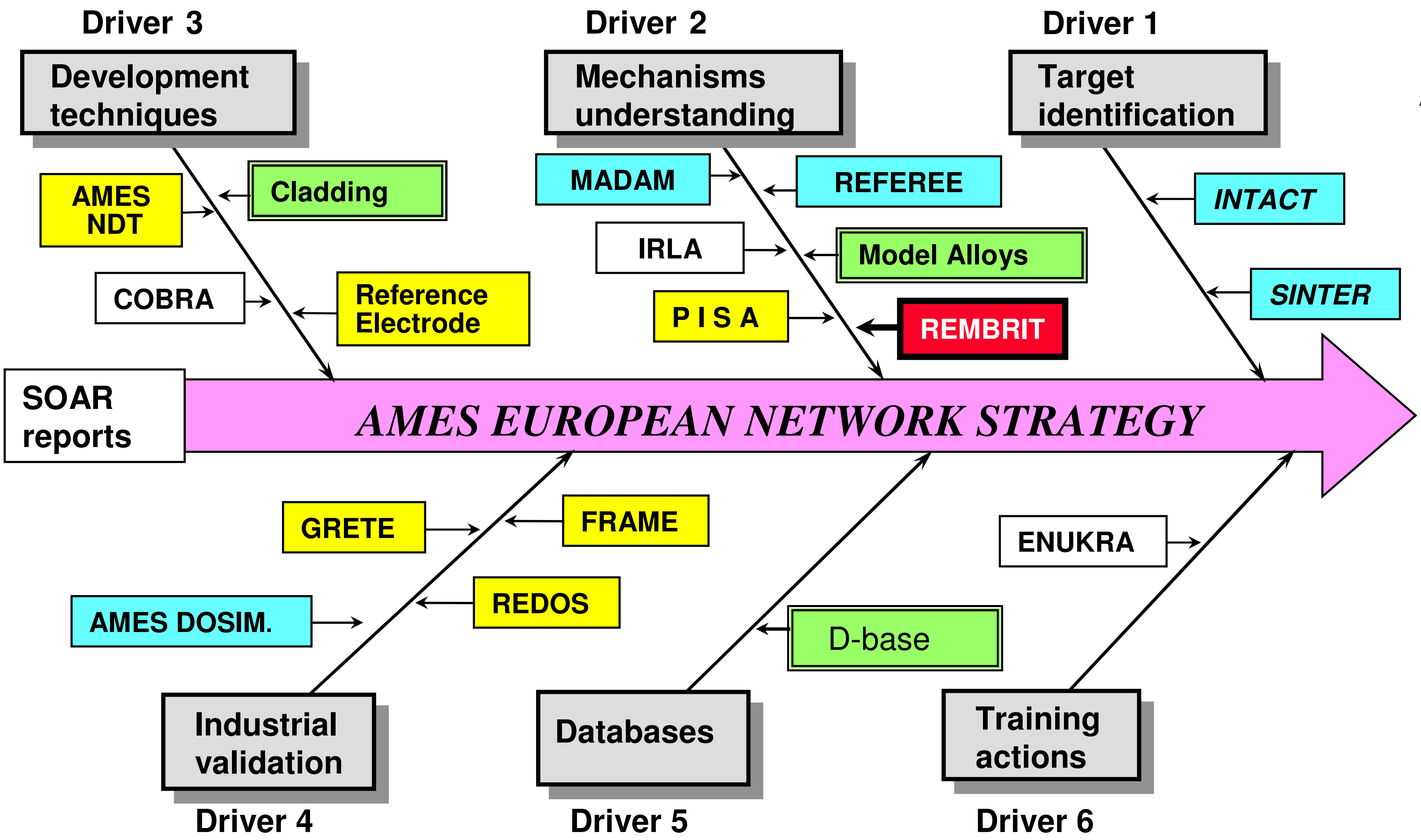
SAFELIFE

AMES STRATEGY



AMES Objectives:

Integrating Fragmented R&D

Amplify R&D Output

Avoid Duplications

Leadership in ‘ageing’

Sustainable success

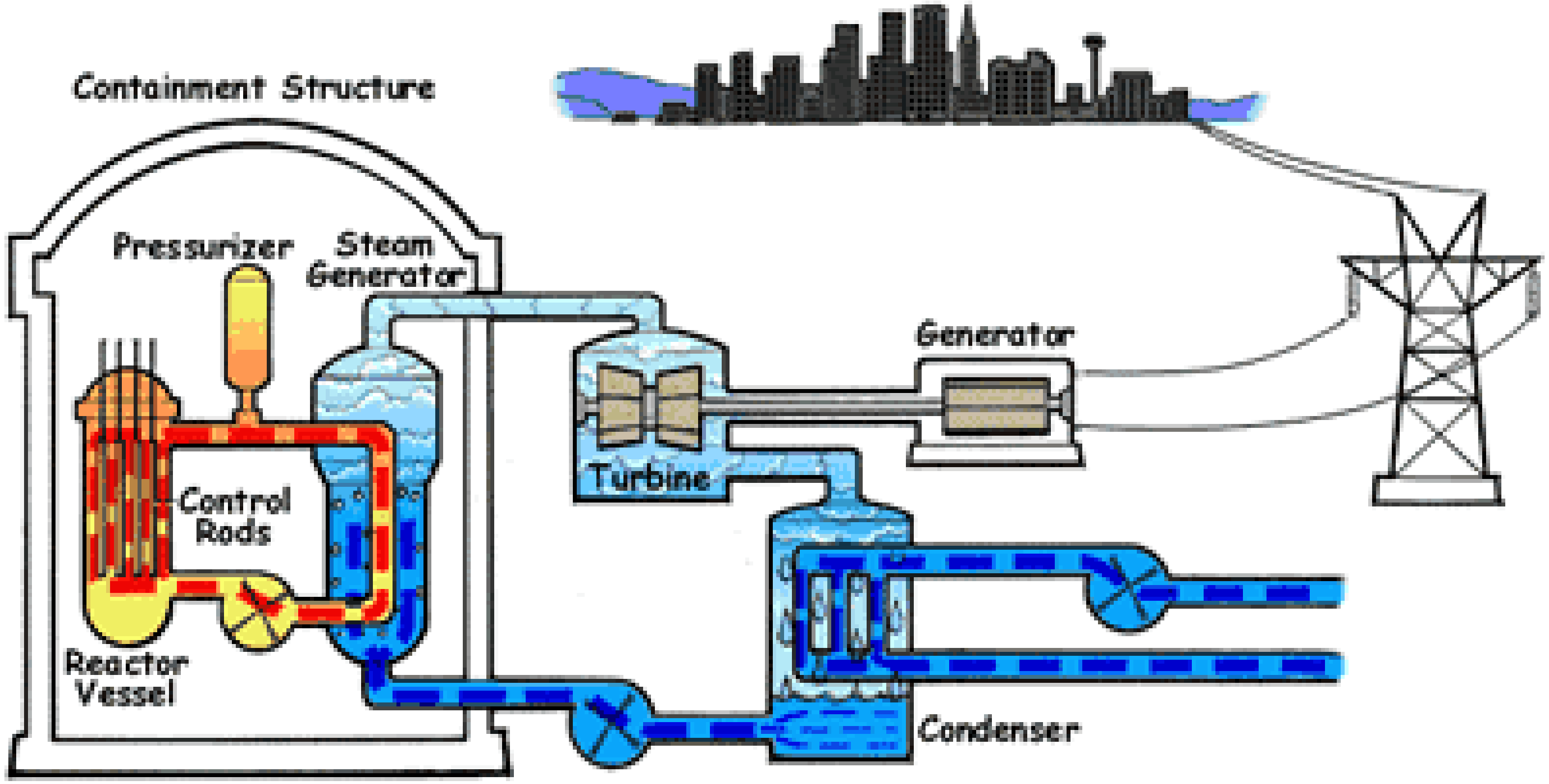
Satisfaction Stakeholder

Brainstorming

VVER-440 Welds Re-Embrittlement Assessment

Petten, 14-15 March, 2011

PrimaVERA Co-operation



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Annex 4: Ballesteros' presentation on Annealing and Re-Irradiation

- ✓ Motivation of this Seminar
- ✓Apologies
- ✓Agenda
- ✓Logistic
- ✓Proceedings
- ✓Introduction of the participants

Annealing and Re-Embrittlement of Reactor Pressure Vessel Materials

Antonio Ballesteros

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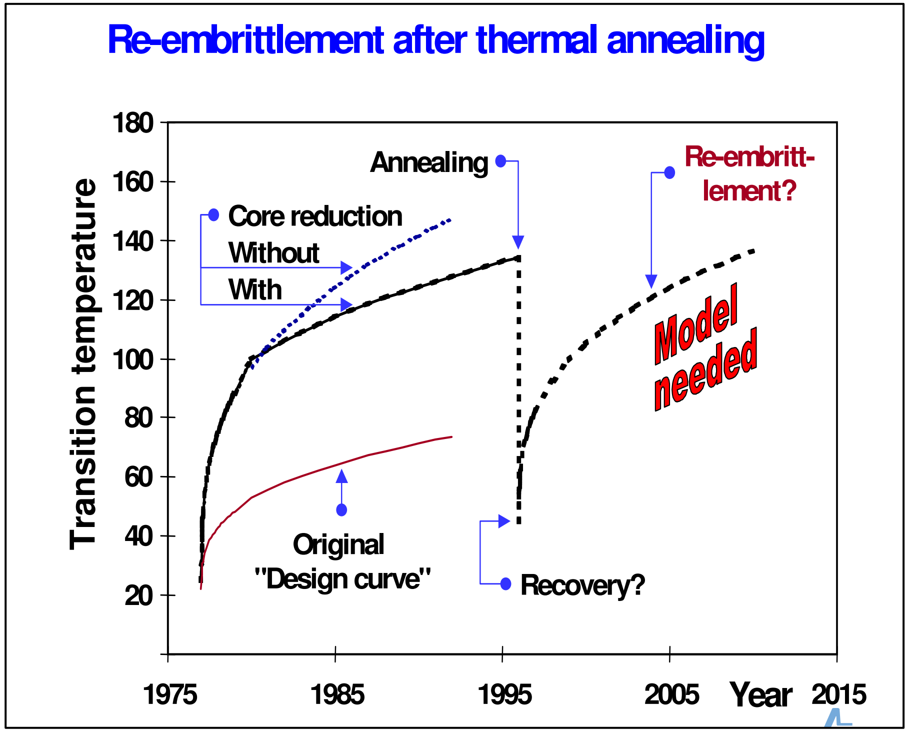
- Mitigation measures
- Annealing
- Re-embrittlement rates and basic models
- Semi-Mechanistic models
- Regulatory requirements
- Conclusions

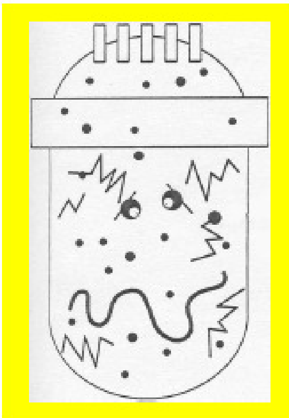
Mitigation Measures

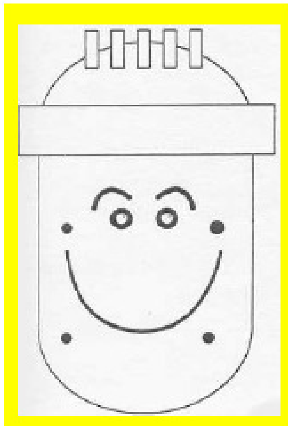
- Use of a "low-leakage core" that could decrease neutron flux on RPV wall by 30-40%.
- Use of "dummy elements" in the core periphery that could decrease the original peak flux by a factor of 4.5, and the new peak flux by 2.5.
- Recovery annealing, as it could practically restore initial mechanical properties of RPV materials.



First RPV Annealings

- The first RPV annealings were done using primary coolant and nuclear heat (USA Army SM-1A) or primary pump heat (Belgian BR-3).
- The annealing temperature for the SM-1A reactor was 293-300 °C (72-79 °C above the service temperature). The degree of recovery in this case was about 70%.
- In the BR-3 reactor the service temperature was 260 °C and the vessel was annealed at 343 °C. The recovery was estimated to be at least 50%.



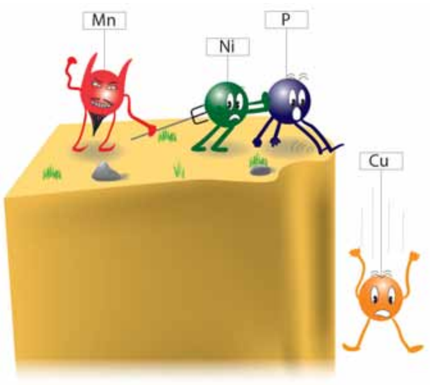


Annealing of WWER-440 RPVs

- At least 16 vessel thermal annealings have been realized.
- An annealing temperature at least 150 °C more than the irradiation temperature is required for at least 100 to 168 hours to obtain a significant benefit.
- A good recovery of all of the mechanical properties was observed when the thermal annealing temperature was about 450°C for about 168 hours (1 week).
- The re-embrittlement rates upon subsequent re-irradiation were similar to the embrittlement rates observed prior to the thermal anneal.

Dominant Factors in Annealing

- Annealing temperature relative to the irradiation (service) temperature
- The time and at the annealing temperature
- The impurity and alloying elements levels
- The type of product (plate, forging, weldment, etc.)

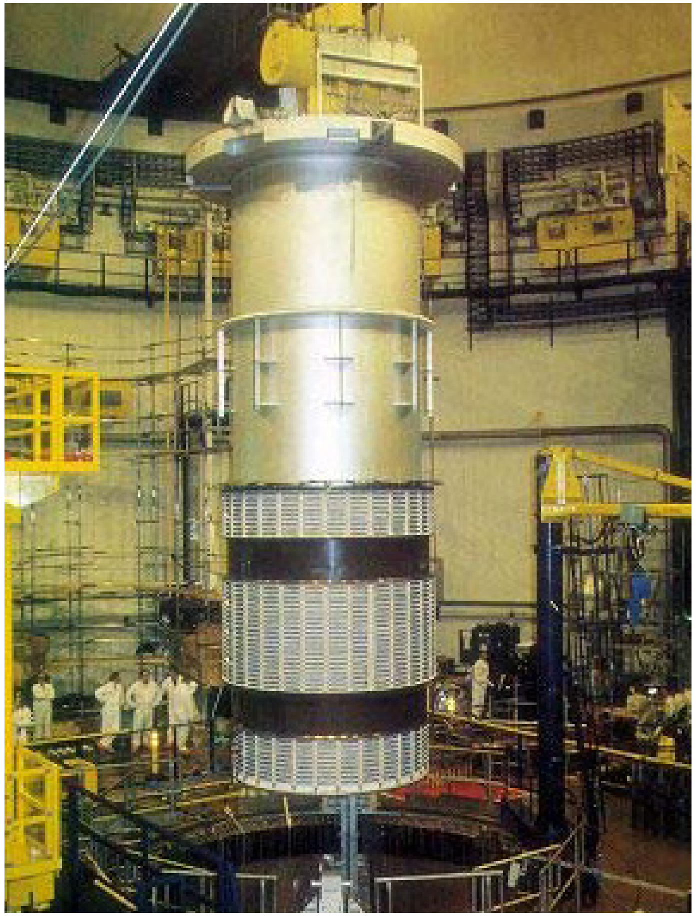


Wet Annealing

- The “wet” annealing method was applied to the SM-1Aand BR-3 reactors. The annealing temperature was reached without external heating, but by increasing the coolant temperature achieved by the energy of the circulating pumps.
- The “wet” procedure produced an insignificant recover of RPV materials properties. The temperature ~340 °C is the maximum possible in “wet” annealing.
- Advantages of the “wet” annealing are the possibility of heat treatment applied to the whole RPV, and the absence of a special heating device.

Dry Annealing

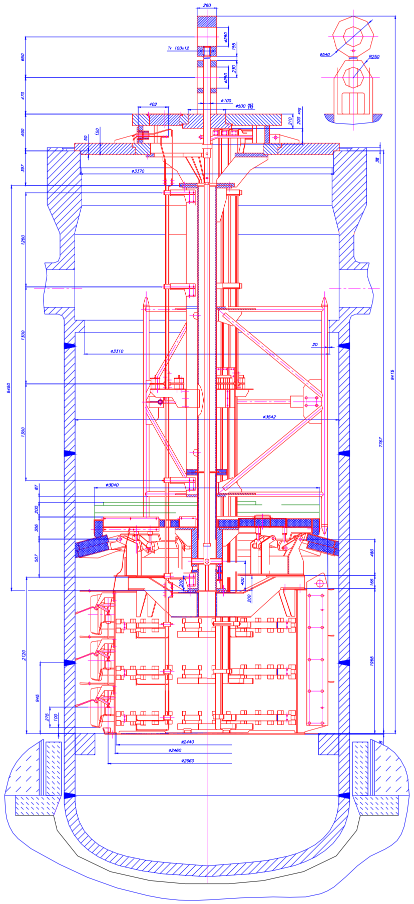
- To achieve a temperature higher than 340 °C it is necessary to remove the core and all reactor internals, and also to use an external source of heating inside the RPV.
- The "dry" annealing permits the recovery heat treatment with a difference between annealing and irradiation temperatures up to 230 °C.
- It is recognized that the "dry" annealing option is a practical solution

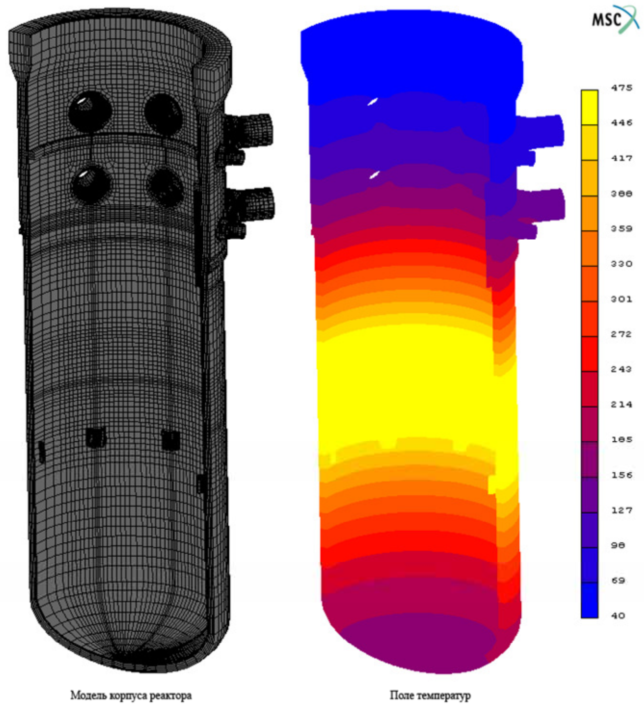


Annealing of WWER-440 RPVs in Russia

NPP	Year of Unit start-up	Year of annealing	Annealing parameters
NV NPP, Unit 3	1971	1987	430±20 ^{0}C, 150 h
		1991	475±15 ^{0}C, 100 h
NV NPP, Unit 4	1972	1991	475±15 ^{0}C, 150 h
KNPP, Unit 1	1973	1989	475±15 ^{0}C, 150 h
KNPP, Unit 2	1974	1989	475±15 ^{0}C, 150 h

Annealing of RPV Rovno 1





Source: Piminov et al, TAREG Project 2.01.00, Kiev, Nov. 2010

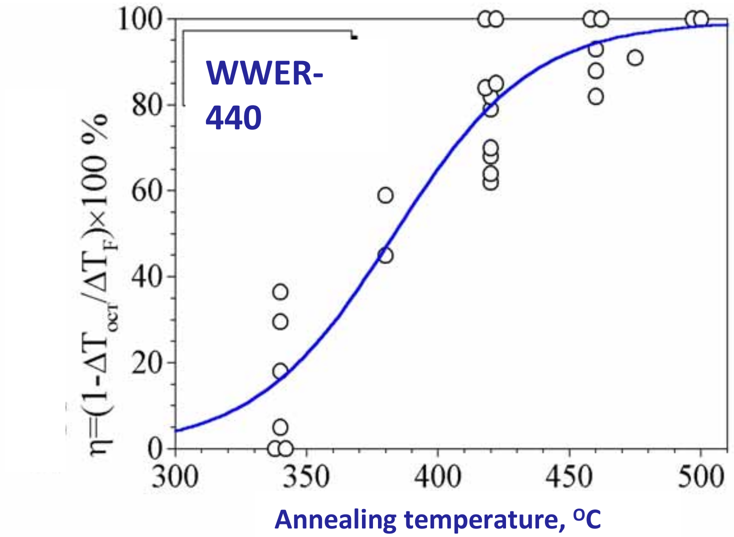
Annealing Effectiveness

- For temperatures in the interval 340 to 420 °C the dependence of Tk recovery is close to linear.

- At temperatures 450 - 470 °C the recovery is about 80 % or more, which corresponds to a residual embrittlement after annealing not bigger than 20 - 30 °C.

- At an annealing temperature of 340 °C only an insignificant recovery in Tk for irradiated materials was observed, 20 % on average.

$$\eta = \frac{(T_F - T_a)}{(T_F - T_{k0})} \cdot 100$$

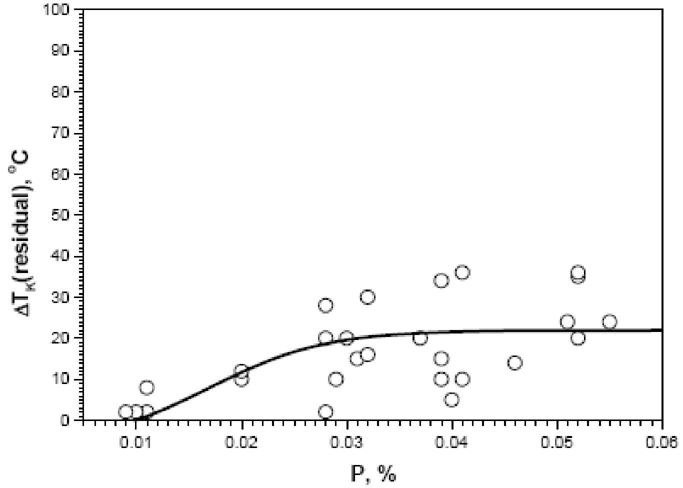


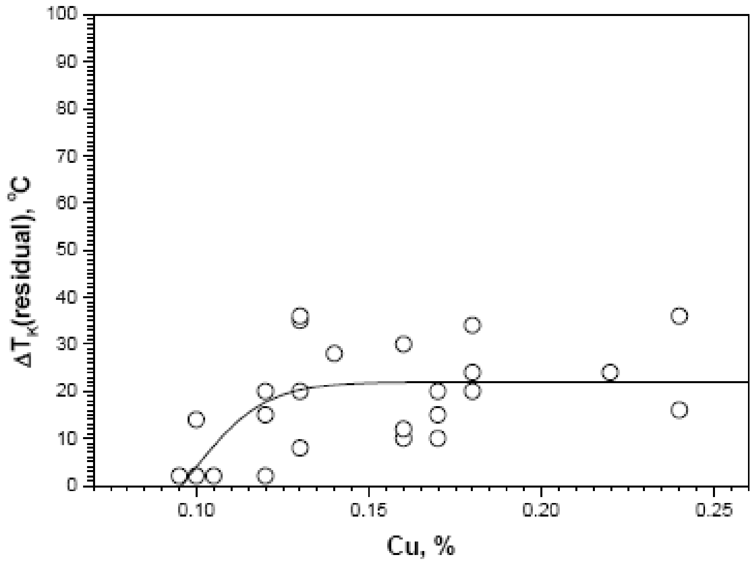
Annealing effectiveness for WWER-440 base metal and welds as a function of annealing temperature. Tirr= 270 °C.

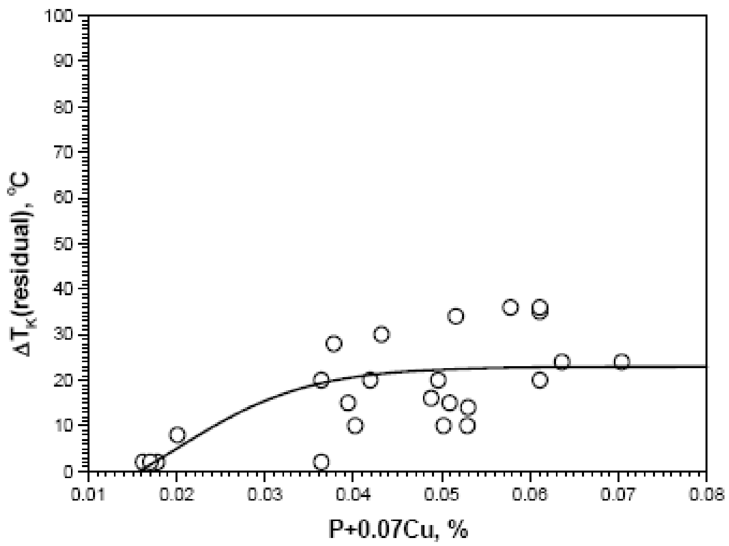
Amayev et al, 1993

Residual after Annealings for WWER-440 Materials

- For material with low level of P and Cu annealing at temperatures of 450-470 ℃ leads to nearly full recovery of Tk.
- If phosphorus content is more then 0.02 % and copper content is more than 0.2 %, the residual shift of Tk could be up to 30-40 ℃.

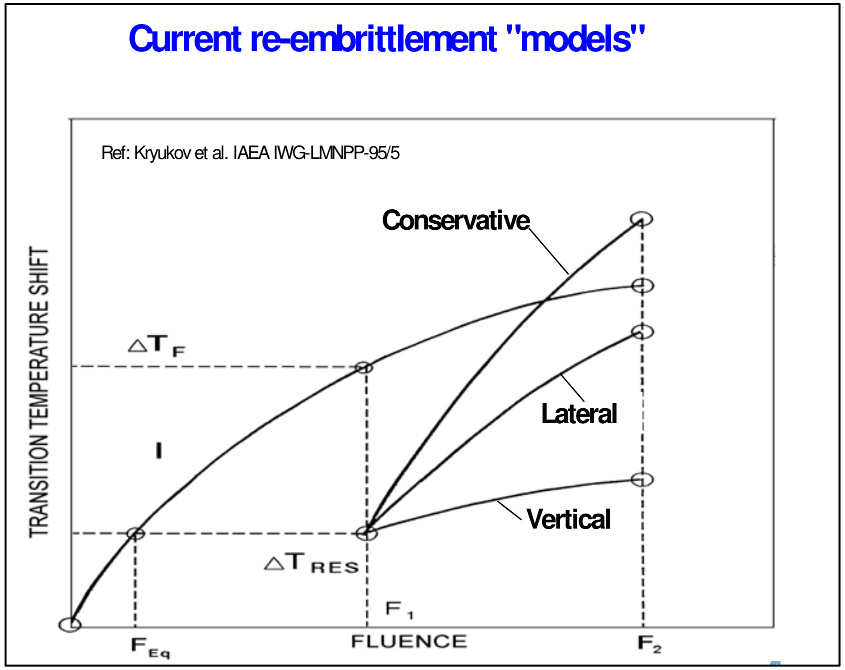






Re-Embrittlement Rate and Models

- **The efficiency of recovery annealing and, consequently, the lifetime of operating after annealing RPV are defined by two factors:**
  - The degree of Tk shift recovery or residual irradiation embrittlement value
  - The rate of irradiation embrittlement during re-irradiation.



Conservative Method

$$T_r = T_{ko} + \Delta T_{res} + A_F \times F_r^{1/3}$$

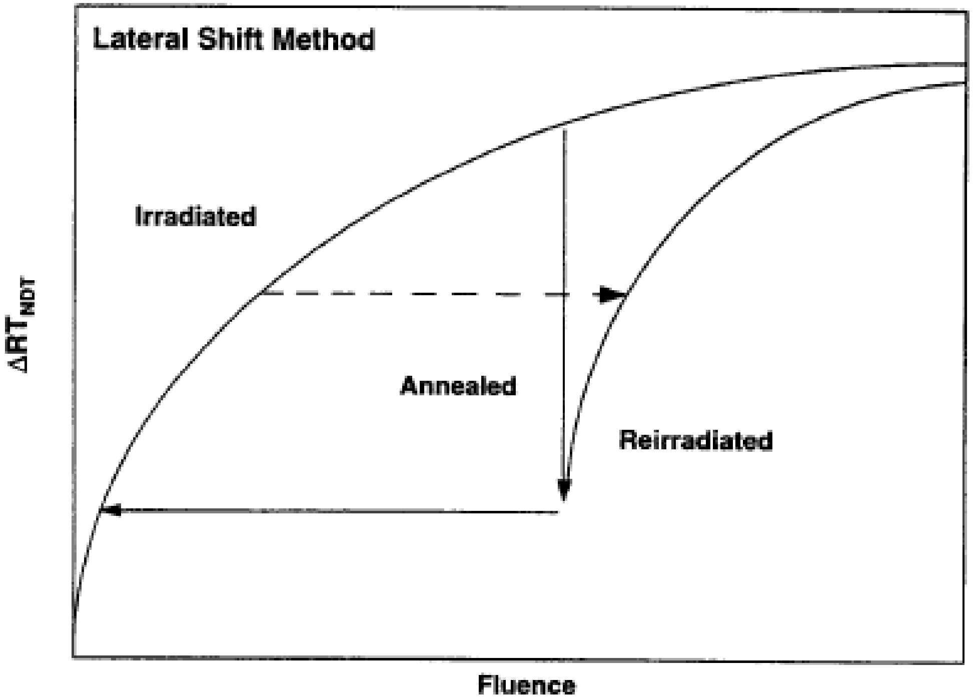
- **This formula has been applied in the assessment of irradiation lifetime for WWER-440 pressure vessels annealed from 1987 until 1992.**

- **This approach contradicts the mechanistic concepts concerning the nature of irradiation embrittlement of materials, because it does not follow adequately the processes of radiation damage and annealing of RPV materials.**

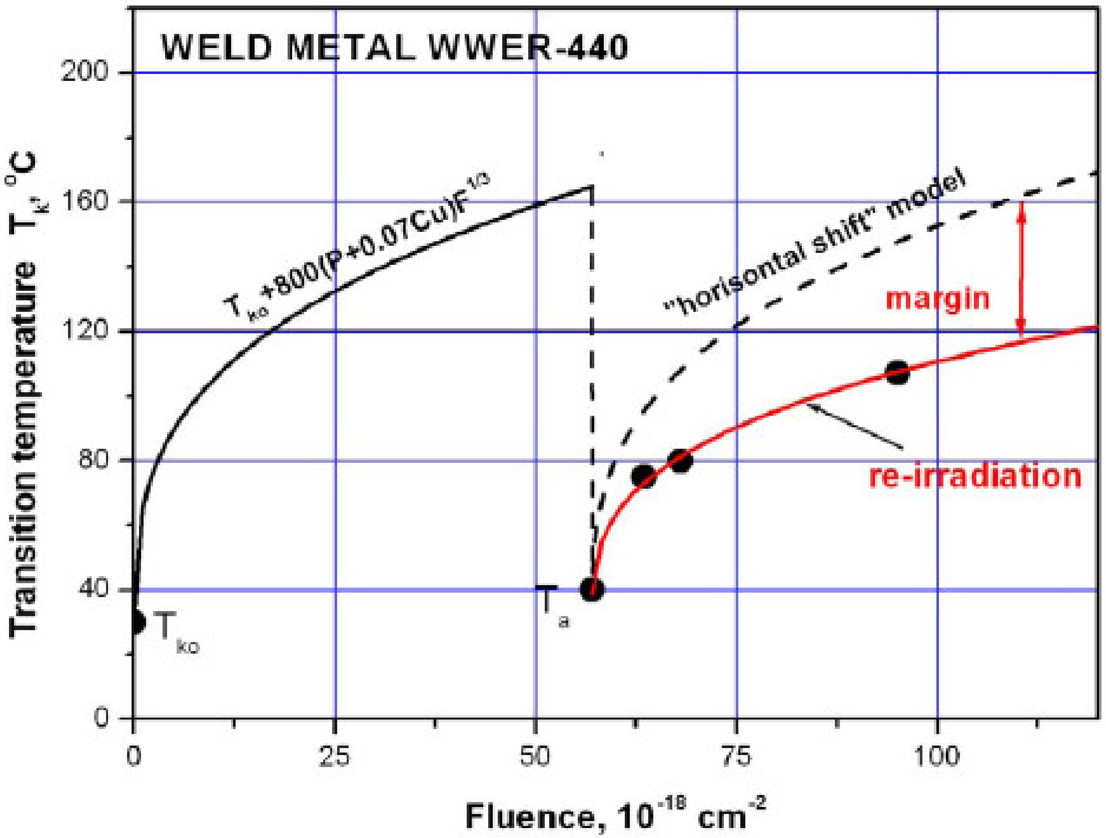
Lateral Shift Method

$$\Delta T_R = -\Delta T_{res} + (\Delta T_{res}^3 + A_F^3 \times \Delta F_R)^{1/3},$$

$$\text{Where } A_F = 800(P + 0.07Cu);\quad \Delta T_{res} = T_{\kappa 0} - T_{\kappa A}$$



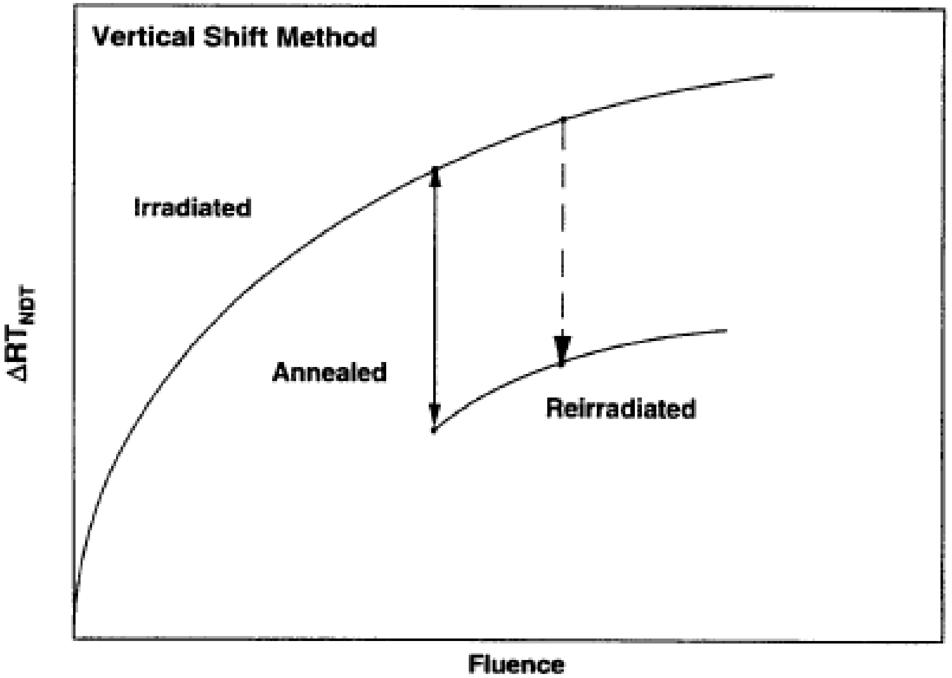
Typical Templet Re-Irradiation data

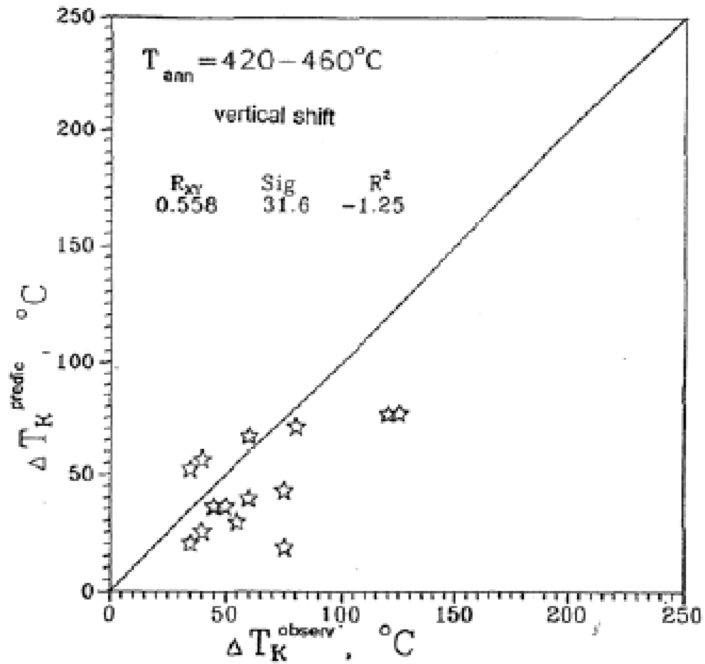


Source: Dmitry Erak

Vertical Shift Method

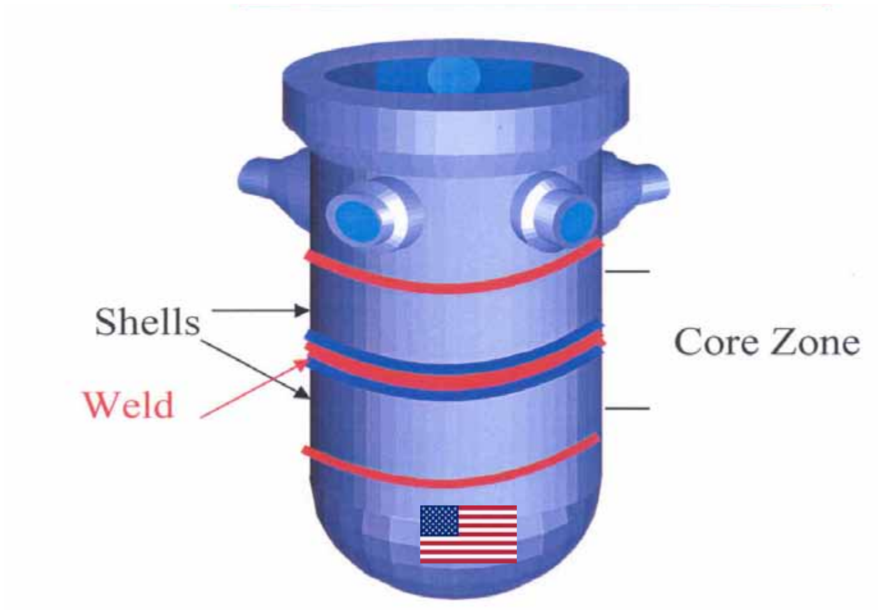
- In general, the predicted values are lower that the measured value.
- Clearly the method is not adequate





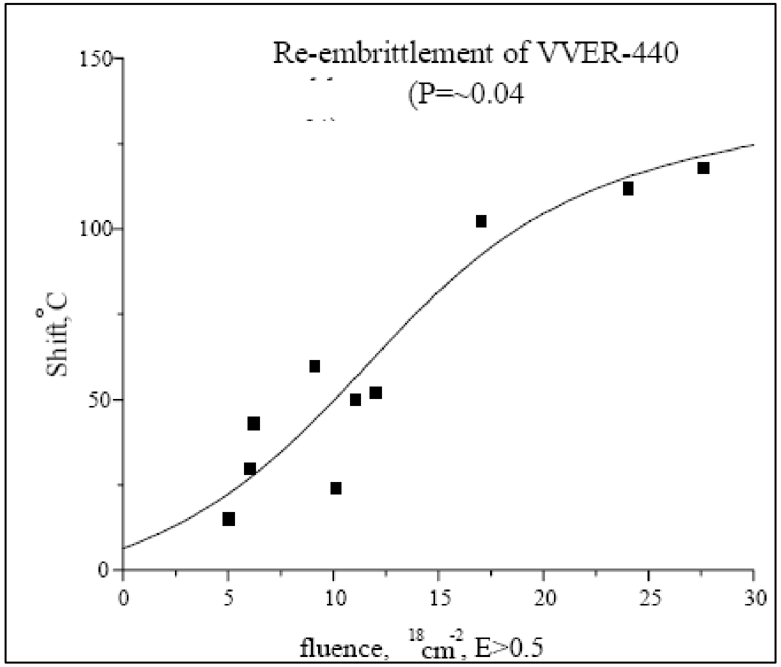
Some Findings from the American Database

- Annealing recovery generally follows NUREG/CR-6327 model.
- Re-embrittlement falls between the lateral shift and vertical shift models.
- EPRI computer code allows prediction based on a mix of lateral and vertical shift.
- Flux effects must be considered for reirradiation, similar to current surveillance concerns for initial irradiation.



Need for a Semi-Mechanistic Model

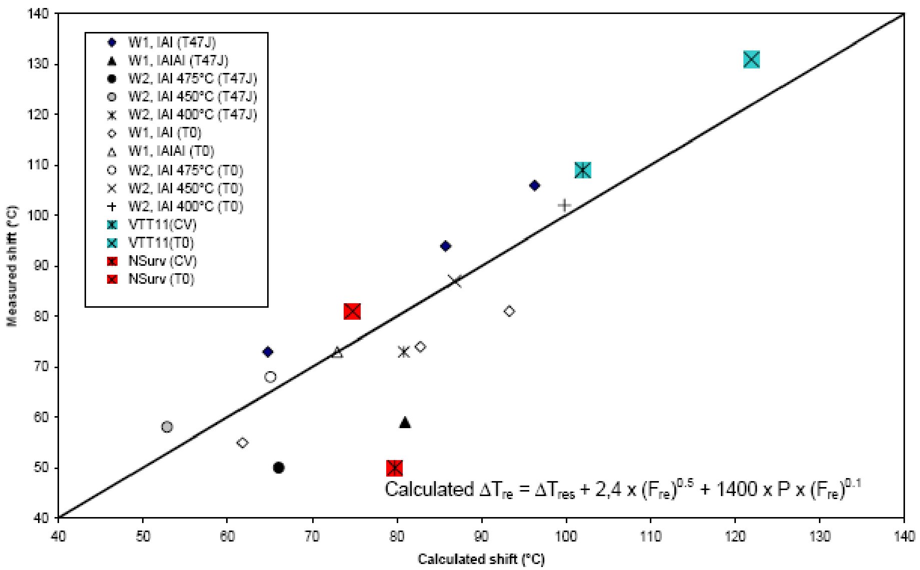
- **The traditional models are not able to describe the peculiar behavior of re-embrittlement after annealing of high phosphorus steels, like some WWER-440 high P welds.**
- **After annealing the embrittlement seems to start with a certain delay and afterwards increases rapidly.**



Source: Kryukov et al, IAEA SM, Gloucester, 2001

- **It is the first attempt to deviate from traditional models.**
- **In this approach the solute P is considered the governing active element in the post annealing re-embrittlement. It is supposed that the Cu-precipitates are growing and not dissolving during annealing.**

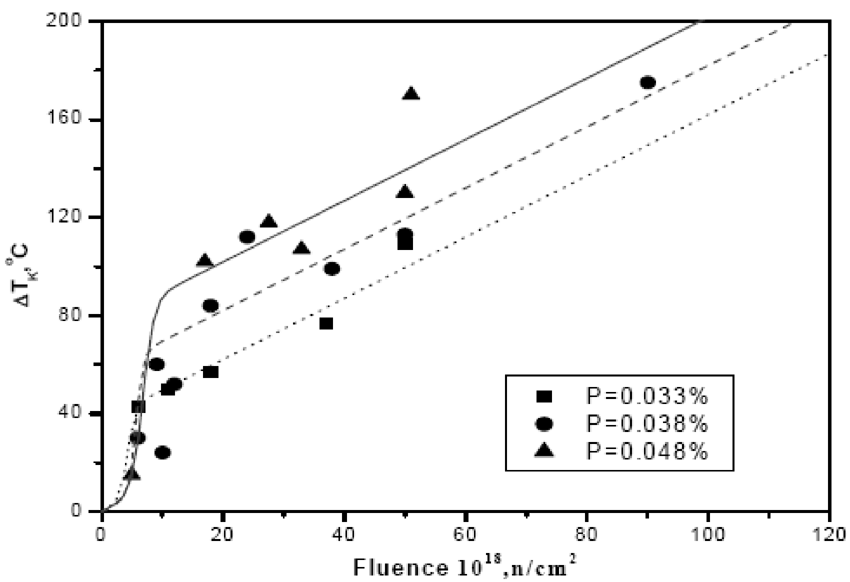
$$\boxed{\Delta T_{re} = \Delta T_{res} + 2.4\,(F_{re})^{0.5} + 1400\,P\,(F_{re})^{0.1}}$$



Debarberis Model

- **It was postulated that the basic mechanism of radiation embrittlement (primary) of steels and welds is based on three major contributions to damage:**
  - Direct matrix damage,
  - Precipitation (mainly copper)
  - Element segregation (mainly phosphorus)

$$\Delta T_{shift} = a \cdot \Phi^{n} + b1 \cdot \left[1 - e^{\left(-\Phi/\Phi_{sat}\right)} \right] + c1 \cdot [1/2 + 1/2 \cdot Tanh(\frac{\Phi - \Phi_{start}}{c2})]$$

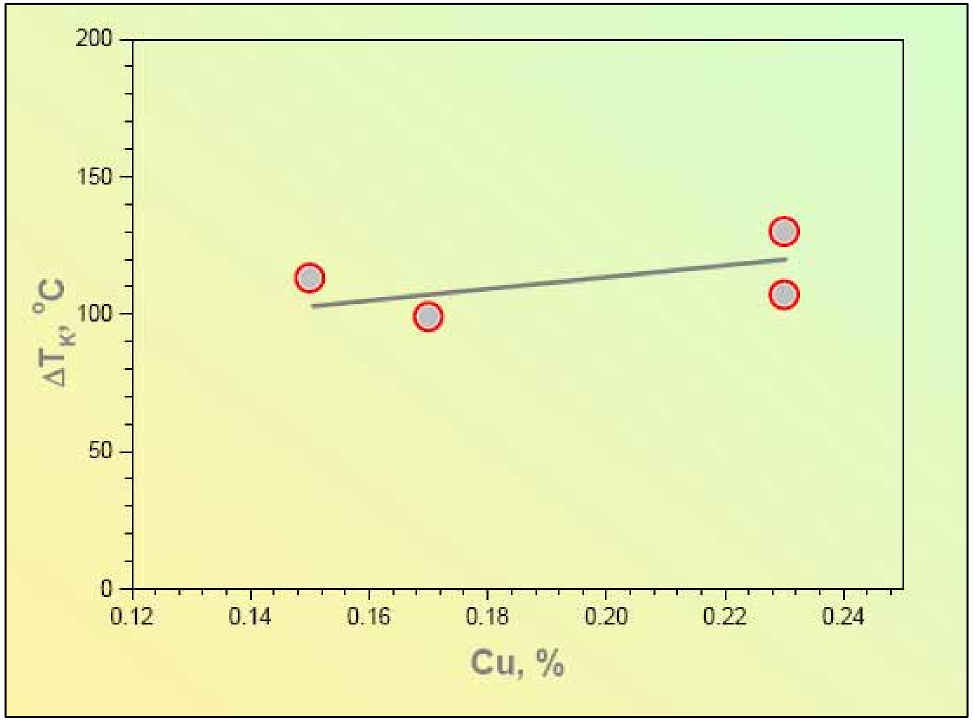


$$\Delta T_k = 5.675 \cdot F^{1/2} + 1860 \cdot P \cdot \left\{ 0.5 + 0.5 \cdot \tanh\left[\frac{(F - 13.433)}{10.12} \right] \right\}$$

Cu Influence after Re-Irradiation

T_k shifts for WWER-440 pressure vessel steels.

Cu influence is insignificant for re-irradiation



Source: Dmitry Erak, AMES Conference, 2006

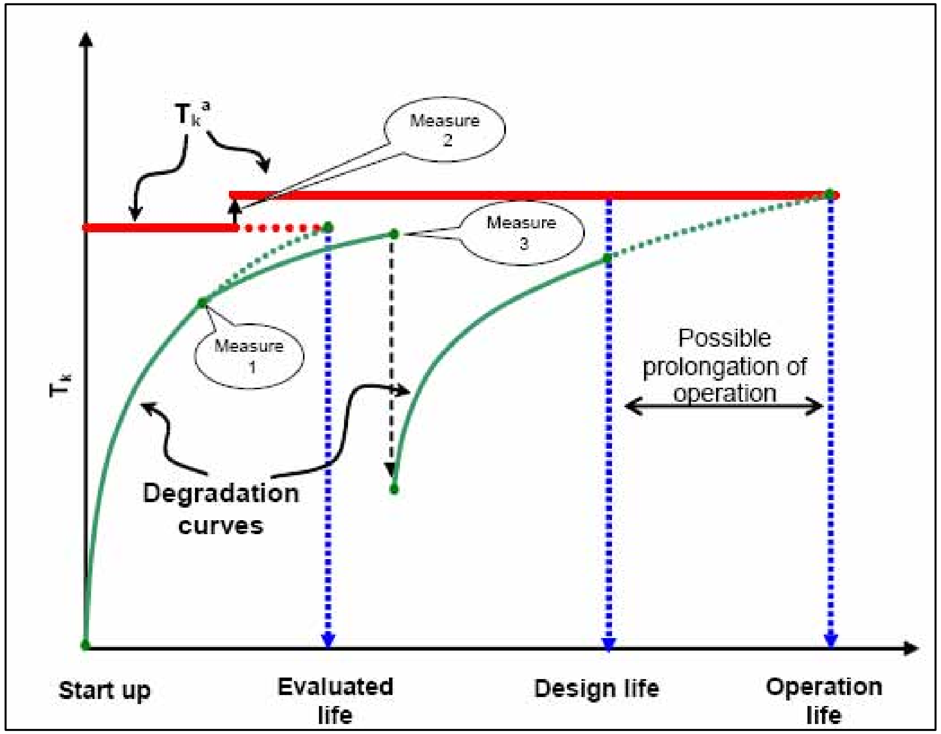
Regulatory Requirements. USA

- **Annealing Rule in 10 CFR Part 50.66.**
- **Regulatory Guide 1.162 on Annealing Program requirements and reporting.**
- **Annealing Rule and Regulatory Guide 1.162 contain reference to NUREG/CR-6327.**
- **ASTM E 509 "Standard Guide for In-Service Annealing of LWR Nuclear Reactor Vessels"**

Regulatory Requirements. Russia

- **There are no specific regulatory requirements for the annealing procedure of WWER RPVs. Practically, each annealing is approved by a special procedure.**

- **The procedure and residual lifetime evaluation should be based on experimental data from irradiation of similar RPV materials and analysis based on transition temperature shifts prediction based on Russian Code.**



Conclusions

- **Only dry annealing can be effectively applied for substantial recovery of RPV material properties.**

- **More general validation of re-embrittlement models based on studies of mechanical properties, as well as on microstructural investigations, is still needed.**

- **A better understanding of re-embrittlement mechanisms is essential for accurate prediction.**

Annex 5: Chernobaeva’s presentation on PRIMAVERA Results

НАЦИОНАЛЬНЫЙ ИССЛЕДОВАТЕЛЬСКИЙ ЦЕНТР
“ КУРЧАТОВСКИЙ ИНСТИТУТ ”

THE RESULTS OF PRIMAVERA PROJECT

Presented by A.A. Chernobaeva

14-15 March 2011

JRC Petén, The Netherlands

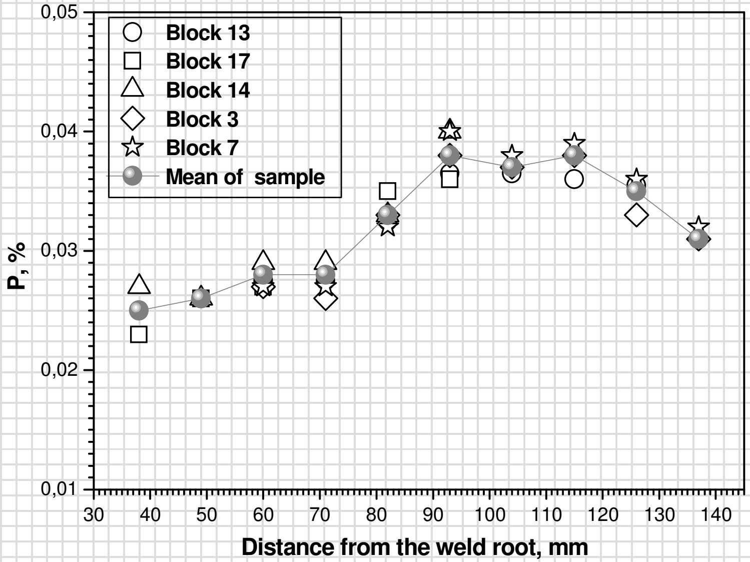
Materials

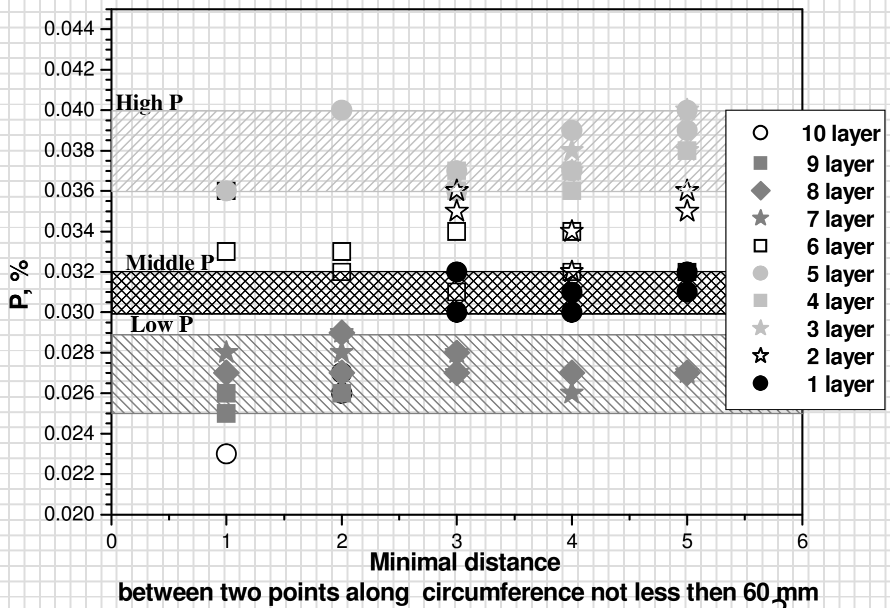
	C	Si	Mn	**P**	S	Cr	Ni	Mo	**Cu**	V
LP	0.04	0.04	1.12	**0.027**	0.013	1.42	0.13	0.49	**0.16**	0.19
MP	0.04	0.39	1.15	**0.031**	0.013	1.42	0.13	0.50	**0.16**	0.18
HP	0.05	0.36	1.09	**0.038**	0.014	1.54	0.13	0.51	**0.16**	0.19

[1] The weld with «low» phosphorus content

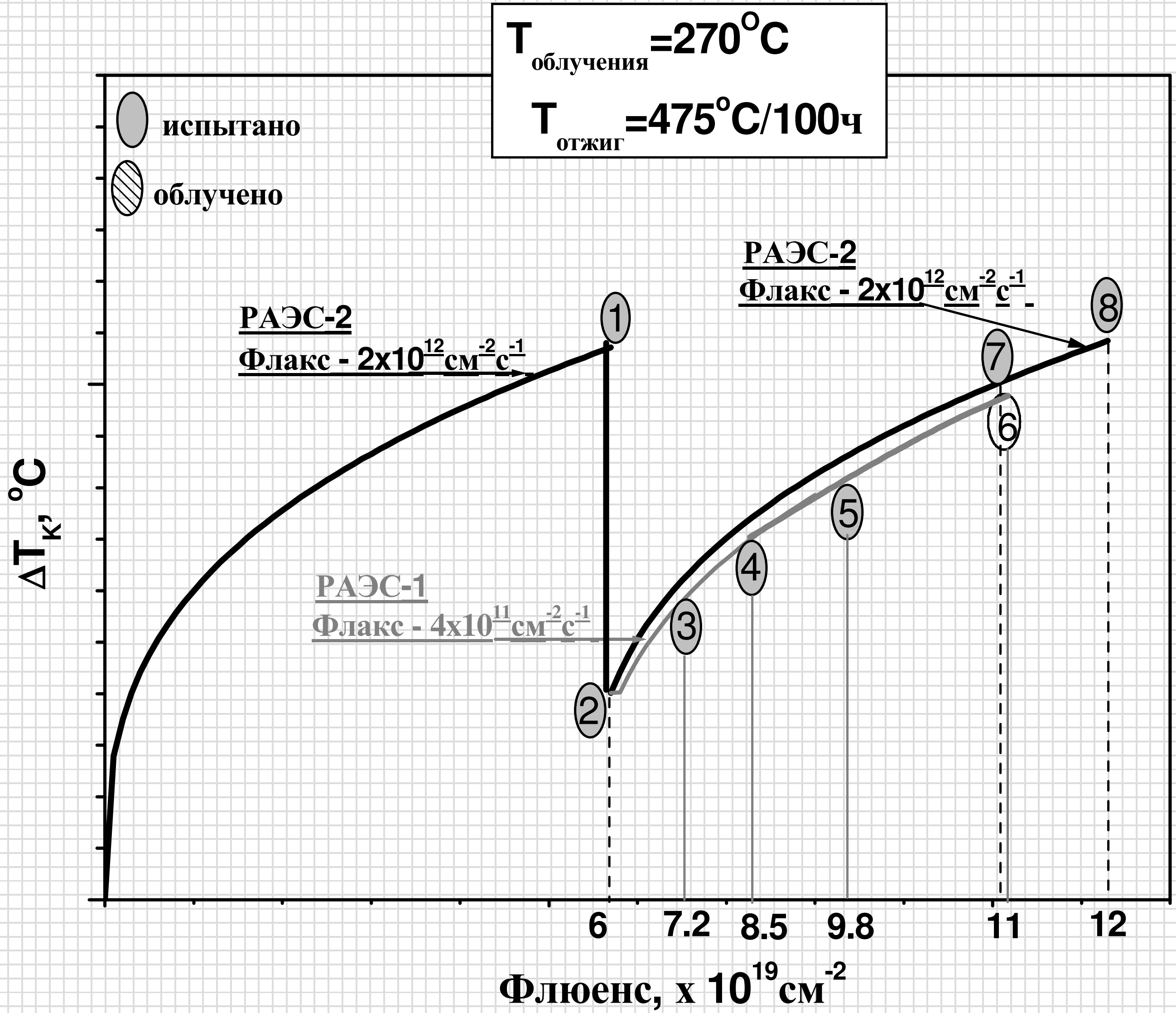
[2] The weld with «medium» phosphorus content

[3] The weld with «high» phosphorus content





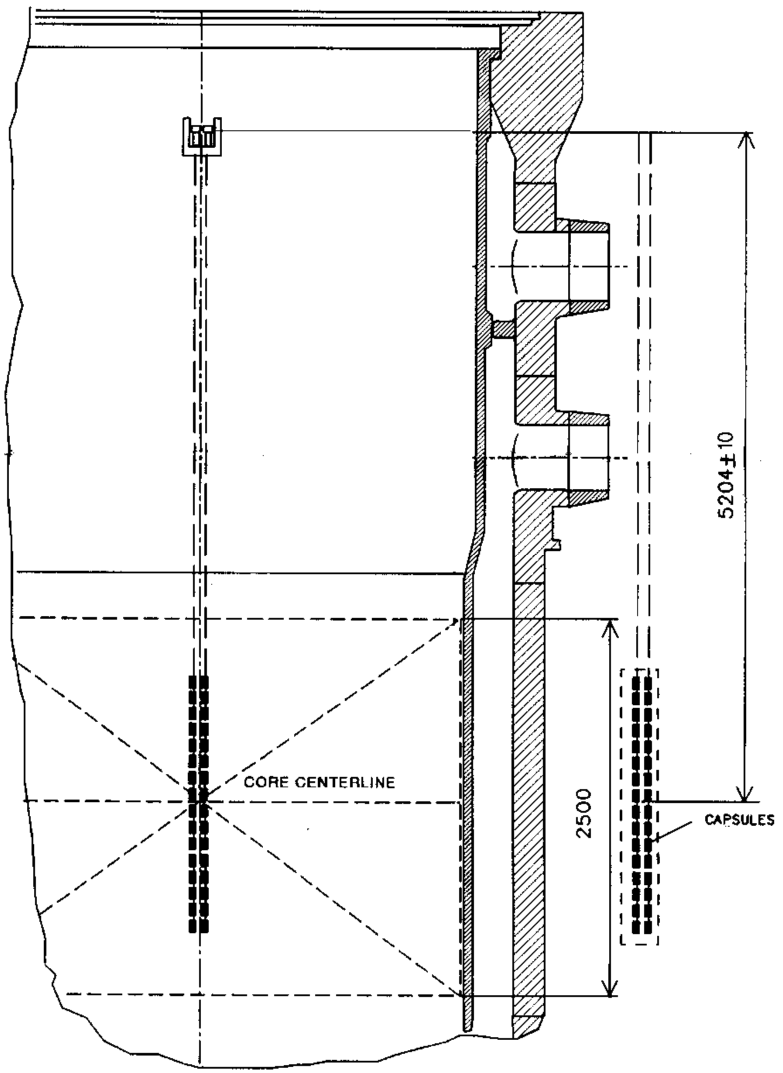
Irradiation program

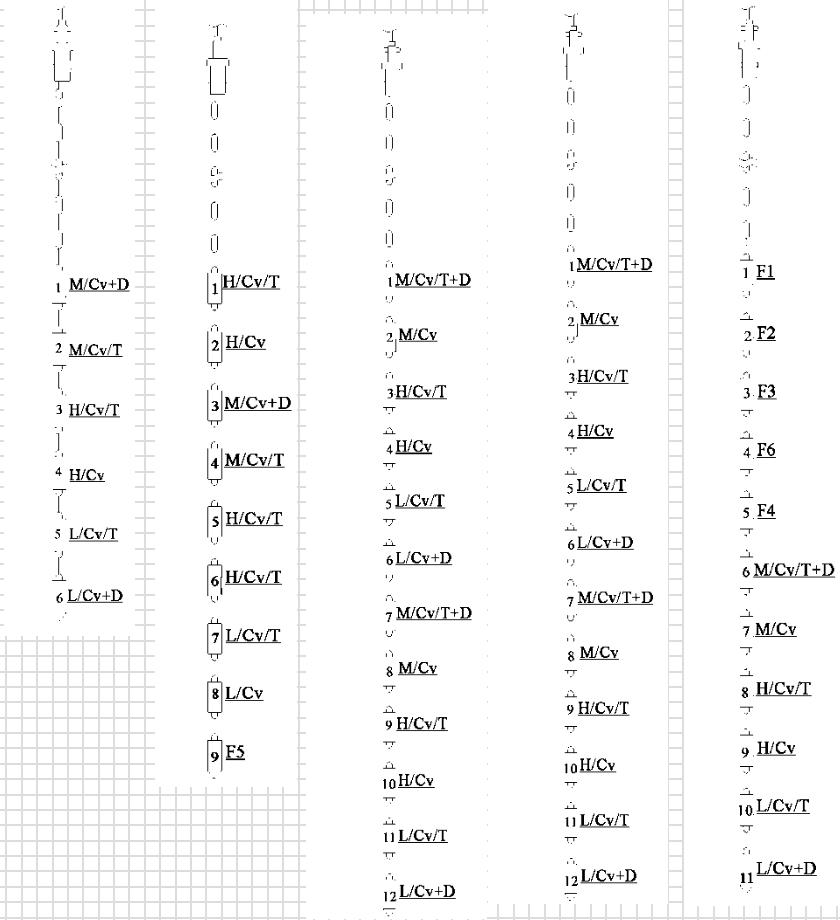


Test matrix

Material	State	Specimens	
		Charpy	Tensile
LM	Unirradiated	11	2
	Irr. Rovno-1	10	2
	Irr. Rovno -2	11	2
	Irr. Rovno -2 + ann.	9	2
	Irr. Rovno -2 + ann. + Irr. Rovno -1 (1 year)	11	2
	Irr. Rovno -2 + ann. + Irr. Rovno -1 (2 year)	11	2
	Irr. Rovno -2 + ann. + Irr. Rovno -1 (3 year)	10	2
	Обл. Rovno -2 + ann. + Irr. Rovno -2 (1 year)	11	2
MP	Unirradiated	15	2
	Irr. Rovno-1	10	2
	Irr. Rovno -2	11	2
	Irr. Rovno -2 + ann.	9	2
	Irr. Rovno -2 + ann. + Irr. Rovno -1 (1 year)	11	2
	Irr. Rovno -2 + ann. + Irr. Rovno -1 (2 year)	11	2
	Irr. Rovno -2 + ann. + Irr. Rovno -1 (3 year)	11	2
	Обл. Rovno -2 + ann. + Irr. Rovno -2 (1 year)	11	2
HP	Unirradiated	15	2
	Irr. Rovno-1	11	2
	Irr. Rovno -2	12	2
	Irr. Rovno -2 + ann.	11	2
	Irr. Rovno -2 + ann. + Irr. Rovno -1 (1 year)	12	2
	Irr. Rovno -2 + ann. + Irr. Rovno -1 (2 year)	12	2
	Irr. Rovno -2 + ann. + Irr. Rovno -1 (3 year)	10	2
	Обл. Rovno -2 + ann. + Irr. Rovno -2 (1 year) (1)	12	2
	Обл. Rovno -2 + ann. + Irr. Rovno -2 (1 year) (2)	12	2

Irradiation

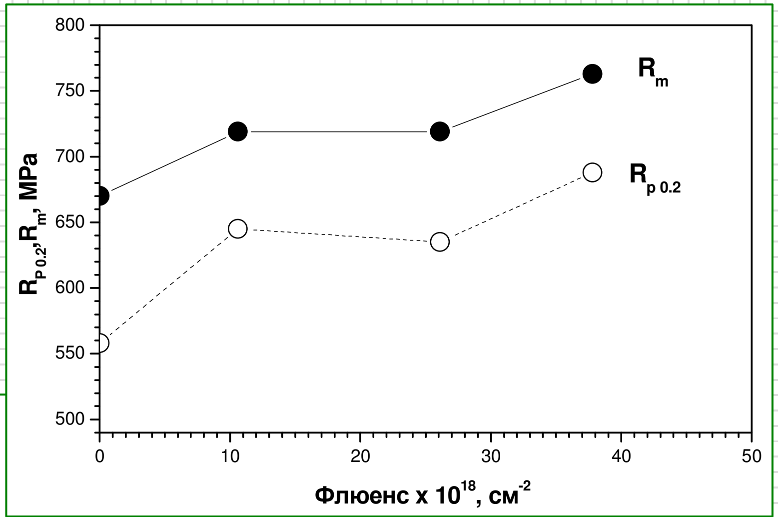




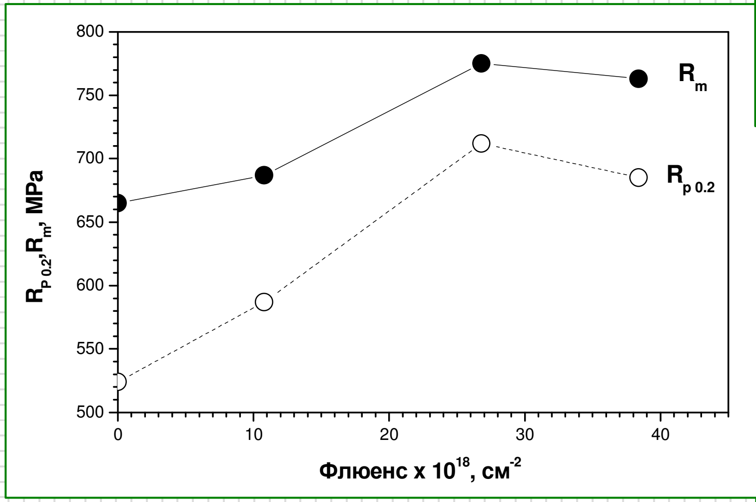
Контейнер 1-6 РАЭС-2 +А(475/100) + РАЭС-2	Контейнер 1-2 РАЭС-2 +А(475/100) + РАЭС-2 (I)	Контейнер 1-6 РАЭС-2 +А(475/100) + РАЭС-1 (5 лет)	Контейнер 1-6 РАЭС-2 +А(475/100) + РАЭС-1 (3 года)	Контейнер 1,2,3,4 РАЭС-2 +А(475/100) + РАЭС-1 (4,3,2,1 года)
	Контейнер 3-9 РАЭС-2 +А(475/100)	Контейнер 7-12 РАЭС-2 +А(475/100) + РАЭС-1 (1 год)	Контейнер 7-12 РАЭС-2 +А(475/100) + РАЭС-1 (2 года)	Контейнер 5-11 РАЭС-2

L – сварной шов LP ~ 0.027%;
M – сварной шов MP ~ 0.031%;
H – сварной шов HP ~ 0.038%;
Cv-вставки для изготовления образцов Шарпи;
T- разрывные образцы;
D – комплект мониторов нейтронного потока;
F1÷F6 VTT capsules.

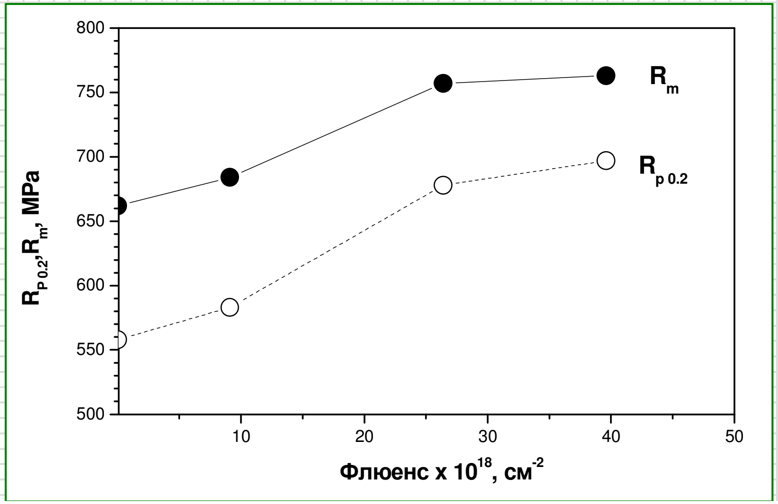
$\Delta R_{p\ 0.2}$ under re-irradiation in Rovno-1



P-0.038



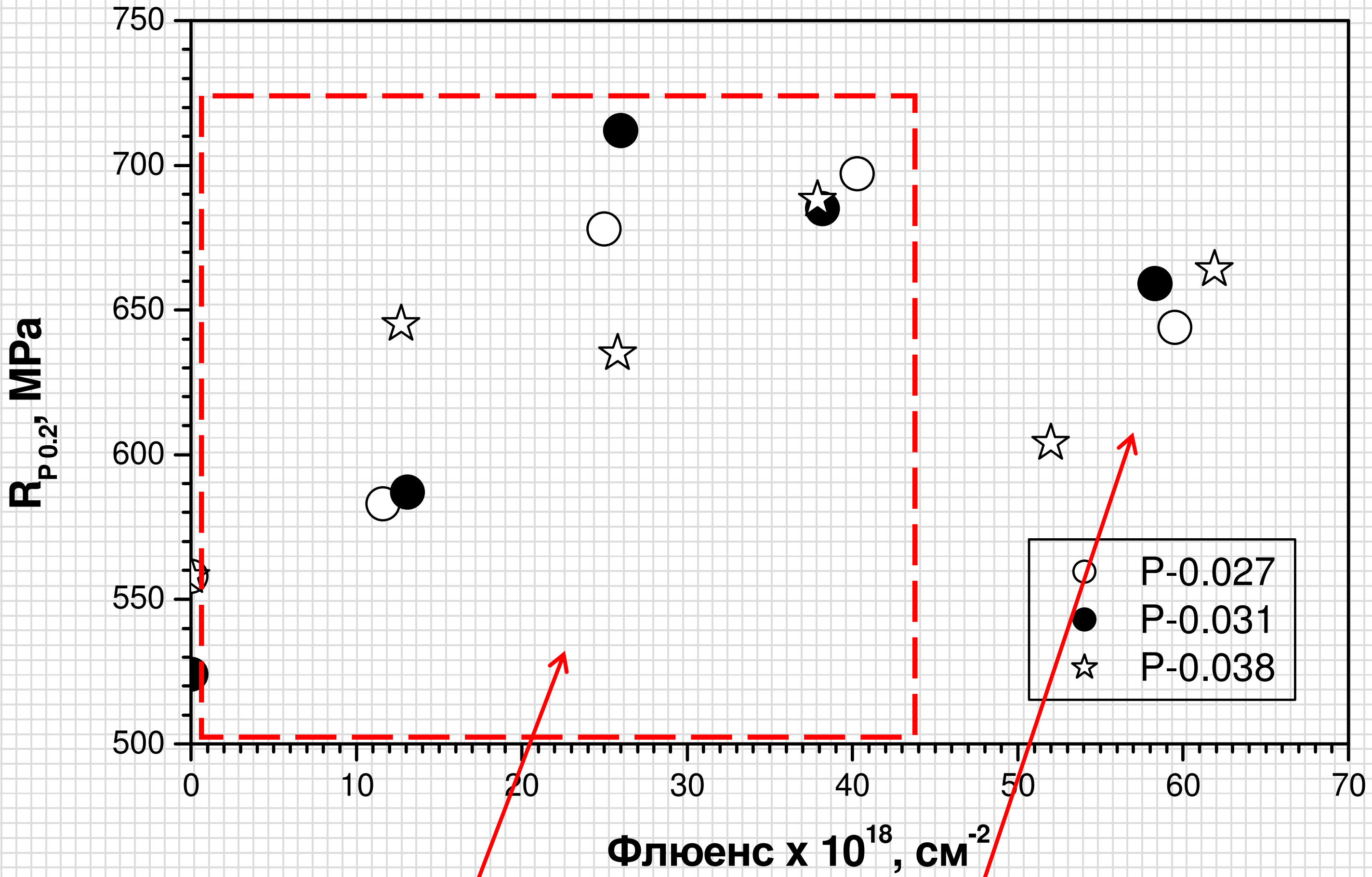
P-0.031



P-0.027

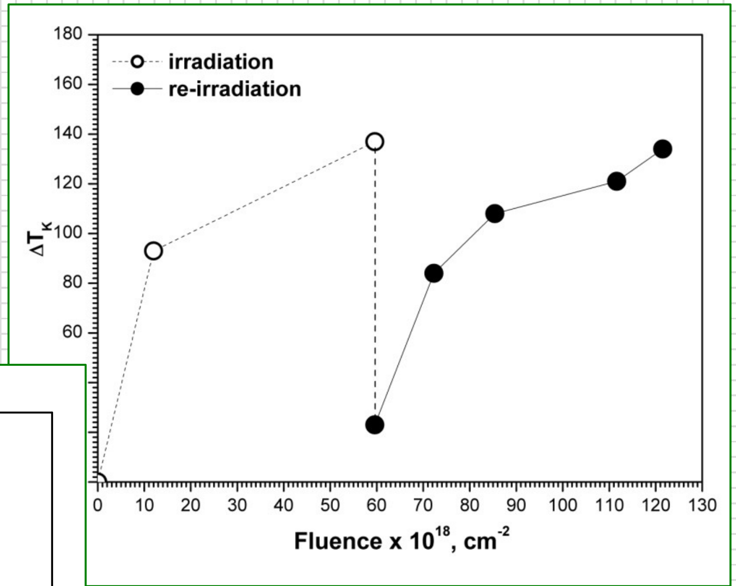
re-irradiation: $\Delta R_{p0.2} = R_{p0.2} - R_{p0.2}(\overset{6}{a}nn)$

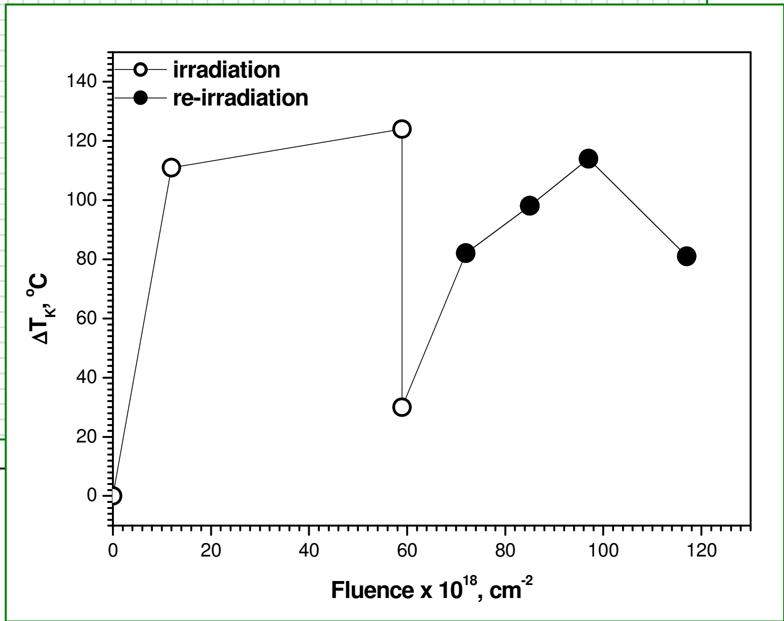
$\Delta R_{p\,0.2}$ under re-irradiation in Rovno-1 & 2

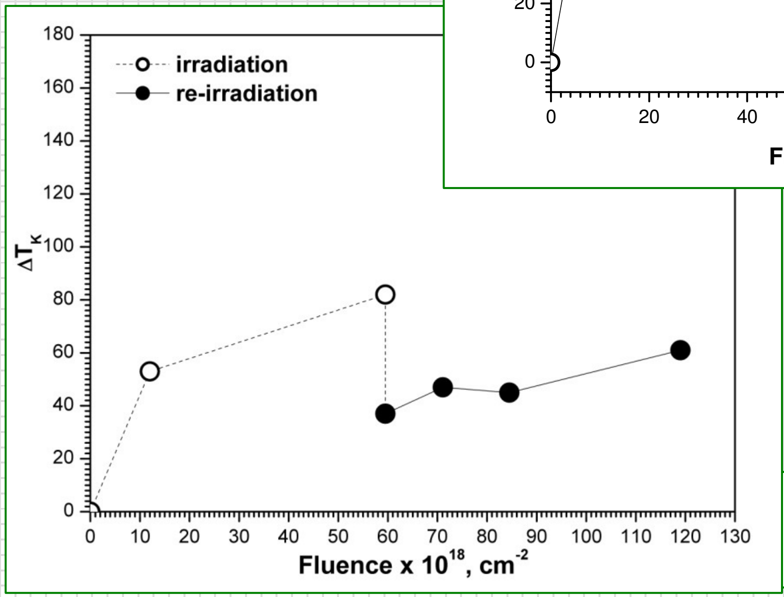


Re-irradiation in Rovno-1 & in Rovno-2

ΔT_K under irradiation and re-irradiation





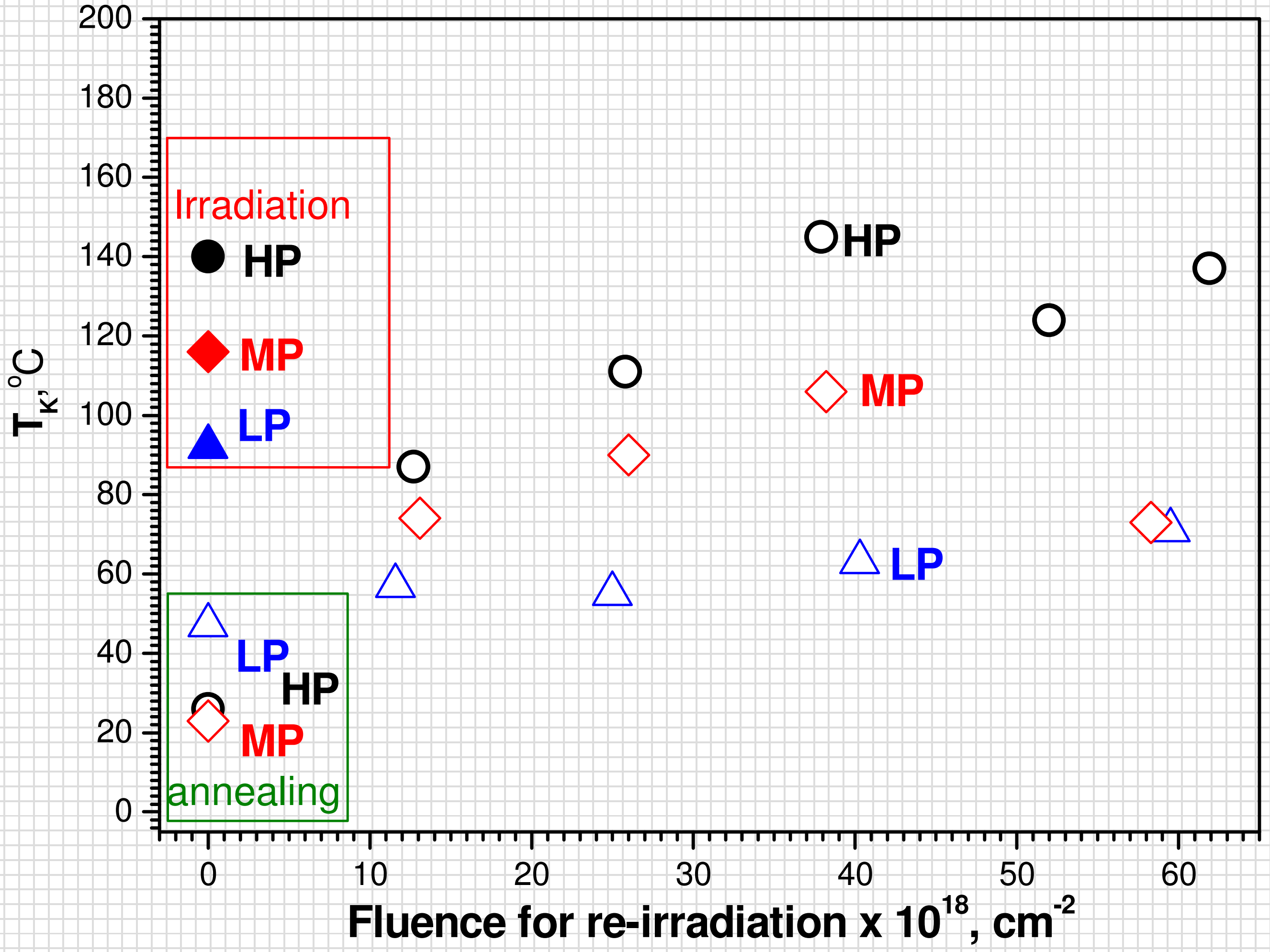


P-0.038

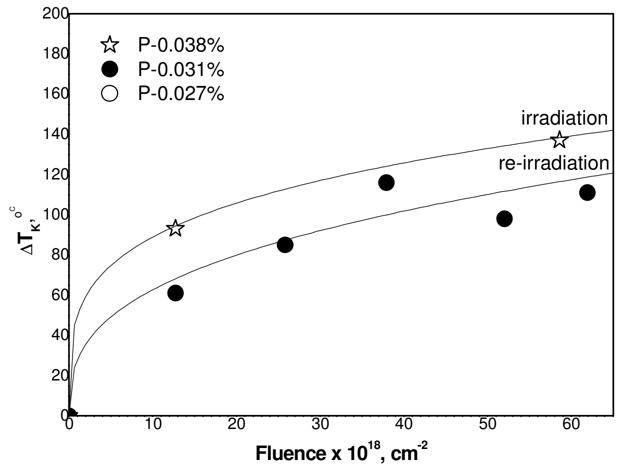
P-0.031

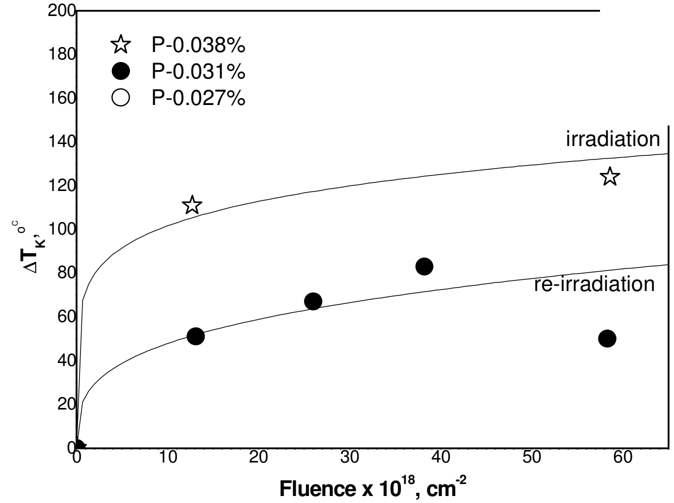
P-0.027

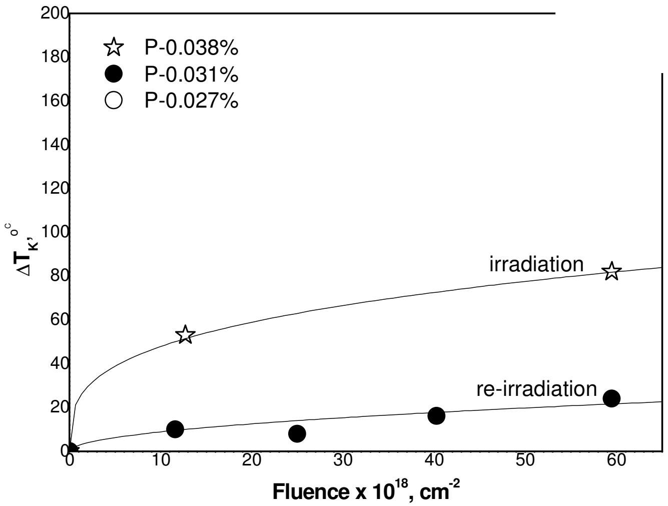
ΔT_K under re-irradiation for different P



ΔT_K under irradiation and re-irradiation







P-0.038

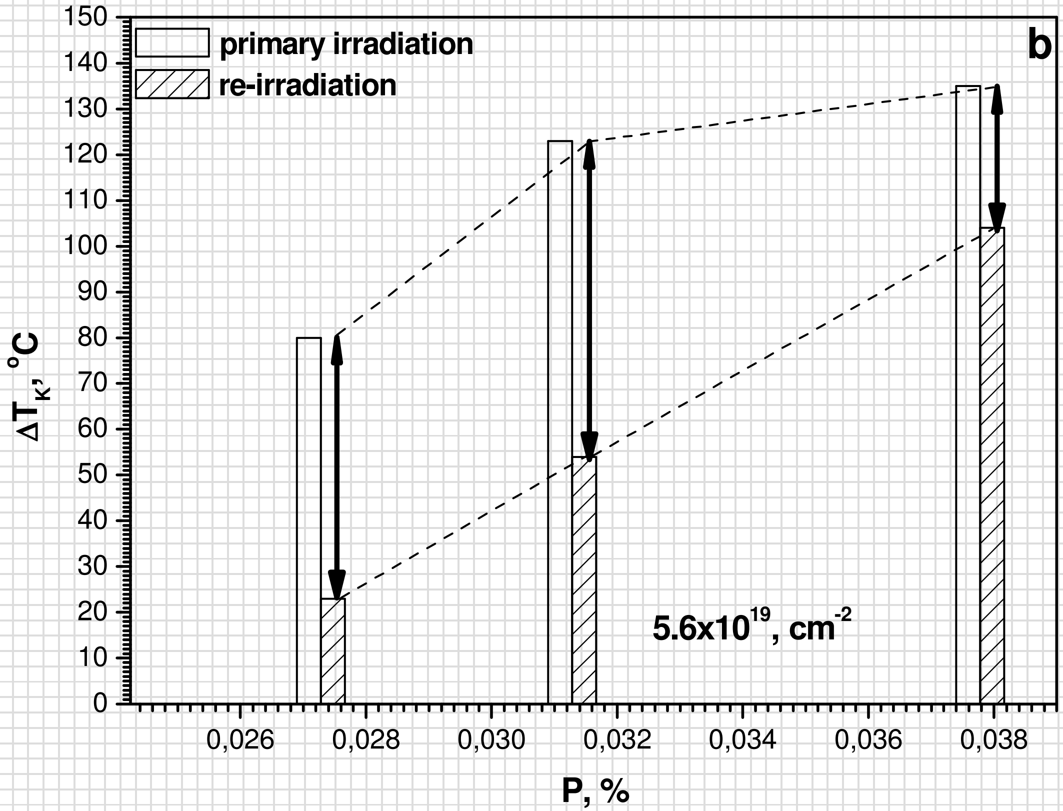
P-0.031

P-0.027

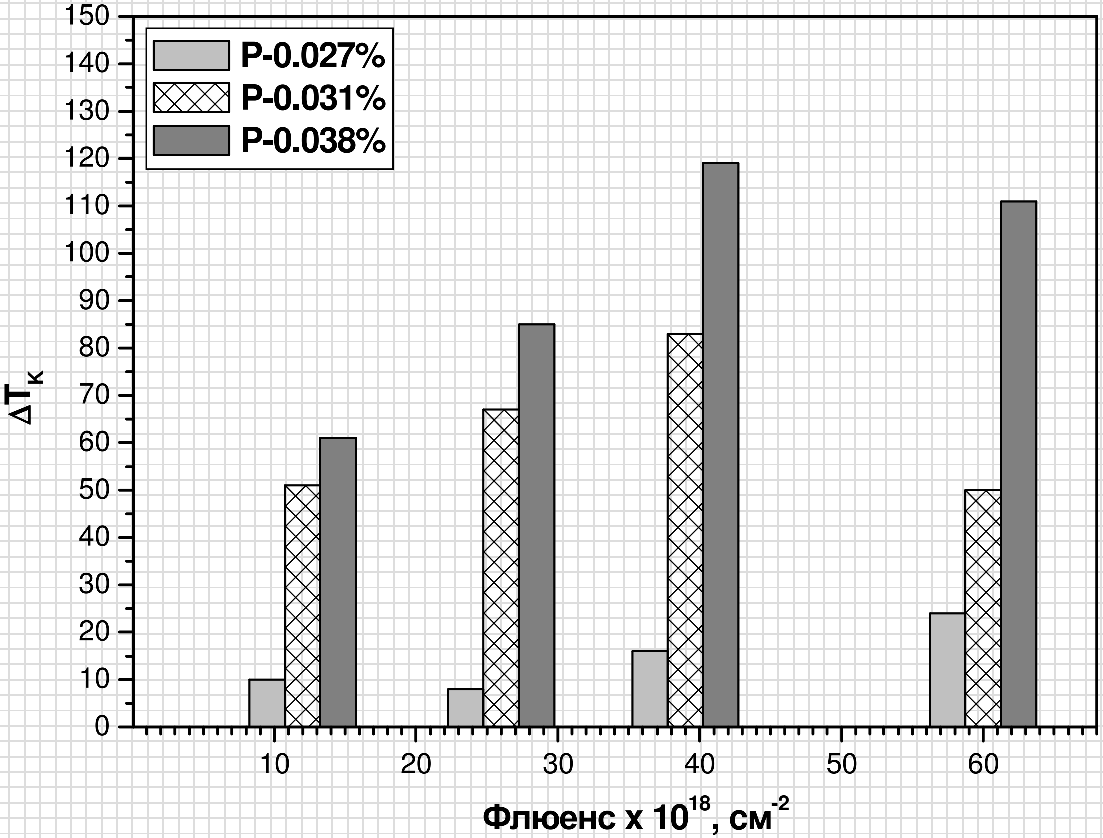
irradiation: $\Delta T_K = T_K - T_K(\text{unirr})_{10}$

re-irradiation: $\Delta T_K = T_K - T_K(\text{ann})$

Difference between embrittlement and re- embrittlement versus *P* content

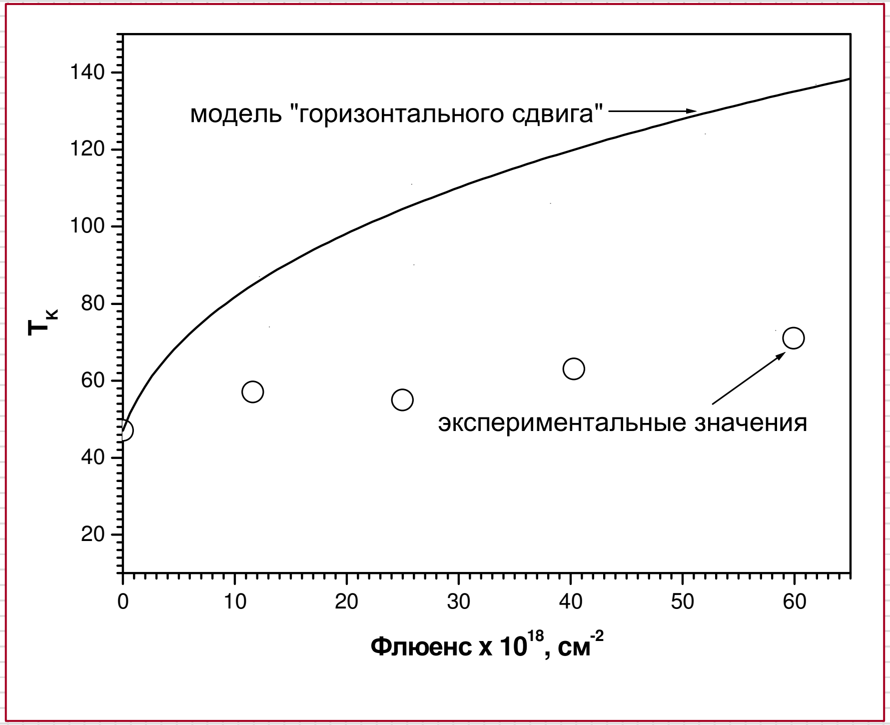


Re-embrittlement versus *fluence*

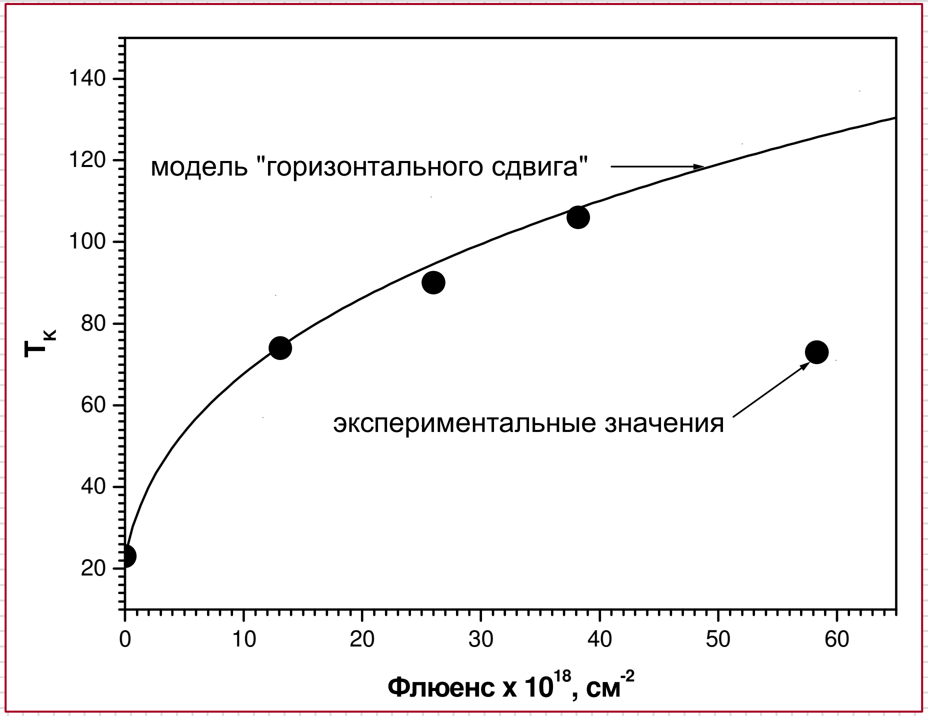


Conclusions

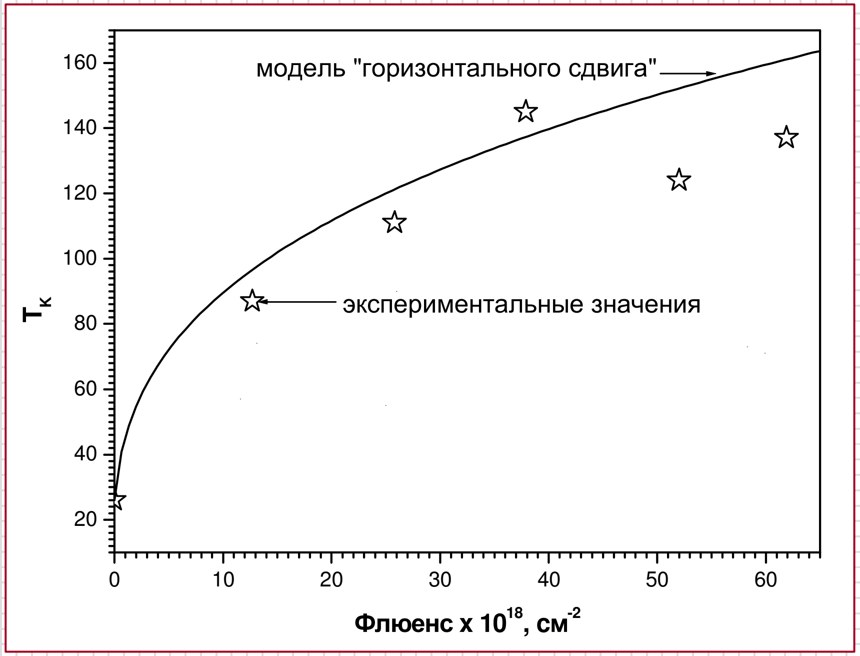
- The absolute values of strength properties and absolute values of T_K are lower at re-irradiation than at primary irradiation under comparable dose conditions
- Use of annealing allows approximately twice irradiation dose extension for reaching some fixed value as compared to irradiation without annealing
- Rates of hardening and embrittlement under re-irradiation are lower, than under primary irradiation. This effect is the largest for the weld with phosphorus content 0.027 % and it is minimum for the weld with phosphorus content 0.038%



модель "горизонтального сдвига"
экспериментальные значения
Tк
Флюенс x 10^{18}, см$^{-2}$



модель "горизонтального сдвига"
экспериментальные значения
Tк
Флюенс x 10^{18}, см$^{-2}$



модель "горизонтального сдвига"
экспериментальные значения
Tк
Флюенс x 10^{18}, см$^{-2}$

Annex 6: Rogozkin’s presentation on APT results

FINE STRUCTURE INVESTIGATION OF VVER-440 REACTOR PRESSURE VESSEL WELD AFTER IRRADIATION, ANNEALING AND RE-IRRADIATION

S. Rogozkin[1], A. Chernobaeva[2], A. Aleev[1], A. Nikitin[1], A. Zaluzhnyi[1], D. Erak[2], Ya. Shtrombakh[2], O. Zabusov[2], L. Debarberis[3], A. Zeman[3]

[1] Institute for Theoretical and Experimental Physics, Moscow, Russia
[2] Kurchatov Institute, Moscow, Russia
[3] Institute for Energy – Joint Research Centre, Petten, The Netherlands

PRIMAVERA Seminar, March 14-15, 2011, JRC-IE Petten

Contents

- Introduction
- Tomographic atom probe (TAP) study of “Primavera” weld metal with high phosphorus concentration in irradiated, annealed and re-irradiated states
- Comparison between our TAP results for Primavera samples and other TAP results for Novovoronezh-3 NPP
- Conclusions

Radiation embrittlement of the pressure vessels is a key issue for plant lifetime assessment

Ductile-to-brittle transition temperature shift

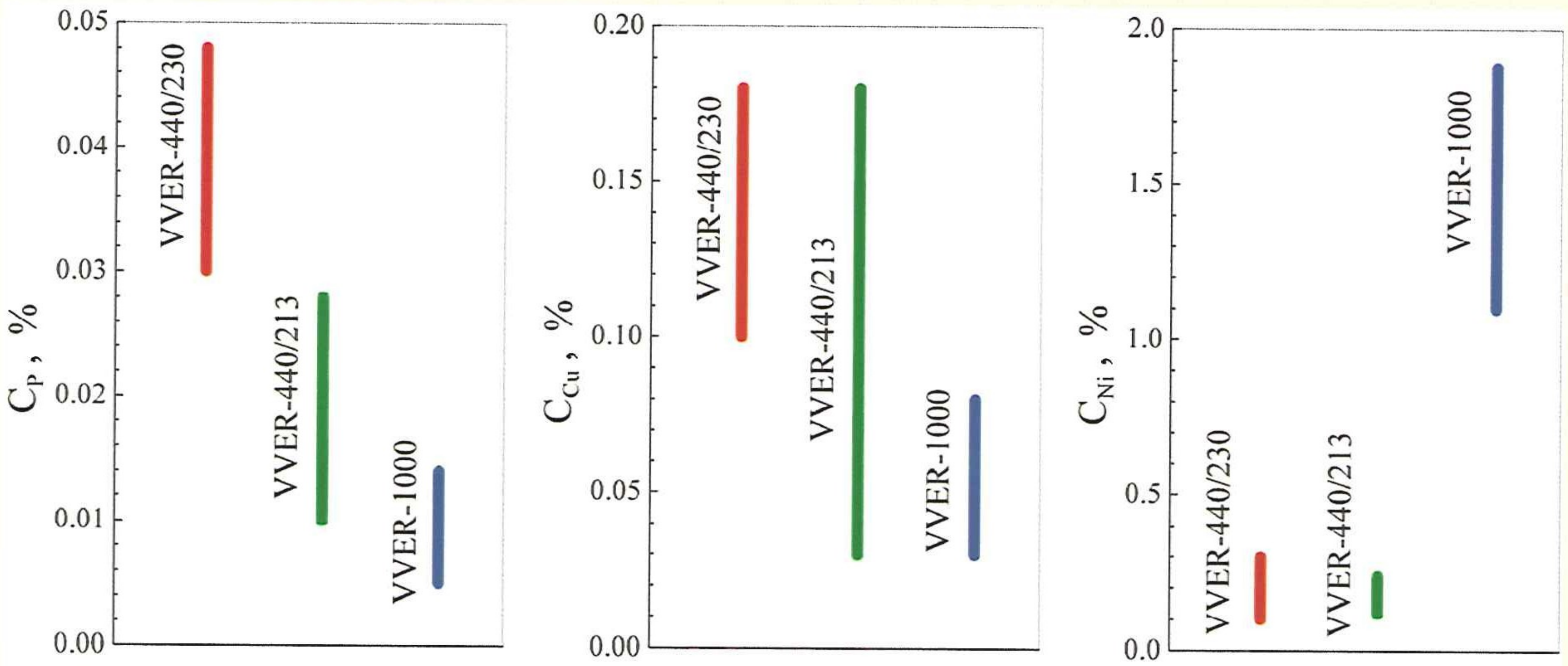
$\Delta T_K(F)$ - !

The guide foresees for VVER-440 RPV

$$\Delta T_K = 800\left(\mathrm{P} + 0.07\mathrm{Cu}\right) F^{1/3}$$

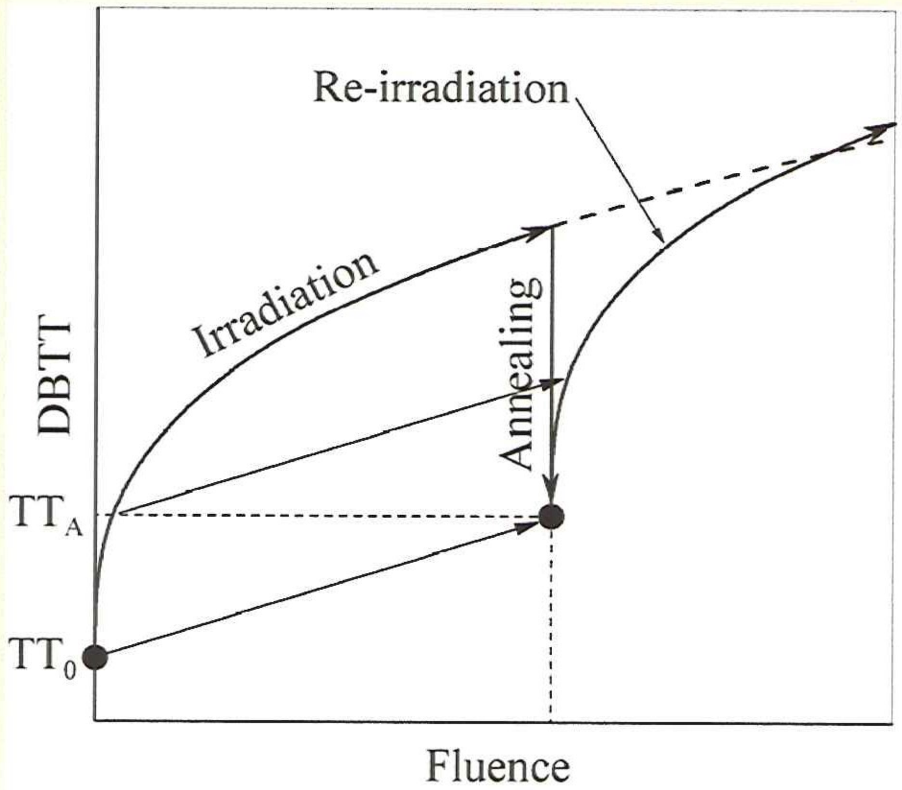
Radiation embrittlement of VVER-440 RPV steels depends mainly on P and Cu contents

P and Cu contents in RPV steels of the First VVER Generation are relatively high

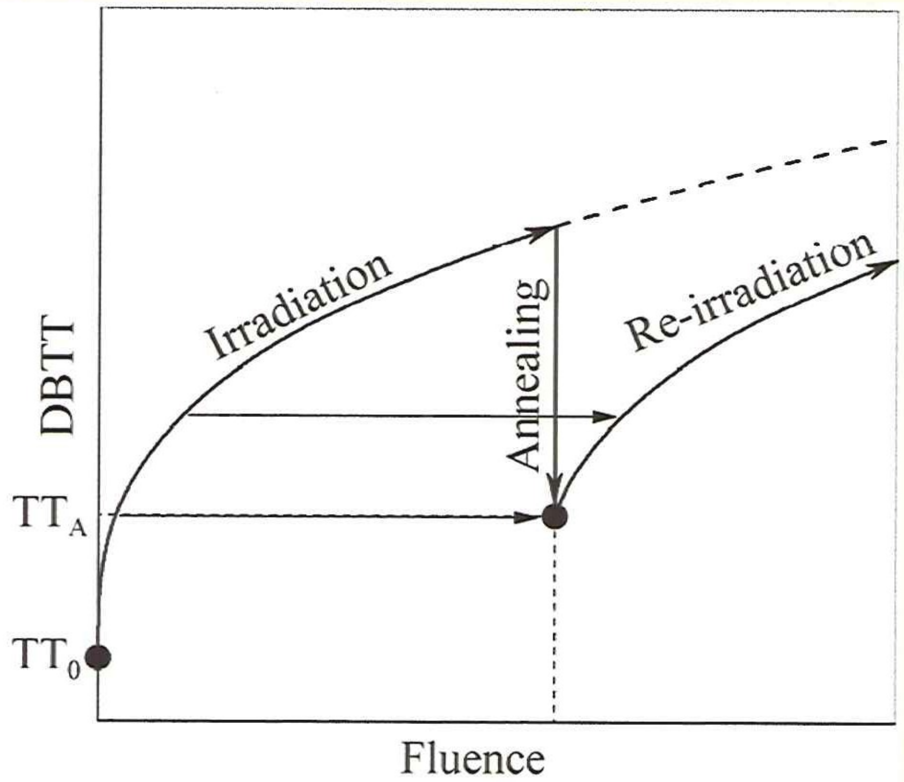


Models for re-irradiation embrittlement evaluation

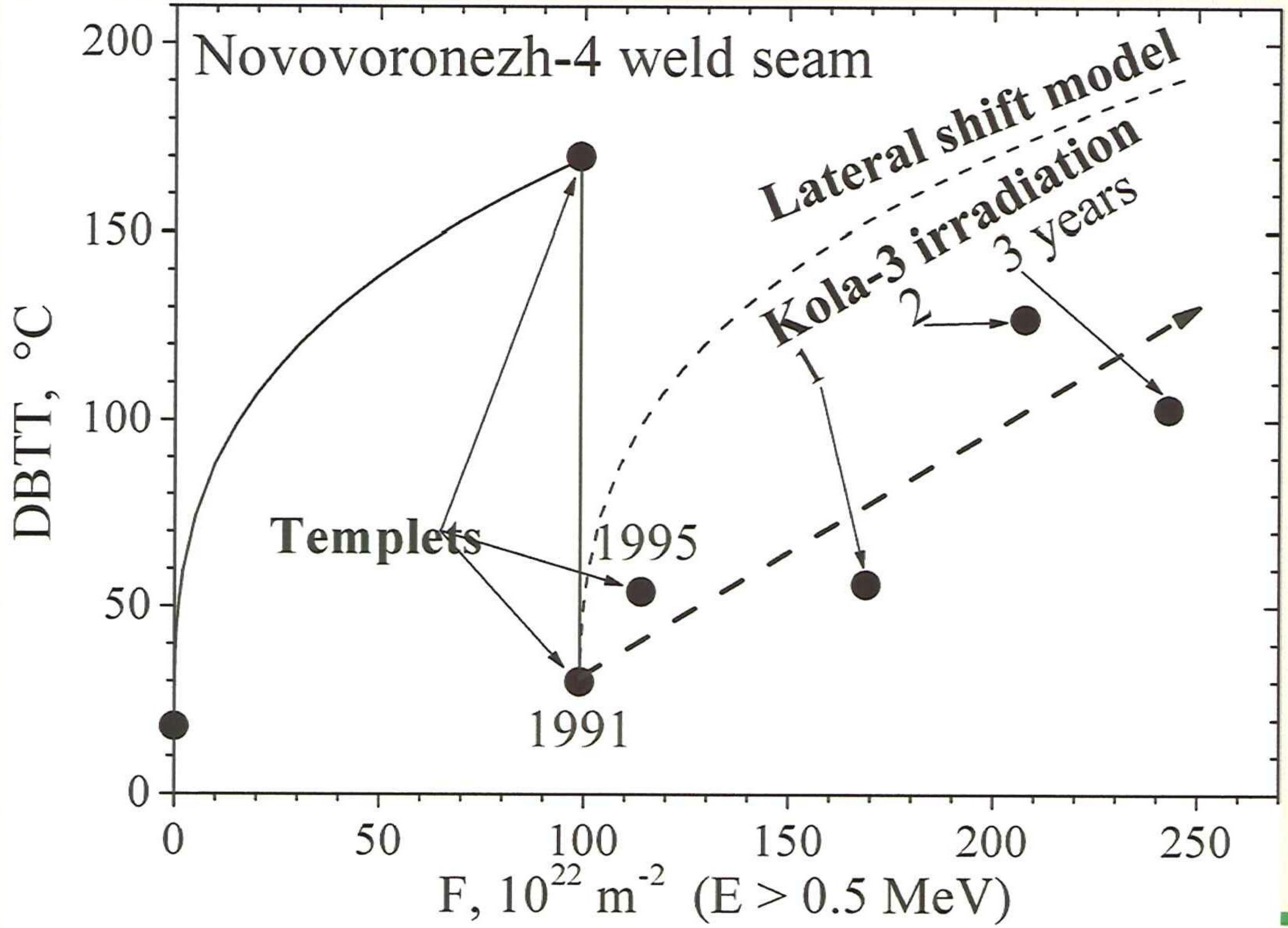
Conservative scheme



Lateral shift model



Novovoronezh-4 templets in as-received, annealed and re-irradiated in VVER-440/213 surveillance channels



Project "PRIMAVERA"

Developing a physically validated prediction model for $\Delta T_K(F)$ of VVER-440 weld metals after reactor pressure vessel annealing

RRC «Kurchatov Institute» (Russia), JRC (The Netherlands), Fortum, VTT (Finland) and ISM (Bulgaria) participate in this project. Tomographic atom probe study was carried out in Institute for Theoretical and Experimental Physics (Russia)

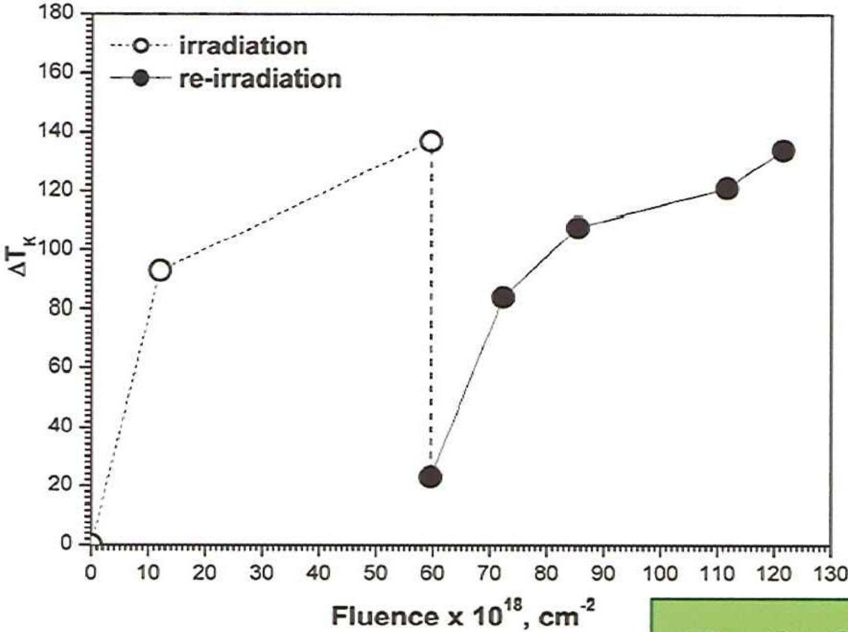
MATERIALS

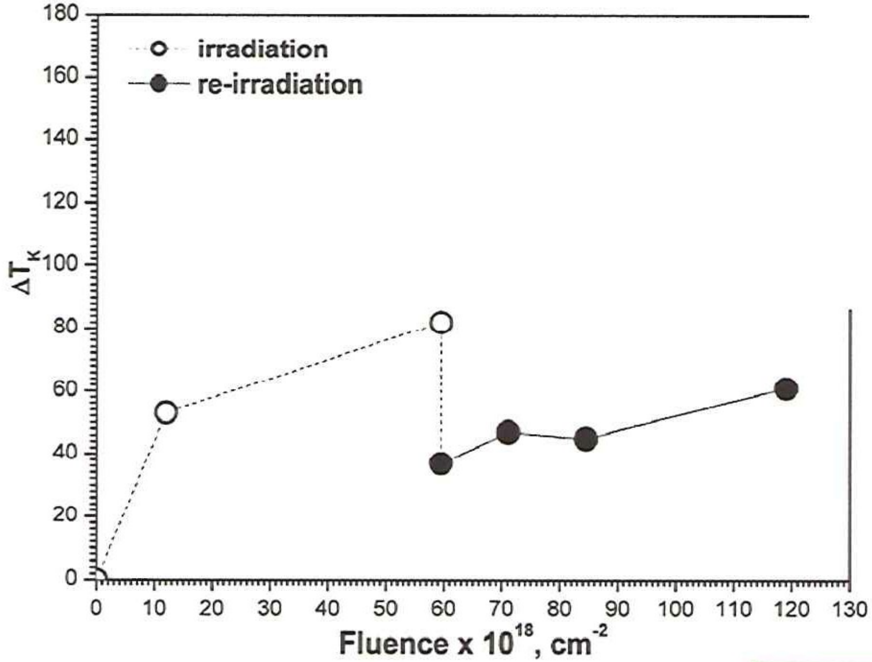
- The weld 501, produced in accordance with the standard technology for the first generation of VVER-440 by “Izhora” plant, was used in this study.
- The range of phosphorus contents in this weld is 0.025-0.040 wt.%.
- The materials studied in this work are the layers of weld 501 with high phosphorus concentration.

BULK COMPOSITIONS OF VVER-440 WELD MATERIALS WITH HIGH (HP) PHOSPHOROUS CONCENTRATION

	C	Si	Mn	**P**	S	Cr	Ni	Mo	**Cu**	V
HP (wt%)	0.05	0.36	1.09	**0.038**	0.014	1.54	0.13	0.51	**0.16**	0.19
HP (at%)	0.23	0.72	1.10	**0.068**	0.024	1.65	0.12	0.30	**0.14**	0.21

THE VALUES OF ΔT_K FOR IRRADIATED, ANNEALED AND RE-IRRADIATED WELDS VERSUS FLUENCE

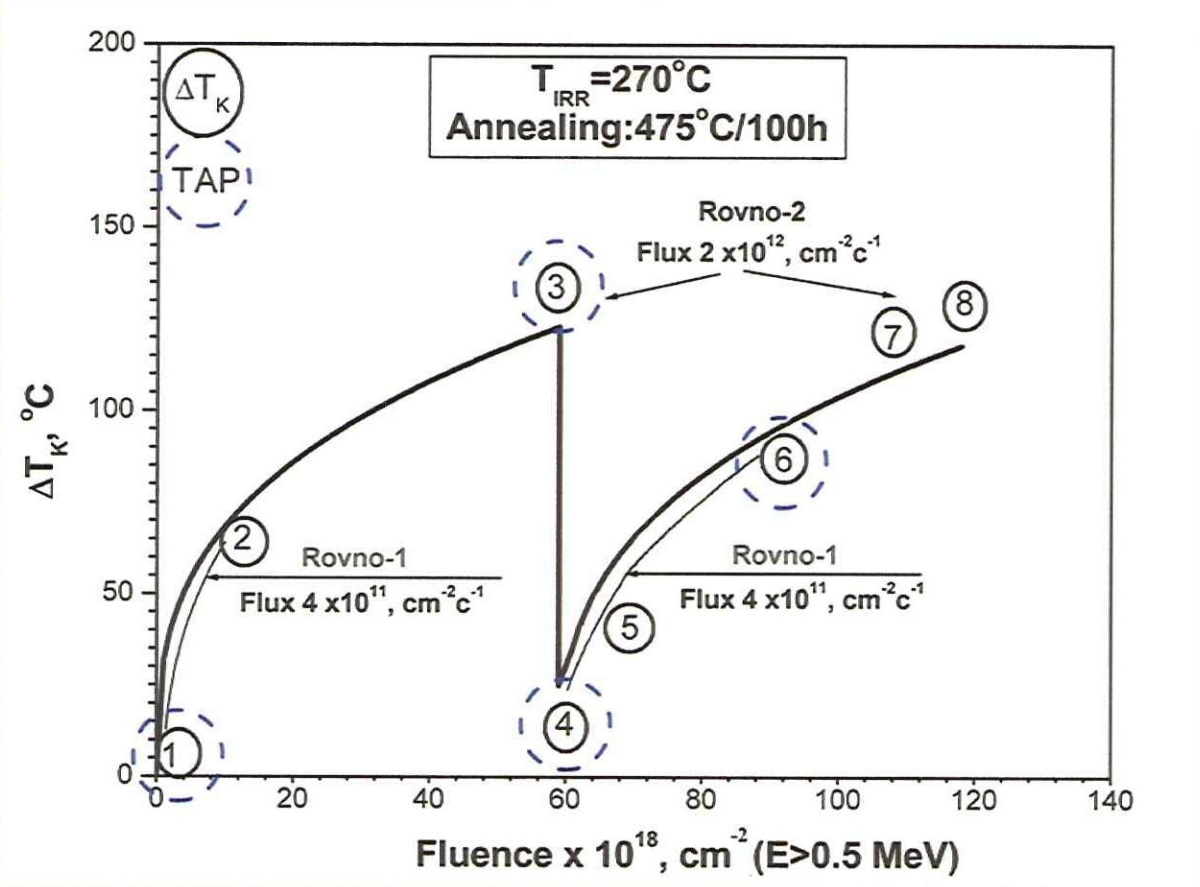




P-0.038

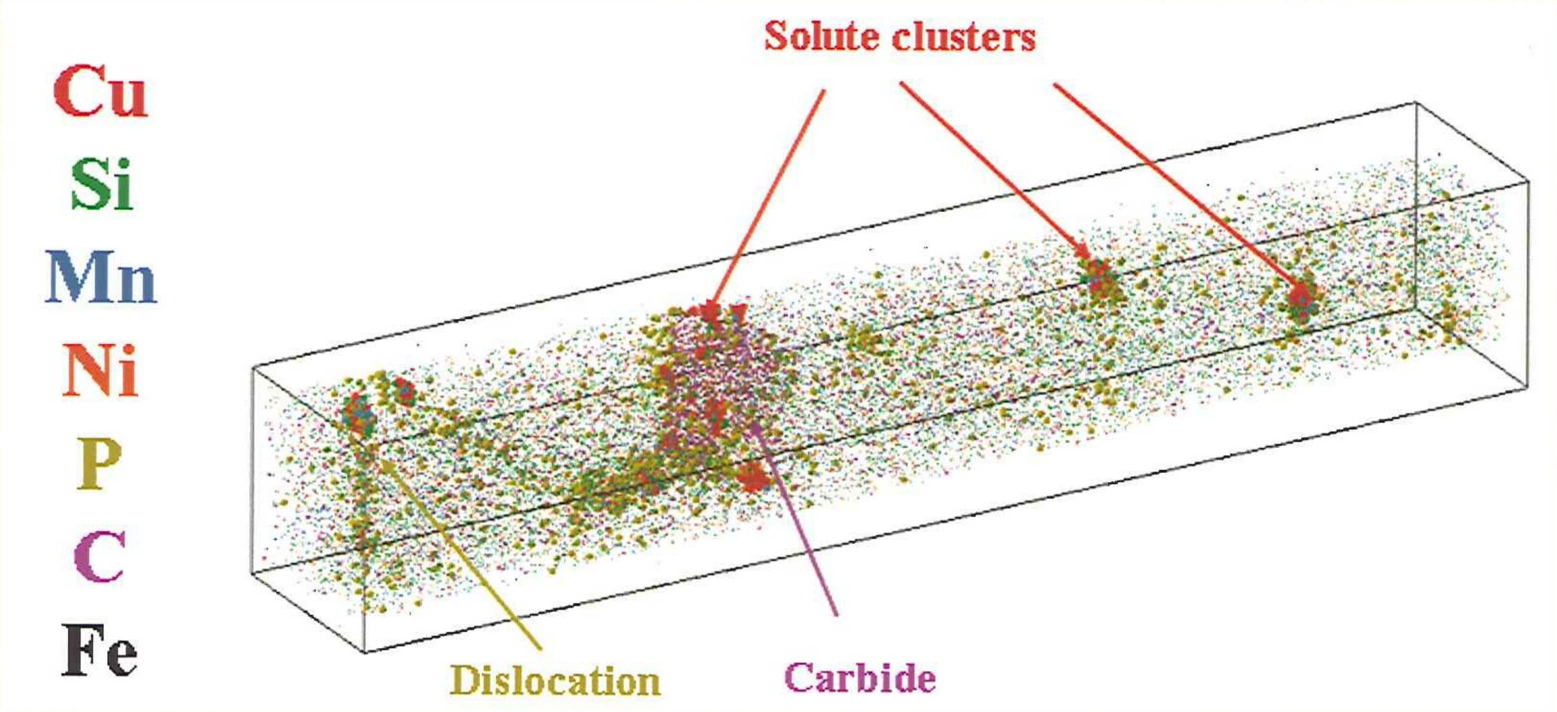
P-0.027

THE EXPERIMENT DESIGN ON THE DEPENDENCE OF DUCTILE-TO-BRITTLE TRANSITION TEMPERATURE SHIFT VERSUS NEUTRON FLUENCE



States under TAP investigation (blue dashed circles)

TOMOGRAPHIC ATOM PROBE STUDY OF THE VVER-440 WELD METAL

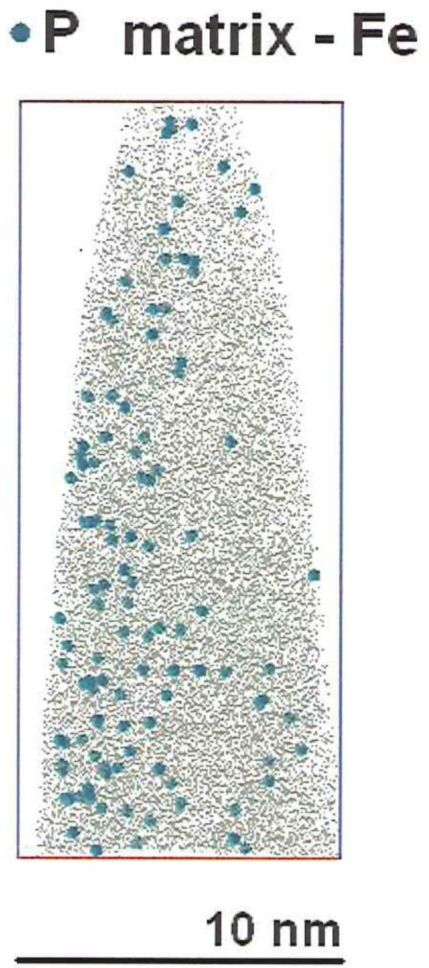


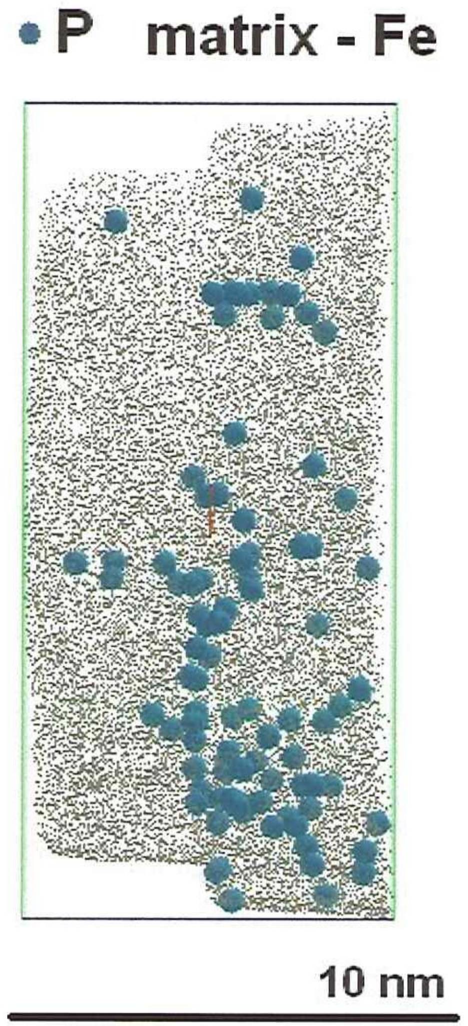
Reconstructed volume ~$10 \times 10 \times 100$ nm^3

TAP characterization of unirradiated weld metal

- Nanosize features were not detected by TAP,
- There is V and C depletion in the matrix,
- Significant inhomogeneous phosphorus distribution was found.

Atom maps of unirradiated weld metal



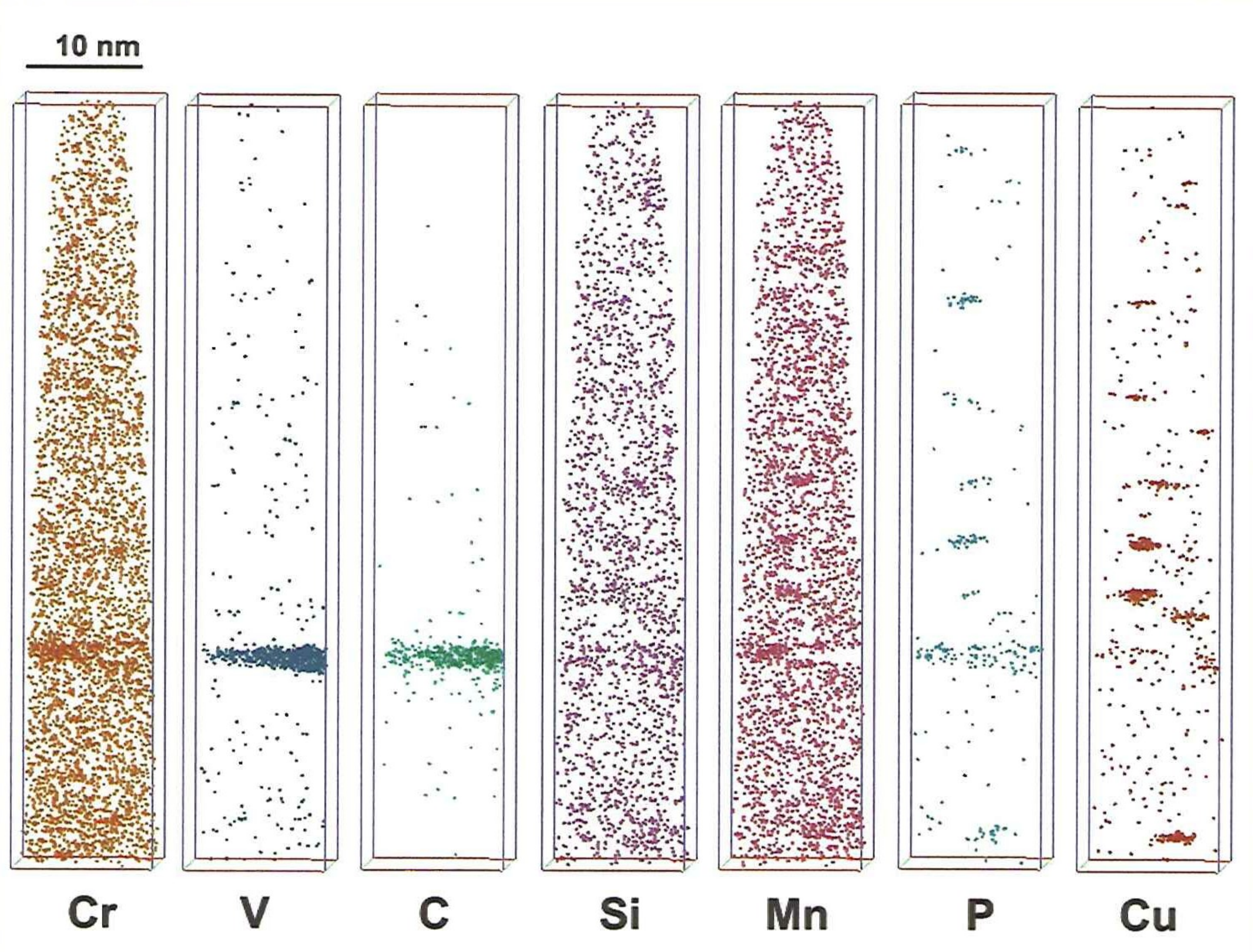


Weld irradiated up to 59.5×10^{18} n/cm^2

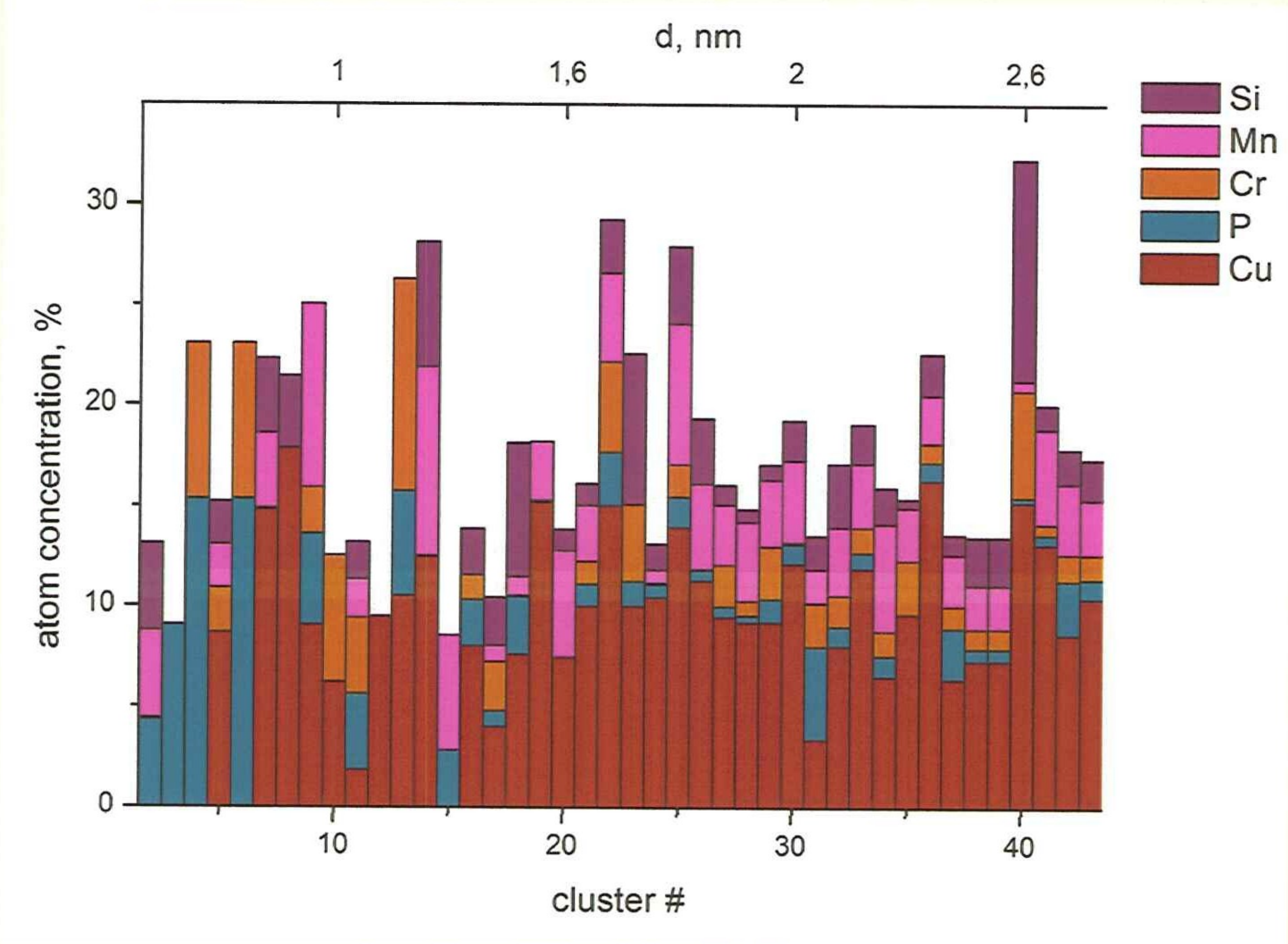
Four types of nanoscale structure features were found:

- nanoclusters enriched in copper atoms (Cu-clusters);
- fine clusters mainly enriched in phosphorus atoms (P-clusters);
- small V-C enriched clusters (carbide clusters);
- V disc carbides.

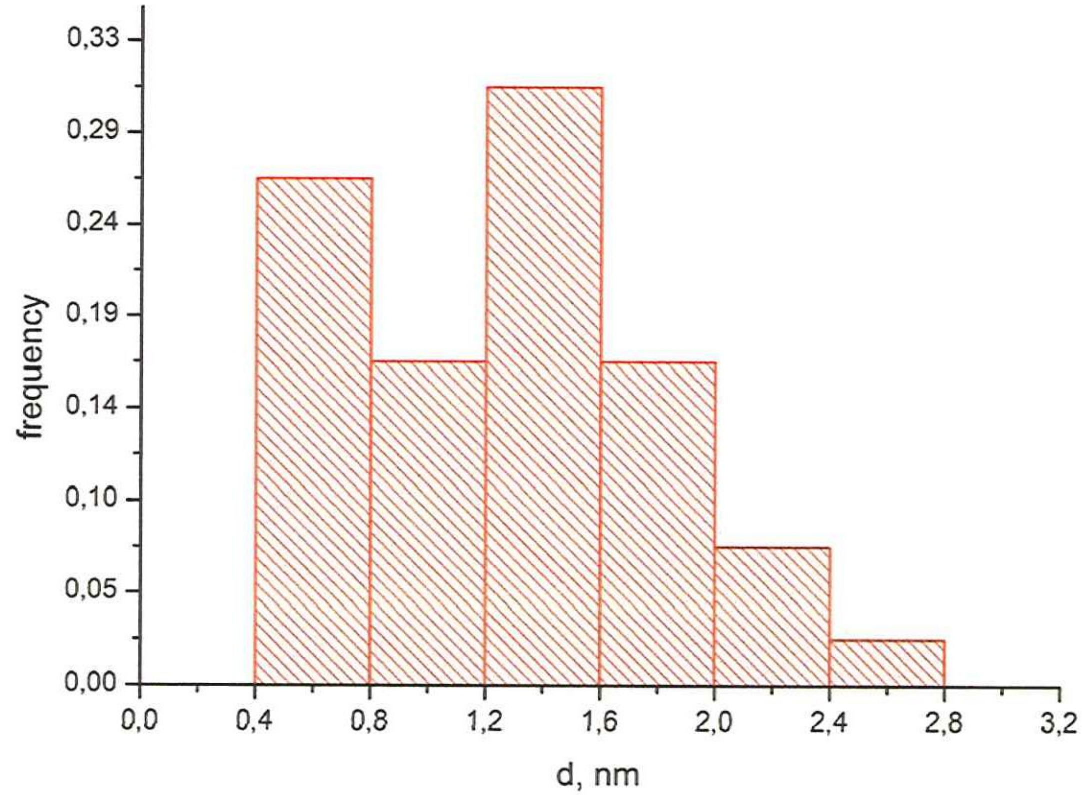
Atom maps for irradiated weld metal



Composition of Cu-P clusters in irradiated weld

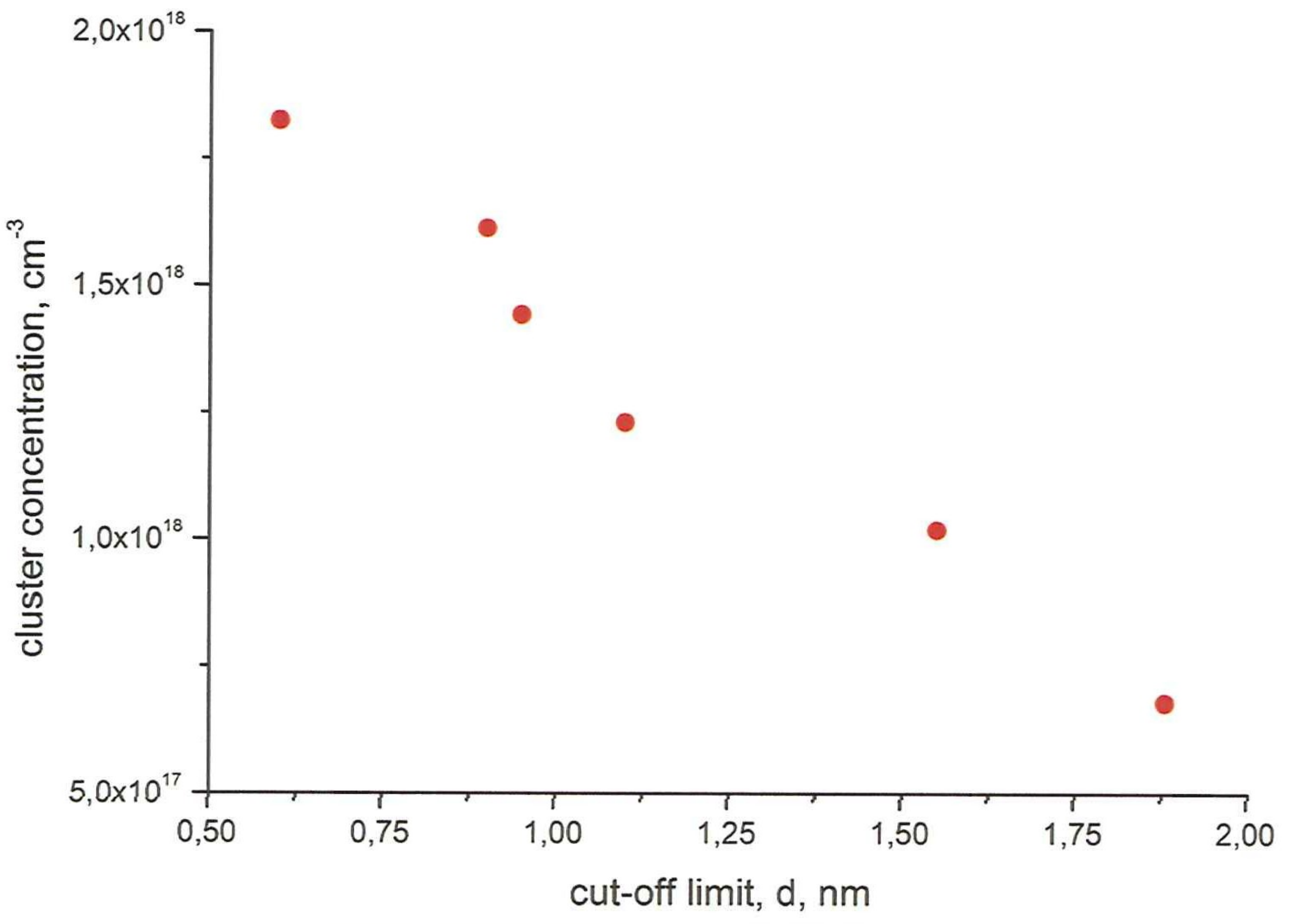


Size distribution of Cu-P clusters in irradiated weld

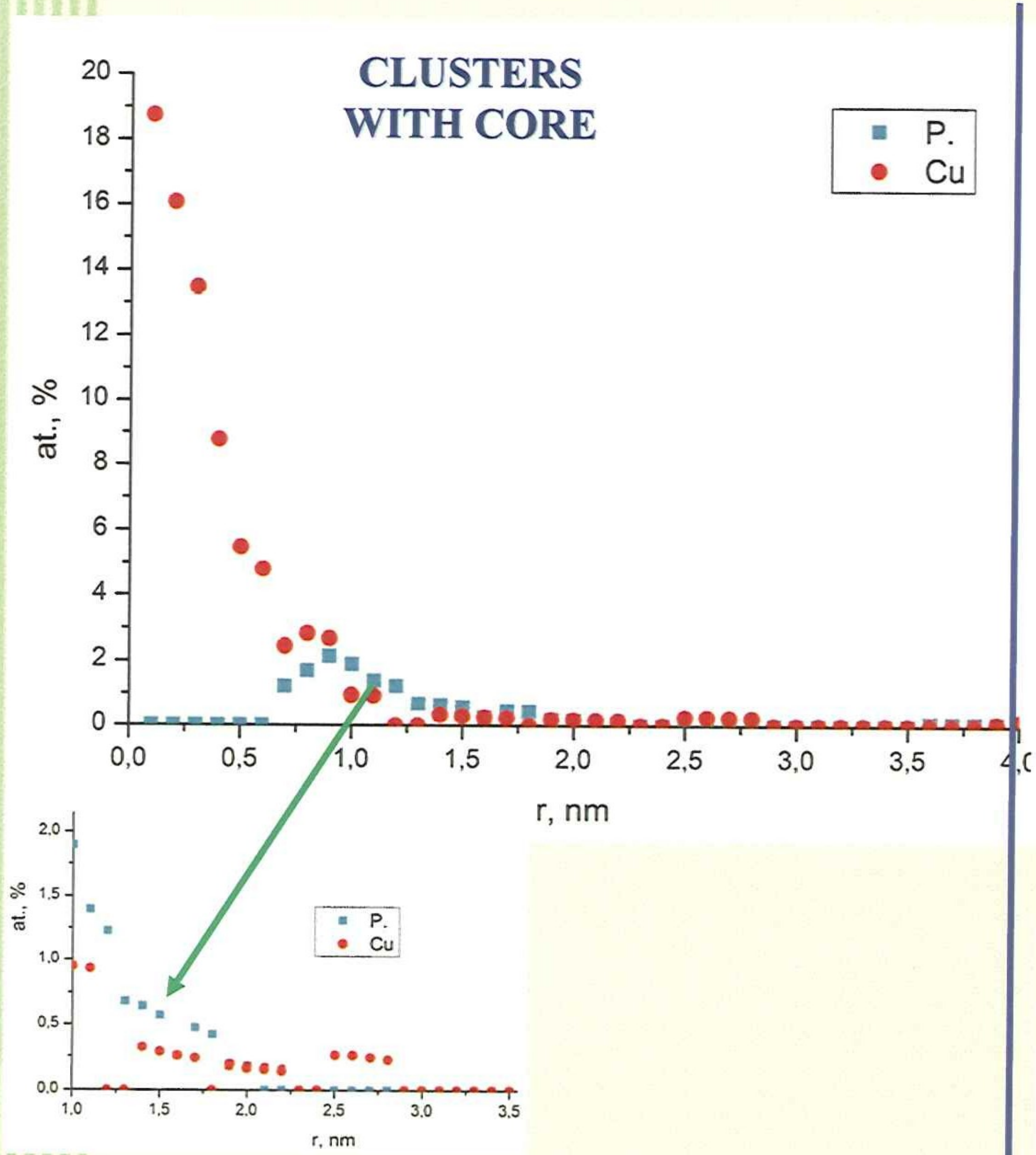


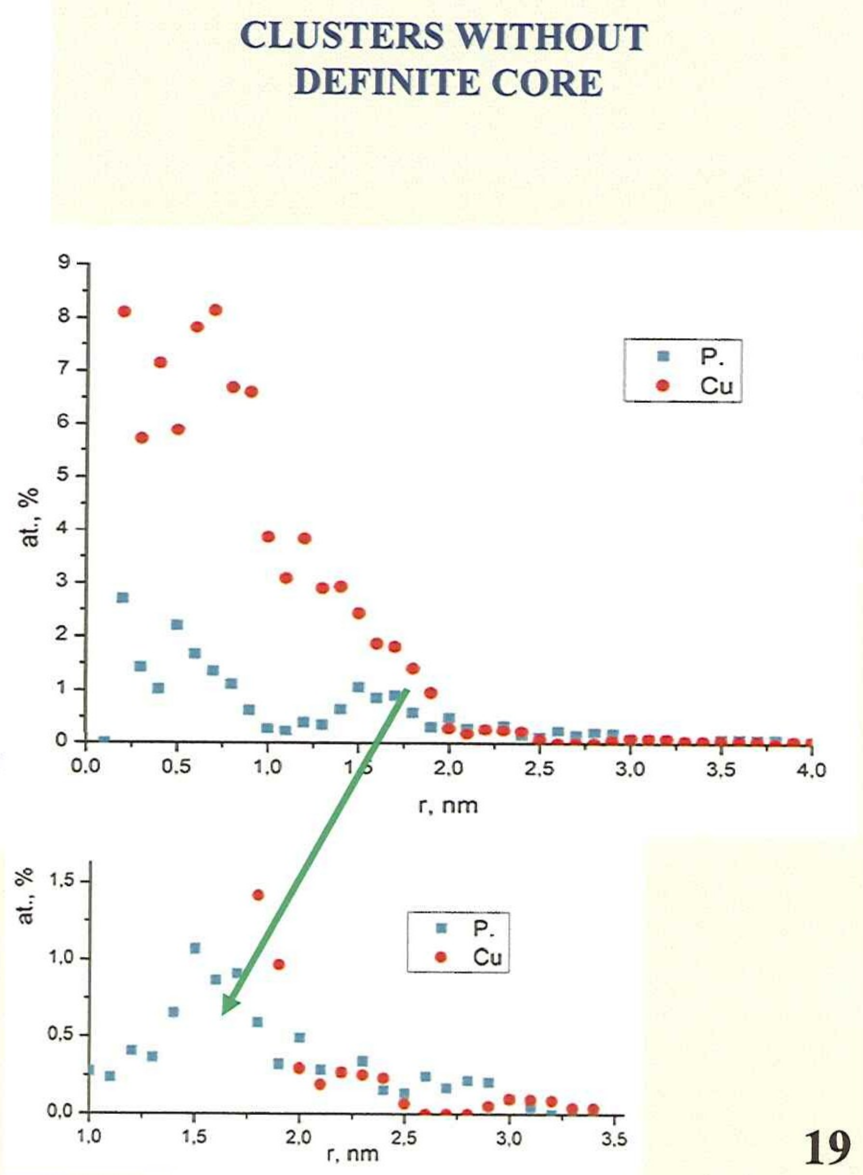
Cluster sizes are 0.5-2.5 nm,
number density is about $(1 \div 2) \times 10^{18}$ cm^{-3}.

Cluster number density as function of minimal size taken into account

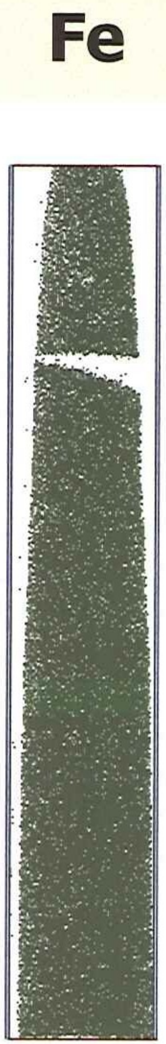


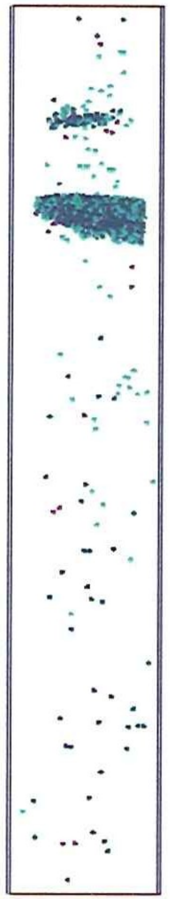
RADIAL CONCENTRATION DISTRIBUTION OF TWO DIFFERENT COPPER ENRICHED CLUSTERS

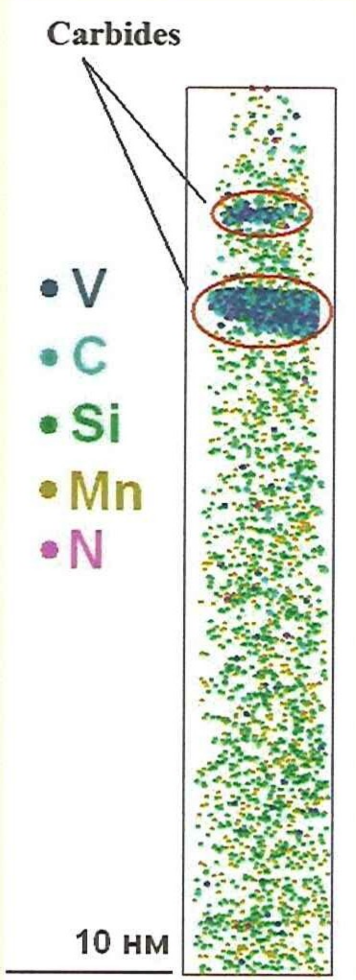




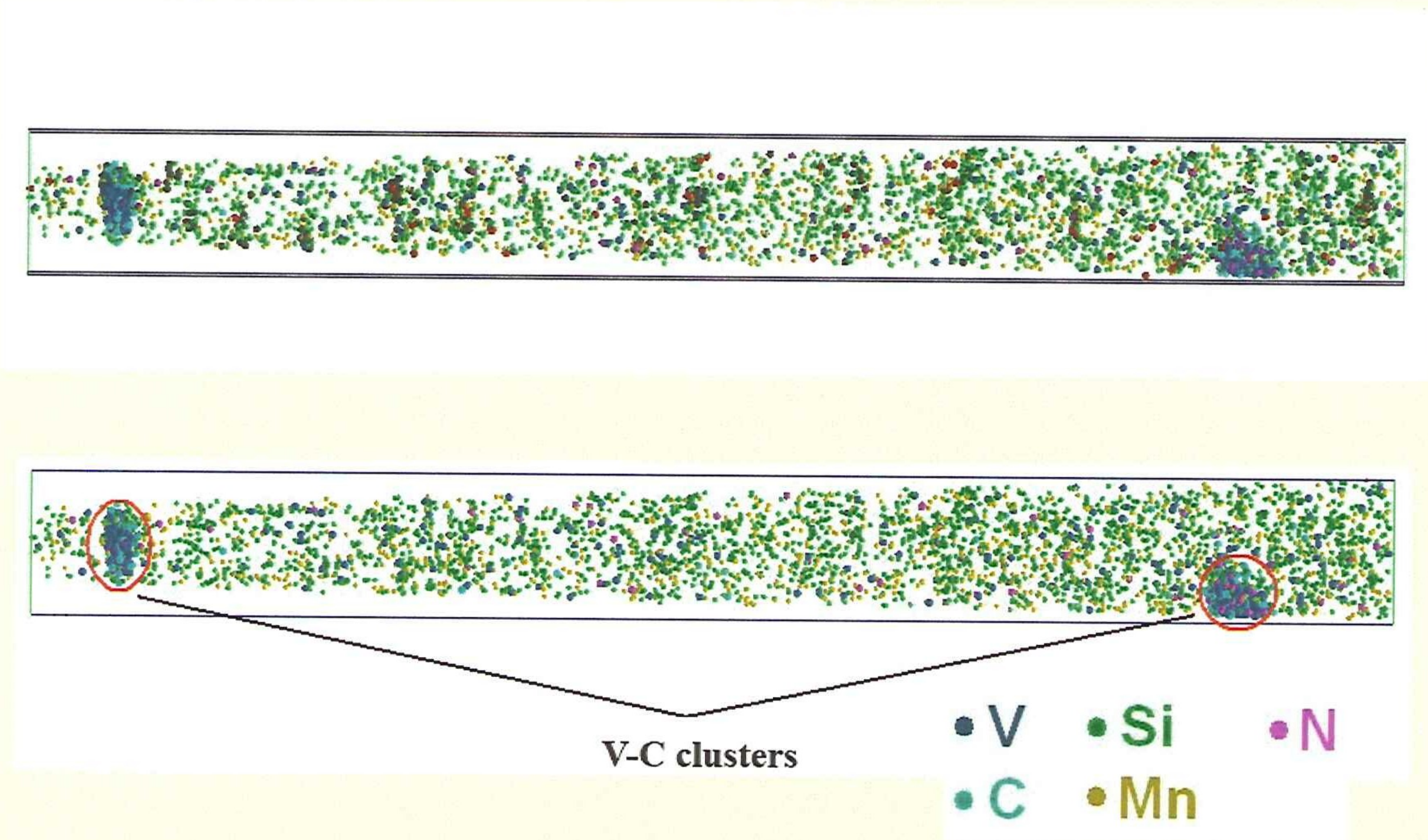
Reconstructed volume of irradiated weld







Reconstructed volume of irradiated weld



ELEMENT CONCENTRATIONS IN INVESTIGATED VOLUMES

at.%	Cr	V	Mn	C	Si	P	Cu	Ni	Mo	N	S
bulk	1,65	0,21	1,10	0,23	0,72	0,068	0,14	0,12	0,30	-	0,024
Irradiated, average concentration	1,62	0,20	1,03	0,10	0,75	0,055	0,134	0,11	0,24	0,007	-
Irradiated, matrix concentration	1,62	0,19	1,02	0,09	0,74	0,048	0,086	0,11	0,25	0,007	-

TAP study of the annealed weld

Irradiated up to 57.1×10^{18} n/cm^2 and annealed (475°C, 150 h)

- **no clusters were found,**
- **P contents increase during annealing.**

Chemical composition of investigated volumes

at.%	Cr	V	Mn	C	Si	P	Cu	Ni	Mo	N	S
bulk	1,65	0,21	1,10	0,23	0,72	0,068	0,14	0,12	0,30	-	0,024
Irradiated, average concentration	1,62	0,20	1,03	0,10	0,75	0,055	0,134	0,11	0,24	0,007	-
Irradiated, matrix concentration	1,62	0,19	1,02	0,09	0,74	0,048	0,086	0,11	0,25	0,007	-
Annealed	1,69	0,10	0,99	0,06	0,61	0,07	0,10	0,10	0,24	0,02	-

TEM study*: pure-copper precipitates with low number density ($\leq 10^{16}$ cm^{-3}) were observed

*Gurovich, Kuleshova, Shtrombakh, Zabusov, Krasikov, JNM, 279 (2000) 259-272)

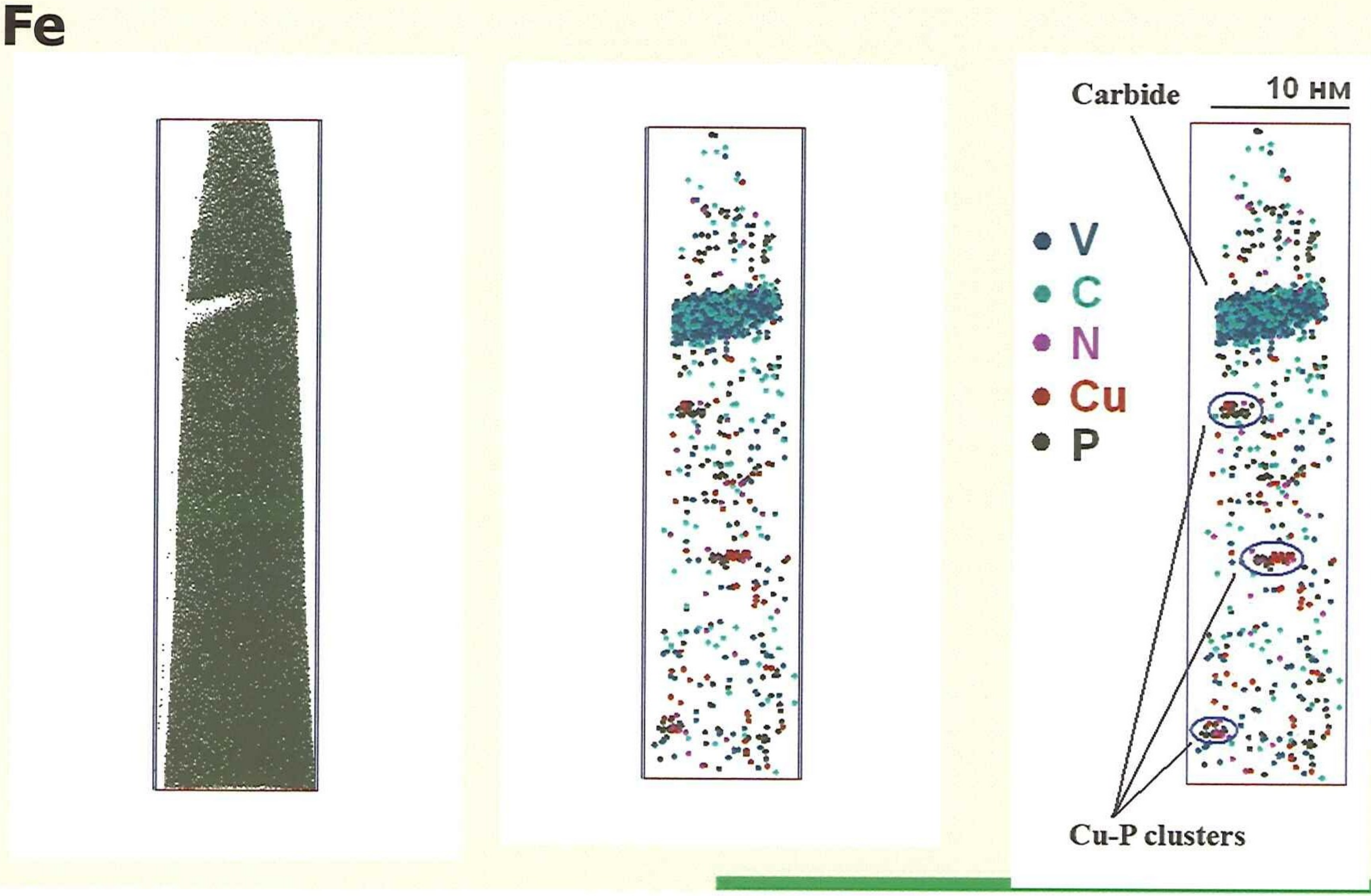
TAP study of the re-irradiated weld

Irradiated up to 57.1×10^{18} n/cm^2, annealed and irradiated up to 25.8×10^{18} n/cm^2

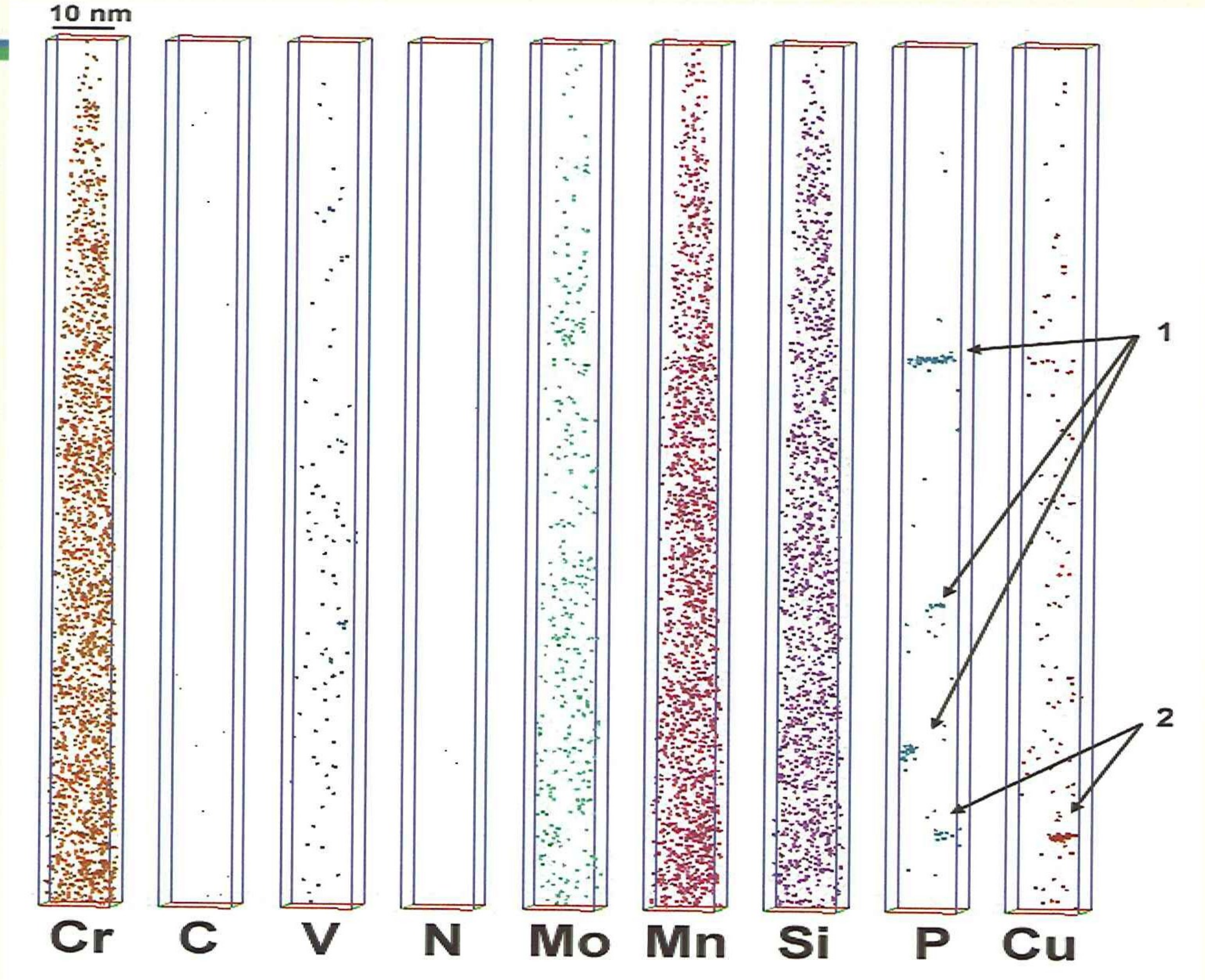
Three types of nanoscale structural features have been found:

- nanoclusters enriched in copper and phosphorus atoms (Cu-P clusters);
- Cu precipitates,
- V disc carbides.

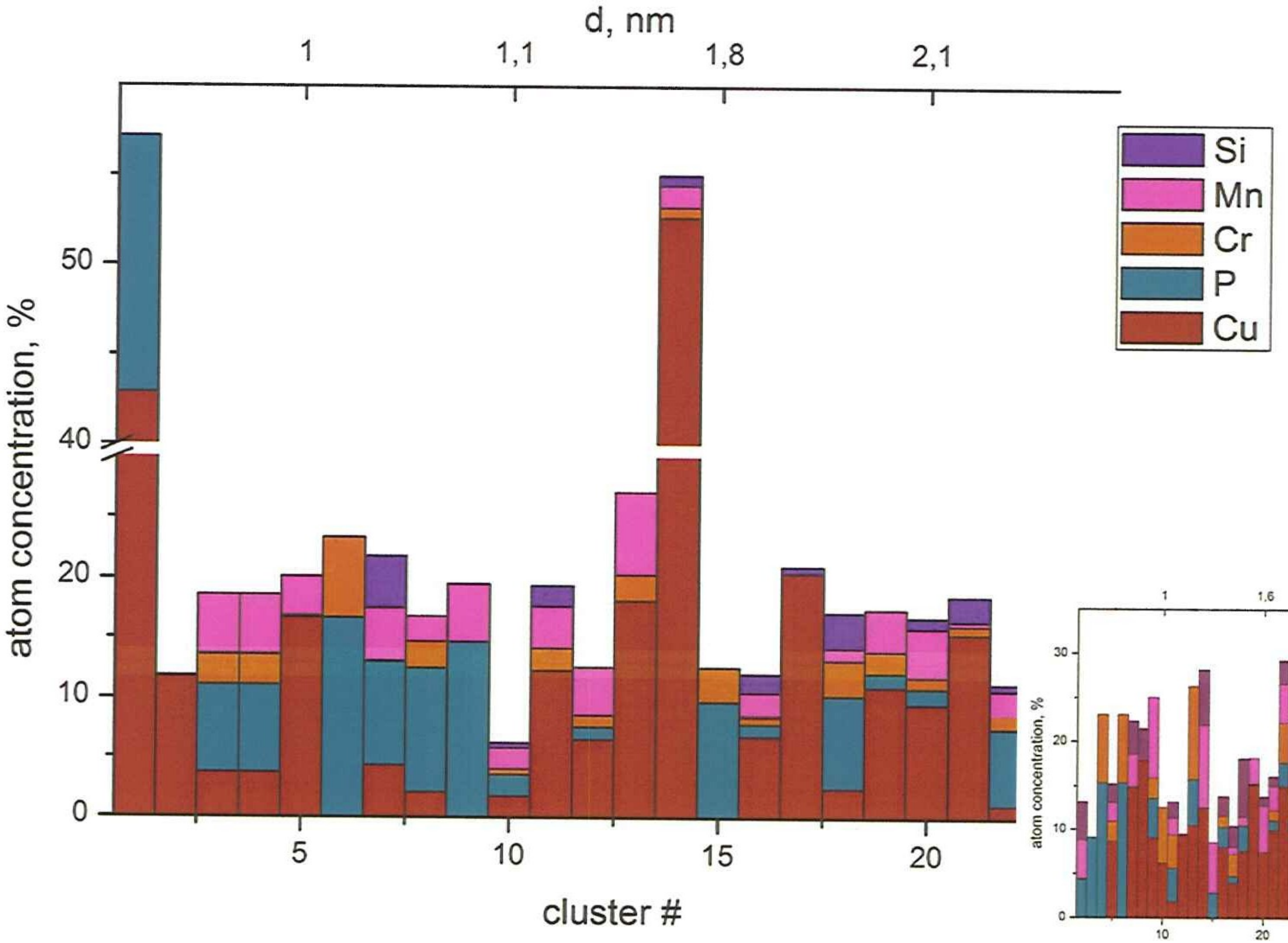
Reconstructed volume showing the results of 3D AP analyses of re-irradiated weld

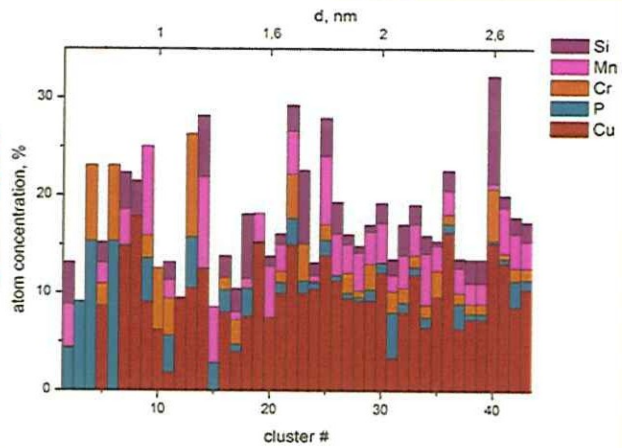


Atom maps for the re-irradiated weld

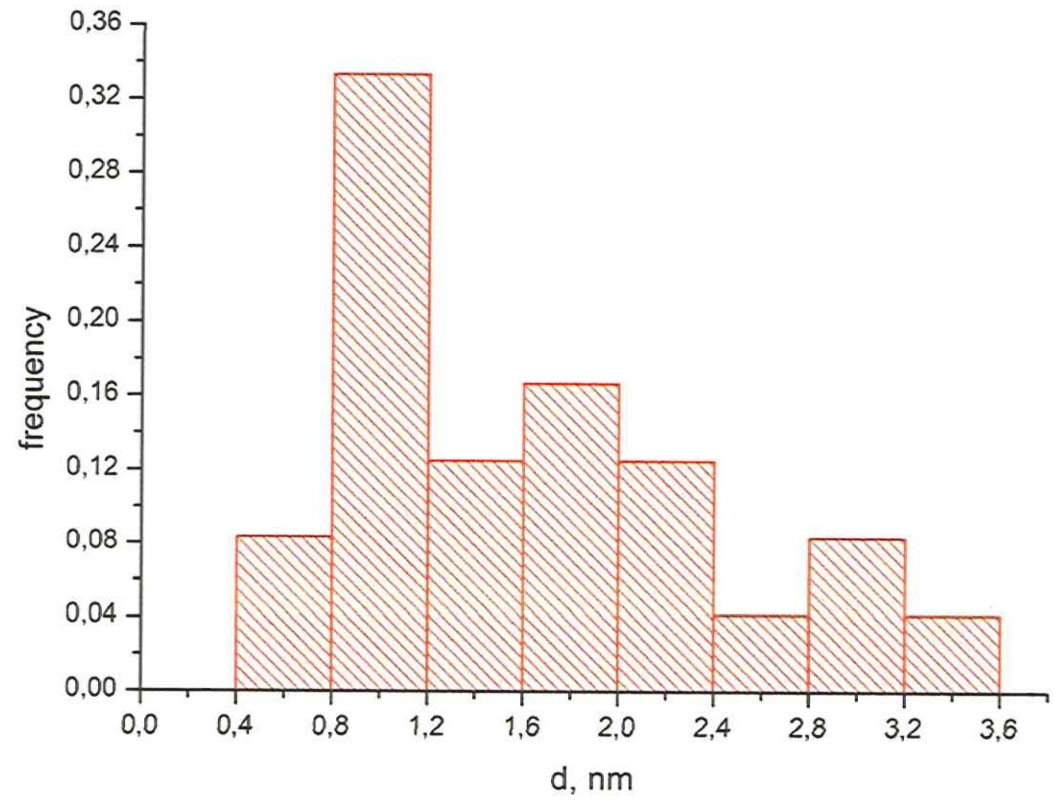


Cluster (precipitates) composition in the re-irradiated weld



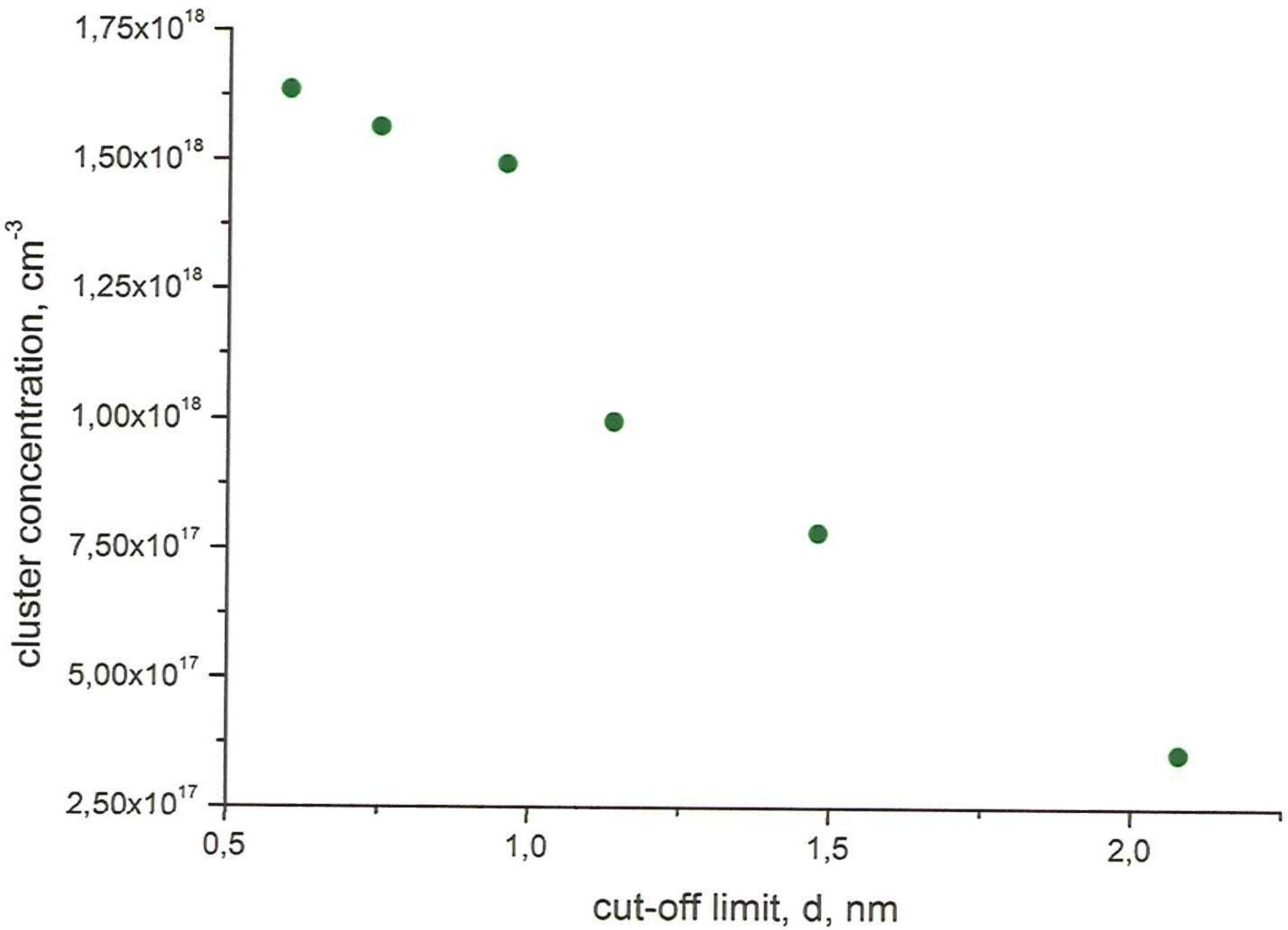


Size distribution of Cu-P clusters in re-irradiated weld



Cluster size is 1-2 nm,
number density is about $(5 \div 17) \times 10^{17}$ cm^{-3}.

Cluster number density as function of minimal size taken into account



TAP study of the re-irradiated weld

Irradiated up to 57.1×10^{18} n/cm^2, annealed and irradiated up to 25.8×10^{18} n/cm^2

Chemical composition of investigated volumes

at.%	Cr	V	Mn	C	Si	P	Cu	Ni	Mo	N	S
bulk	1,65	0,21	1,10	0,23	0,72	0,068	0,14	0,12	0,30	-	0,024
Irradiated, average concentration	1,62	0,20	1,03	0,10	0,75	0,055	0,134	0,11	0,24	0,007	-
Irradiated, matrix concentration	1,62	0,19	1,02	0,09	0,74	0,048	0,086	0,11	0,25	0,007	-
Annealed	1,69	0,10	0,99	0,06	0,61	0,073	0,10	0,10	0,24	0,02	-
Re-irradiated, average concentration	**1,66**	**0,26**	**1,04**	**0,82**	**0,66**	**0,063**	**0,14**	**0,11**	**0,24**	**0,03**	-
Re-irradiated, matrix concentration	**1,70**	**0,15**	**1,08**	**0,14**	**0,66**	**0,061**	**0,11**	**0,11**	**0,24**	**0,03**	-

Comparison of TAP results for the "Primavera" weld and trepanned samples from RPV weld

wt%	C	Si	Mn	P	S	Cr	Ni	Mo	Cu	V
trepanned material Novovoronezh-4	0.04	0.38	0.97	0.029	0.022	1.49	0.24	0.46	0.16	0.14
HP (this study)	0.05	0.36	1.09	0.038	0.014	1.54	0.13	0.51	0.16	0.19

*P. Pareige B. Radiguet, A. Suvorov, M. Kozodaev, E. Krasikov, O. Zabusov, J.P. Massoud, Surface and Interface Analysis, 2004, 36(5/6), 581-584

*P. Pareige, B. Radiguet, R. Krummeich-Brangier, A. Barbu, O. Zabusov, M. Kozodaev, Philosophical Magazine, Vol. 85, Nos. 4–7, 2005, 429–441

Comparison of irradiation parameters

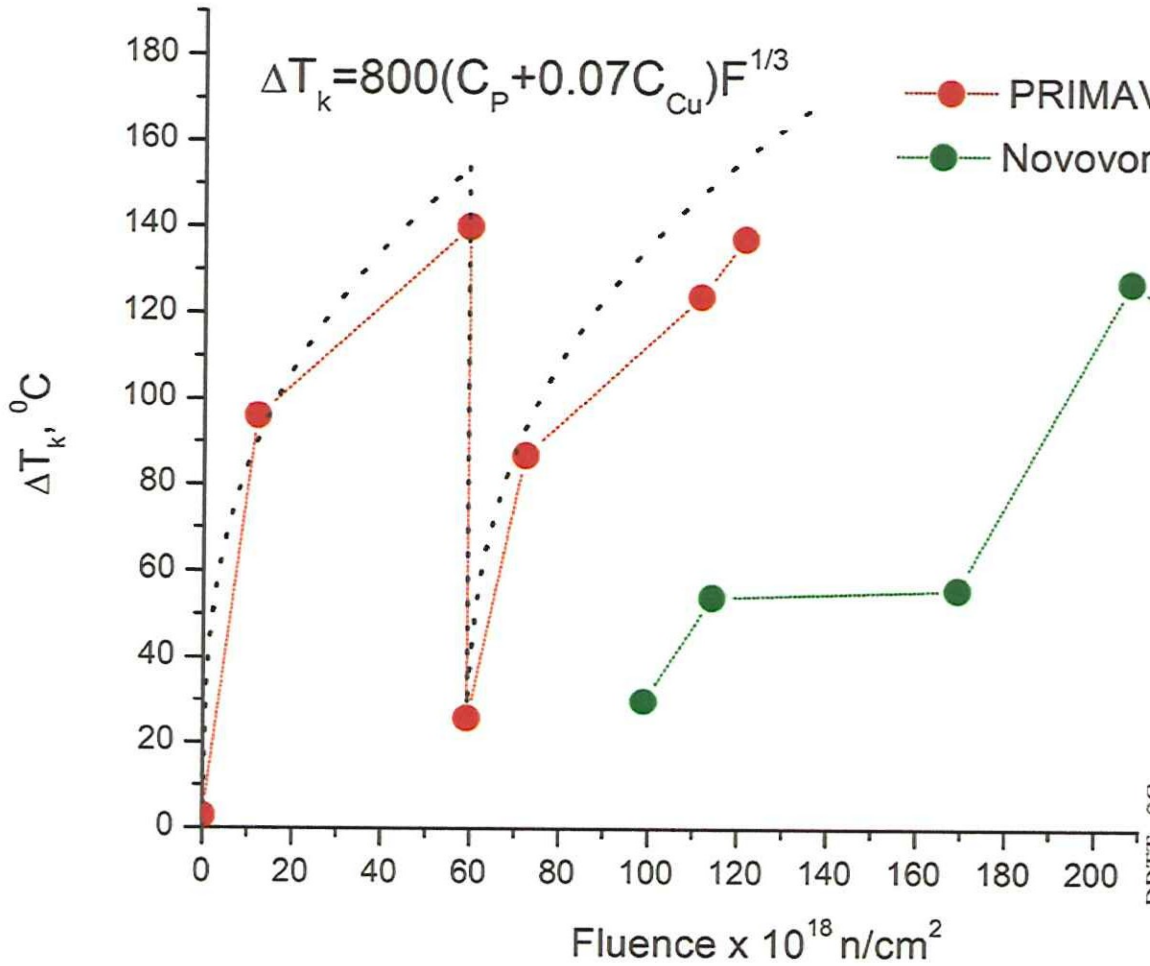
Irradiation parameters

	Fluence	Flux	Irradiation T
Primavera	5.9×10^{23} m^{-2}	2×10^{16} m^{-2} s^{-1}	270°C
Novovoronezh-4 NPP	9.7×10^{23} m^{-2}	1.5×10^{15} m^{-2} s^{-1}	270°C

Re-irradiation parameters (irradiation after recovering annealing)

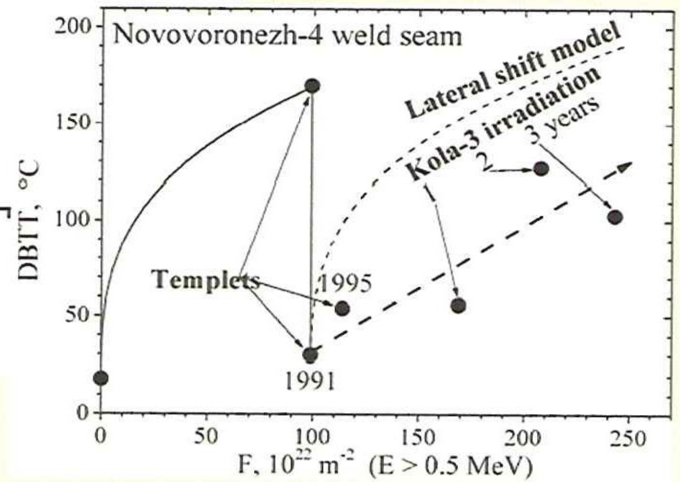
	Fluence	Flux	Irradiation T
Primavera	2.6×10^{23} m^{-2}	4×10^{15} m^{-2} s^{-1}	270°C
Novovoronezh-4 NPP	1.5×10^{23} m^{-2}	1.5×10^{15} m^{-2} s^{-1}	270°C

DBTT for irradiated, annealed and re-irradiated states



(C$_P$=0.038 wt.%, C$_{Cu}$=0.16wt.%)

Novovoronezh-4 templates



Primary irradiation. Comparison of atom probe tomography data

Novovoronezh-4 NPP templets	Primavera samples

Dose

Flax = 1.5×10^{11} cm^{-2} c^{-1}
Fluence = 9.7×10^{19} cm^{-2}

Flax = 2×10^{12} cm^{-2} c^{-1}
Fluence = 5.9×10^{19} cm^{-2}

Cluster chemistry (at.%)

Weld material	Cr	Mn	Si	P.	Cu	Ni
Novovoronezh-3 NPP	1,7	4,2	3,7	3,4	20,3	3,3
Primavera	1,3	3,3	2,0	1,2	10,0	0,6

Number density and sizes

d ~ 2 nm, Number density ~ $5\text{x}10^{17}$ cm^{-3}

d ~ 1-2 nm, Number density ~ 10^{18} cm^{-3}

Re-irradiation. Comparison of atom probe tomography data

Novovoronezh-4 NPP templets | Primavera samples

Dose

Novovoronezh-4 NPP templets:

Flax = 1.5×10^{11} cm^{-2} c^{-1}

Fluence = 1.5×10^{29} cm^{-2}

Primavera samples:

Flax = 4×10^{11} cm^{-2} c^{-1}

Fluence =2.6×10^{19} cm^{-2}

Cluster chemistry (at.%)

Weld material	Cr	Mn	Si	P	Cu	Ni
Novovoronezh NPP	-	1,85	-	2.0 (atm)	80,7 (precipitates)	-
Primavera	0,91	1,8	1,2	2,7	7,3 (clusters) > 50 (precipitates)	0,2

Number density and sizes

Novovoronezh-4 NPP templets:

Cu-precipitates: d ~ 5 nm, number density < 10^{16} cm^{-3}

Cu-clusters were not observed

P- cluster (atm), d ~ 3-12 nm, number density ~ 10^{17} cm^{-3}

Primavera samples:

Cu-precipitates: 1-2 nm,

Cu-P-clusters: d ~ 1-3 nm, number density ~ $(5-10)\times10^{17}$ cm^{-3}

Conclusions

The study of weld metal with high concentration of phosphorus in different states (irradiated, annealed and re-irradiated) has been done.

- Under primary irradiation of the weld, formation of Cu -P enriched clusters, disk carbides and carbide clusters takes place.
- Under re-irradiation after recovering annealing, new generation of Cu-P-enriched clusters was observed.

Annex 7: Zeman’s presentation on Microstructural Investigation

Microstructure Evolution of VVER-440 RPV Steel after irradiation and annealing

A.Zeman 1,2

1 IAEA / Department of Nuclear Sciences and Application (AT)
2 Institute for Energy, Joint Research Centre EC (NL)

Outline

* Introduction
* On-going issues
* Published data
* Discussions and summary
* Conclusions

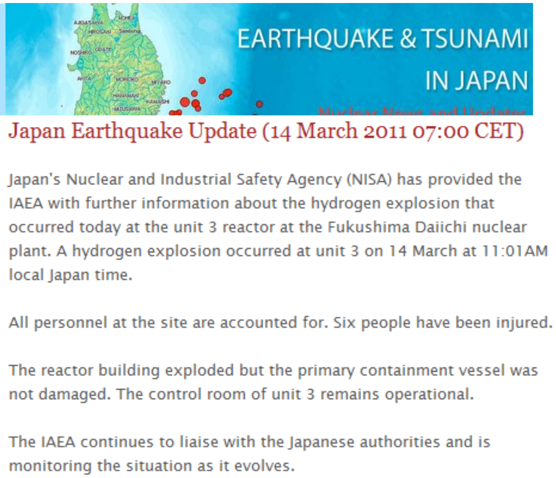
Introduction

- RPV steel - shift of ductile-to-brittle transition temperature
- Yield and hardness ↑ due to defects acting as barriers to motion of dislocations
- Thermal ageing: long-term degradation process of mechanical properties
- Chemical composition (alloying elements: Ni, Cr, Mn; impurities: P, Cu, S)
- More-complicated for multi-component system - complex issue, many parameters and variables

❖ Emergency situation - Pressurised-Thermal-Shock (PTS) transient

❖ Small break LOCA: fast-cooling of RPV (as consequence to the water safety inject-system), Initial pressure decrease, followed with a re-pressurisation

❖ Consequence: HP combined with low temperature can cause the brittle fracture of the RPV (VVER-440 critical scenario - weld near by core)



EARTHQUAKE & TSUNAMI IN JAPAN

Japan Earthquake Update (14 March 2011 07:00 CET)

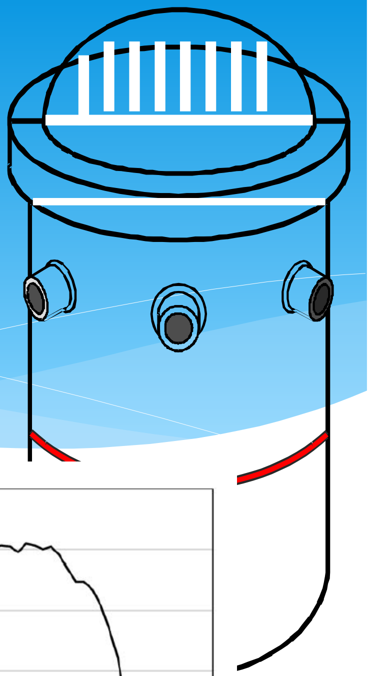
Japan's Nuclear and Industrial Safety Agency (NISA) has provided the IAEA with further information about the hydrogen explosion that occurred today at the unit 3 reactor at the Fukushima Daiichi nuclear plant. A hydrogen explosion occurred at unit 3 on 14 March at 11:01AM local Japan time.

All personnel at the site are accounted for. Six people have been injured.

The reactor building exploded but the primary containment vessel was not damaged. The control room of unit 3 remains operational.

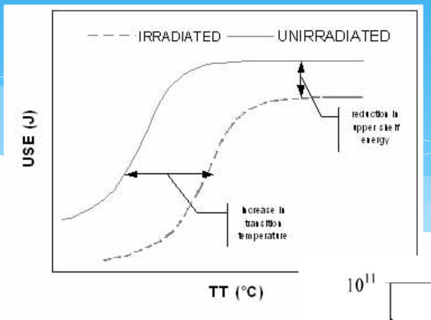
The IAEA continues to liaise with the Japanese authorities and is monitoring the situation as it evolves.

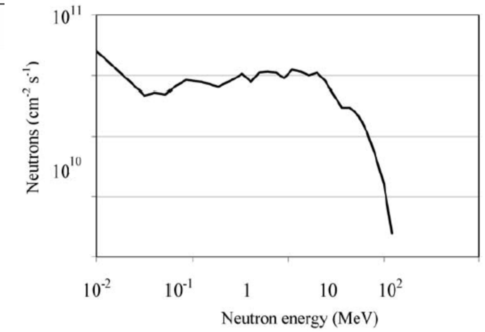
On-going issues



DESIGN LIMITS:

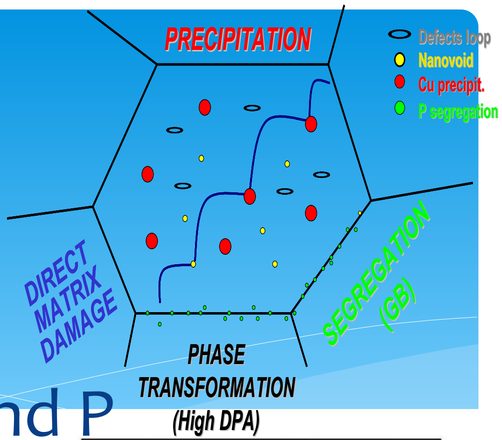
* No less than 40 y of service life or 2.10E5 h of operation at normal power
* Up to 30 planned shutdowns
* Coolant working pressure at the core outlet of 10-16 MPa ,
* Coolant temperature at steady operation of 250 to 289°C (inlet) and 269 to 324°C (outlet)
* RPV temperature (considering heating due to radiation) up to 300°C,
* Maximum neutron flux density at the level of the core center of around 10E11 n/(s cm2) with respect to neutrons with energy greater than 0.5 MeV (1 MeV).



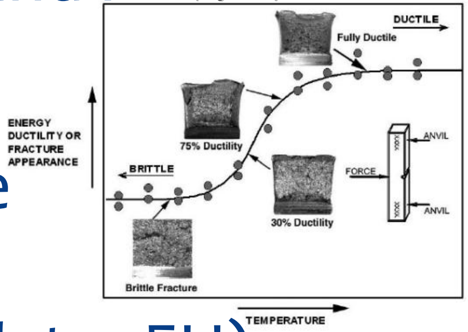


PART OF RPV	*VVER 440 (230)*	*VVER 440 (213)*	*VVER 1000 (320)*
	(E_N > 0,5 MEV)		
BASE MATERIAL	2,3 X 10^{24}	2,6 X 10^{24}	6,3 X 10^{23}
WELD MATERIAL	1,6 X 10^{24}	1,8 X 10^{24}	5,7 X 10^{23}
	(E_N > 1 MEV)		
BASE MATERIAL	1,4 X 10^{24}	1,6 X 10^{24}	3,7 X 10^{23}
WELD MATERIAL	1,0 X 10^{24}	1,1 X 10^{24}	3,4 X 10^{23}

On-going issues



- Older RPV grades = higher content of Cu and P
- Increased sensitivity to “RD diseases”
- Unaccaptable DBTT shift at higher fluence

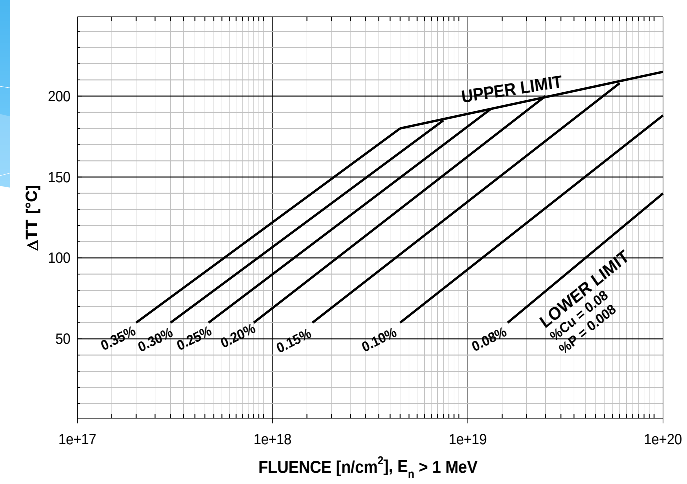


Several studies at international level (IAEA, later EU)

- *TECDOC Series No. 659 (1992) Reactor Pressure Vessel Embrittlement - programme on the Safety of WWER-440 Model 230 Nuclear Power Plants*
- *TECDOC Series No. 710 (1993) Applicability of the Leak Before Break Concept - programme on the Safety of WWER-440 Model 230 Nuclear Power Plants) Status Report on a Generic Safety Issue Details*
- *IAEA TECDOC Series No. 1442 (2005) Guidelines for Prediction of Irradiation Embrittlement of Operating WWER-440 Reactor Pressure Vessels*
- *TECDOC Series No. 1610 (2009) Safety Analysis of WWER-440 Nuclear Power Plants: Potential Consequences of a Large Primary to Secondary System Leakage Accident*

On-going issues

- Coordinated Research Projects (IAEA)
- Engineering margins analysis: RPV prediction formulas (COVERS)
- Basic interactions – modelling (PERFECT)
- Irradiation – Annealing – Reirradiation (PRIMAVERA)



Recovery annealing was needed in case of several NPPs (EU relevant activities Greisfaild, Bohunice, Lovisa, etc.),

Steel type/ element[1]		Cu	Co	As	S	P	Sb	Sn
AZ	15Ch2MFA (V-230)	0,30	0,025	0,040	0,020	0,020	-	-
	15Ch2MFA (V-213)	0,10	0,025	0,010	0,015	0,012	0,05	0,015
	15Ch2NMFA (V-320)	0,10	0,03	0,010	0,012	0,010	0,005	0,005

Reactor	Year	Temperature/time (°C/h)	SS clad
Novovoronezh 3	1987	430 ± 20°C / 150 h	no
Armenia 1	1988	450 + 50°C / 150 h	no
Greifswald 1 (Nord 1)	1988	475 - 10°C / 150 h	no
Kola 1	1989	475°C / 150 h	no
Kola 2	1989	475°C / 150 h	no
Kozloduy 1	1989	475°C / 150 h	no
Kozloduy 3	1989	475°C / 150 h	yes
Greifswald 2 (Nord 2)	1990	475 - 10°C / 150 h	no
Greifswald 3 (Nord 3)	1990	475°C/150 h	yes
Novovoronezh 3 (re-annealing)	1991	475 ± 15°C / 100 h	no
Novovoronezh 4	1992	475°C / 150 h	no
Kozloduy 2	1992	475°C / 150 h	no
J. Bohunice V-1/2	1993	475 - 503°C / 160 h	yes
J. Bohunice V-1/1	1993	475 - 496°C / 168 h	yes

Reijo Pelli, Kari Törrönen, AMES report, EUR16278EN

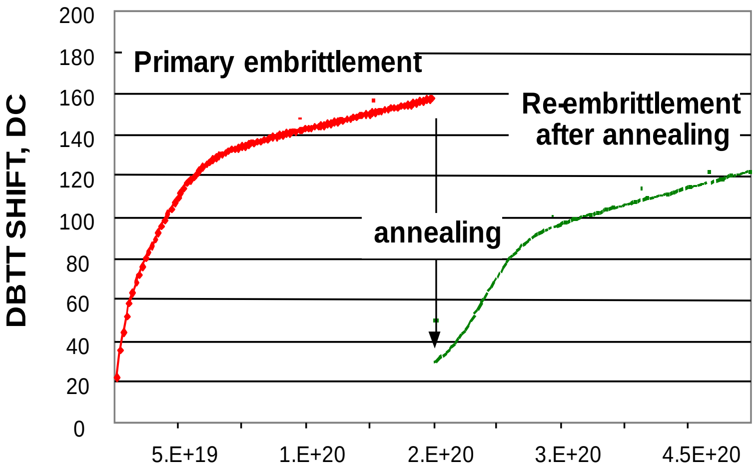
Issues

- Post irradiation annealing arises from the fact that some early NPP RPVs were fabricated in such a way that they may not meet some pertinent regulatory requirements as they near end-of-life.
- Predictions suggest that several vessels may exceed the DBTT limits set by regulations concerned with pressurized-thermal shock.
- In case of PWR reactors, thermal annealing may be performed to mitigate the effects of neutron embrittlement.

- Quantification of microstructural changes of irradiated materials including response to recovery annealing and residual shift is needed.
- Evolution of degradation process and interactions of alloying elements and impurities, specifically further precipitation /segregation and direct matrix damage acceleration.

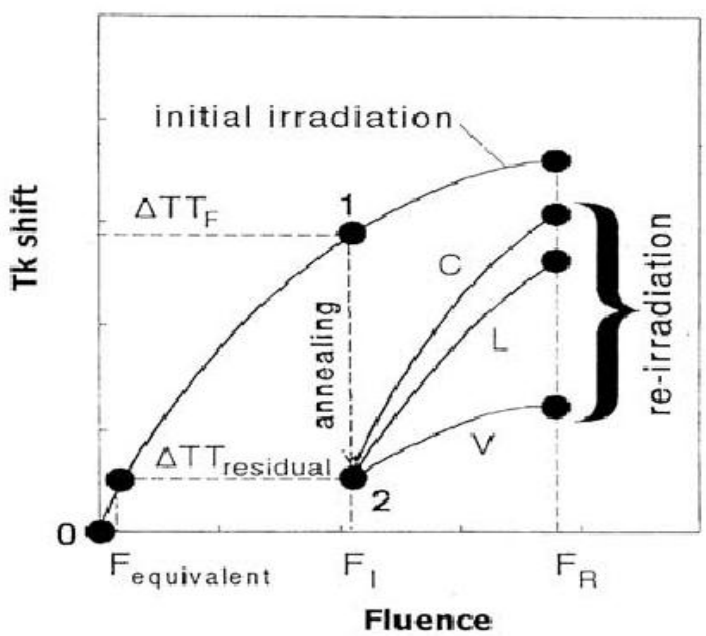
Recovery annealing

* One of the greatest risks in recovery annealing is exceeding the acceptable stress level, resulting in residual strains.
* In case of annealing only one ring weld, this can be avoided using sufficiently low heat-up and cool-down rates and controlling temperature gradients.
* In WWER-440 RPVs, the calculations have shown the maximum rate to be about 20°C/h.



Re-irradiation

* Conservative shift approach was used previously in the assessment of the residual lifetime of annealed vessels.
* At present, adjusted initial embrittlement curve with lateral shift approach is used.
* Recent data confirmed that models do not satisfactorily explains the kinetics of re-embrittlement, in particular during the early re-embrittlement phase (DBTT shift is lower than the predicted values).
* Following phase, the data rapidly increase to align with the lateral shift model.
* In order to account for 'delayed' early embrittlement after annealing, a model is based on the fact that data show a 'logistic' shape without saturation at high fluence.



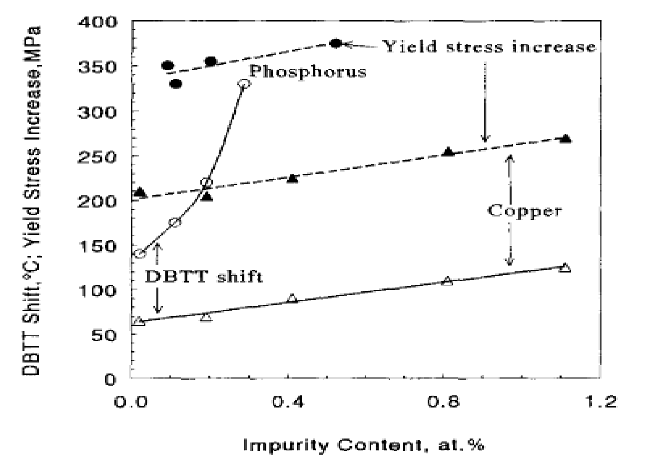
$\Delta Tshift = [a + \tanh(F - b)]\,(1 + c \times F^{1/3})$

– $\Delta Tshift$ is the transition temperature shift;
– F is the re-embrittlement fluence;
– a, *b*, *c* are the model fitting constants.

Published data

B.A. Gurovich et al. / JNM 246 (1997) 91-120

- Formation of radiation defects plays crucial role.
- Phase transformations accompanied by the generation of various precipitate populations.
- Formation of impurity-vacancy clusters (for instance, Cu-vacancy type).
- P-segregation and probably some other impurities to grain boundaries (i.e. intergranular segregation).
- Impurities segregate (P) at interfaces between secondary phases and matrix and/or radiation defects.



Dependence of steel irradiation response on impurity content (fluence 4. 10E23 n m-2, Tirr = 50°C), TEM available from WWER-440 trepans Sv-IOKhMFT 0.034% P 0.155% cu (same paper).

Density and dimensions of radiation defects and disk-shaped precipitates in weld metal of NVNPP-2 pressure vessel

Layer	Conditions	n_{loops} ($\times 10^{15}$ cm^{-3})	d_{loops} (nm)	n_{disk} ($\times 10^{15}$ cm^{-3})
Inner (8)	irradiated to $F = 6.5 \times 10^{19}$ n cm^{-2}	7–8	5	50–60
Inner (8)	irrad. + anneal. 475°C/150 h	–	–	3.5–4.0
Inner (8)	irrad. + anneal. 560°C/2 h	–	–	0.7–0.9
Extern (1)	irradiated to $F = 2.4 \times 10^{19}$ n cm^{-2}	5–6	3	30–50
Extern (1)	irrad. + anneal. 475°C/150 h	–	–	2.5–3.0
Extern (1)	irrad. + anneal. 560°C/2 h	–	–	0.9–1.0
	unirradiated	–	–	0.5–0.6

Irradiation – Cu reach precipitates with density and radius may reach
~ 2 × 10E19 cm -3 and ~ 1-2 nm

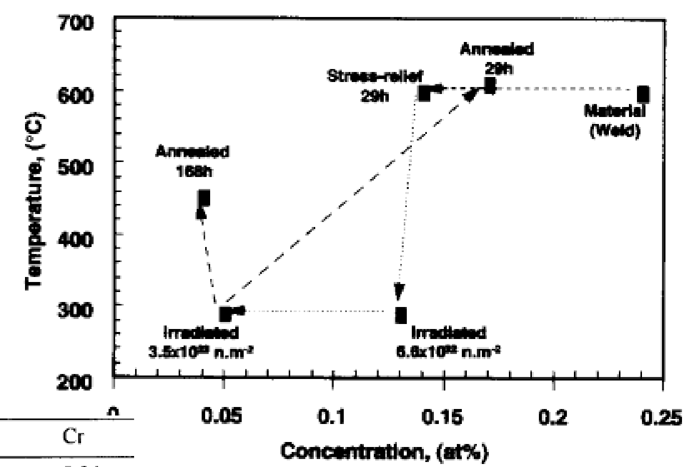
CONCLUSIONS

- Embrittlement is driven by 3 effects: matrix hardening, grain boundary segregation of impurities and segregation of impurities to precipitate interfaces.
- Essential part of RPV embrittlernent is attributed to P-segregation to interfaces induced by irradiation.
- GB P-segregation in irradiated RPV is responsible for insignificant portion of the radiation-induced DBTT shift (exceeding ~ 10-20%).

Published data

P. Pareigr et al. / JNM 249 (1997) 165- l74

- Intermediate-copper level weld and a low-copper forging material were investigated.
- The maximum neutron fluence of the materials was 3.5 ×10E23 nm -2 (E>1 MeV).
- The irradiated weld was also examined after two post-irradiation heat treatments: 168 h at 454°C and 29 h at 610°C.



Influence of neutron irradiation and annealing on Cu content in the matrix in WM

		Cu	Ni	Mn	Si	P	C	S	Mo	Cr
Forging	wt%	0.02	0.76	0.72	0.21	0.014	0.24	0.012	0.62	0.34
	at.%	0.017	0.72	0.72	0.41	0.025	1.11	0.021	0.36	0.36
Weld	wt%	0.28	0.59	1.49	0.51	0.016	0.09	0.016	0.39	0.06
	at.%	0.24	0.56	1.5	1.01	0.03	0.42	0.03	0.23	0.06

Conclusions:

- Presence of neutron-induced copper clusters after neutron irradiation is in agreement the measured transition temperature shift.
- Their dissolution after annealing is in agreement with the high percentage of recovery (168 h at 454°C, the Cu concentration in the matrix is of the order of 0.04 + 0.01 at.% which is in agreement with the copper solubility limit at this T).
- This indicates that the low number density of copper particles in the ferrite matrix after annealing has little influence on the mechanical properties of the recovered weld material.

Published data

G.R. Odette, B.D. Wirth/JNM 251 (1997) 157-171

- Low alloy RPV steels (plates, forgings and welds) contain Mn (0.7-1.7%), Ni (0.2 to l.4%), MO (= OS%), Si (0.25-0.5%) and, in the case of forgings, Cr (0.25-0,50).

Summary of nanofeatures formed in irradiated RPV steels[a]

Description (acronym)	Rad. (nm), Conc. ($/m^3$)	Compositions	Comments
Copper-rich precipitates (CRPs)	0.5–1.5 nm, $0.1–2 \times 10^{24}/m^3$	Cu(> 50%)–Mn/Ni/Si	CRPs rapidly nucleate at Cu > 0.1% growing and finally slowly coarsening near the peak volume fraction
Manganese/nickel-rich precipitates (MNPs)	similar to CRPs	Mn/Ni/Si (> 50%)–Cu	MNPs are favored by high Mn, Ni and low T_i, and Cu and *may* form at low Cu at high ϕt
Vacancy cluster–solute complexes	< 0.5 nm, up to $10^{24}/m^3$	vacancies–Cu/Mn/Ni/Si/...	thermally unstable (dissolve) in typical irradiations, but reach a steady state concentration dependeing on T_i and ϕ; mediate ϕ effects
Nanovoid vacancy complexes	< 1 nm, up to $10^{24}/m^3$	vacancies–Cu/Mn/Ni/Si/...	stable (grow) under irradiation and increase with $\approx \sqrt{\phi t}$ and lower T_i but independent of ϕ
Dilute solute atmospheres	< 2 nm, up to $10^{24}/m^3$	Fe–Cu/Mn/Ni/Si/...	may contain VCCs and NVCs

[a] Other nano-features may include alloy carbonitrides and phosphides as well as interstitial clusters/dislocation loop–solute complexes; however, these features are not normally believed to result in a major contribution to embrittlement in western-type Mn–Ni low alloy steels.

Conclusions:

- In intermediate-to-high Cu steels, Cu- reached precipitates are well formed precipitates, however with complex chemical structures.
- Metastable vacancy cluster-solute complexes are formed in displacement cascades. Continuum clustering models predict that stable nano-void complexes nucleate on some of the vacancy cluster-complexes.
- Cascades also produce a significant amount of Cu (and presumably other solute) clustering. Thus in high Ni steels, cascades may promote the formation of MNPs that could ultimately result in high levels of hardening and embrittlement even at low Cu levels.

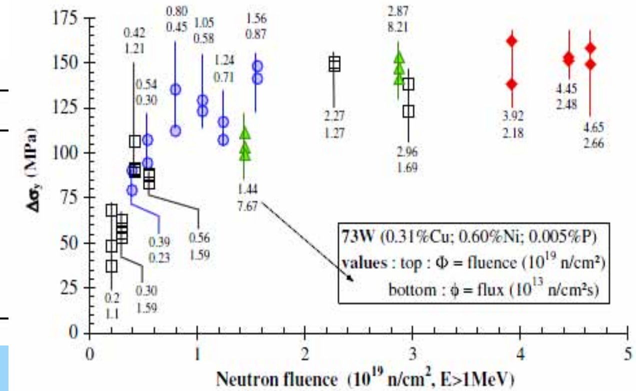
Published data

R. Chaouadi, R. Gerard/ JNM 345 (2005) 65–74

- Research aimed to summarise data (chemistry, heat treatments, fluence, Tirr) in order to study irradiation-induced hardening of RPV steels and welds with copper contents ranging 0.06-0.31% at 300/265C. Dose rate effects on the irradiation hardening was studied as well.
- Experiments on re-irradiation after annealing were performed to investigate the re-irradiation kinetics.

Chemical composition (wt%)

Material	Cu	Ni	P	C	Si	Mn	S	Cr	Mo
73W	0.31	0.60	0.005	0.10	0.45	1.56	0.005	0.25	0.58
72W	0.23	0.60	0.006	0.09	0.44	1.60	0.006	0.27	0.58
18MND5	0.13	0.64	0.008	0.18	0.25	1.55	0.002	0.18	0.50
16MND5	0.06	0.69	0.013	0.14	0.04	1.37	0.009	0.13	0.52
JRQ	0.14	0.84	0.017	0.18	0.24	1.42	0.004	0.14	0.51
A508	0.07	0.83	0.015	0.07	0.15	1.15	0.005	0.14	0.55



Conclusions:

- Irradiation effect on Cu-precipitation was experimentally evaluated by selecting a number of materials where Cu is the major variable (0.06–0.31% Cu) while the other elements are essentially similar (0.6% Ni).
- Two-component damage mechanism, (i) precipitate hardening and (ii) matrix hardening.
- Irradiation-induced precipitates are essentially Cu-rich precipitates.
- Precipitate hardening reaches its saturation value, corresponding to peak hardening, already around 1x10E19 n/cm2, E > 1 MeV while matrix hardening increases continuously with neutron exposure.
- Based on exp. data authors derived the peak hardening resulting from the copper-rich precipitates as matrix damage is basically similar for all the materials under consideration.
- They found that the re-irradiation kinetics after annealing depends strongly on the material under consideration, moreover, re-irradiation after annealing experiments were also used to question the relationship between the precipitate and matrix hardening components.

Published data

M.K. Miller, K.F. Russell / JNM 371 (2007) 145–160

- Atomic level characterization of the microstructure (2-nm) Ni, Si, Mn-enriched clusters in neutron irradiated low copper and copper free alloys.
- Quantification of solute segregation to, and precipitation on, dislocations and grain boundaries

Atom probe tomography results of the copper content (at.%) in the matrix of different steels after the stress relief treatment (SR), irradiation (I), annealing (IA), and re-irradiation (IAR)

Material	Cu after SR	Fluence 10^{23} m^{-2}	Cu after I	PIA	Cu after IA	Fluence 10^{23} m^{-2}	Cu after IAR	Ref.
Midland weld	0.119 ± 0.007	1.1 $E > 1$ MeV	0.06 ± 0.01	168 h at 454 °C	0.05 ± 0.01			[44]
B&W weld	0.14 ± 0.03	3.5 $E > 1$ MeV	0.05 ± 0.01	168 h at 454 °C	0.04 ± 0.02			[45]
Weld 73W	0.12 ± 0.01	1.8 $E > 1$ MeV	0.06 ± 0.01	168 h at 454 °C	0.04 ± 0.01	0.8 $E > 1$ MeV	0.04 ± 0.01	[49]
15Kh2MFA	0.14 nominal	9.7 $E > 0.5$ MeV	0.05 ± 0.02	150 h at 475 °C	0.07 ± 0.03	9.7 $E > 0.5$ MeV	0.05 ± 0.02	[46,47]
JRQ	0.12 ± 0.01	5 $E > 1$ MeV	0.07 ± 0.01	168 h at 460 °C	0.06 ± 0.01			[48]
JRQ	0.12 ± 0.01	0.85 $E > 1$ MeV	n/a	168 h at 460 °C	n/a	0.85 $E > 1$ MeV	0.09 ± 0.01	[48]

Conclusions:

- Post weld stress relief treatment reduces the matrix copper content in high copper alloys thereby making these alloys less susceptible to embrittlement.
- Small (2-nm) Cu, Ni, Mn and Si-enriched precipitates formed during neutron irradiation in copper containing RPV.
- Cu-enriched precipitates coarsened during post irradiation heat treatments and a second finer distribution formed during re-irradiation.
- Solute segregated to and precipitated on dislocations and grain boundaries.
- Small (2-nm) Ni, Si and Mn-enriched clusters formed in neutron irradiated high nickel, low copper and copper free alloys.
- Fine copper-enriched precipitates formed during long term thermal exposure at the reactor temperature.

Published data

G.E. Lucas / JNM 407 (2010) 59–69

- Fundamental understanding of RD and property changes have led to a number of embrittlement correlations that have been used by regulatory agencies to assess the degree of embrittlement of operating RPVs.
- Models are used to craft a mathematical framework which is calibrated by multivariable regression analysis on RPV embrittlement data bases, leading to a correlation between transition temperature shift, as measured in Charpy V-notch tests

Conclusions:

- Models of irradiation hardening and DBTT shift in RPV steels based on the evolution of several predominant defect types in irradiated RPV steels, including precipitates (e.g., Cu rich for high Cu steel, Mn–Ni rich in low-Cu steels at high fluences), stable matrix defects, and unstable matrix defects (UMDs – vacancy agglomerates, partially affiliated with Cu and/or other alloys).
- Role of Cu, Mn, Ni in mitigating the damage microstructure, specifically (a) threshold level of bulk Cu before the onset of hardening; (b) upper level of bulk Cu beyond which hardening no longer increases (due to pre-precipitation of some Cu during heat treatment prior to service); (c) attraction of Mn and Ni to the surface of Cu precipitates leading to Cu-Mn–Ni precipitates that depend on irradiation flux, fluence and temperature as well as matrix composition prior to irradiation.
- Effect of thermo-mechanical treatment of RPV steels in mitigating their response to irradiation (heat treatment time and temperature), especially (a) Cu pre-precipitation, which mitigates the amount of Cu in solution prior to irradiation and thus available to contribute to radiation-enhanced precipitation hardening; (b) dislocation densities, which serve as sinks for point defects, mitigating radiation-enhanced diffusion and precipitation processes (c) carbide populations determining the pre-existing barrier strengths in the superposition of contributions of both the unirradiated and irradiated microstructures to hardening.

Published data

G.E. Lucas / JNM 407 (2010) 59–69

- Fundamental understanding of RD and attendant property changes have led to a number of embrittlement correlations that have been used by regulatory agencies to assess the degree of embrittlement of operating RPVs.
- Models are used to craft a mathematical framework which is calibrated by multivariable regression analysis on RPV embrittlement data bases, leading to a correlation between transition temperature shift, as measured in Charpy V-notch tests

Conclusions:

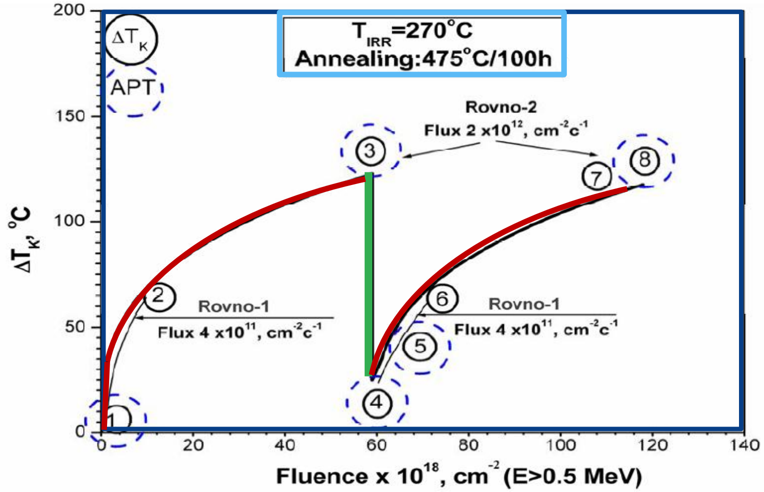
- Multiple roles of flux and hence the various flux dependences that can and have been observed. For instance: (a) at high fluxes, UMD's provide increasing hardening with increasing flux, but serve as sinks for point defects thereby reducing the contribution of radiation-enhanced precipitation to hardening; (b) at low fluxes, thermal diffusion can predominate leading to an apparent flux (time) dependence ; (c) at intermediate fluxes, where-irradiation-enhanced precipitation predominates hardening and embrittlement, the fluence to achieve a given level of hardening is flux independent, but solute trapping can provide a small degree of flux dependence.
- Effect of irradiation temperature to the evolution of defect population, thus hardening and embrittlement, main conclusions: (a) increasing irradiation temperature reduces the population of UMD's at higher temperatures – leading to reduced hardening at higher temperatures; (b) contributions of thermal diffusion at higher temperatures can also affect both flux and temperature dependence; (c) Mn–Ni rich precipitates are promoted at lower irradiation temperatures.
- Defect populations in both post-irradiation annealing and re-irradiation embrittlement, PIA can lead to annihilation of UMD's and dissolution/coarsening of precipitates with increasing time and temp; re-irradiation embrittlement is then affected by the degree of solute returned to solution during PIA.

Primavera results

❖ Various P : 0.027, 0.031 and 0.038 % respectively.

	C	Si	Mn	P	S	Cr	Ni	Mo	Cu	V
LP	0.04	0.04	1.12	0.027	0.013	1.42	0.13	0.49	0.16	**0.19**
MP	0.04	0.39	1.15	0.031	0.013	1.42	0.13	0.50	0.16	**0.18**
HP	**0.05**	**0.36**	**1.09**	**0.038**	**0.014**	**1.54**	**0.13**	**0.51**	**0.16**	**0.19**

Ref. Int. Journal of Pressure Vessels and Piping, 84 (2007) 151-158

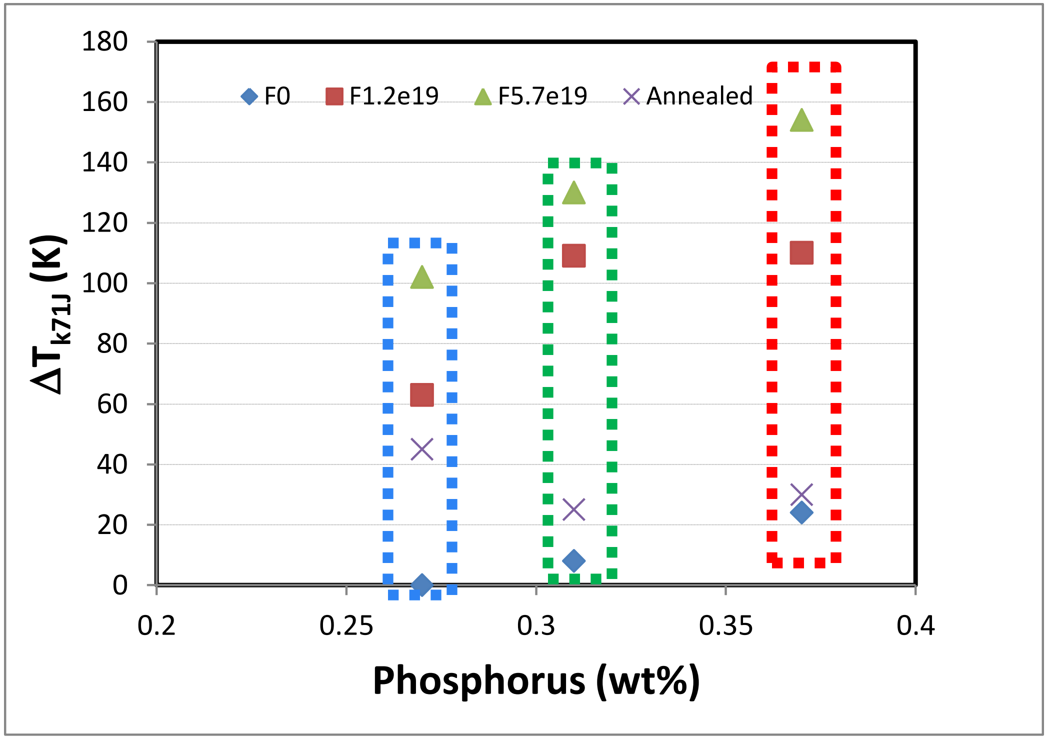


Primavera results

* Full data set of T_{k71J} for non-irradiated, irradiated (1.2 and 5.7 E+19 n/cm2)
* Deviation of Transition temperature (T_{k71J})

Fluence	LP	MP	HP
0	16	24	40
1.2E+19 n/cm2	89	133	126
5.7E+19 n/cm2	108	146	170
Annealed	61	41	46

Ref. Non-irradiated LP



Discussions & conclusions

PRIMAVERA SAMPLES:

* **Annealing caused partial disolution of Cu-clusters and larger precipitates were formed**, however, it is hardly expected that dissolution of such radically different clusters will run in similar ways during annealing.
* **Secondary nucleation of Cu-clusters took place under re-irradiation** after annealing.
* Formation of **similar clusters under re-irradiation was also observed** Western RPV steel (A533B).
* It is necessary to note that **the composition of Cu-enriched clusters depends on both dose rate** and mainly composition of irradiated material.
* **HP concentration** in material (0.038 wt%) **led not only to copper enriched cluster formation but also to P-segregation into relatively small clusters,** however such behaviour had not been observed in LP specimens.

Conclusions

- **Harmonization of tools and measurement procedures** in order to assure that are sure what we measure as well as common understandings of experimental results.
- Mechanistic approach **further investigations of microstructure still needed**.
- **Strengthening of multi-tools approach**, only combination of various techniques and computer simulation could bring right answer.
- **Key tools** in terms of microstructure characterisation: AP, (HR)TEM, nD, PAS, SANS.

Conclusions

* Available tools for microstructure evolution.
* Qualitative and quantitative analysis.

SELECTIVITY	PAS	TEM	APFIM	MS	TEP	SANS	n-DIFFR.	MAGNTIC
Precipitates	☺	☺	☺	?	☺	☺	_	?
Vacancies	☺	_	?	_	_	_	_	_
Grain boundary effect	?	☺	?	☺	?	☺	_	?
Dislocation density	☺	☺	?	_	?	-	_	?
Phase transformation	?	☺	☺	☺	?	☺	_	☺
Grain size	?	☺	?	_	_	☺	_	?
Stress	-	_	_	_	?	_	☺	?
Chemical composition	?	_	☺	?	?	?	_	_
Solid solution evolution	_	_	?	?	?	?	_	?

Annex 8: Krsjak's presentation on Positron Annihilation Results

V. Kršjak, V. Grafutin, R. Burcl

Positron annihilation spectroscopy studies in frame of the PRIMAVERA project

PRIMAVERA seminar 14/15 March 2011

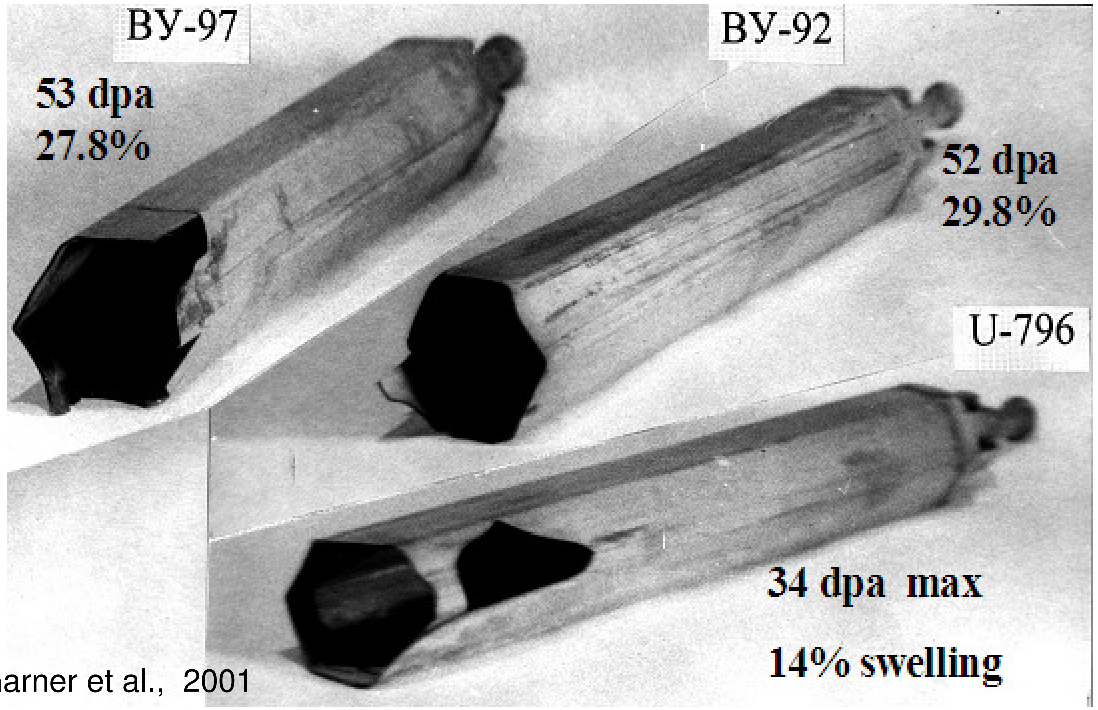
Outline:

- Why positron annihilation?
- Positron production - Radioisotope sources
- Positron annihilation spectroscopy – Techniques
    - Angular correlation of annihilation radiation (ACAR)
    - Positron annihilation lifetime spectroscopy (PALS)
- Defect spectroscopy by ACAR
- Defect spectroscopy by PALS
- PRIMAVERA PAS experiments results

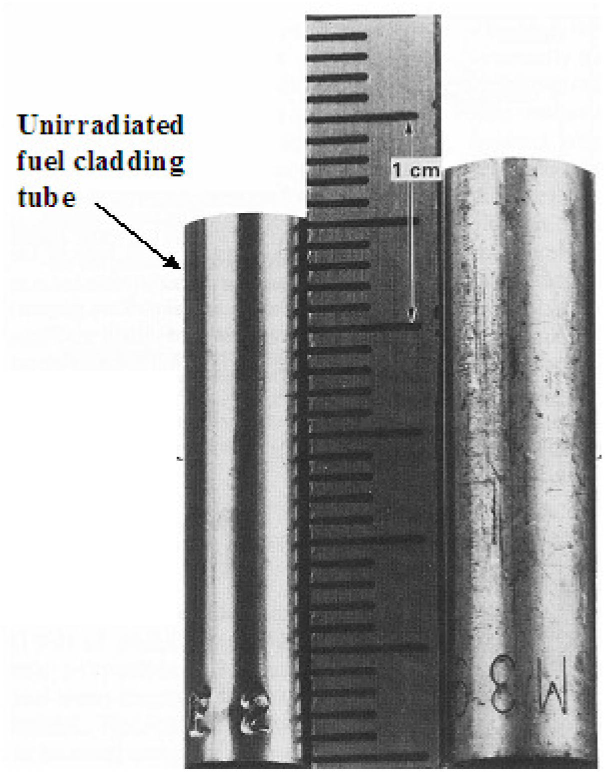
Why positron annihilation?

Point defects determine properties of materials

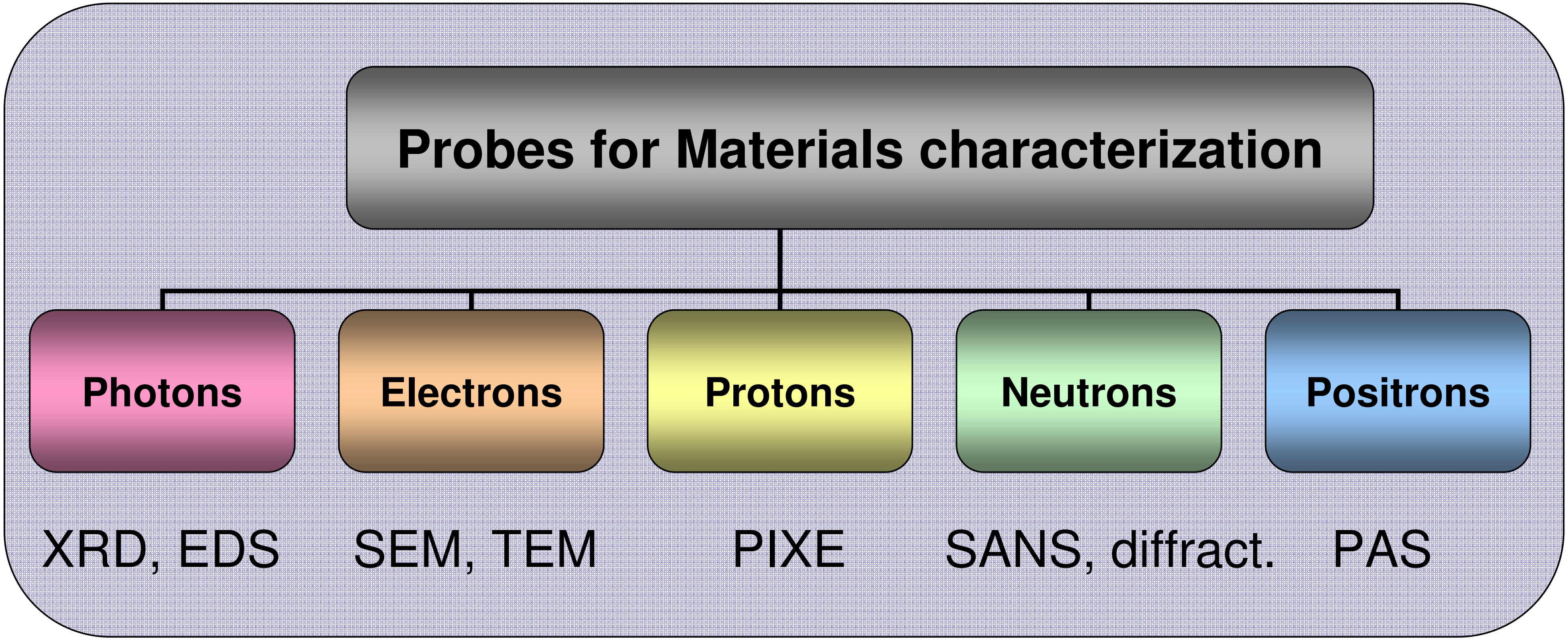
Point Defect Production - Quenching, i.e. rapid cooling; Plastic deformation; **Irradiation** with electrons, ions, neutrons; Oxidation; Reactive Interfaces; Precipitation



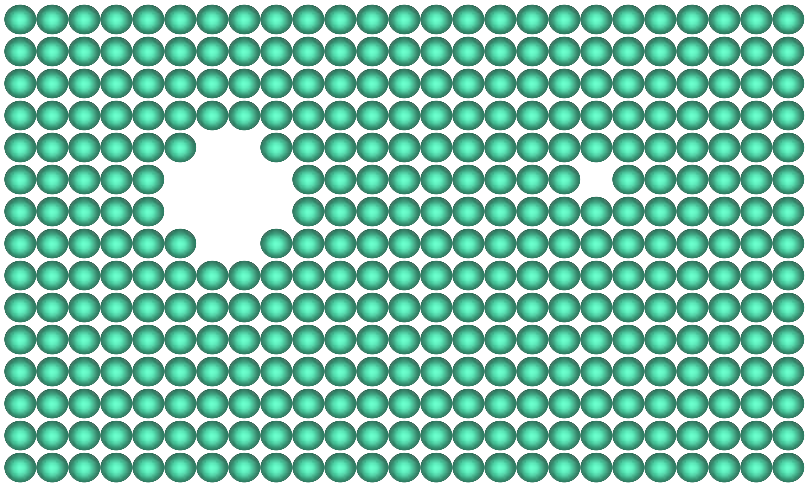
Garner et al., 2001

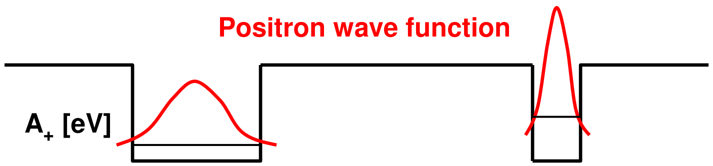


Why positron annihilation?



Why positron annihilation?





Self-Seeking

(positron diffuse typically ~100nm in metals and seek for sites with higher positron affinity than bulk)

Sensitive

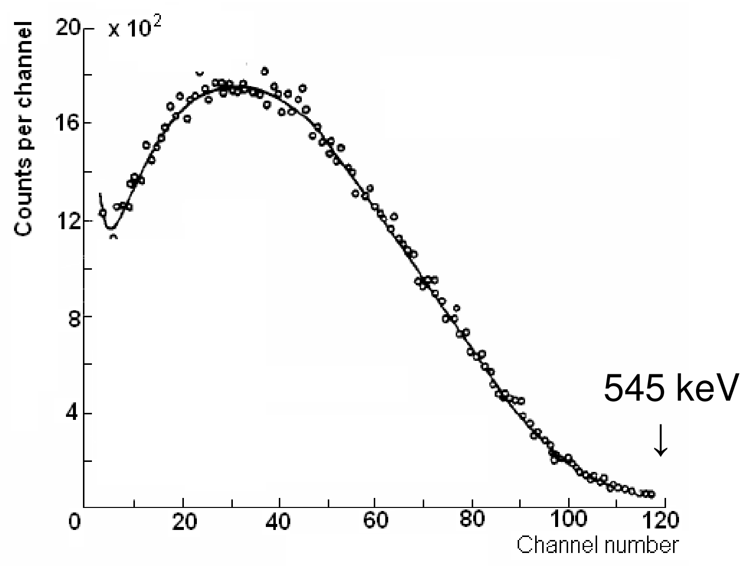
Defect type	Sensitivity range (detection limit vs. saturated trapping)
neutral vacancies	5×10^{21}... 10^{25} m^{-3}
dislocations	10^{12} ... 5×10^{15} m^{-2}
precipitates (r=2 nm)	10^{20} ... 10^{23} m^{-3}
grain boundaries	5 µm ... 200 nm (particle size)
microvoids (>50 atoms)	10^{20} ... 5×10^{23} m^{-3}

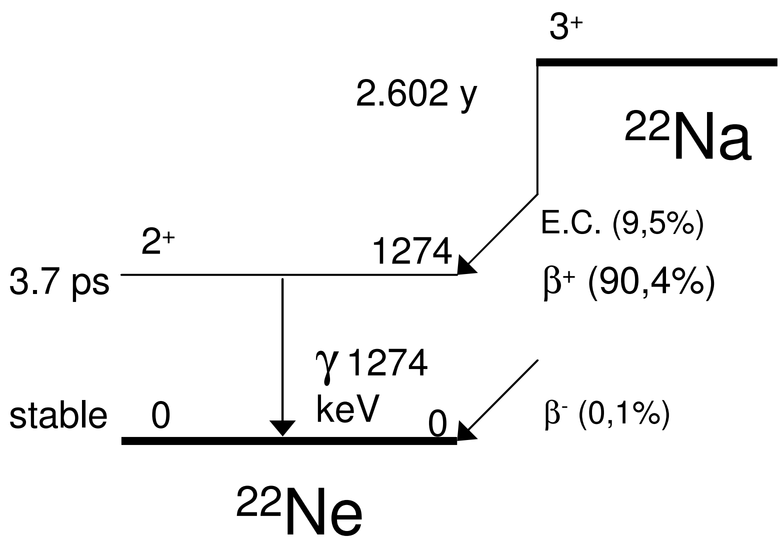
Radioisotope positron source

Positrons are obtained for laboratory setups usually by the β+ decay of isotopes ^{22}Na, ^{64}Cu, ^{58}Co and ^{44}Ti

$$^{22}Na \rightarrow {}^{22}Ne + \beta^+ + \nu_e + \gamma(1.27MeV)$$

Physical Half-Life: 2.602 Years





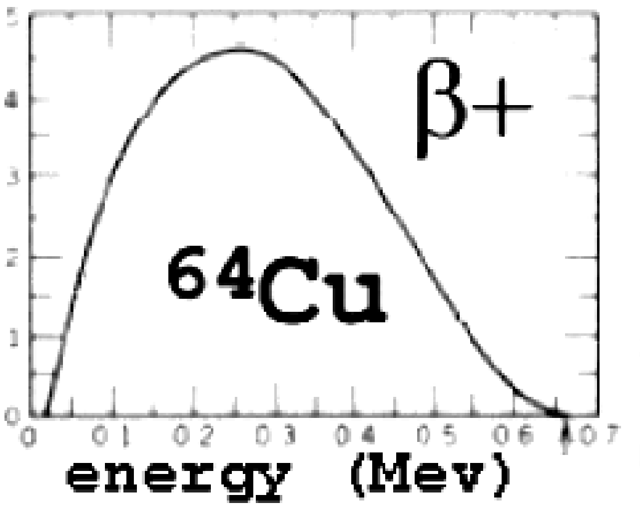
- ^{22}Na positron source - continuous spectra 0 – 545 keV
- correspondent depth in bcc iron 0 – 130 µm

Radioisotope positron source

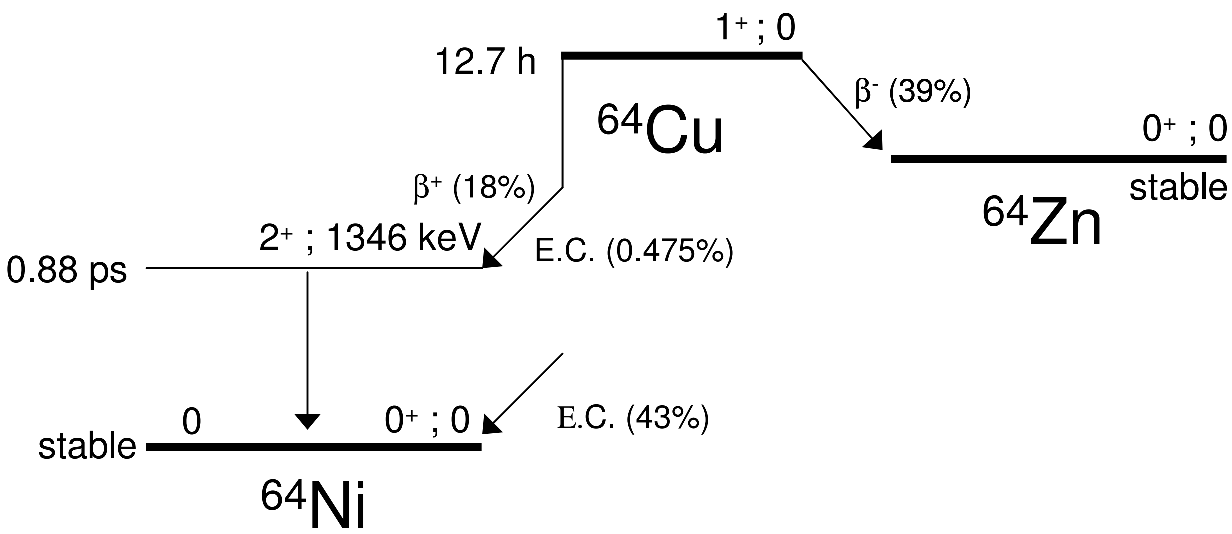
Positrons are obtained for laboratory setups usually by the β+ decay of isotopes ^{22}Na, ^{64}Cu, ^{58}Co and ^{44}Ti

$$^{64}Cu \rightarrow {}^{64}Ni + \beta^+ + \nu_e + \gamma(1.35 MeV)$$

Physical Half-Life: 12.7 hour



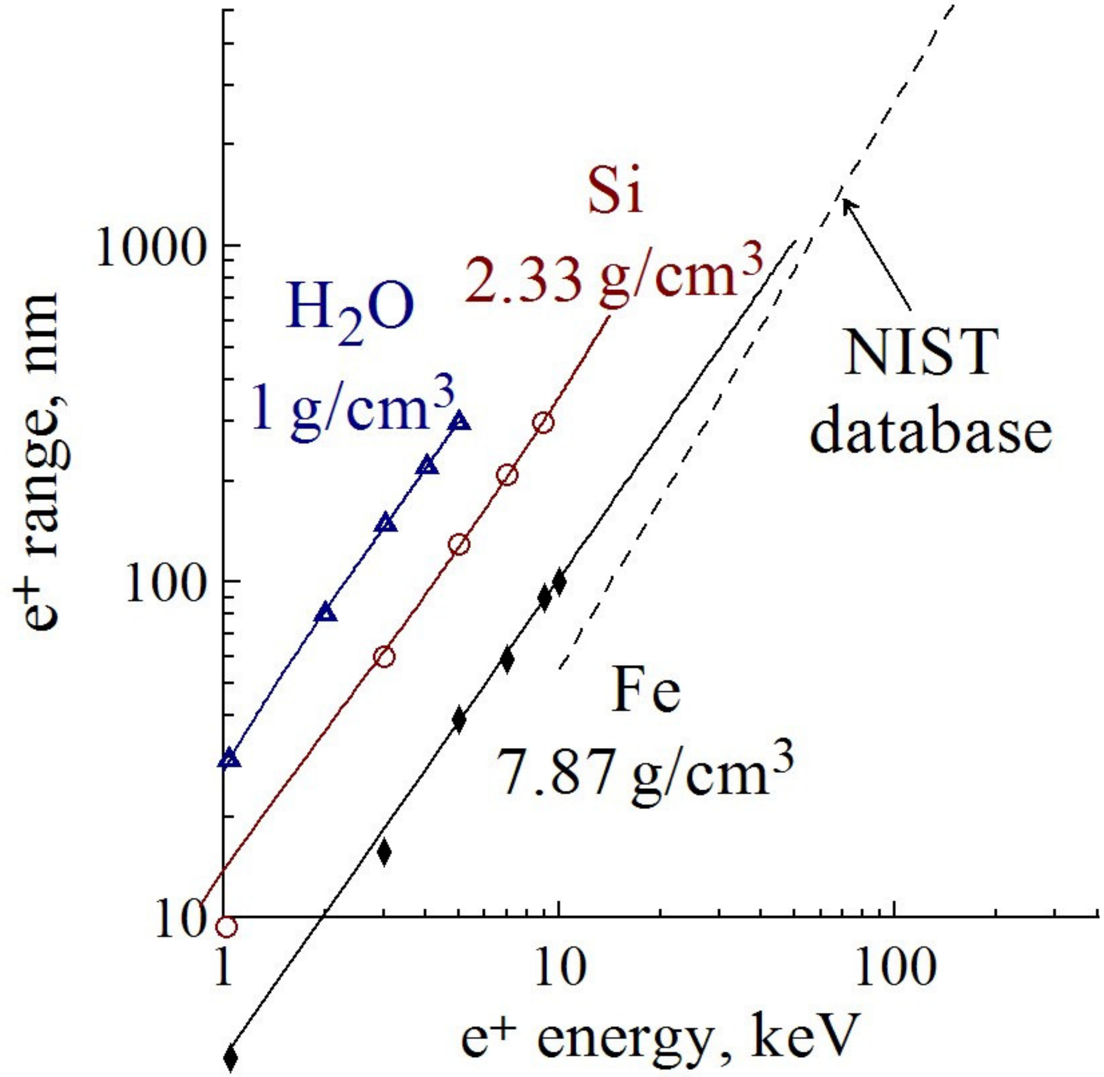
Brusa et al. presentation Verona 2009



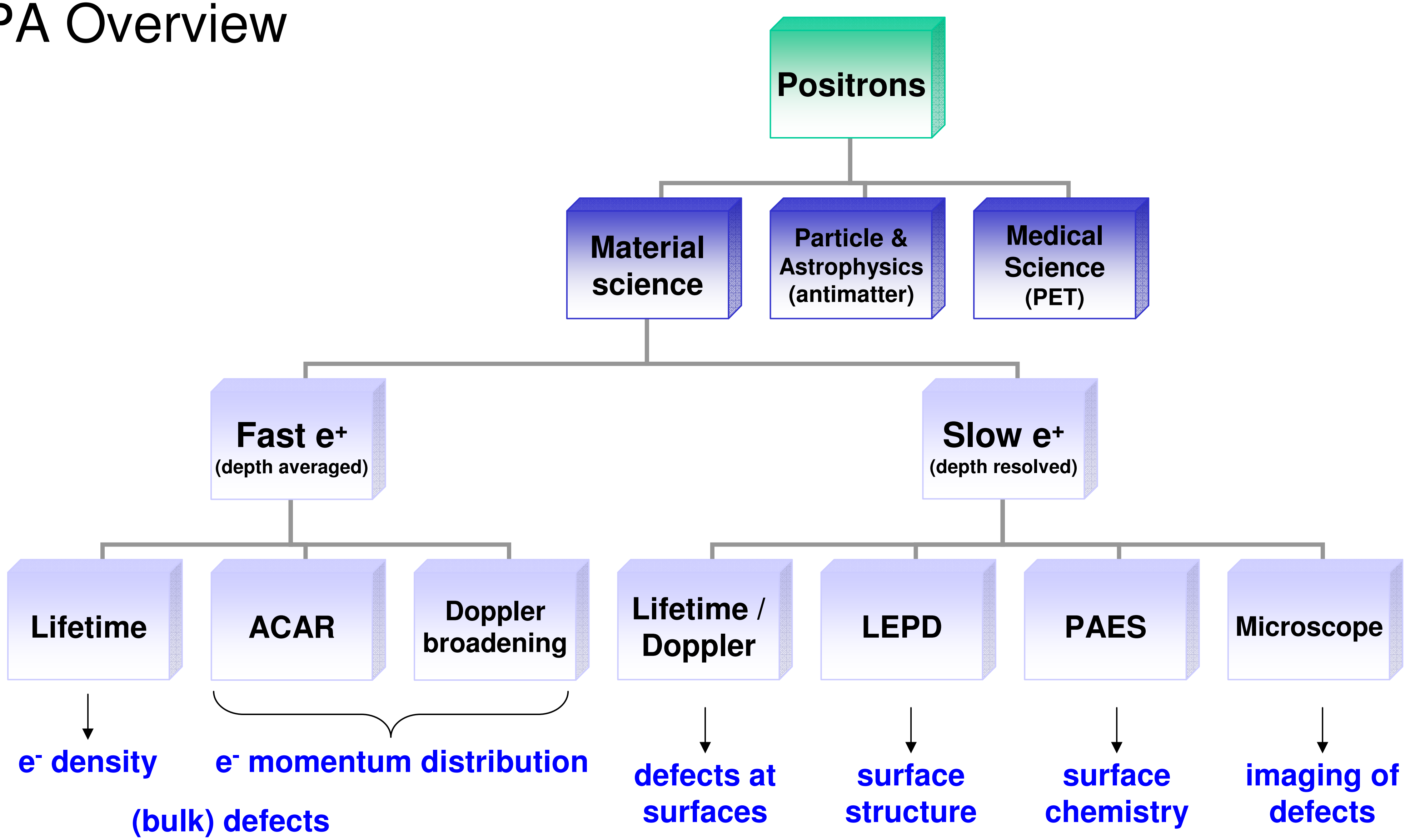
Radioisotope positron source

The dependence of the penetration depth of the positron on its energy

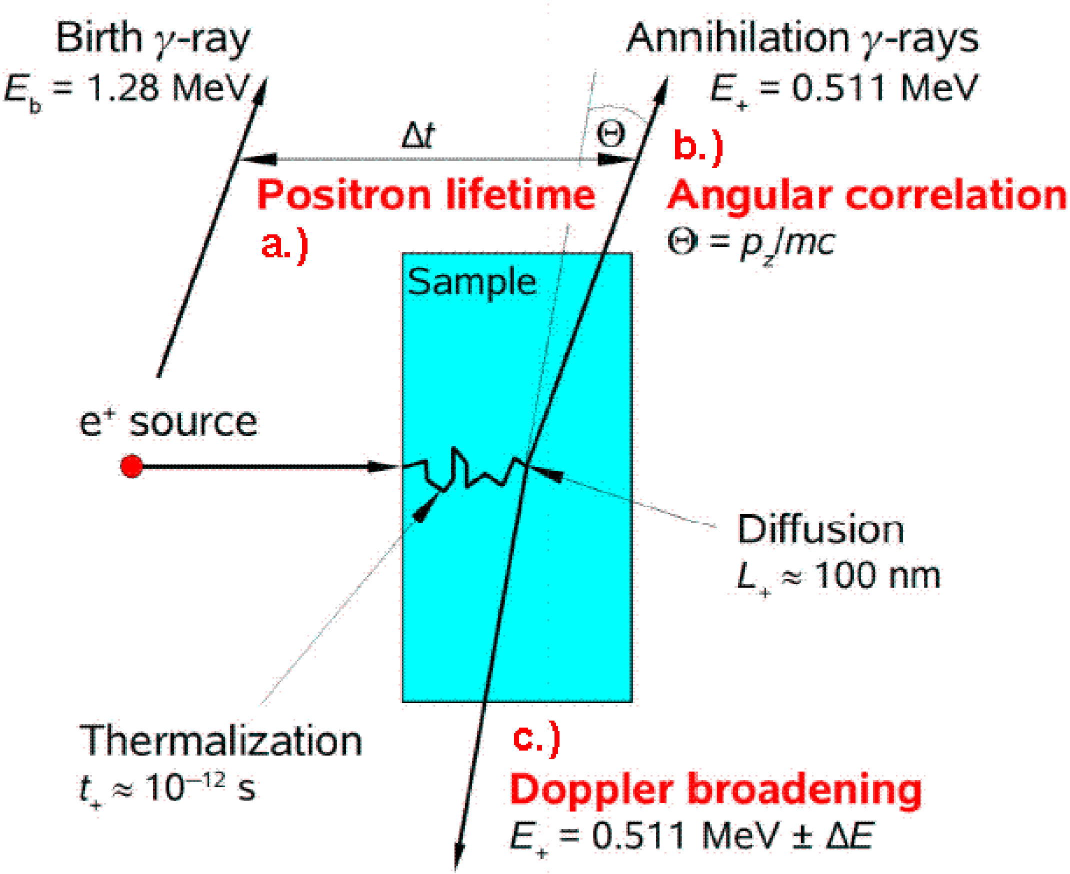
- ^{22}Na positron source - continuous spectra 0 – 545 keV (mean energy 150keV)
- correspondent depth in bcc iron 0 – 130 µm (mean implantation depth 26.6µm)



PA Overview


Positrons
Material science
Particle & Astrophysics (antimatter)
Medical Science (PET)
Fast e+ (depth averaged)
Slow e+ (depth resolved)
Lifetime
ACAR
Doppler broadening
Lifetime / Doppler
LEPD
PAES
Microscope
e- density
e- momentum distribution
(bulk) defects
defects at surfaces
surface structure
surface chemistry
imaging of defects

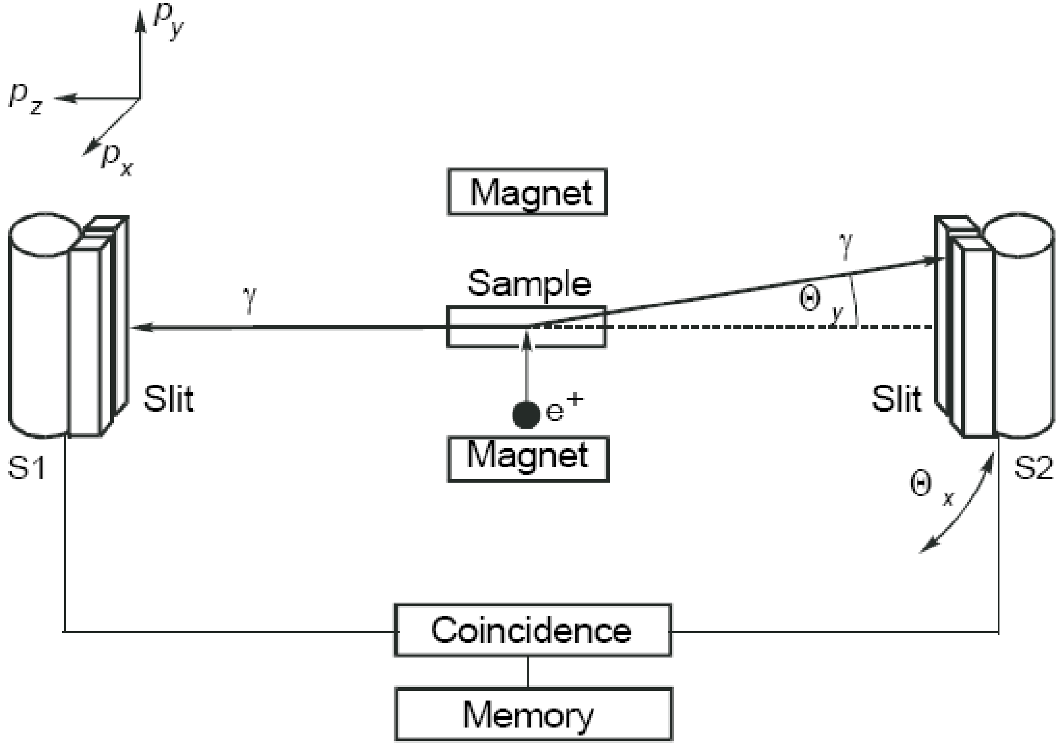
Techniques used in the PRIMAVERA project.

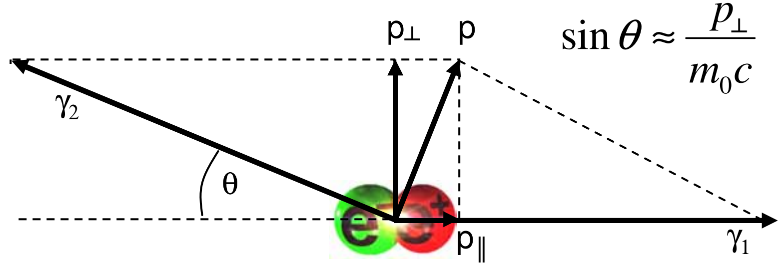


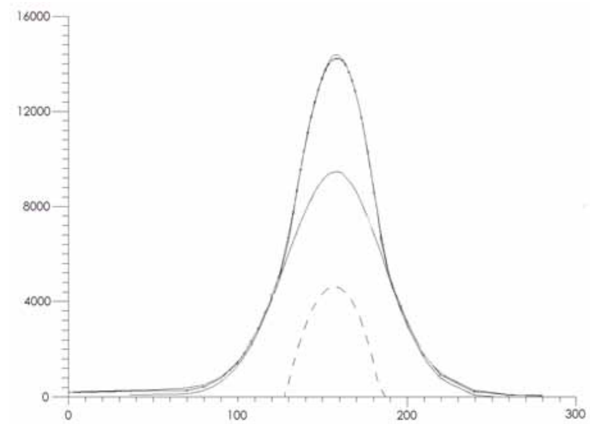
a) Positron-lifetime measurements (PAS LT) – sensitivity to electron density
b) Angular correlation of annihilation gamma (PAS ACAR) – sensitivity to electron momentum distribution
c) Doppler broadening of annihilation line (PAS DB) – sensitivity to electron momentum distribution

Angular correlation of annihilation radiation (PAS ACAR).

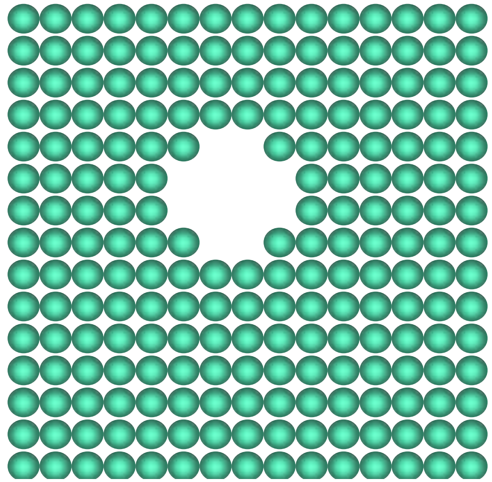
- measures deviation of annihilation gamma quanta from the 180°
- annihilation photons are detected in coincidence by scintillation counters
- lead collimators in front of the detectors define the instrumental angular resolution (1 mrad)
- slits are made in the x direction as long as possible
- single channel analyzer (SCA) is tuned for 511 keV photons and the device simply counts the coincidence pulses as a function of the angle Θ_z.







Angular correlation of annihilation radiation (PAS ACAR).



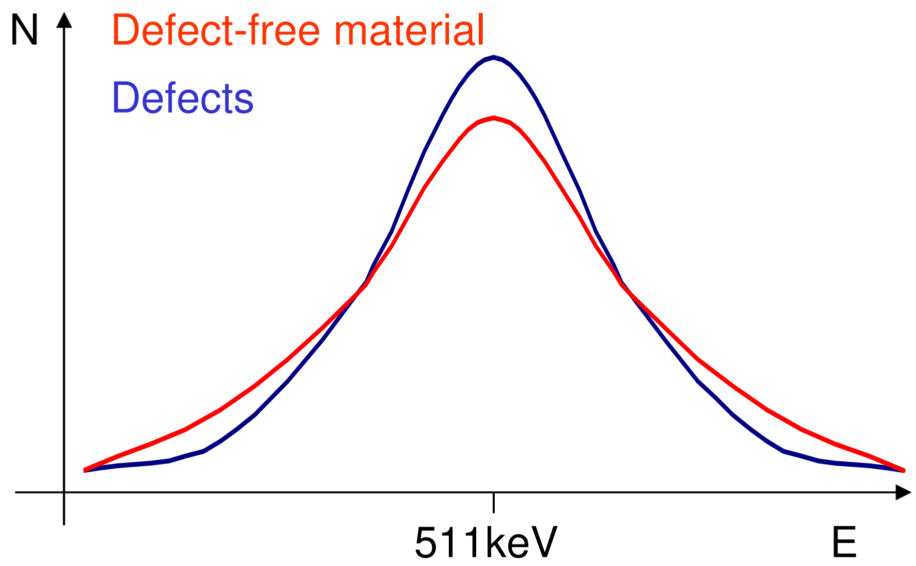
1. localization of positrons in open-volume defects

2. fraction of valence electrons (low momentum) taking part in the annihilation process increases compared with that of core electrons (high momentum)

3. momentum distribution of annihilating electrons shifts to smaller values

4. smaller angular deviation for ACAR

5. The curve is higher and narrower than that of defect-free reference material



Angular correlation of annihilation radiation (PAS ACAR).

Chemical information:

Fermi momentum $p_F = \theta_p mc$

Fermi energy $\varepsilon_F = \dfrac{\theta_p^2 mc^2}{2}$

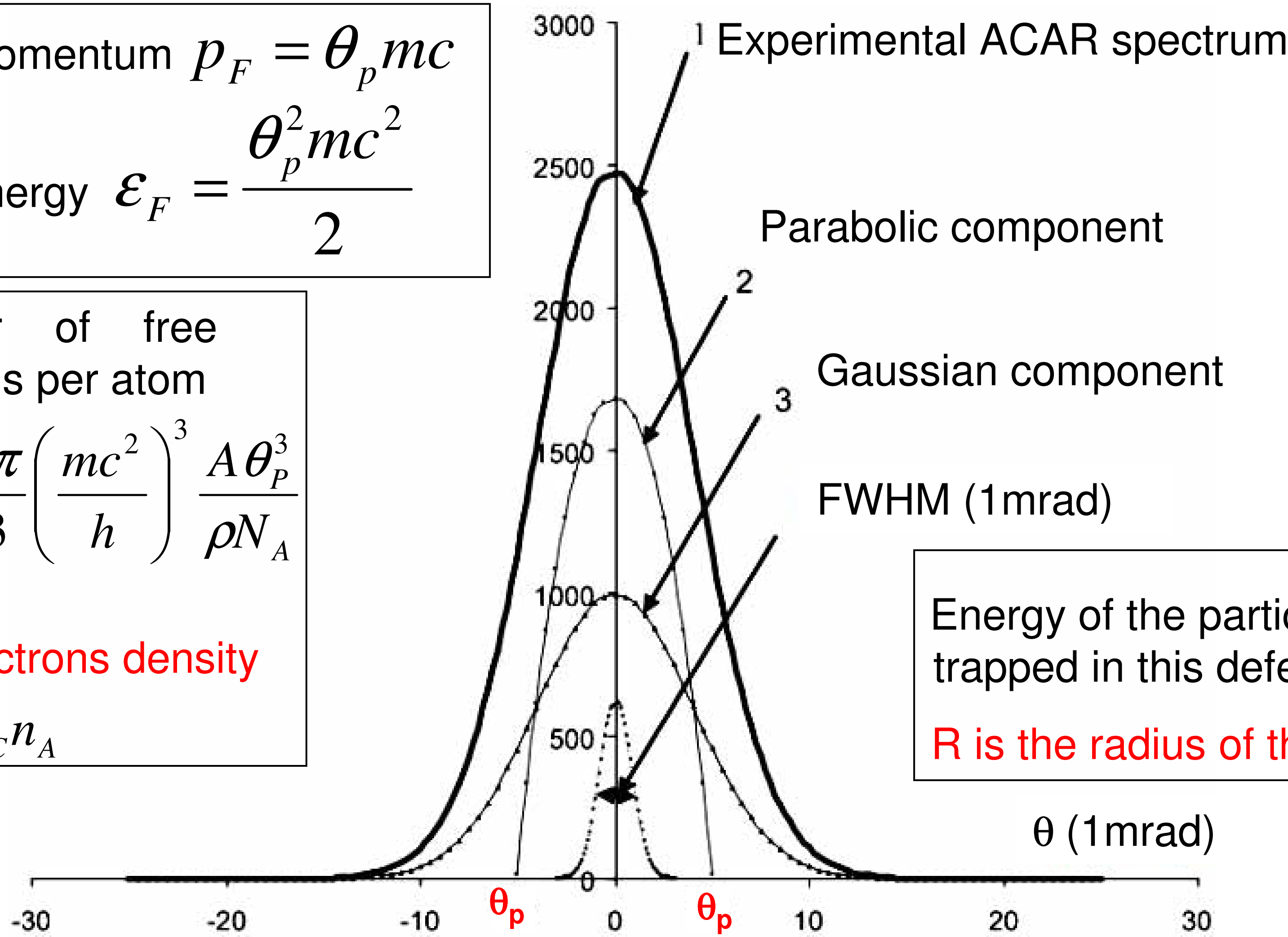
Number of free electrons per atom

$$Z_C = \frac{8\pi}{3}\left(\frac{mc^2}{h}\right)^3 \frac{A\theta_P^3}{\rho N_A}$$

Free electrons density

$$n_P = Z_C n_A$$

Defect information:



Energy of core electron

$$\varepsilon_g = \frac{3}{4} mc^2 \theta_g^2$$

Energy of the particle trapped in this defect $E = \dfrac{\pi^2 h^2 n^2}{2mR^2}$

R is the radius of the potential well

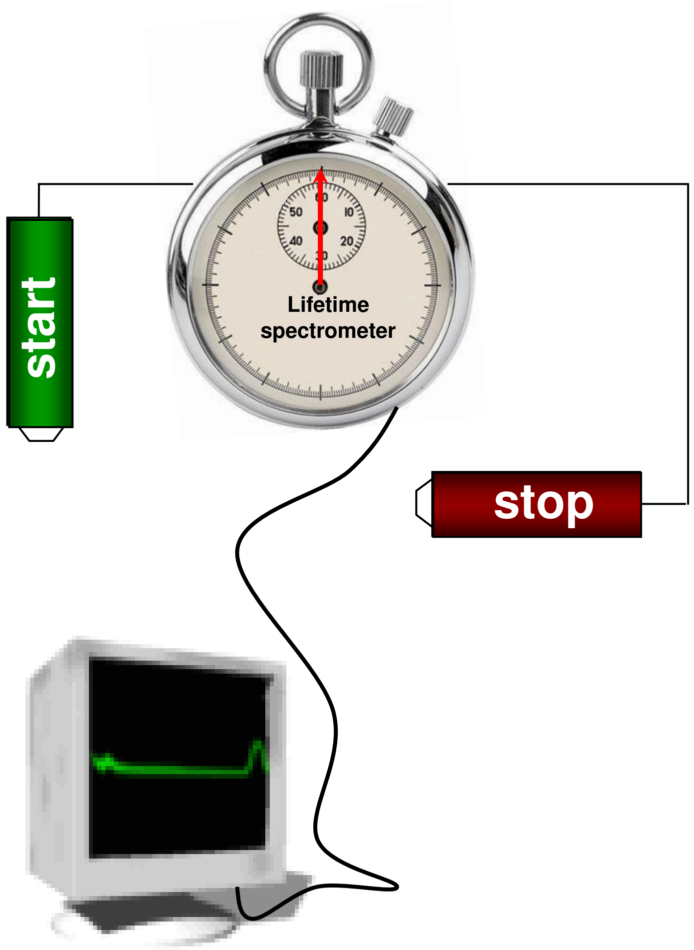
Angular correlation of annihilation radiation (PAS ACAR).

positron sources – electrolytic copper foils (10x10x2mm), irradiated for 24 hours in IRT reactor (flux $2.10^{13}\ cm^{-2}s^{-1}$)

Angle resolution of the ACAR facility is 0.4mrad. Number of counts in peak – $10\text{-}16.10^{3}$

Positron Annihilation Lifetime Spectroscopy (PALS)

-Measuring of time between the generation of positron and the electron-positron annihilation
-The positron lifetime (usually less than 1 ns) is determined with the environment (electron density)



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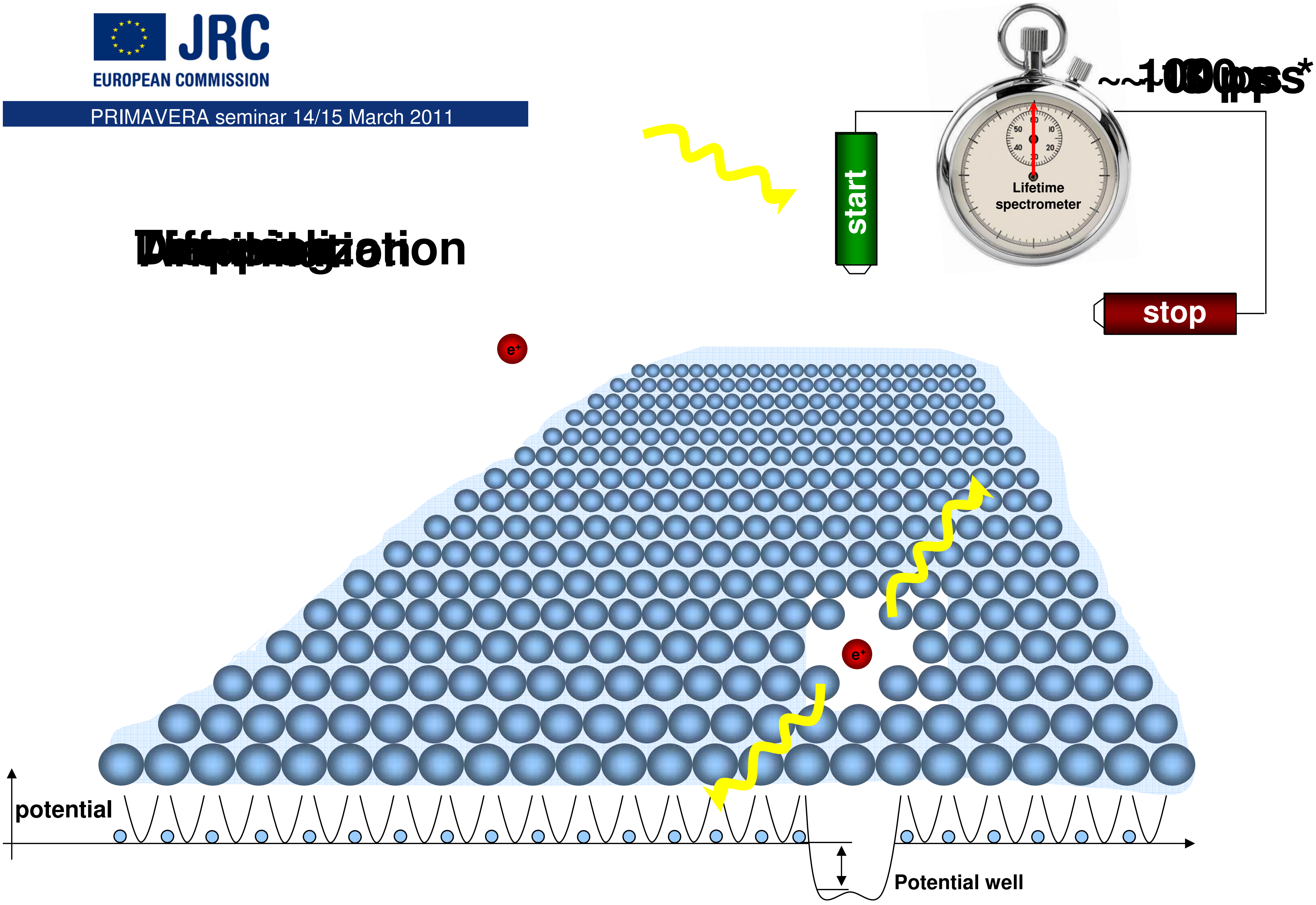
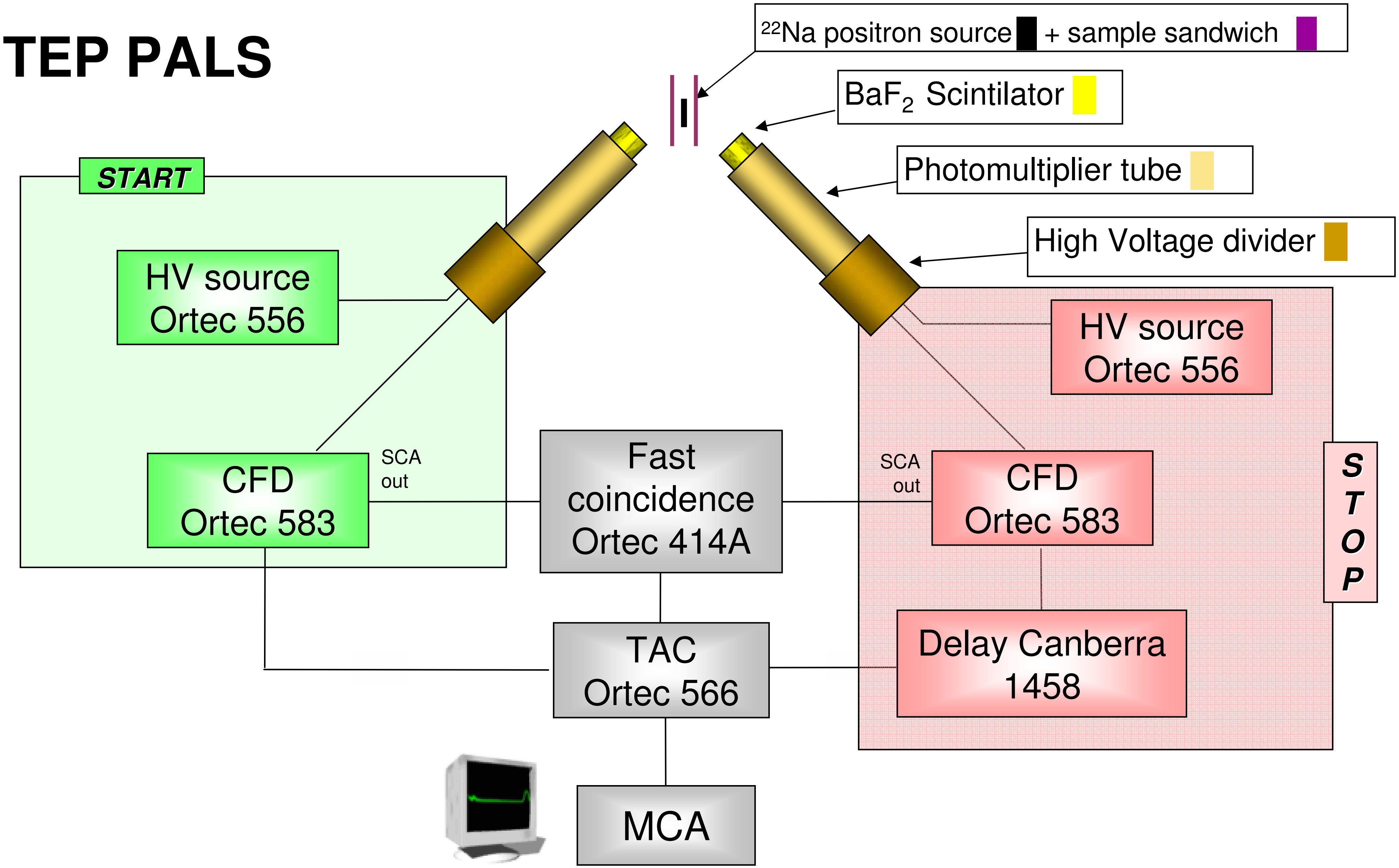
PRIMAVERA seminar 14/15 March 2011

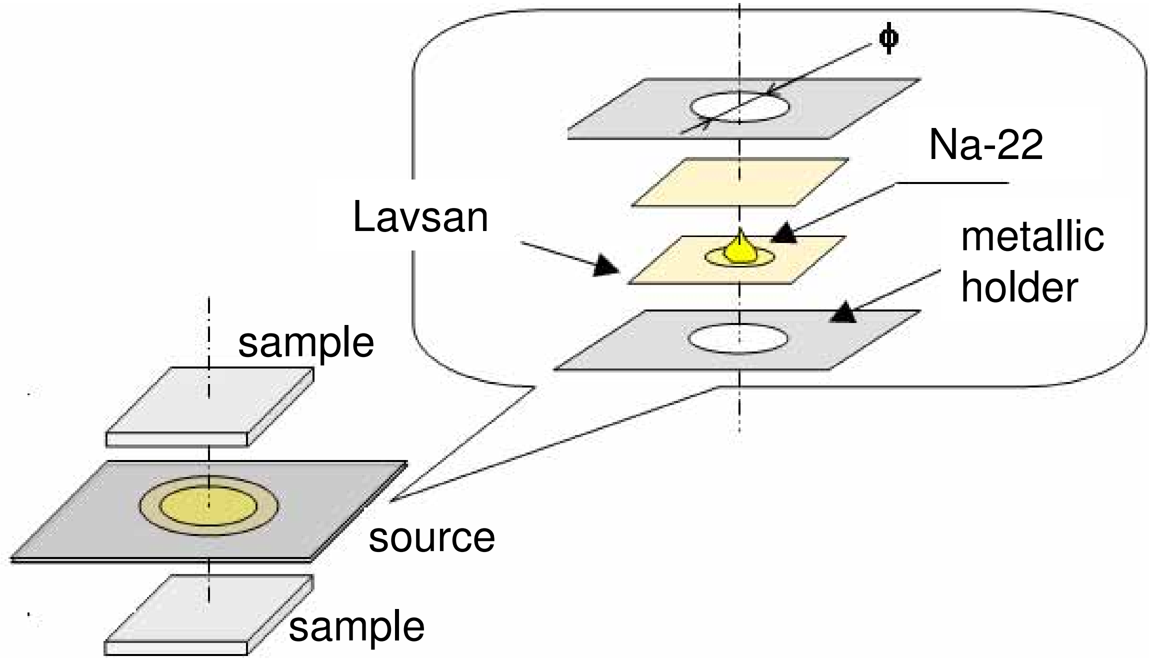


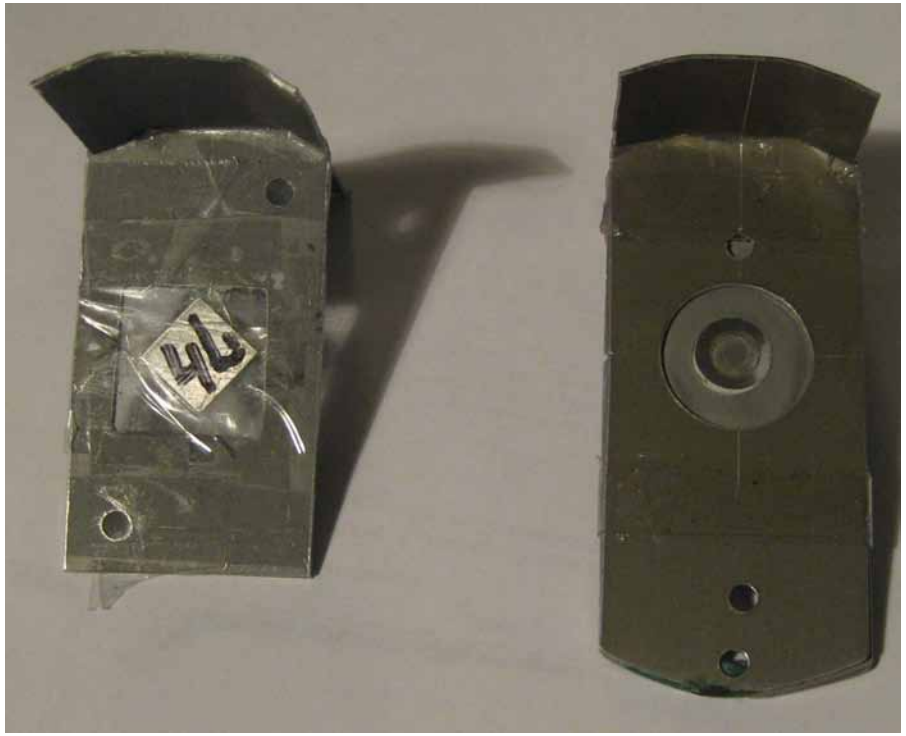
ITEP PALS


22Na positron source + sample sandwich
BaF2 Scintilator
Photomultiplier tube
High Voltage divider
START
HV source
Ortec 556
CFD
Ortec 583
SCA
out
Fast
coincidence
Ortec 414A
SCA
out
CFD
Ortec 583
HV source
Ortec 556
S
T
O
P
TAC
Ortec 566
Delay Canberra
1458
MCA

ITEP PALS – positron source

Na-22 radionuclide was supplied by V/O "Isotope" in aqueous solution of sodium chloride form. Calculated activity of about 100 µCi (3.7MBq) was sealed by polymer foil (Lavsan) of 7.5 µm thick. Sandwich was placed inside a metallic holder. Studied sample was fixed to the holder by adhesive tape.





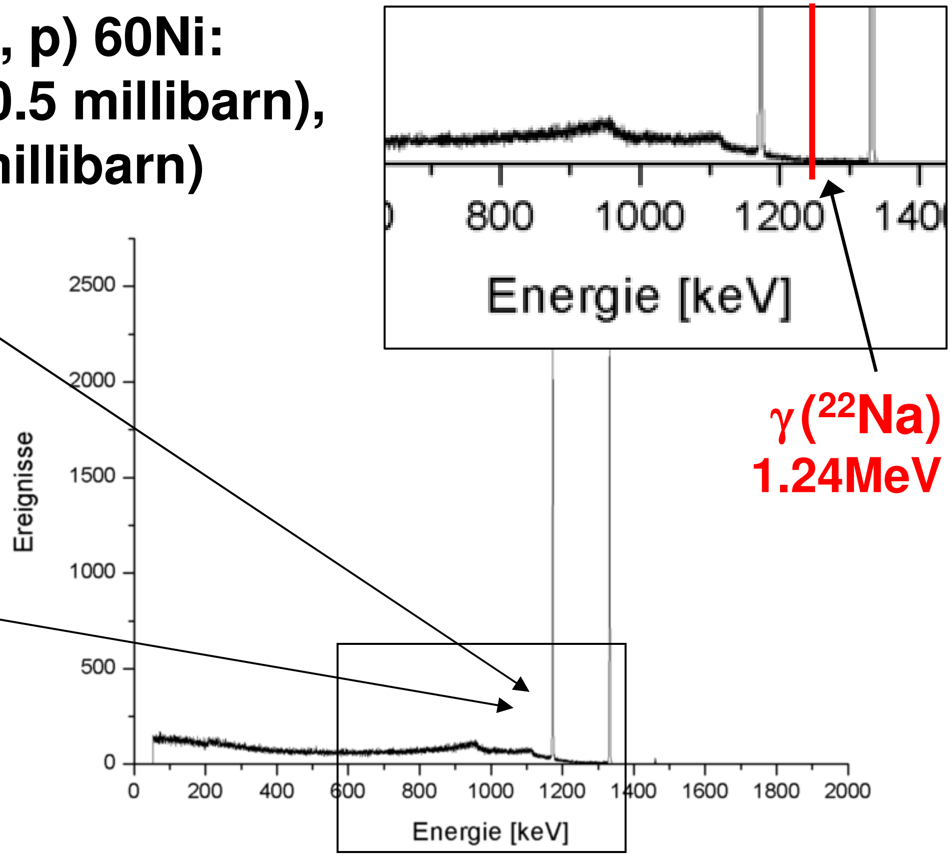
Estimated fraction of positrons, annihilating in the source (source contribution) was approximately 30%. Characteristic lifetime of positrons annihilating in the positron source was found as 0.175ns (foil), 0.427ns (NaCl), 1.84 ns (foil).
70% of positrons annihilated in the sample material.

Cobalt 60 problem

Pathway of cobalt 60 in reactor steels containing Ni (~ 0.13%) or Cu (~ 0.16%):

1. (reaction n, alpha) ^{63}Cu and (reaction n, p) 60Ni:
   - ^{63}Cu (69,1%) (n, alpha) → ^{60}Co (0.5 millibarn),
   - ^{60}Ni (26,16%) (n, p) → ^{60}Co (2.3 millibarn)

2. (n, p) reaction 58Ni:
   - ^{58}Ni (n, p) → ^{58}Co (113 millibarn)
   - ^{58}Co + n → ^{59}Co (37 millibarn)
   - ^{59}Co + n → ^{60}Co (58 millibarn)



<u>1.17</u> and <u>1.33MeV</u> γ cause a false start (stop) signals in lifetime spectrometer

Cobalt 60 problem

The experimental PALS spectra of the irradiated steels are a superposition:

1. annihilation of positrons in steel
2. annihilation of positrons in the source material
3. coincidence of Na-22 γ - Co-60 γ and Co-60 γ - Co-60 γ – background effect
4. coincidence (interference) of γ from Co-60 present in the irradiated samples – contribution to the peak

In a separate experiments, we measured the annihilation spectra in the unirradiated and irradiated steels, as well as the spectra of instantaneous coincidences of γ from Co-60 (without positron source).
The analyses of experimental results allow us to assess the impact of each of these factors and outline a methodology for the conventional positron lifetime measurement on irradiated materials containing Co-60 (both experiments and data treatment).

Cobalt 60 problem

Low-P material measurements

Sample no.	Condition	Contribution Co-60 in the PAL spectrum (%)	Contribution Na22 in the *background* (%)
L1-Na-L1	**unirradiated**		**100**
L2-Na+Co-L2	**irradiated**		**87,0**
L2-Co-L2	irradiated	2,0	0
L3-Na+Co-L3	**irradiated**		**62,0**
L3-Co-L3	irradiated	7,7	0
L4-Na+Co-L4	**Irradiated + annealing**		**61,6**
L4-Co-L4	Irradiated + annealing	8,3	0

To obtain 4 experimental spectra of individual material (unirradiated, low fluence, high fluence, high fluence + annealing) 7 measurements have been done.

Absolute values of sample activity can be determined - <u>precise characterization of the neutron fluence</u> for each individual sample

Cobalt 60 – evaluation of the measurements

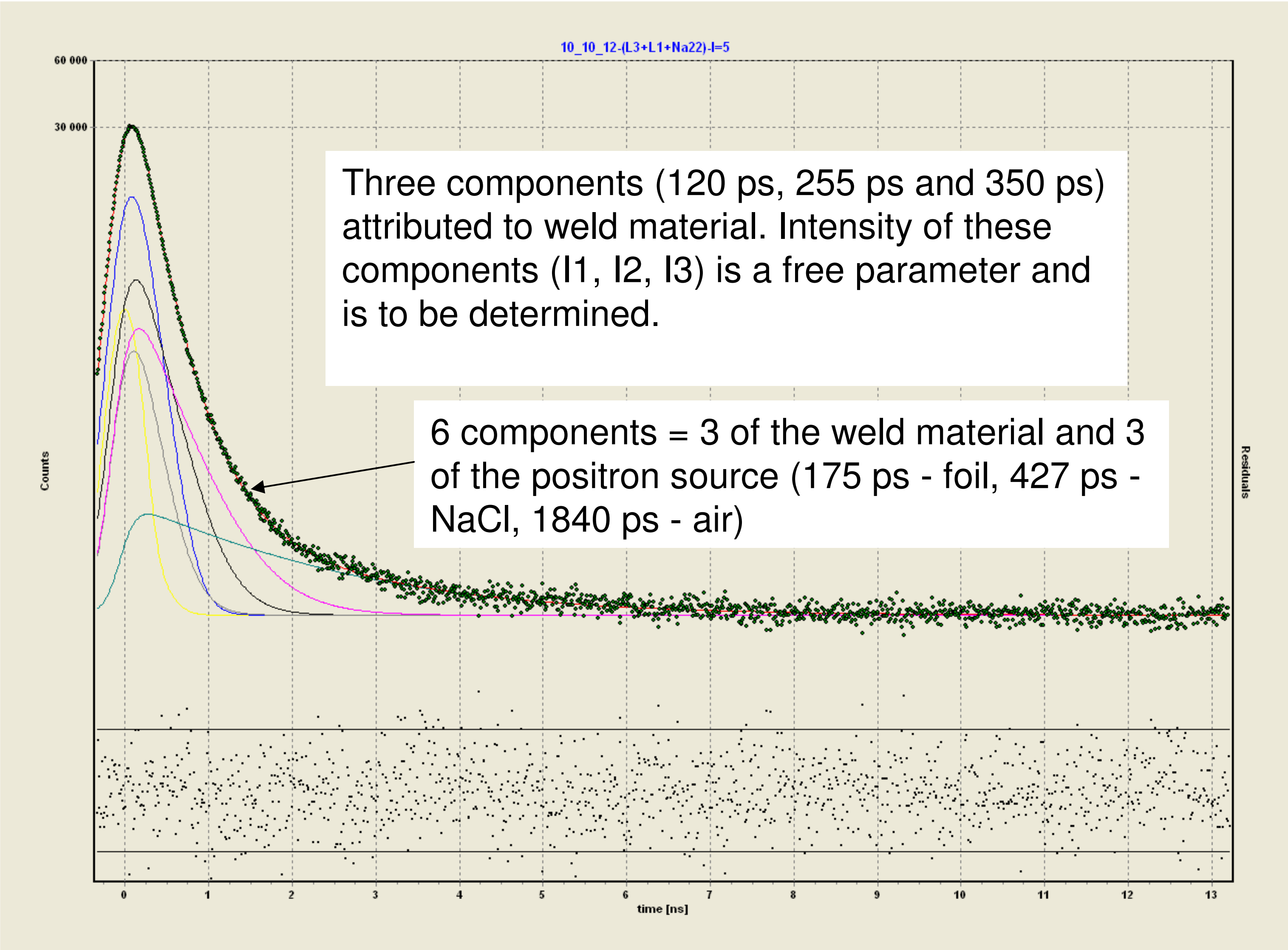
Relative activity of the Co-60 in the low-irradiated samples was ~ 5% of the Na-22 activity, while the relative activity of the high-irradiated sample was ~ 25% of the Na-22.

Coincidences of γ(Co-60) with γ(Na-22) increase the background by approximately 10 - 15% for the low-irradiated samples and 35 - 40% for the high-irradiated steels.

Co-Co coincidences contribute to the total spectrum as a spectrum as small Gaussian with peak shifted by 80-100 ps left from the center of the lifetime peak. Contribution of this coincidences to the lifetime spectrum is ~ 2% for the low-irradiated samples and ~ 7 - 9% for the high-irradiated samples.

The contribution of Co-60 to the background is ~ 1 - 2% depending on the fluence.

PALS data treatment



PAS results

PALS results

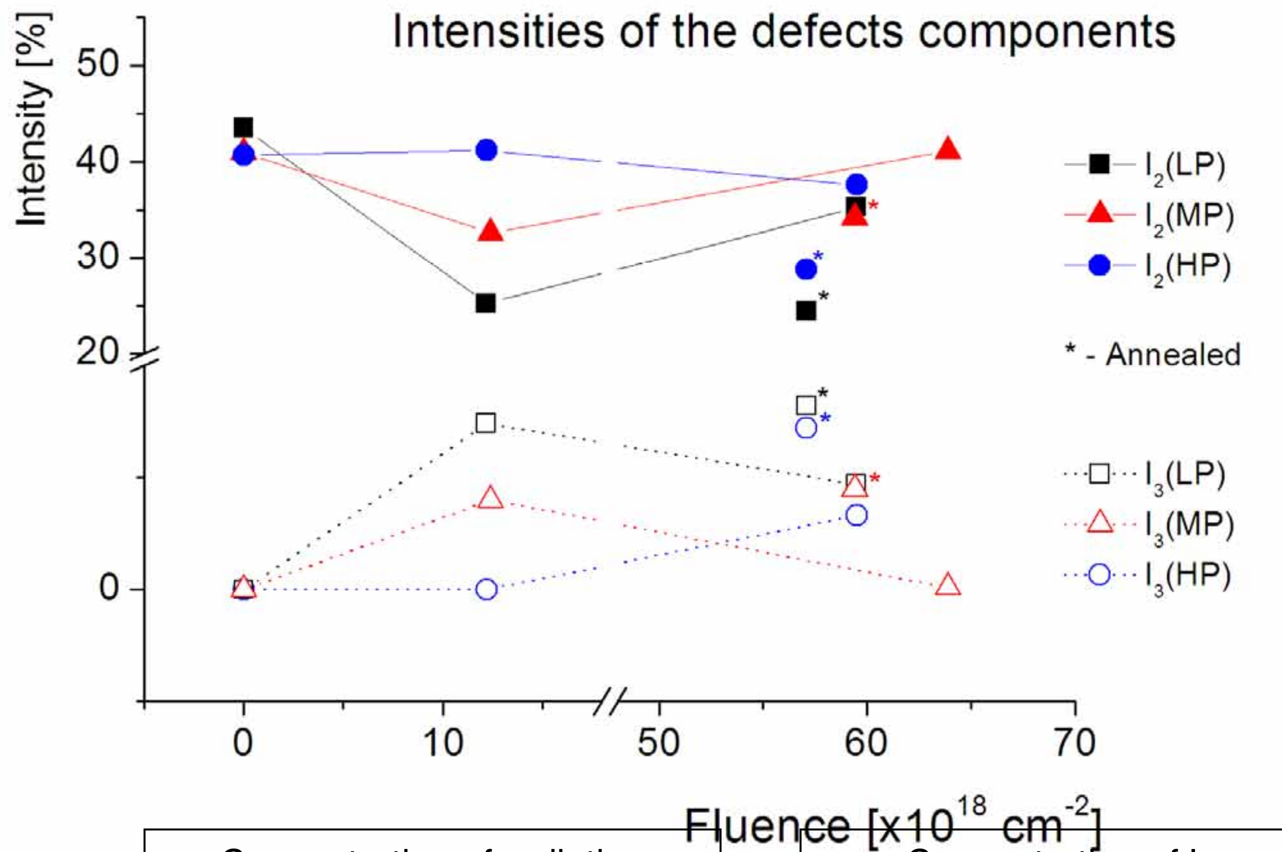
Sample no.	I_1 (%)	I_2 (%)	I_3 (%)	MLT (ps)	χ^2	BKGD
L1	56.5%	43.5%	0.0%	178.7	0.97	95.0
L2	67.4%	25.2%	7.4%	171.0	1.36	117.7
L3	60.1%	35.3%	4.7%	178.6	1.08	169.2
L4	67.4%	24.4%	8.2%	171.7	0.92	167.7
M1	59.0%	41.0%	0.0%	175.3	1.00	106.3
M2	63.4%	32.6%	4.0%	173.1	1.01	124.8
M3	58.8%	41.1%	0.1%	175.8	1.10	173.4
M4	61.3%	34.2%	4.5%	176.5	0.83	164.6
H1	59.4%	40.7%	0.0%	174.9	1.06	102.2
H2	58.8%	41.2%	0.0%	175.6	0.93	117.1
H3	59.2%	37.6%	3.3%	178.2	0.89	163.0
H4	64.0%	28.8%	7.2%	175.3	1.03	164.6

Bulk (no defects)
120ps component

Concentration of radiation induced vacancy type defects (vacancies and smal clusters, up to 5-6 vacancies.
255ps component

Concentration of large clusters/cavities ~ 3 – 4Å (10 - 12 vacancies)
350ps component

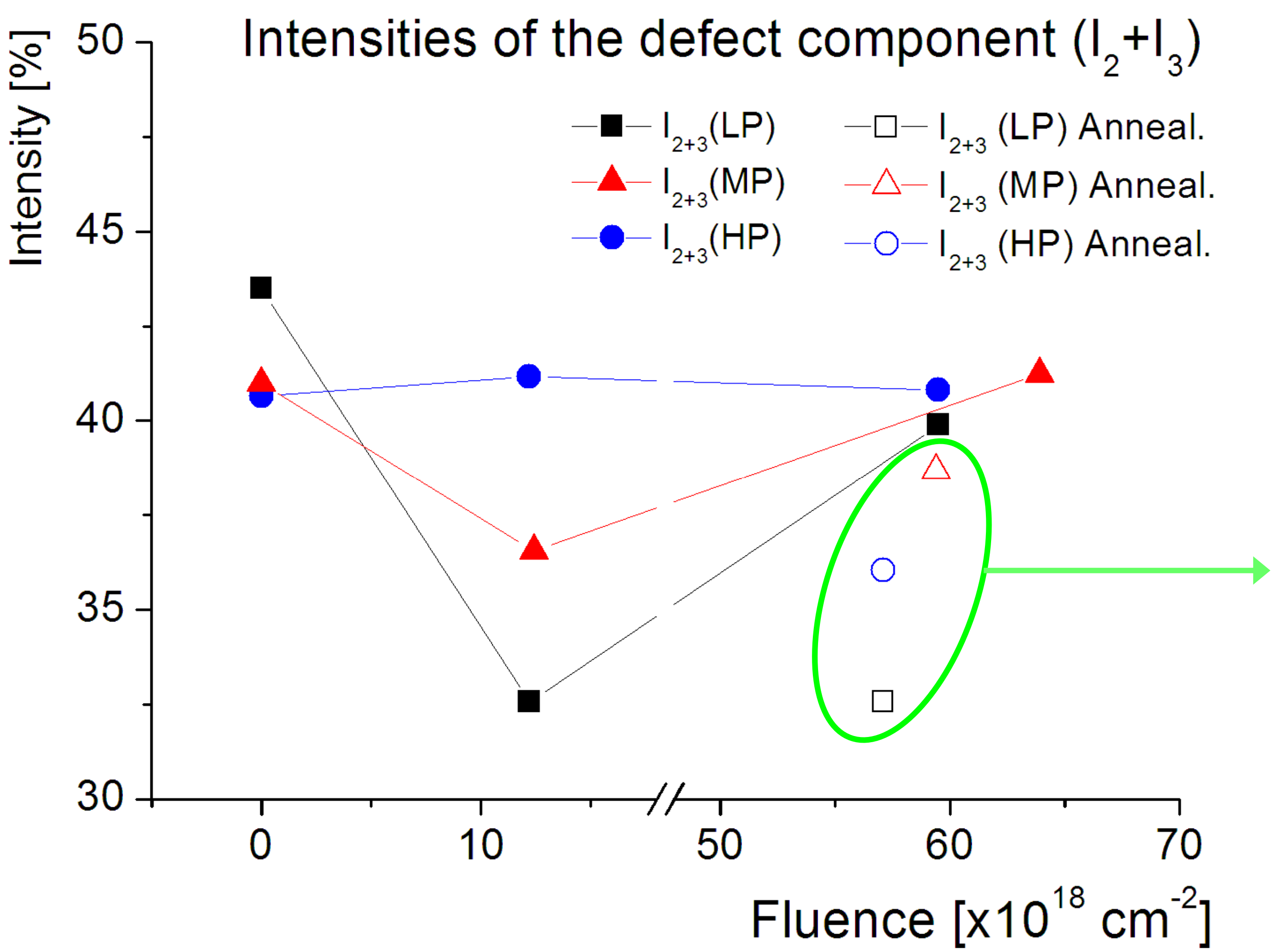
PALS results



Concentration of radiation induced vacancy type defects (vacancies and smal clusters, up to 5-6 vacancies.
255ps component

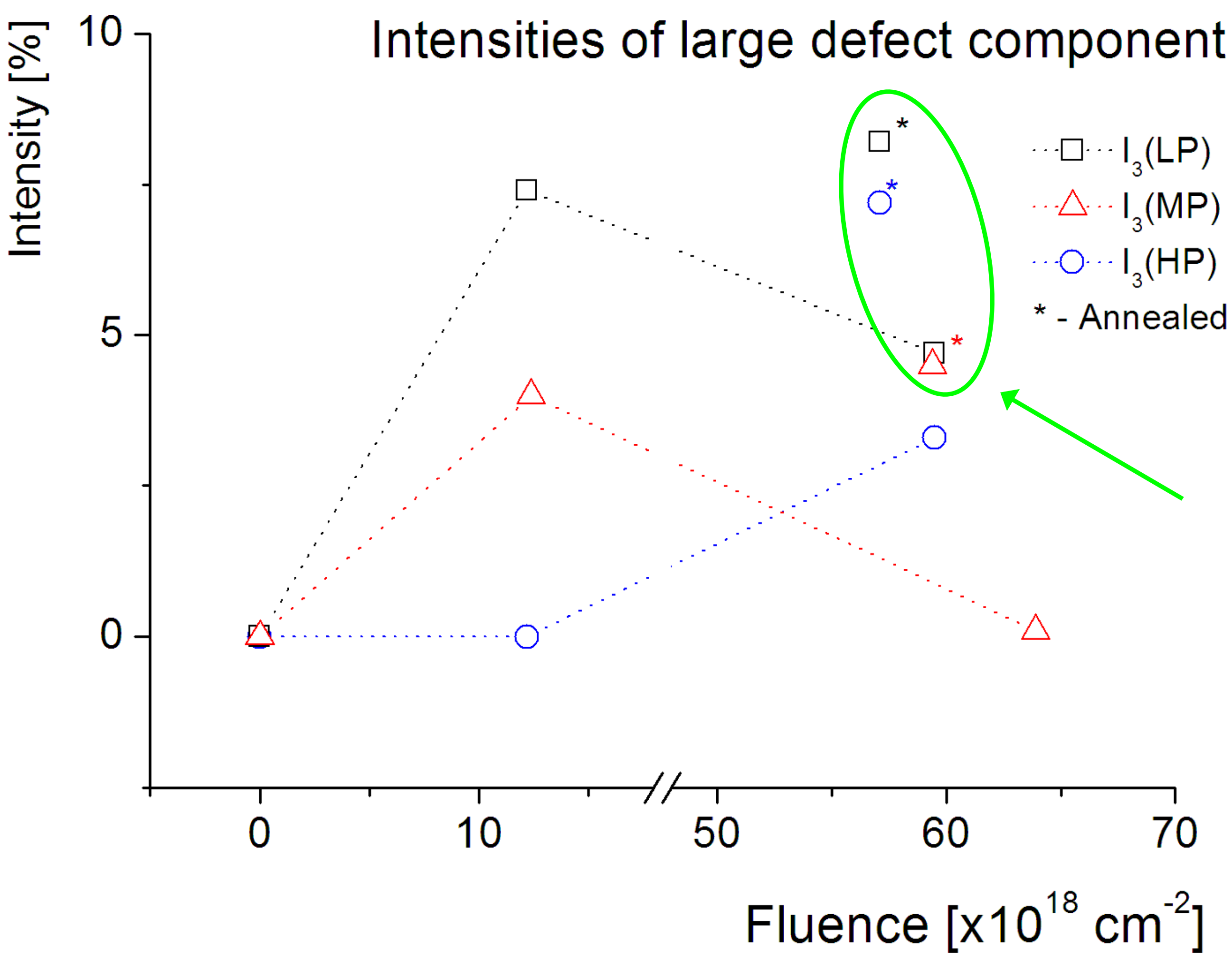
Concentration of large clusters/cavities ~ 3 – 4Å (10 - 12 vacancies)
350ps component

PALS results



General annealing effect can be seen in decreasing of the defect component intensities

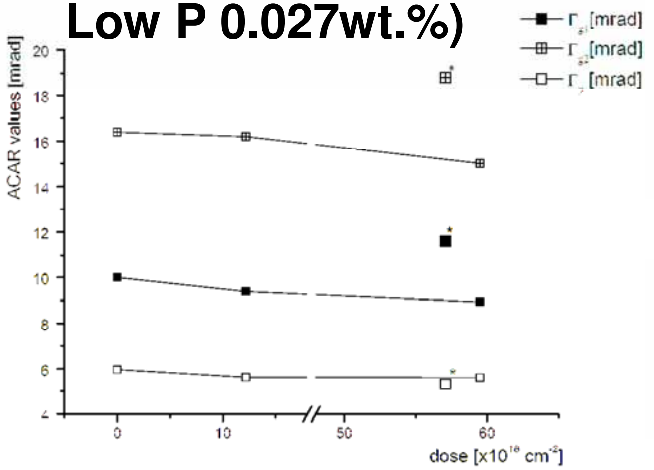
PALS results



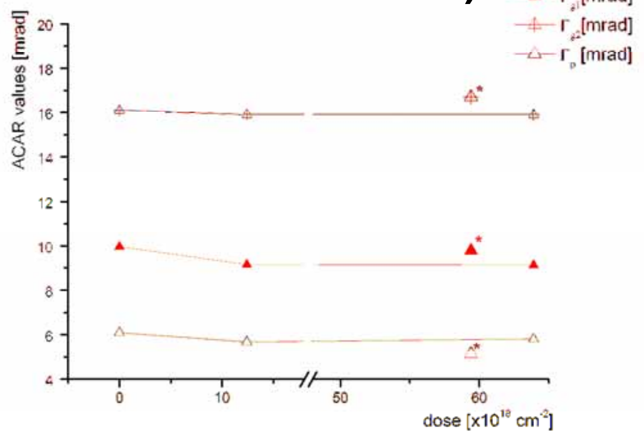
Coarsenning of vacancy clusters

ACAR results

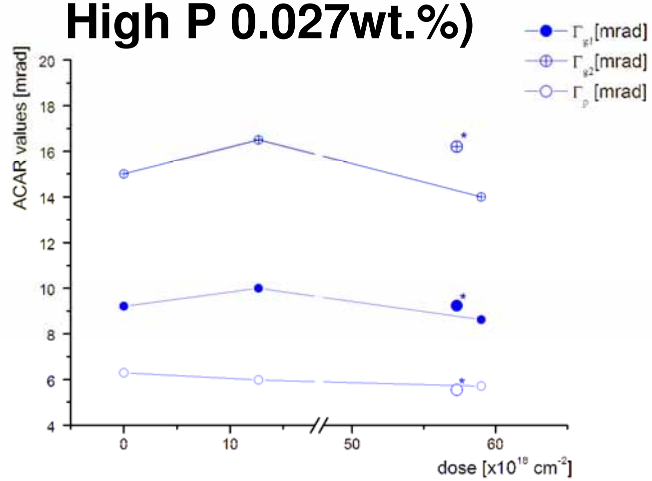
Low P 0.027wt.%)

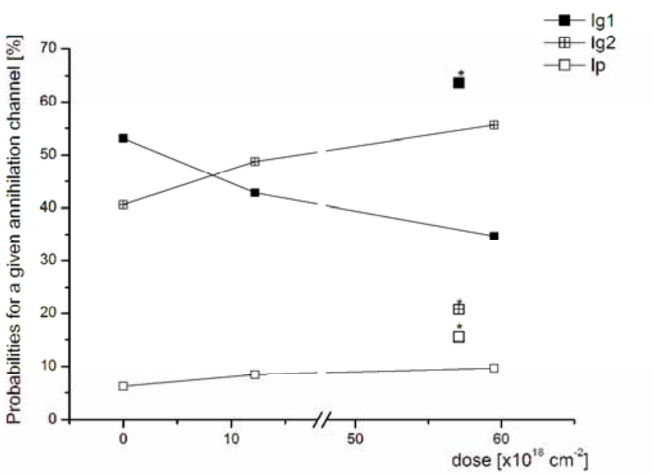


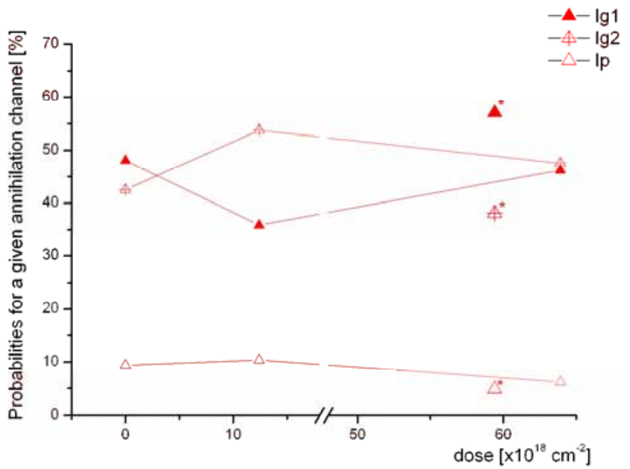
Med P 0.027wt.%)

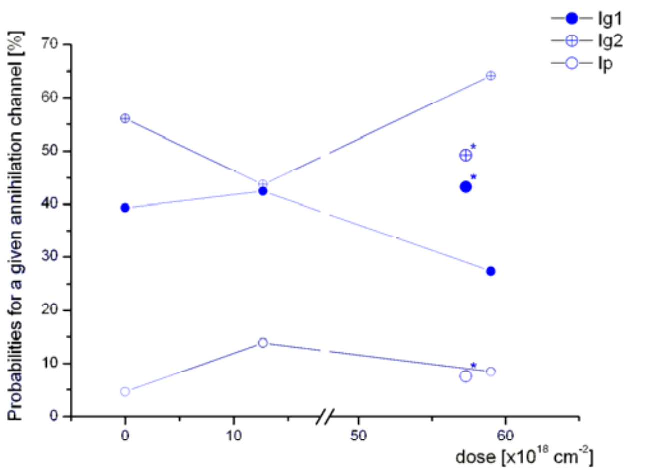


High P 0.027wt.%)









ACAR results

Low P 0.027wt.%	I_{g1} [%]	E_{g1} [eV]	I_{g2} [%]	E_{g2} [eV]	I_p [%]	E_F [eV]	N_p [10^{22} cm^{-3}]
Unirradiated	53,15 ±14,00	6,91 ±0,05	40,61 ±15,00	18,60 ±0,08	6,24 ±2,70	9,08 ±5,10	12,6
Irradiated ($11{,}3 \times 10^{18}$)	42,80 ±11,00	6,09 ±0,05	48,74 ±14,00	18,10 ±0,07	8,46 ±2,90	8,07 ±3,30	10,5
Irradiated ($53{,}1 \times 10^{18}$)	34,69 ±9,10	5,52 ±0,05	55,63 ±14,00	15,50 ±0,05	9,68 ±2,70	8,02 ±2,40	10,4
Irradiated ($56{,}6 \times 10^{18}$) and annealing	63,65 ±17,00	9,23 ±0,06	20,80 ±14,00	24,40 ±0,23	15,54 ±3,60	7,18 ±0,82	8,8

Low energy – valence electrons

Higher energy – ion core electrons

Low energy – conduction electrons

Concentration of free conduction electrons

ACAR results

Concentration of conduction electrons N_p [10^{22} cm^{-3}]			
Material	**Low P 0.027wt.%**	**Med P 0.027wt.%**	**High P 0.027wt.%**
Non-irradiated	14,8	13,3	12,6
Irradiated (1 year)	12,7	10,8	10,5
Irradiated (3 years)	12,0	11,6	10,4
Irradiated (3 years) and annealed	10,1	8,0	8,8

- in all samples annealing is accompanied by reorganization of the electronic subsystem
- Fermi energy and concentration conduction electrons are decreased

ACAR results

Ionization potentials of the elements of the materials studied

Element	Fe	Cr	C	Si	Mn	P	S	Ni	Mo	Cu	V
E^{+}	7.9	6.76	11.3	8.15	7.43	10.56	10.35	7.63	7.13	7.72	6.74
E^{2+}	16.2	16.49	24.4	16.34	15.64	19.65	23.4	18.15	15.75	20.29	14.65

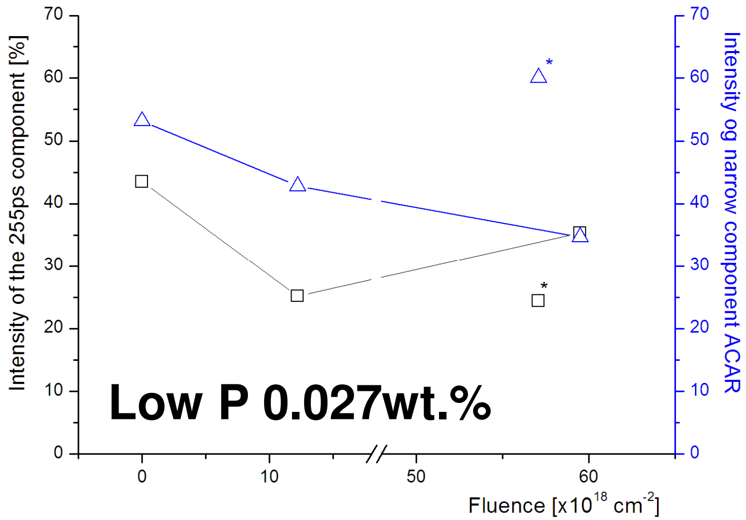
Parameters of the ACAR spectra for pure Fe and Cr samples

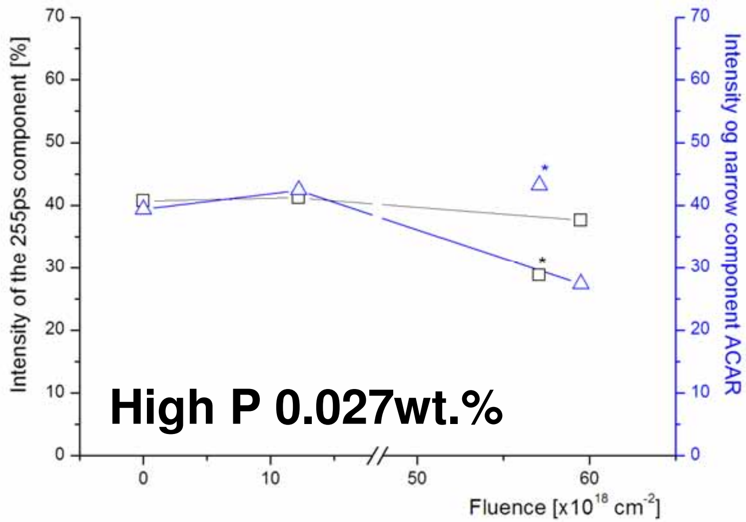
	I_{g1} [%]	E_{g1} [eV]	I_{g2} [%]	E_{g2} [eV]	I_p [%]	E_F [eV]	N_p [10^{22} cm^{-3}]
Fe	64,99	7,05	32,29	19,20	2,71	6,40	7,45
Cr	54,60	6,68	41,76	14,60	3,63	10,48	15,6

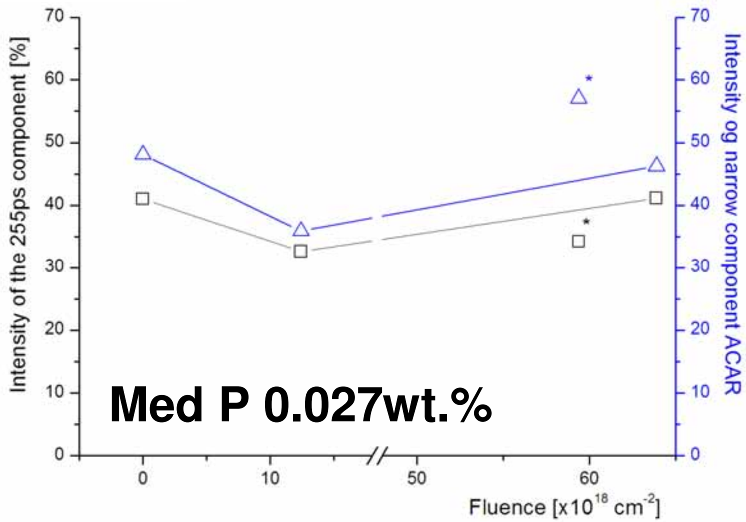
Parameters of the ACAR spectra for PRIMAVERA samples

	I_{g1} [%]	E_{g1} [eV]	I_{g2} [%]	E_{g2} [eV]	I_p [%]	E_F [eV]	N_p [10^{22} cm^{-3}]
Unirradiated	53,15	6,91	40,61	18,60	6,24	9,08	12,6
Irradiated ($53,1 x 10^{18}$)	42,80	6,09	48,74	18,10	8,46	8,07	10,5
Irradiated ($53,1 x 10^{18}$)	34,69	5,52	55,63	15,50	9,68	8,02	10,4

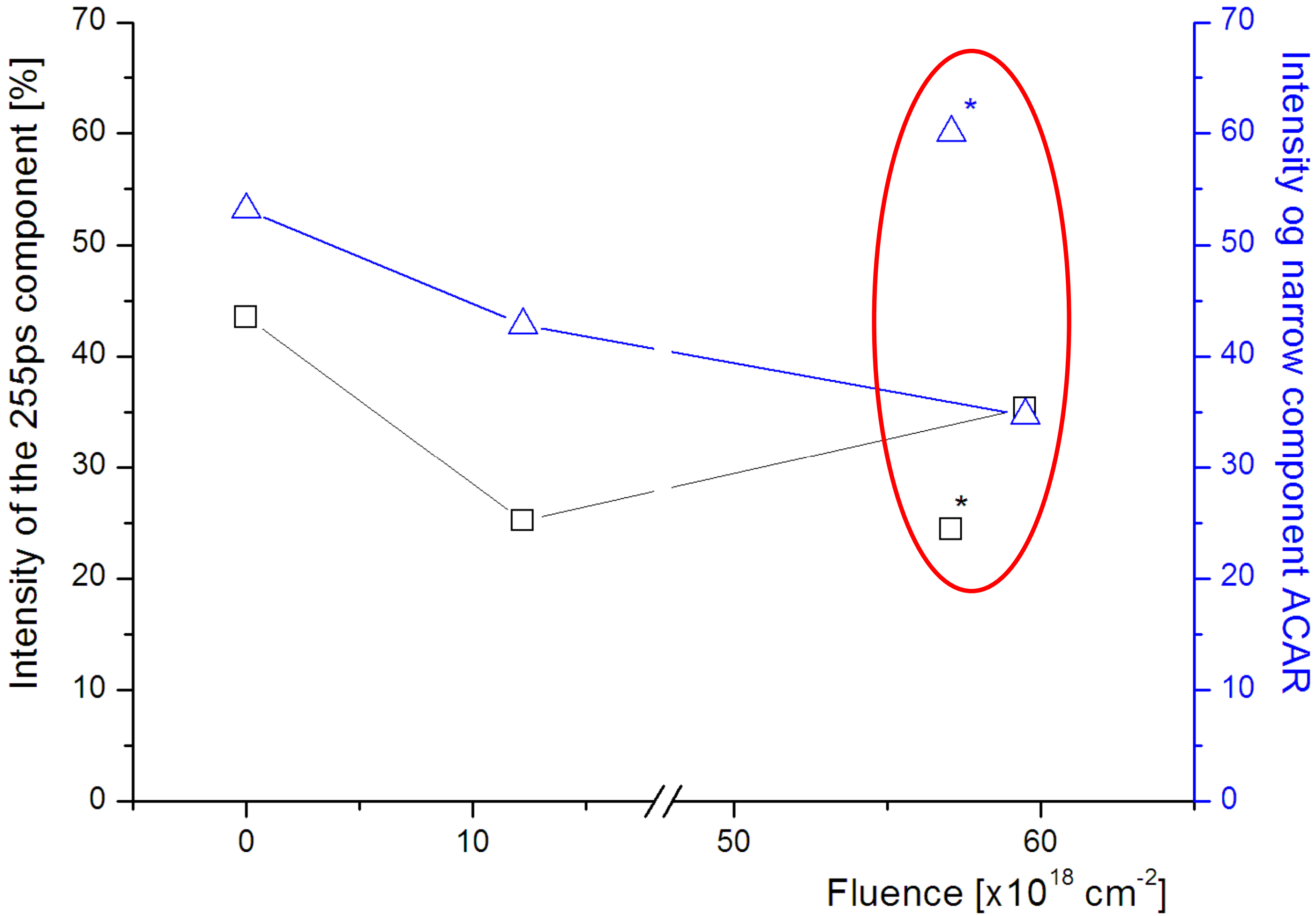
ACAR + PALS results

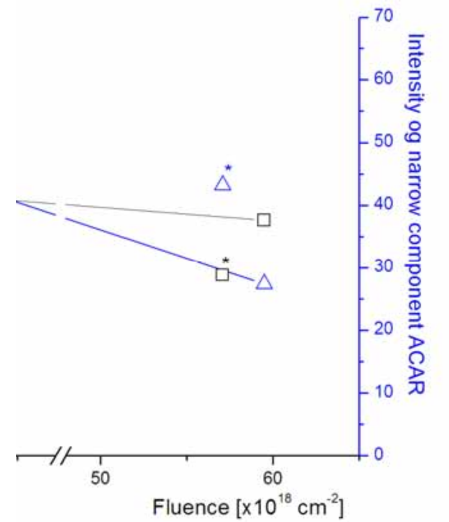






ACAR + PALS results

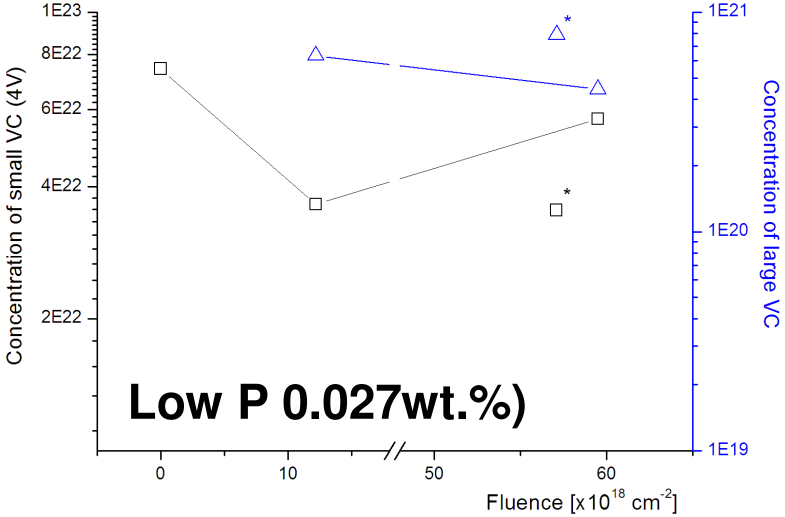


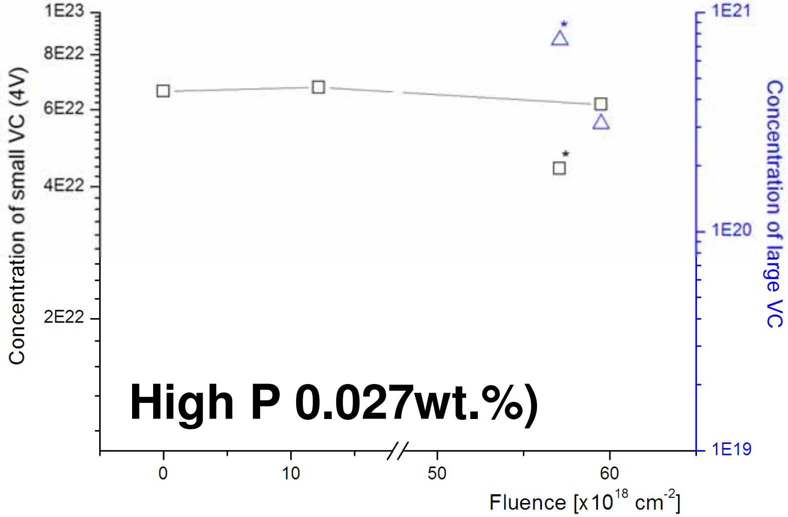


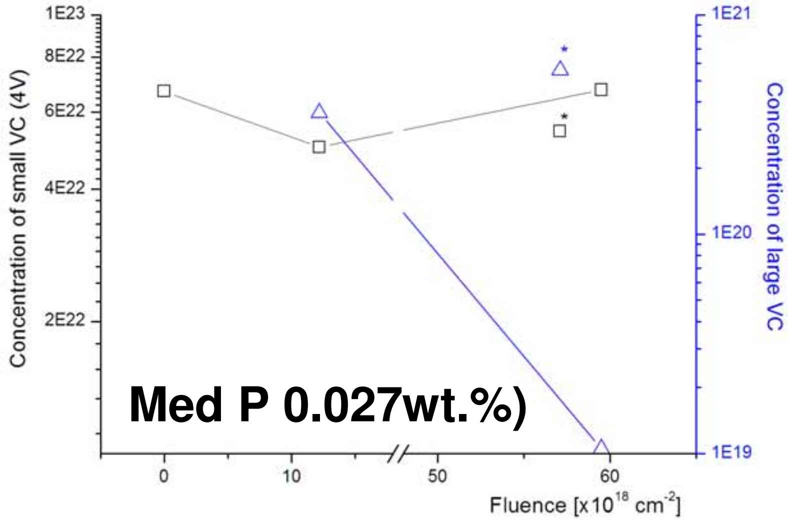
Annealing:

- Small defects are annealed out (partially)
- Narrow component – increasing of intensity given by large defects

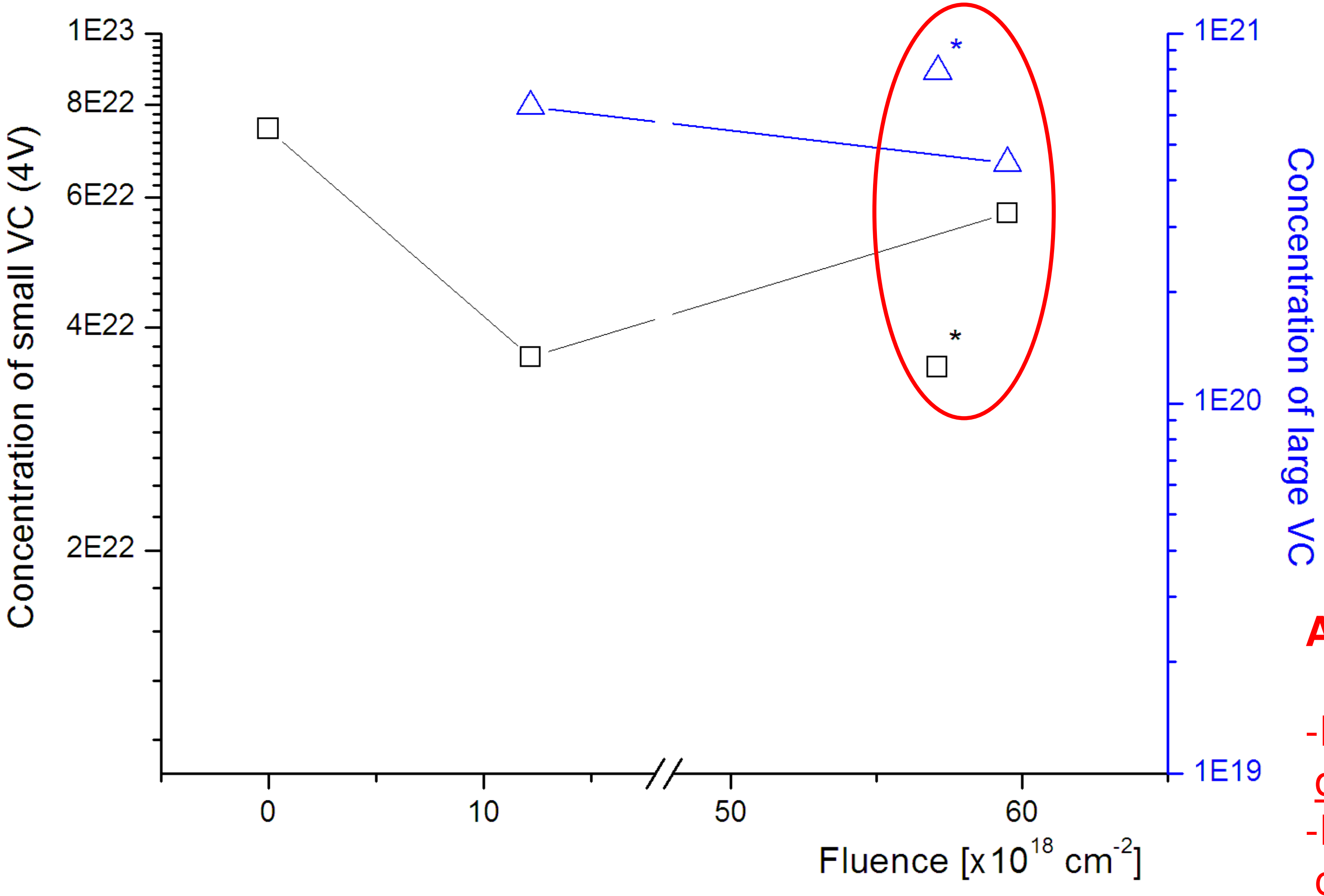
Evolution of the defects concentration

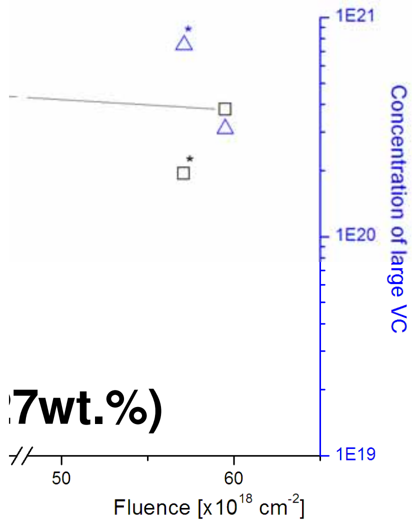






Evolution of the defects concentration



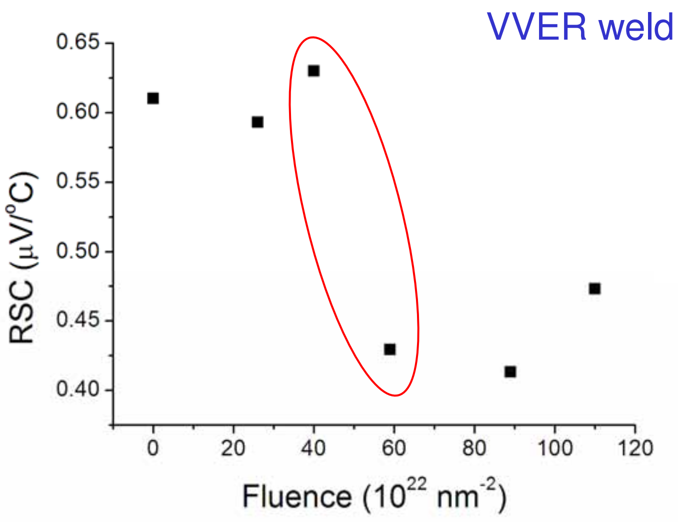


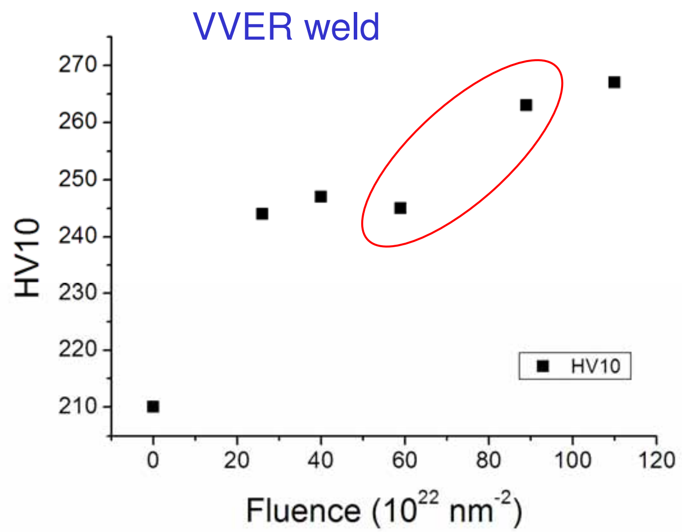
Annealing:

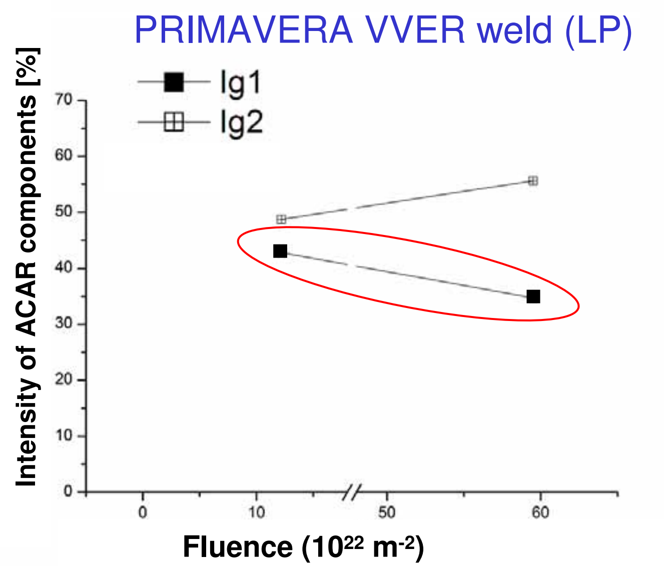
-Intensity of small defects is decreasing

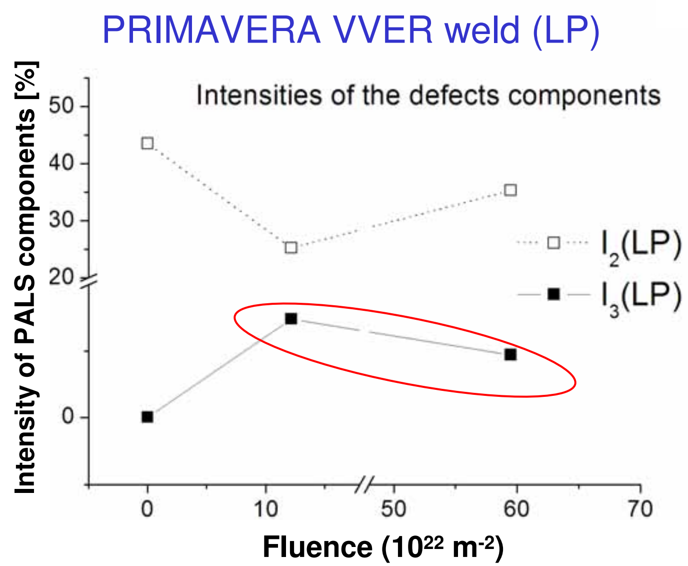
-Intensity of large clusters is increasing!

NDT* study of VVER weld









Point defects cluster

Seebeck coefficient ↓

Hardness ↑

Positron lifetime ↓

Annihilation with valence electrons ↓

Dislocation loops

Summary – material characterization

- Definition of two distinctive group of defects (small VC clusters/dislocations; larger voids ~ 3-4Å - observed in irradiated materials)
- Concentration of defects (~10^{16}cm^{-3}), free electrons (~10^{23}cm^{-3}) and Fermi energy (7-8 eV) have been determined for individual materials and treatments
- Decrease of the concentration of delocalized electrons with neutron fluence is interpreted as forming of new covalent bonds at the grain boundary, recovery of metal ions on the surface of large vacancy clusters and the formation of ordered structures.
- Characterization of annealing behavior of individual defects. In general, the positron trapping on defects is lower after annealing (most significant for low-P material), while the large component related to large defects is increasing on intensity after annealing - coarsening of vacancy clusters (observed in Cu-enriched VVER model alloys with SANS, Bergner et al. 2008)
- Behavior of chemical environment in the material after irradiation and annealing depends on the P content (chemical composition) and the evolution of microstructure is given by competition between radiation induced defects production and radiation and thermal induced annealing of the lattice defects

Summary – methodology

- Methodology for application of 22-Na source on the positron lifetime measurements of irradiated materials containing Co-60 (experimental spectra obtained in few hours instead of several tens of hours) was developed
- Absolute values of steel samples activity, containing Co-60, was determined - precise characterization of the neutron fluence for each individual sample
- These values together with absolute value of Na-22 activity were used to determine the individual contributions of the Co-60 to experimental lifetime spectra
- For the first time a study the same objects using different positron techniques PALS and ACAR.
- These techniques are complementary and allow to obtain detailed information about the electronic and defect properties of the material
- For the first time a correlation between ionization potentials of chemical elements (components of nuclear structural materials) and ACAR spectra parameters was revealed

The presented results demonstrated the potential of positron annihilation spectroscopy as a unique analytical tool and a complementary technique to mechanical testing, TAP, TEP and others.

PAS offers specific information on nano objects characteristics and behavior in investigated materials, which are essential for understanding processes in the microstructure of irradiated materials, establishing of the models, and prediction of microstructural development. This information is a significant contribution to the interpretation of the mechanical properties related to radiation embrittlement phenomena and can be used in the development of new nuclear structural materials.
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Publications

1. V.Grafutin, O.Ilukhina, V.Krsjak, R.Burcl, P.Hahner, D.Erak, A.Zeman, Journal of Nuclear Materials, 406(2010), 257-262.
2. V.Grafutin, E.P.Prokoptv, V.Krsjak, R.Burcl, P.Hahner, D.Erak, A.Zeman, O.Ilukhina, M.A.Mogilevskyi, G.G.Myasisheva and Y.V.Funtikov, Physics of Atomic Nuclei, 2011, vol.74, №2, pp.177-188.

3. *V. Grafutin, O. Ilyukhina, V. Krsjak, R. Burcl, Study of PRIMAVERA steel samples by a positron annihilation spectroscopy technique II – Lifetime measurements, drafted for Journal of Nuclear Materials*

Cobalt problem

Markin of the welds	Condition	Fluence· 10^{19}, sm^{-2} E>0.5MeB	Radio activity mBq	Weight mg
Ti-44			1,93	
H4	Irradiated +annealing	5,73	0,84	301+ 200
H3	irradiated	5,90	0,835	218 + 244
H2	irradiated	1,27	0,198	238 + 189
M4	Irradiated +annealing	5,94	0,68	212 + 231
M3	irradiated	~ 6,39	0,75	221 + 225
M2	irradiated	1,24	0,25	238 + 261
L4	Irradiated +annealing	~ 5,66	0,84	266 + 281
L3	irradiated	~5,31	0,846	221 + 312
L2	irradiated	1,13	0,138	263 + 271
Na -22			2,95	

As mentioned above, positron annihilation spectroscopy study of the irradiated reactor steel samples is complicated by the activity, induced in the samples during irradiation in the reactor - gamma quanta of radionuclides, present in the steel samples, interfere in different way with normal signal of PAS spectrometer. Gamma spectrometric analysis of the steel samples, shown that at the time of PAS experiments, the activity of the samples was mainly determined by Co-60 with small admixture of Mn-64.

The experimental PALS spectra of the irradiated steels are a superposition of several spectra - annihilation of positrons in steel, annihilation of positrons in the source material, coincidence (interference) of gamma-quanta from Co-60, contained in the irradiated samples, and coincidence of Co-60 gamma-quanta with decay gamma-quanta of Na-22 from the positron source and with annihilation gamma quanta.

Annex 9:
Kryukov's presentation on PRIMAVERA Results and Open Issues

Petten, 14-15 March, 2011

Technical meeting

PrimaVERA – basic results & open issues

A. Kryukov, L. Debarberis, A. Ballesteros

EC-JRC Petten – Institute of Energy

VVER-440 Welds Re-Embrittlement Assessment

PrimaVERA

PrimaVERA objectives:

• Study of re-embrittlement after annealing

• Role of P and Cu

•Validation of re-embritlement kinetic model

• Micro-structural validation of radiation damage

• Guidelines development

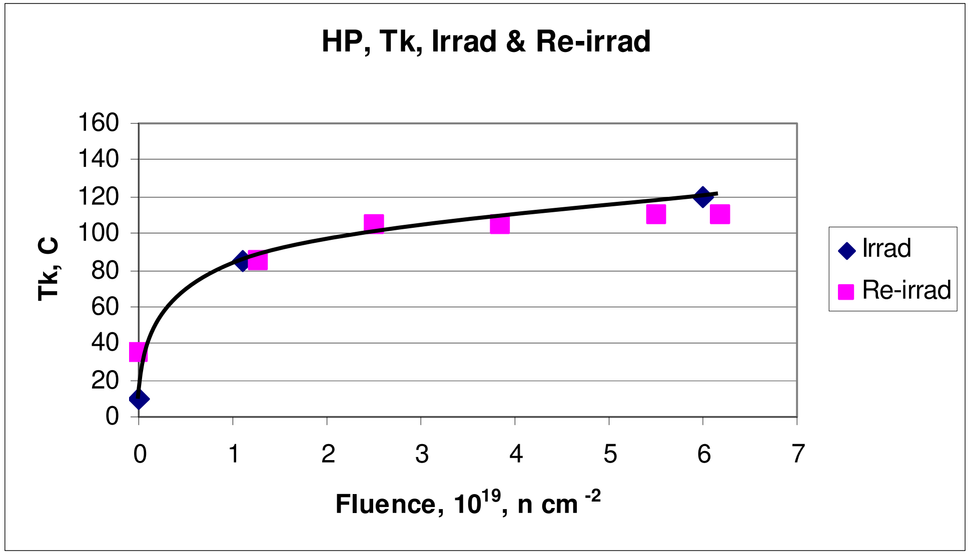
VVER-440 Welds Re-Embrittlement Assessment

PrimaVERA

Metal	P, %	Cu, %
HP	0.038	0.16
MP	0.031	0.16
LP	0.027	0.16

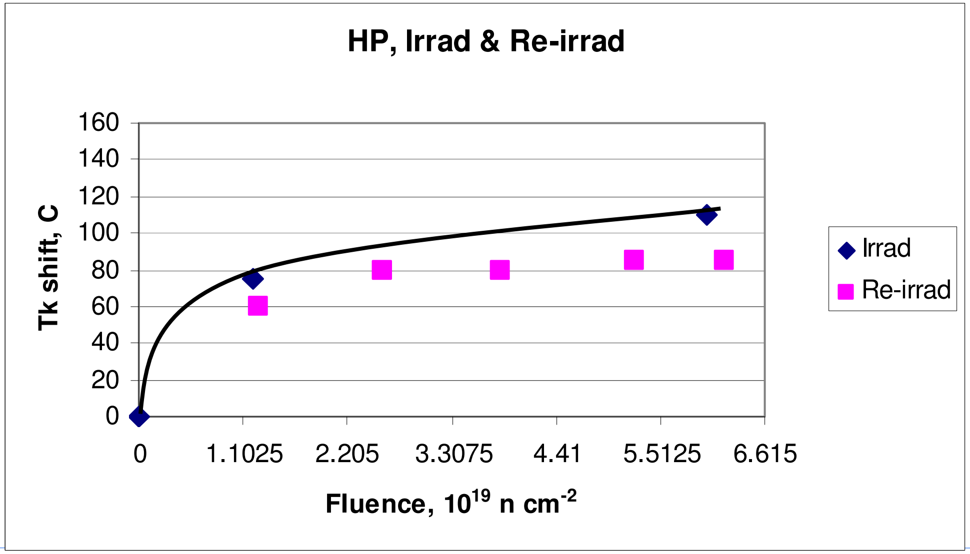
P content in annealed WWER-440 RPVs welds: 0.030 - 0.038 %

Re-embrittlement after annealing

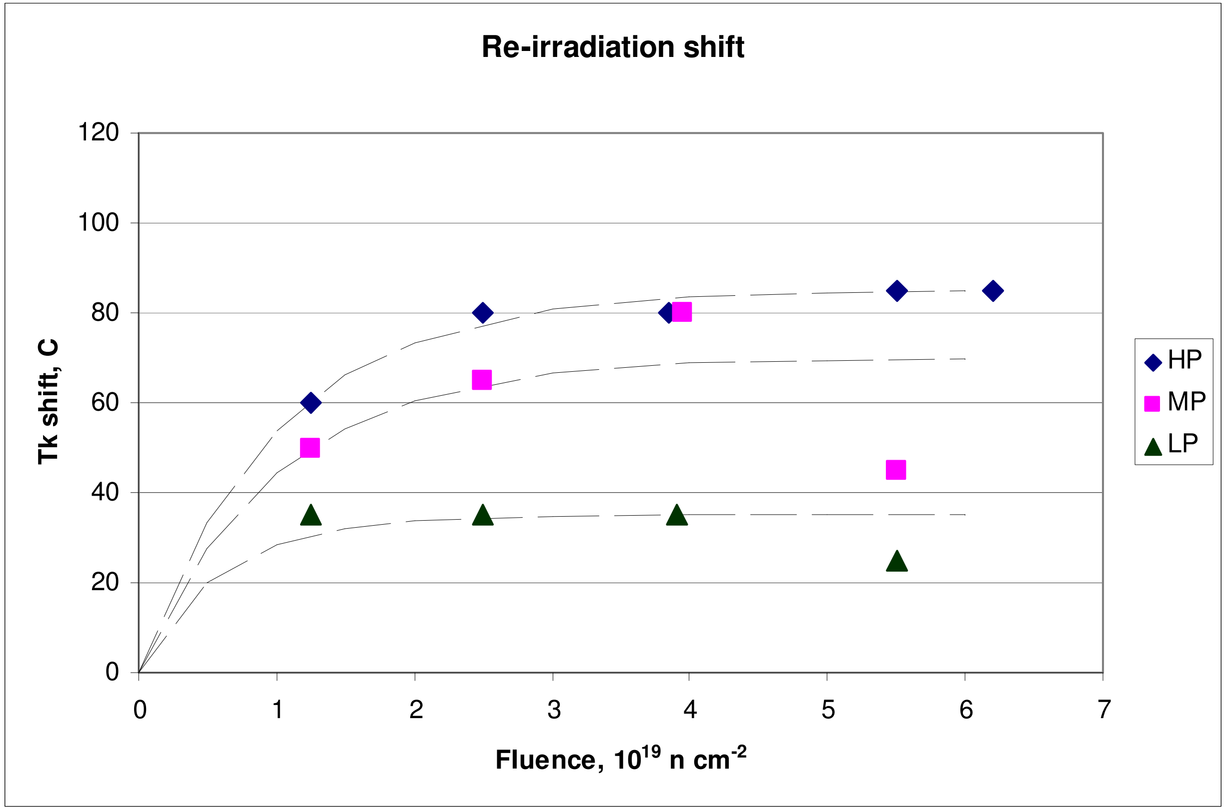


Re-irradiation effect:

- Tk not exceeding primary irradiation
- Tk re-irradiation shifts are less



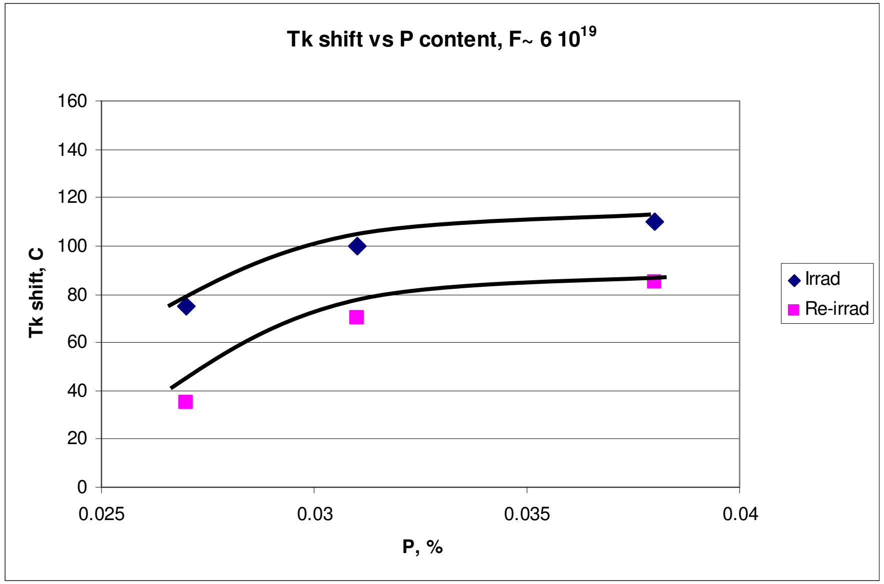
Re-embrittlement after annealing

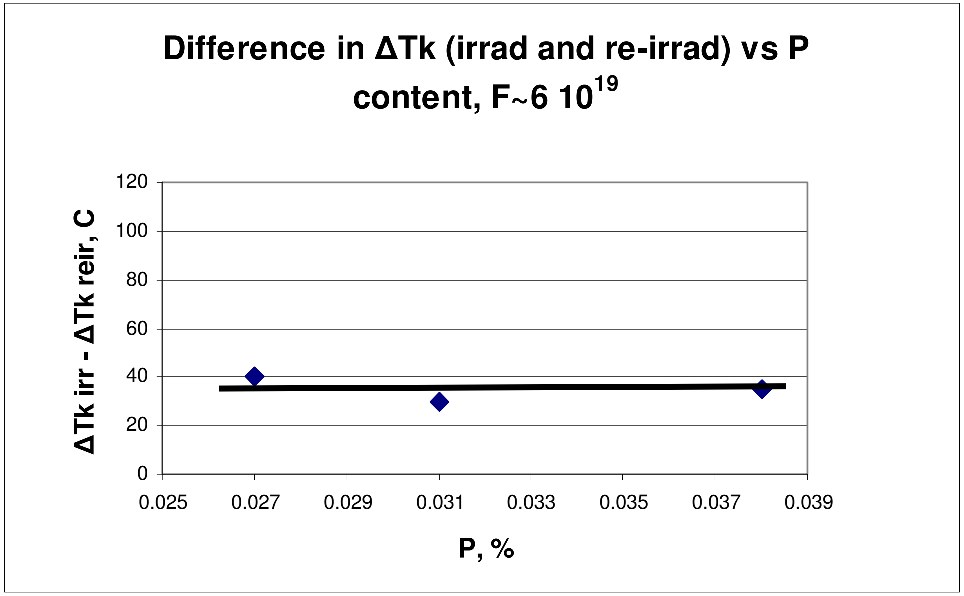


Re-irradiation - Tk shift depends on P content

Role of P and Cu

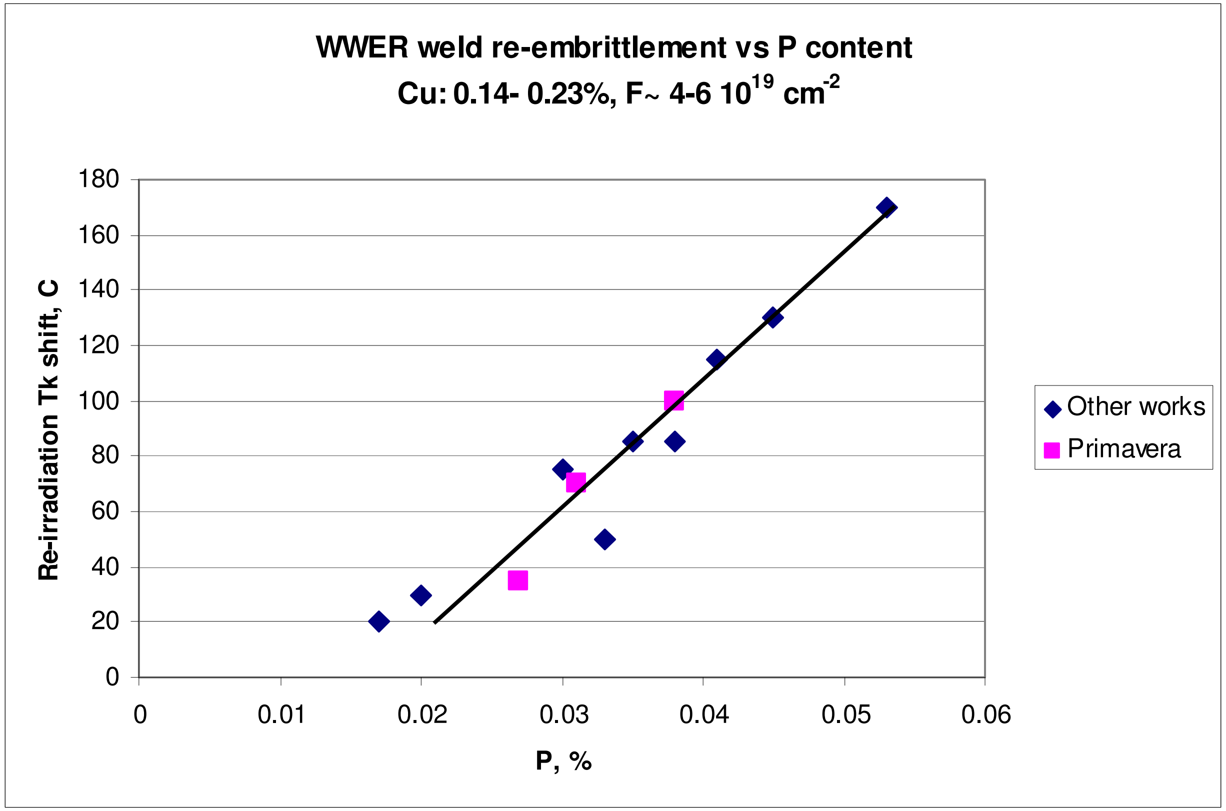
Tk shift reduction **does not depend** on P





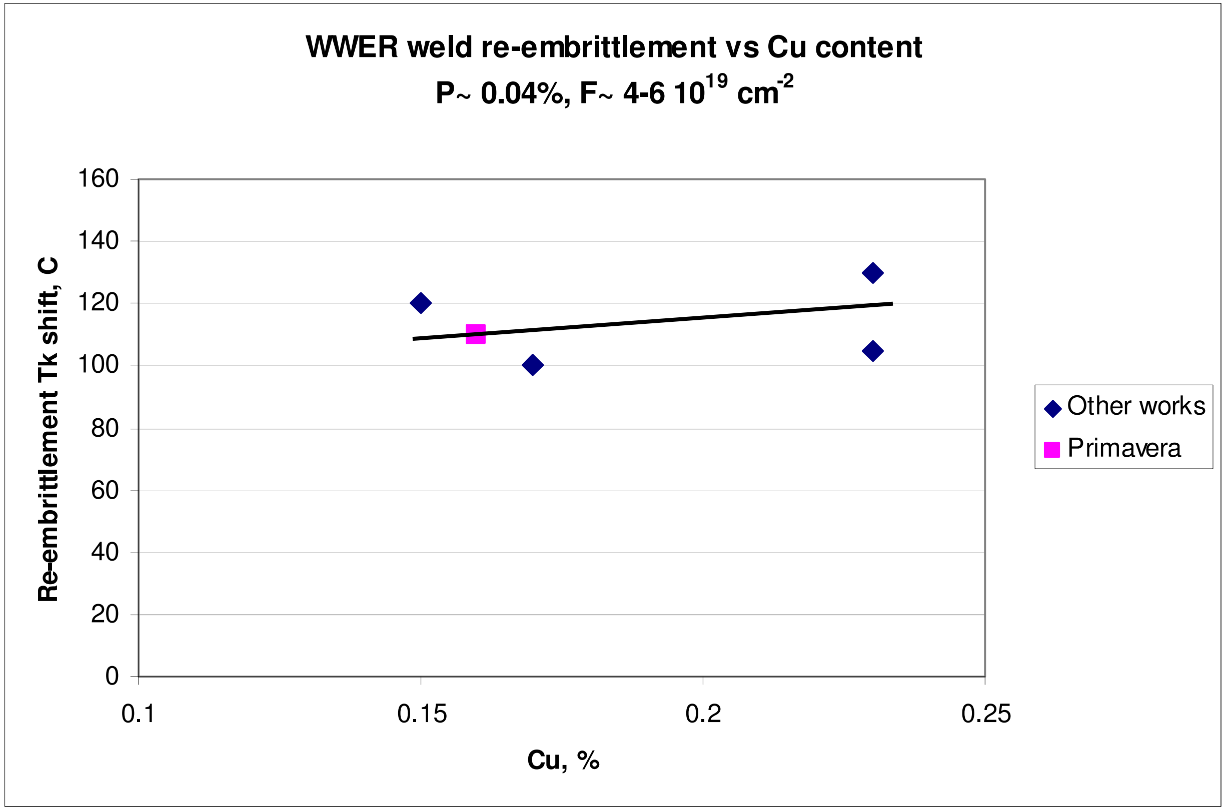
Tk shift reduction **depends on Cu** content?

Role of P and Cu



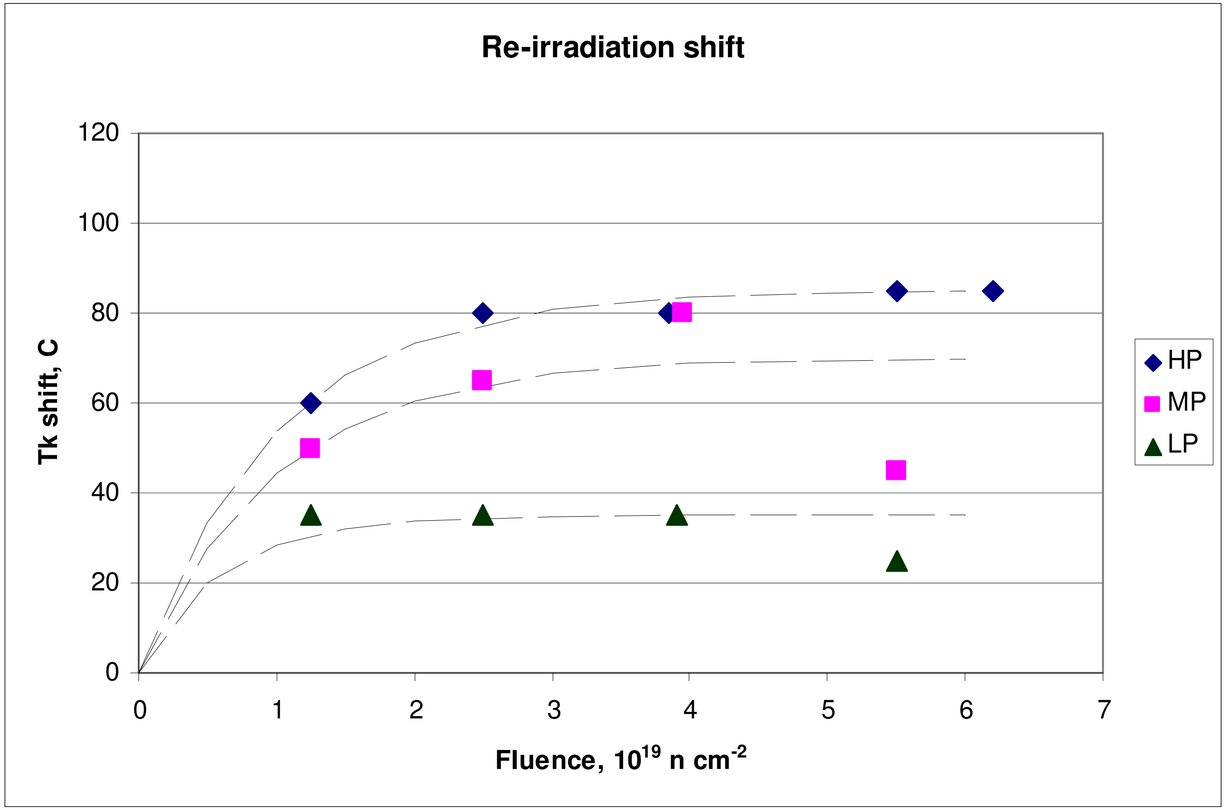
<u>WWER-440 re-embrittlement strongly **depends** on P content</u>

Role of P and Cu



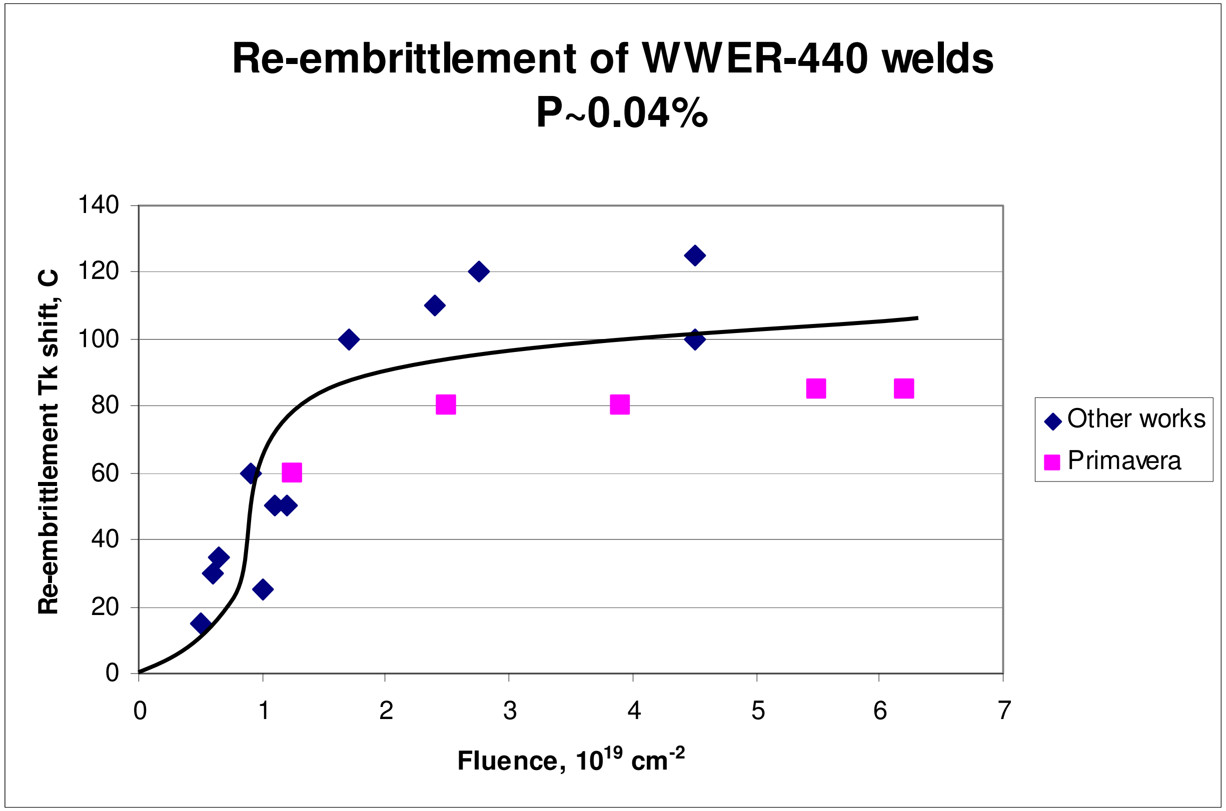
<u>WWER-440 re-embrittlement slightly **depends** on Cu content</u>

Role of P and Cu



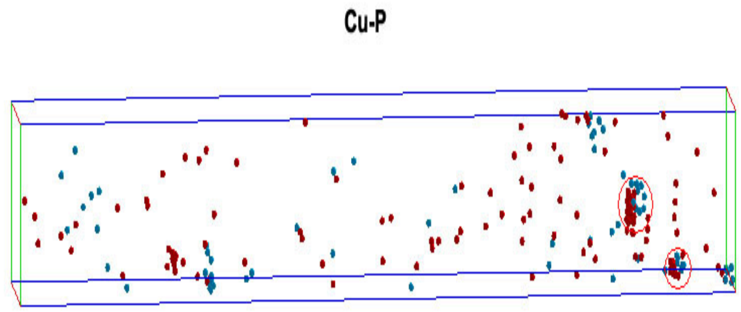
Tendency to ‘saturation’

Role of P and Cu



Micro-structural validation of radiation damage

Primary irradiation:

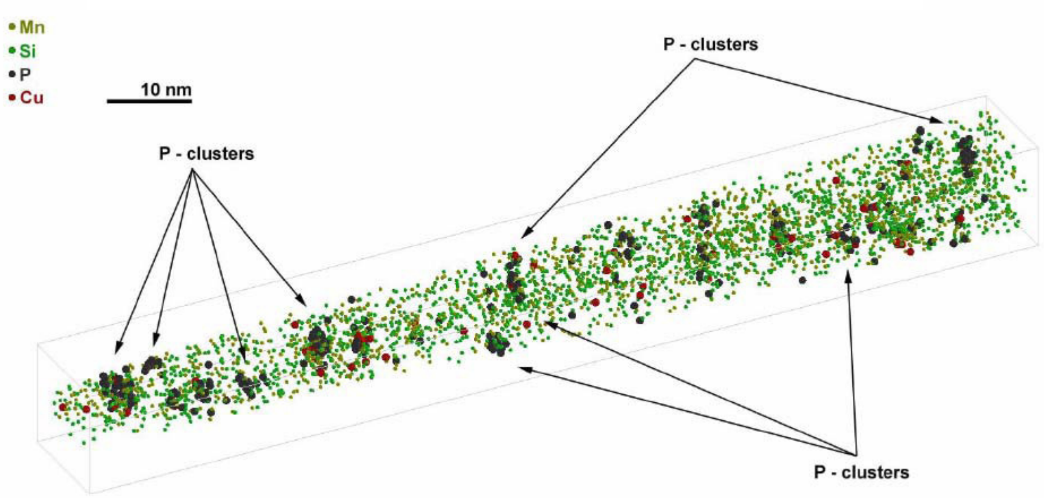


- significant level of Cu (up to 0.03- 0.04%) and P (up to 0.003-0.004%) depletion in irradiated weld ferrite matrix

- ultrafine (2-3 nm) intra-granular clusters enriched in - **Cu, P**, Ni, Mn and Si

- intragranular P atmospheres and P segregation on dislocations

- cluster density and Cu content in cluster increases as fluence increases

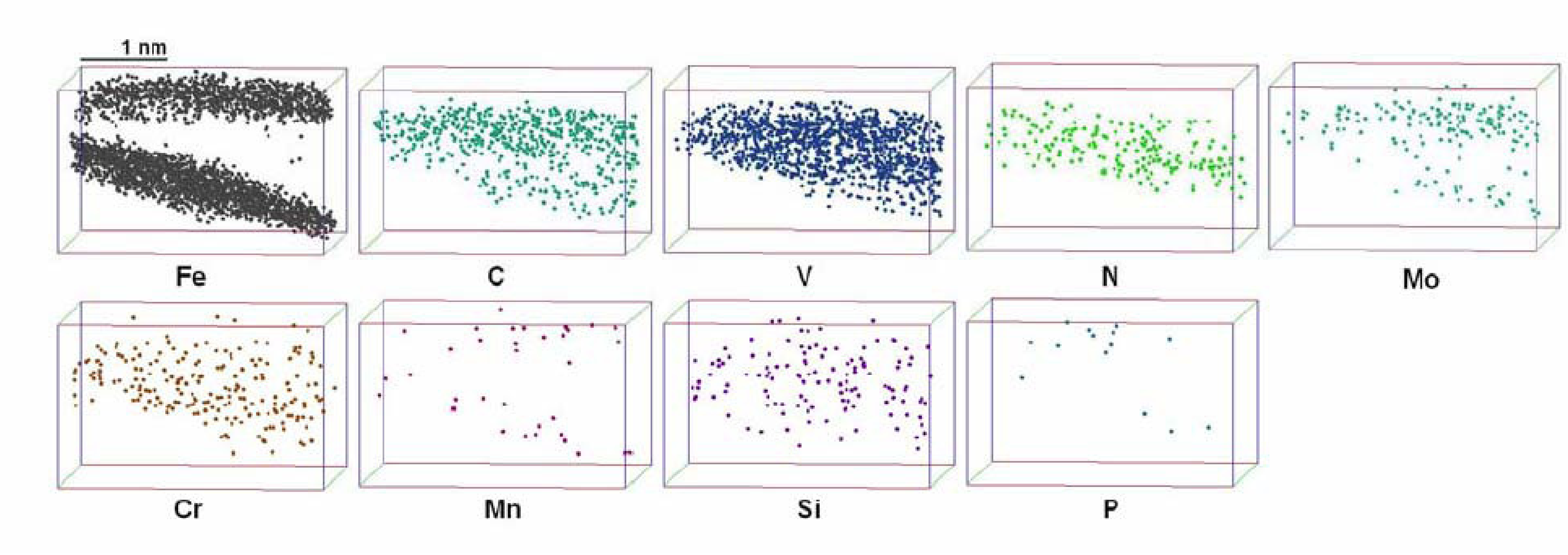


Micro-structural validation of radiation damage

Primary irradiation:

Small V-C enriched clusters and disks

Flat carbide:

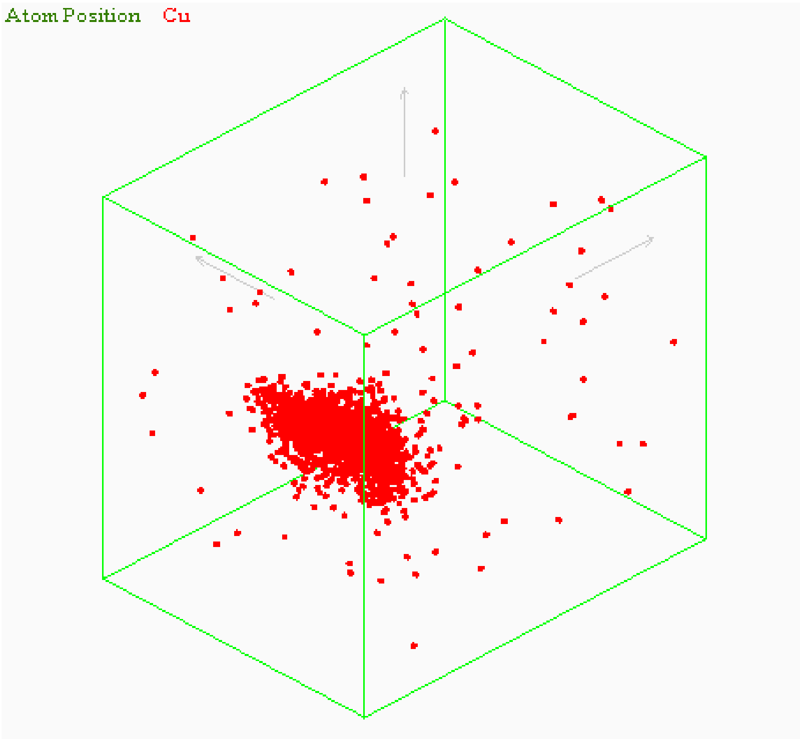


Micro-structural validation of radiation damage

Annealing effect

- Cu matrix content is still ~0.04%, similar to irradiated material
- during annealing the Cu clusters dissolve and growth of Cu precipitates (~5 nm) take place
- Cu content in precipitates is 60-100%
- Cu precipitate density in annealed material is low
- Phosphorus matrix content is 2.3 times higher than before annealing, like as in unirradiated material

Cu precipitate
(P. Pareige et al)

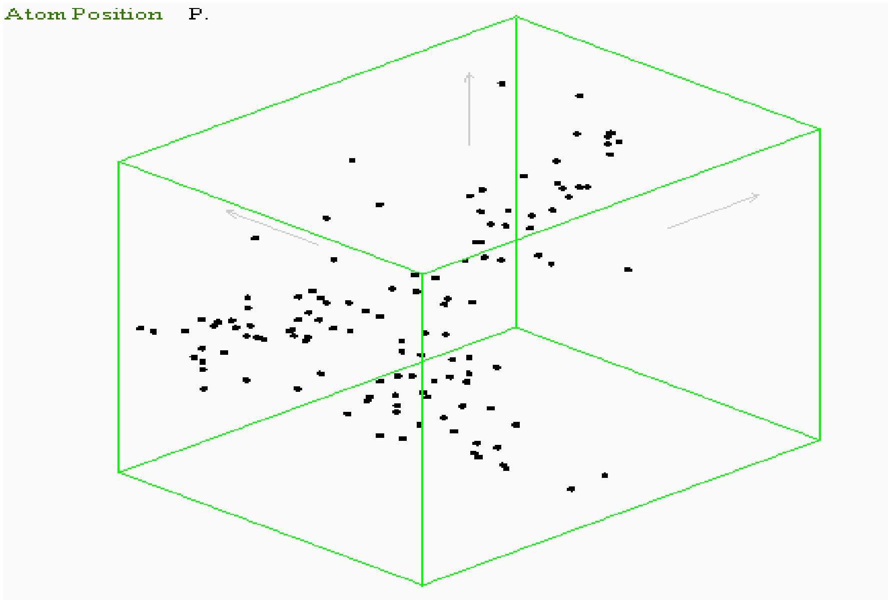


Micro-structural validation of radiation damage

Re-irradiation (very limited results):

P atoms around Cu precipitate
(P. Pareige et al)

- P and Cu atoms form atmosphere around the core
- Disk carbide and Cu-P clusters were observed
- Core of disk carbide is formed by V, C, Cr atoms
- New Cu clusters enriched by P were observed



Validation of re-embrittlement kinetic model

BASIC IDEA

Trend curves are based on d-bases and elaborated by statistical methods

to make a trend curve based on simple additive key mechanisms

Validation of re-embritlement kinetic model

Considered Embrittlement Mechanisms

1

Direct matrix damage

2

Precipitation hardening the matrix

Cu is the leading element

3

Segregation (mainly intra-grain)

P is a recognized segregating element

Validation of re-embrittlement kinetic model

Matrix damage contribution,

assumed to be dependent on fluence, is then described simply as follows:

$$\Delta T_{shift\ \ matrix} = a * \Phi^{1/2}$$

where: ΔT_{shift} is the transition temperature shift component

a - is model parameter

Validation of re-embrittlement kinetic model

The effect of precipitation:

$$\Delta T_{shift\ \ Cu\ \ precipitation} = b * \left[1 - e\left({}^{-\Phi / \Phi_{Cu\ sat}} \right) \right]$$

b - is a model parameter, representing the maximum saturation value of the shift due to precipitation

$\Phi_{Cu\ sat}$ - is the model parameter, representing the fluence at which Cu saturation starts

Validation of re-embrittlement kinetic model

Segregations

$$\Delta T_{shift\ P\ segregation} = c1*[1/2+1/2*Tangh(\frac{\Phi-\Phi_{Inc\ segr}}{c2})]$$

c1 is a model parameter, representing the maximum saturation value due to segregation

$\Phi_{Inc\ segr}$ **is a model parameter, representing the fluence at which segregation starts**

c2 is a model parameter, representing the velocity of increase of the effect to saturation

Validation of re-embritlement kinetic model

Embrittlement re-embrittlement semi-mechanistic model development

direct matrix damage

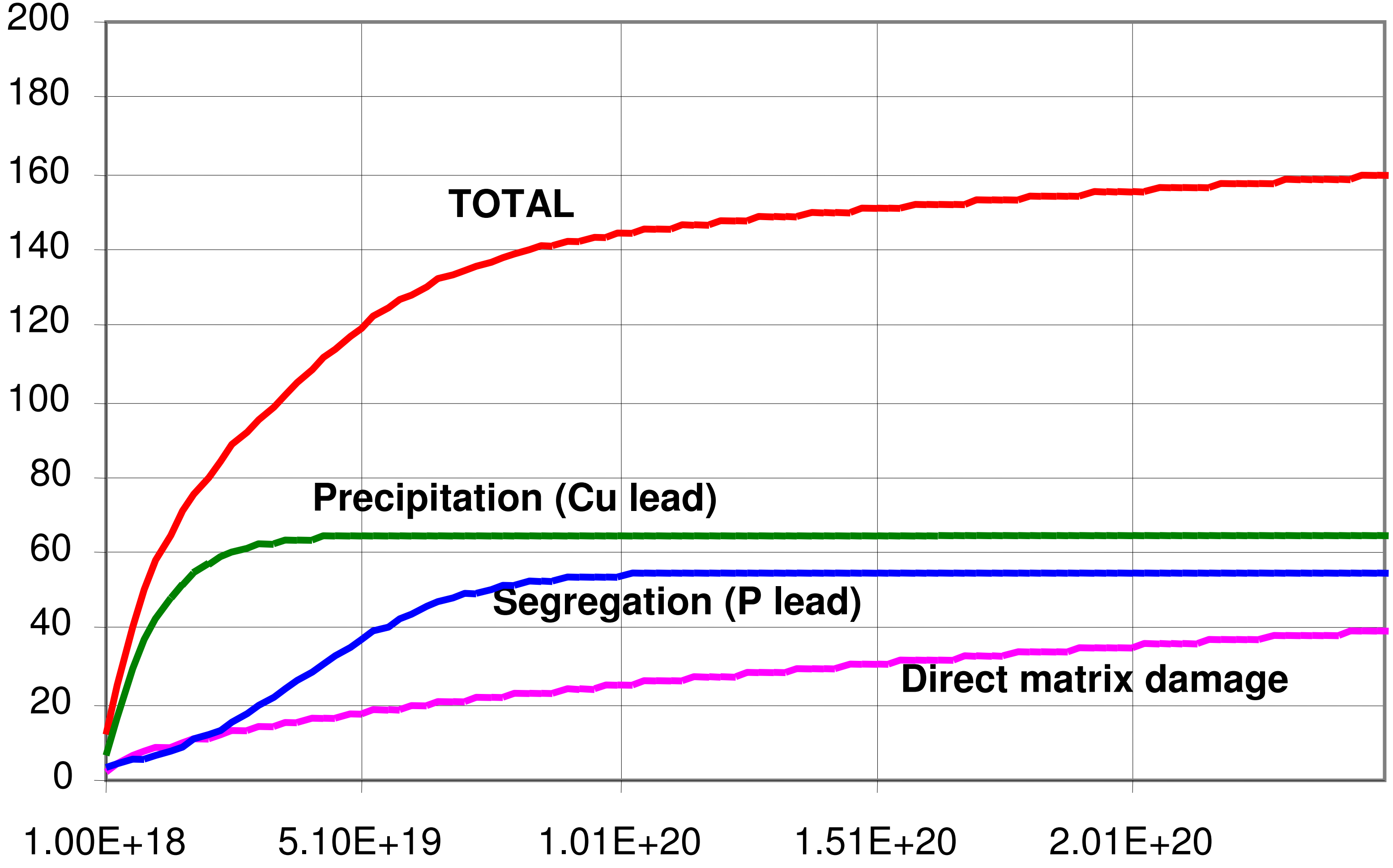
precipitations

$$DBTT_{shift} = a * \Phi^{1/2} + b * \left[1 - e\left(-\Phi / \Phi_{Inc\ pre} \right) \right] +$$

$$+ c1 * [1/2 + 1/2 * Tangh\left(\frac{\Phi - \Phi_{Inc\ segr}}{c2} \right)]$$

segregations

Validation of re-embrittlement kinetic model



Validation of re-embrittlement kinetic model

Annealing effect:

- Cu matrix content is similar to irradiated material
- Cu precipitate density in annealed material is low
- P matrix content is like as in unirradiated material

Validation of re-embrittlement kinetic model

Re-embrittlement after annealing:

direct matrix damage ***precipitations***

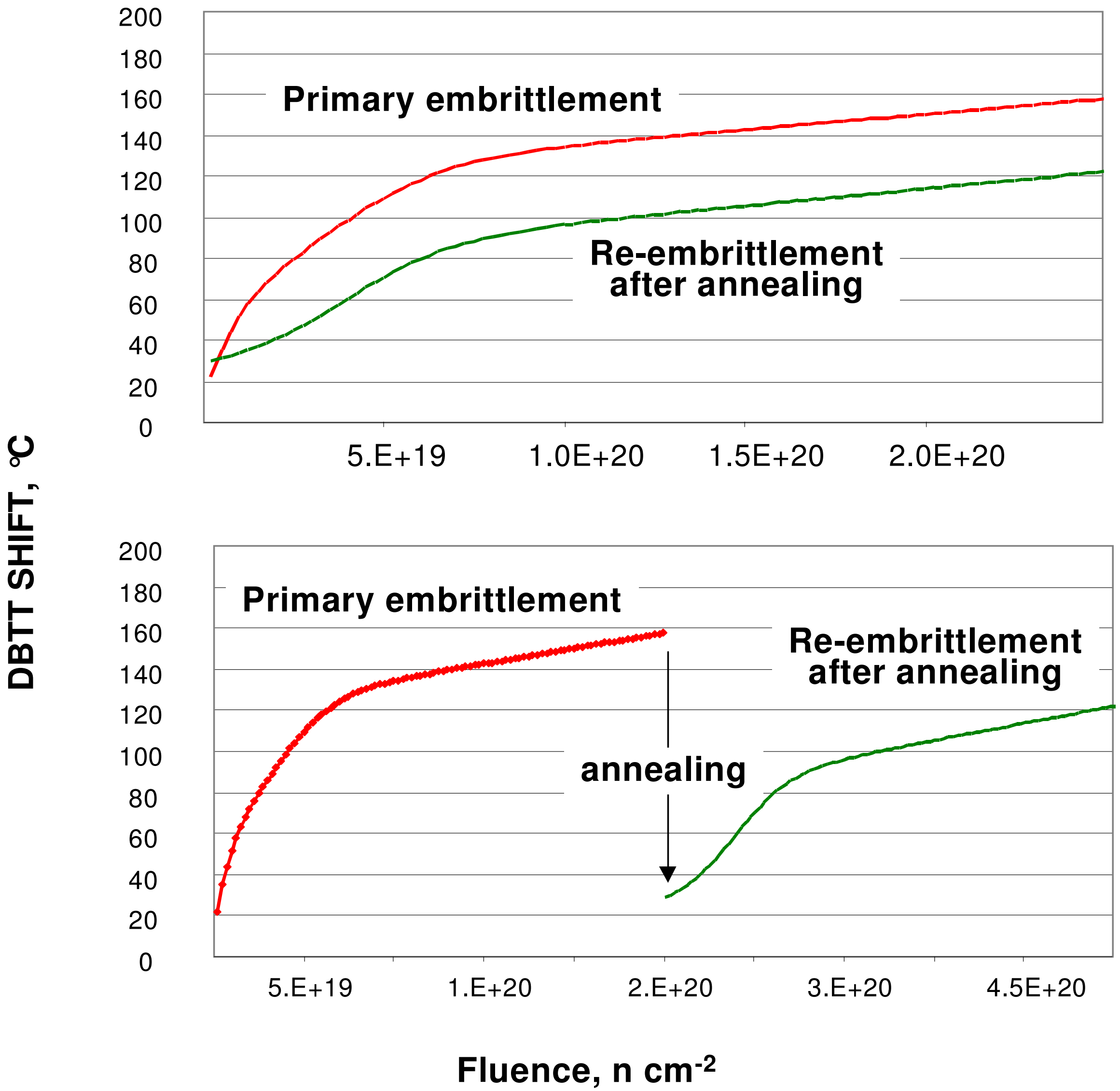
$$DBTT_{shift} = a * \Phi^{1/2} + b * \left[\cancel{1 - e\left(-\Phi / \Phi_{Inc\ pre}\right)} \right] +$$

$$+ c1 * [1/2 + 1/2 * Tangh\left(\frac{\Phi - \Phi_{Inc\ segr}}{c2}\right)]$$

segregations

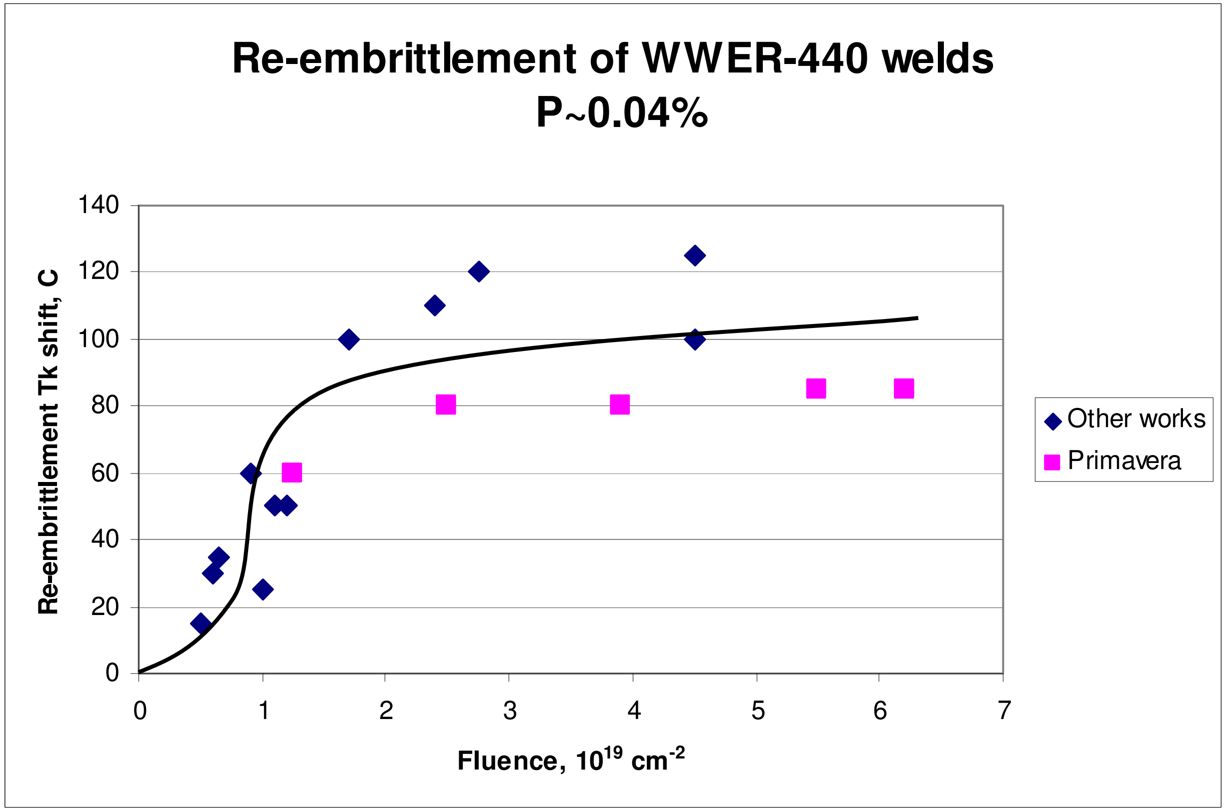
Validation of re-embritlement kinetic model

Annealing and re-embrittlement



- Cu precipitates are stable
- Cu effect is negligible during re-irradiation

Validation of re-embritlement kinetic model



Open issues

1. Evidence of PRIMAVERA results for WWER RPV lifetime assessment (flux effect):
   - Testing specimens irradiated with low flux & high fluence 6 set

2. More comprehensive microstructure studies
   - Re-irradiation
   - Focusing on high phosphorus metal
   - Correspondence with results of other research programmes

3. Integration of positron annihilation technique results to basic picture

4. General analysis of RPV material annealing and re-embrittlement problem

5. Guidelines development
   - Cooperation to IAEA, VTT, Gidropress, Prometey
   - Further elaboration of re-embrittlement kinetic model?

6. Possible use of PRIMAVERA results for GEN IV investigations
7. Date of PRIMAVERA project completion

Conclusions

1. PRIMAVERA is an outstanding example of successful international project among Russian and EU organizations

2. Project results showed that current evaluation methods for embrittlement after annealing are adequate or conservative

3. Tk shift due to re-irradiation is less as compared with primary irradiation
   - Tk shift reduction looks to be independent on P content

4. P plays basic role in RPV re-embrittlement
   - Tk shift strongly depends on P content

5. WWER-440 re-embrittlement slightly depends on Cu content

Conclusions

6. Good agreement between microstructural and mechanical testing results
   - Primary irradiation:
     - Cu precipitation
     - P segregation
   - Annealing:
     - Cu cluster growth
     - P matrix content increase
   - Re-irradiation:
     - P re-segregation
7. Semi-mechanistic model based on simple additive key mechanisms has been proposed

8. Model predicts the behavior difference of re-embrittlement in comparison with primary irradiation

9. Primavera results are in consistence with other relevant works and modelling developments

Conclusions

10. Still open issues:

- Verification of PRIMAVERA results by **low flux & high fluence** irradiation
- Comprehensive **microstructure studies** of re-irradiated weld (APFIM, TEM)
- Integration of **positron annihilation** technique results
- Re-embrittlement Guidelines development
    - Cooperation with IAEA, VTT, Gidropress, Prometey
- PRIMAVERA results for GEN IV investigations

Annex 10: Rogozkin's presentation on EDS Eurofer Steel

Atom probe characterization of nano-scaled features in unirradiated and irradiated ODS Eurofer steel

S. Rogozkin

Institute for Theoretical and Experimental Physics, Moscow, Russia

PRIMAVERA Seminar, March 14-15, 2011, JRC-IE Petten

Outline

- Introduction

ODS Eurofer steel, ODS particles (TEM&SANS results)

- Tomographic atom probe study of unirradiated ODS Eurofer

- ARBOR1 irradiation project & materials

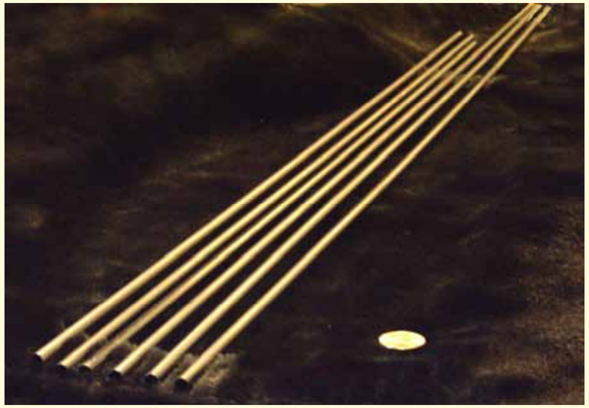
- Tomographic atom probe study of ODS Eurofer irradiated in BOR-60 to 32 dpa

- Discussion & conclusion

New Generation Construction Materials

Requirements:

- Higher damage dose >140 dpa
- Higher operating temperatures >650°C
- Steel should be a reduced activated
- Price …



Reduced Activation Ferritic/Martensitic steels -
Oxide Dispersion Strengthened steels hold much promise

- Oxide hardening: formation of nanosized Y_2O_3 particles
- Decrease of particle sizes and increase of their number density improves material properties

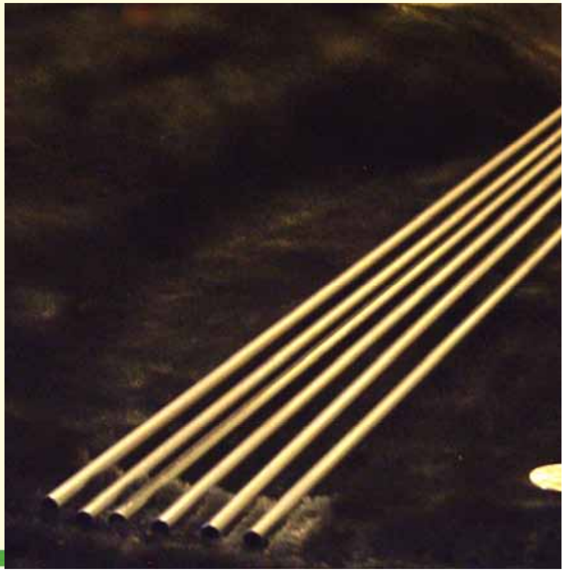
New generation structural materials of reactor core

Requirements

- Radiation stability (>160 dpa)
- Heat resistance (>700 ℃)
- Reduced activation under irradiation

General way

Design of structural materials strengthened by dispersion inclusions (clusters, precipitates, …) – Dispersion-hardening and oxide dispersion strengthened steels

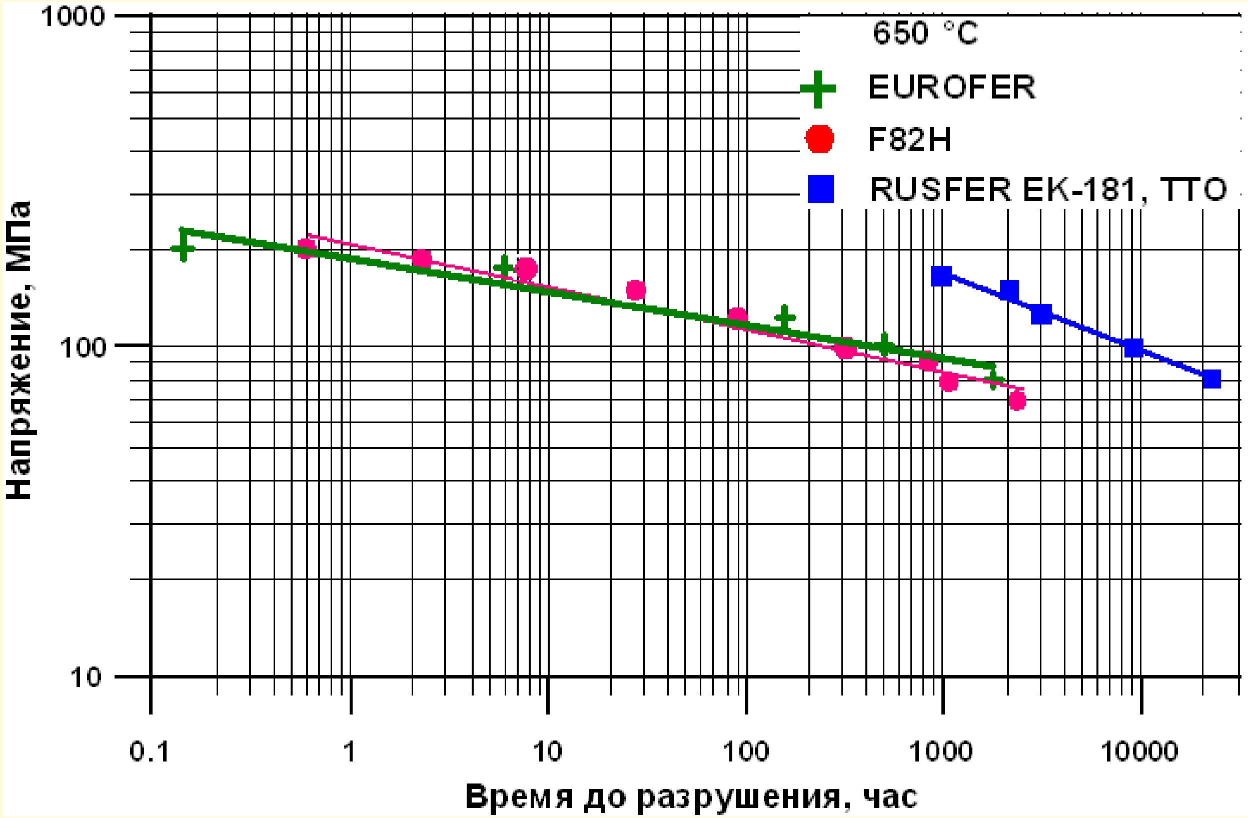


Dispersion-hardening and oxide dispersion strengthened steels

- Rusfer EK-181, Eurofer 97 …, (dispersion hardening steels)
- ODS Rusfer EK-181,ODS EP-450…, ODS Eurofer,… (oxide dispersion strengthened steels)
- vanadium alloys (V-4Ti-4Cr).

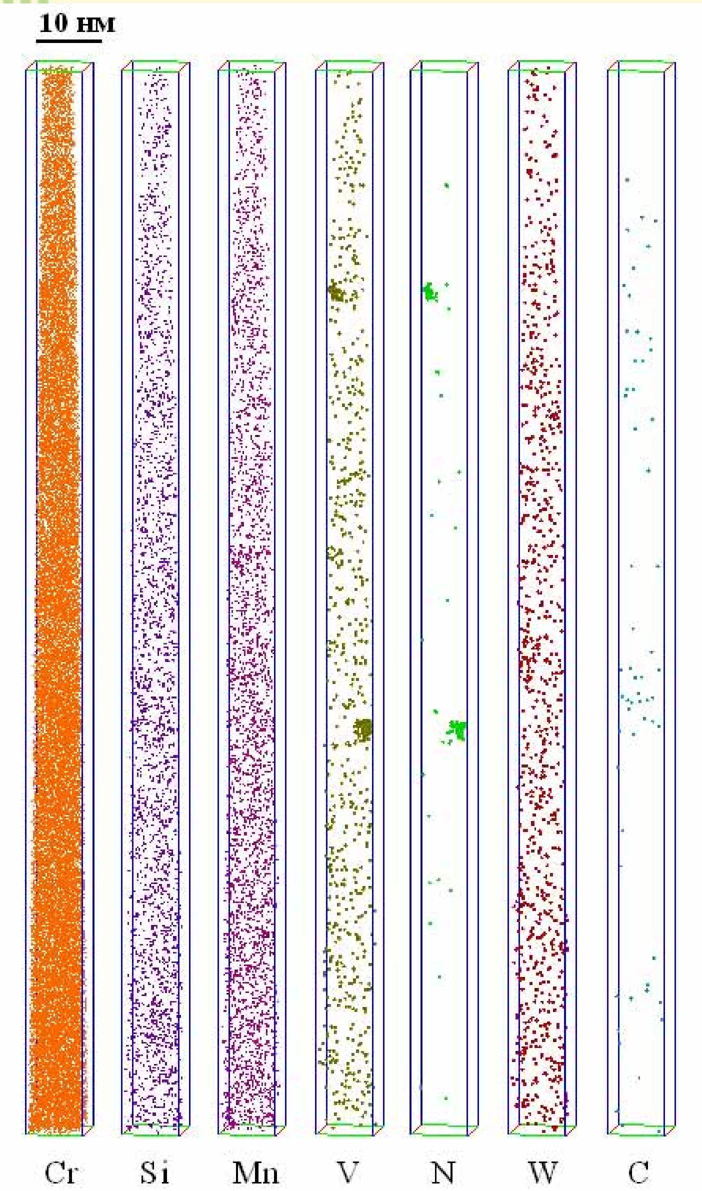
Dispersion-hardening steel Rusfer EK-181
(12%Cr Ferritic–Martensitic Steel)

The most promising mechanical properties (heat resistance and creep rupture strength at 650°C) are after traditional heat treatment (TTO): quenching 1100°C, 40 min + tempering 720°C, 3 h)

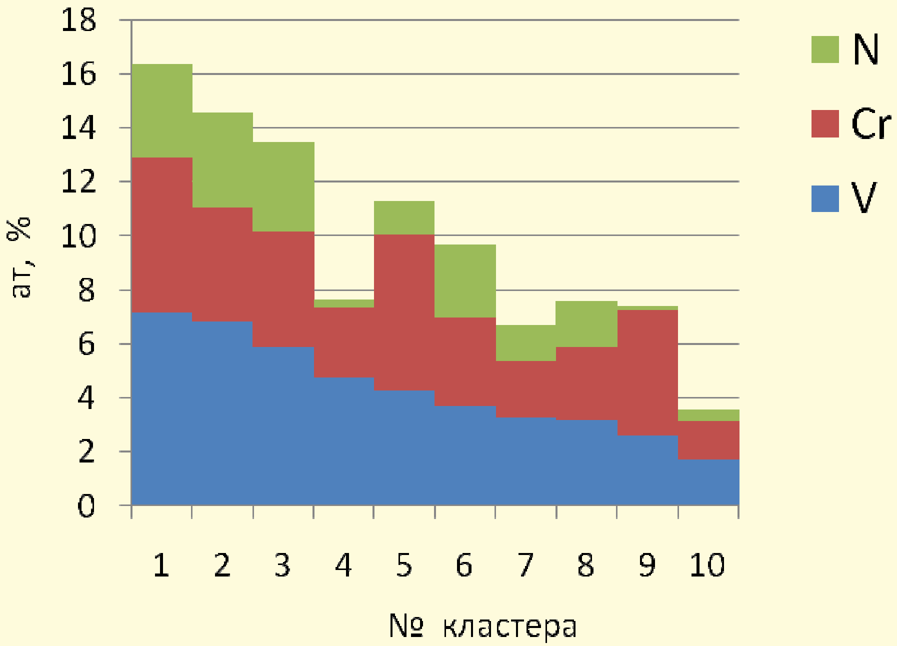


*Leont'eva-Smirnova M.V. et al., Perspectivnye materialy, 2006

Nanostructure of traditional heat treated Rusfer EK-181



Cluster composition

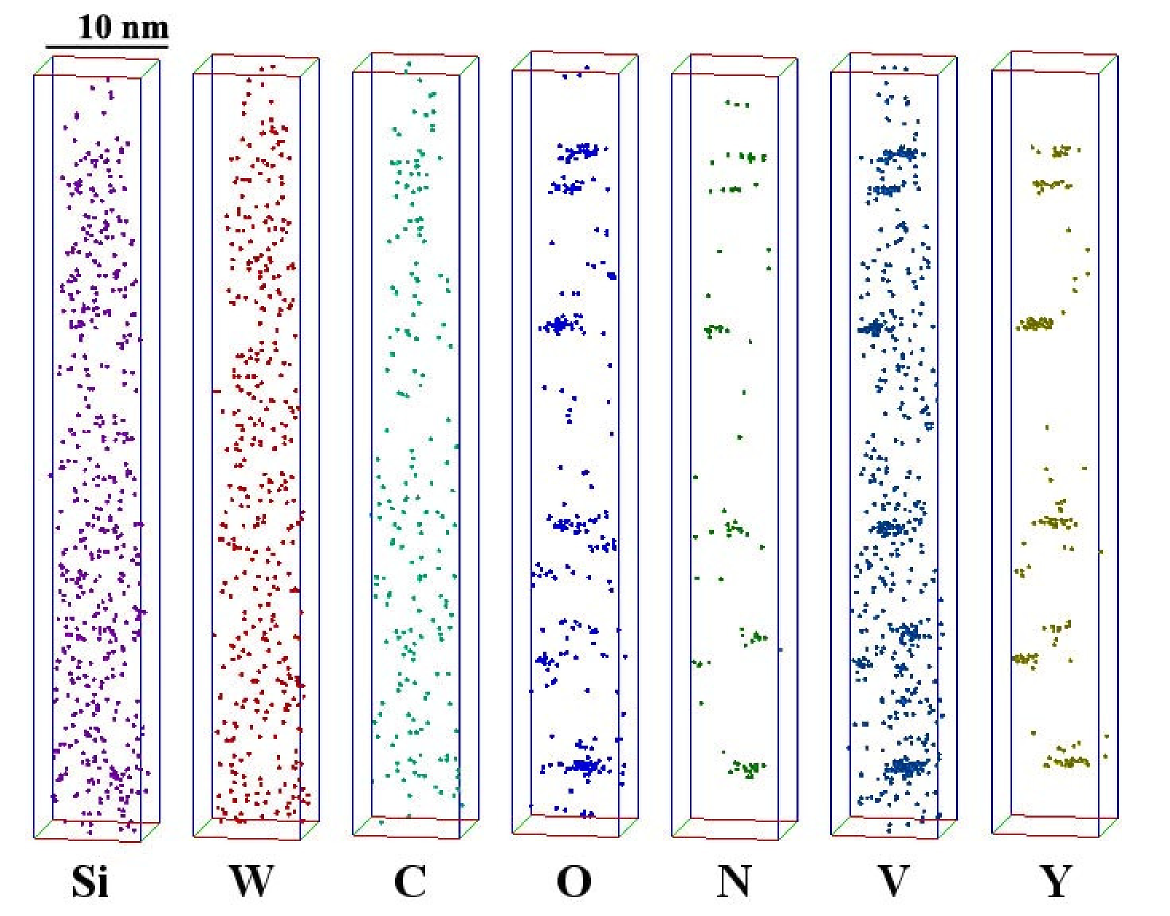


Cluster size is 1÷4 nm,
Number density is 1÷2 × 10^{23} м$^{-3}$.

Rogozhkin S.V. et al., Phys. Metal. and Metallography, 2009

- **Formation of V-N enriched nanoclusters in Rusfer EK-181 takes place under traditional heat treatment**

Tomographic atom probe study of oxide dispersion strengthened steels (V)



9% Cr ODS Eurofer, without Ti, 0.2 at.%V

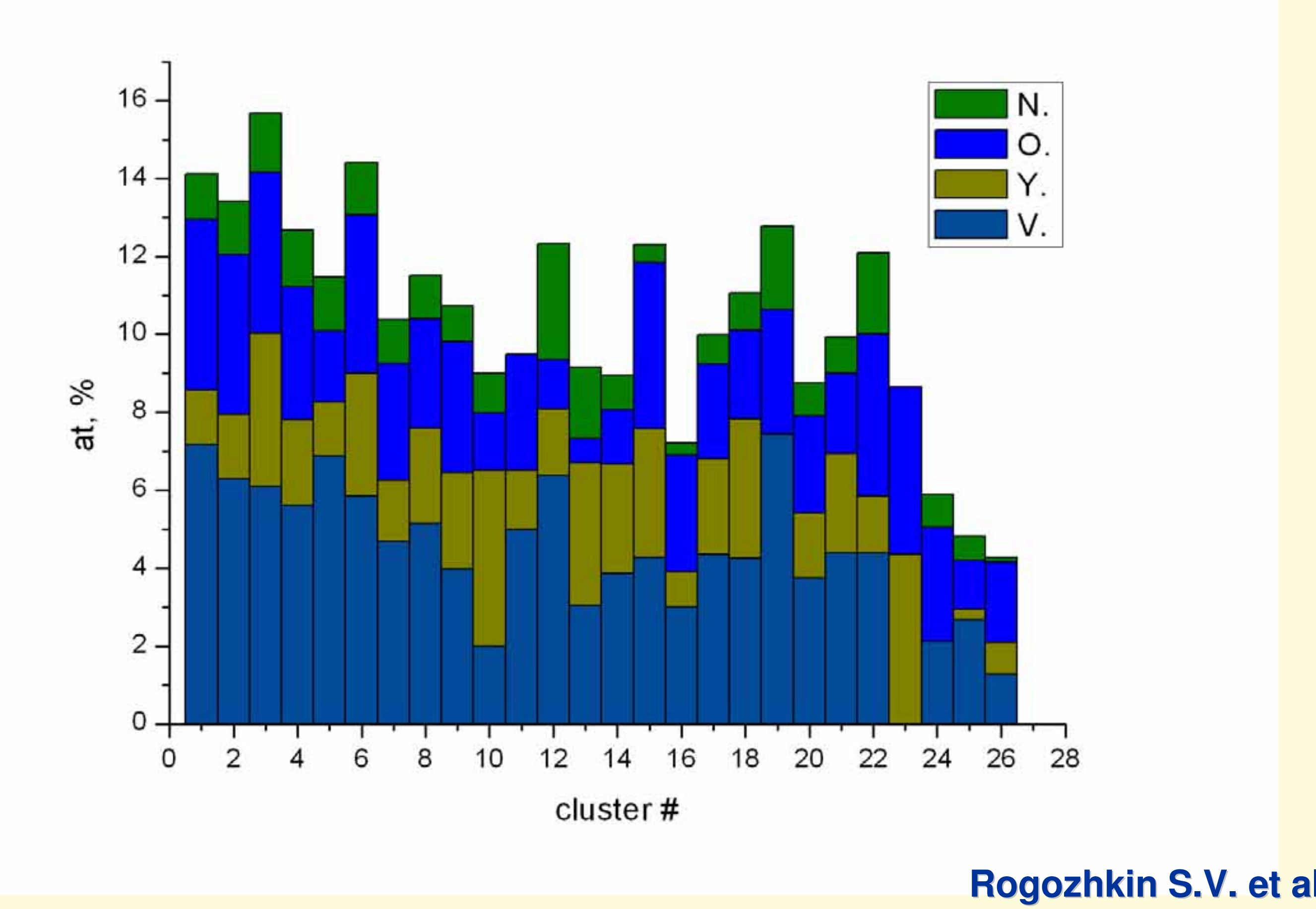
at.%	Cr	W	V	Y	O
	9,6	0,33	0,21	0,25	0,37

Cluster number density: ~ 2× 10^{23} m^{-3}
Cluster size: 2-3 nm

Rogozhkin S.V. et al., JNM, 2011

Cluster composition in ODS Eurofer

9% Cr ODS Eurofer, without Ti, 0.2 at.%V



Rogozhkin S.V. et al., JNM, 2011

- There are considerable evidences showing an important role of vanadium in fine cluster formation in ODS steels;
- Nanoscale clusters in ODS steels cannot be referred as oxide or other type of second phase precipitate as far as concentrations of the enriched elements are much smaller than that of the iron;
- These clusters can be interpreted as ODS particle precursors.

Evolution of nanostructure under irradiation

- ***Materials irradiated in BOR 60 (ODS Eurofer and Eurofer 97 irradiated up to 32 dpa);***
- ***Materials irradiated by heavy ions (simulation of neutron damage).***

‘ARBOR 1’ irradiation project

Impact, tensile and low cycle fatigue specimens of reduced activation ferritic/martensitic steels (e.g. EUROFER 97, F82H mod., OPTIFER IVc) and **ODS EUROFER** have been irradiated in BOR 60 (neutron flux of 1.8×10^{15} n/cm^2 s) up to 32 dpa

Specimens under Tomografic Atom Probe characterization

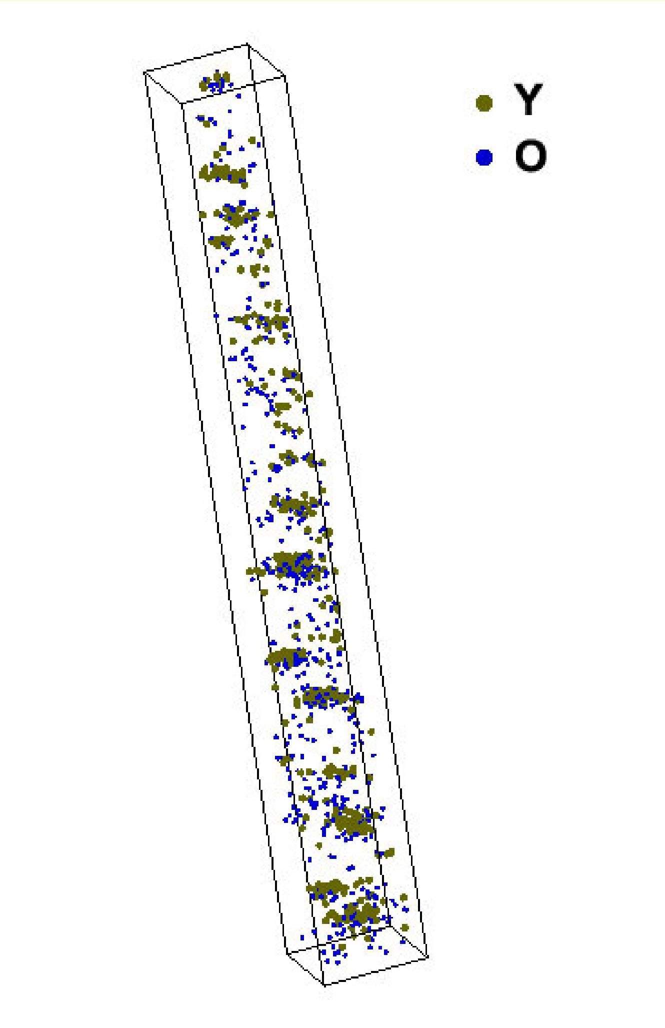
EO01: Heat treatment: 31 min in air @ 980°C + 90 min in air @ 760°C; **Test condition: 330°C** (Charpy impact test)

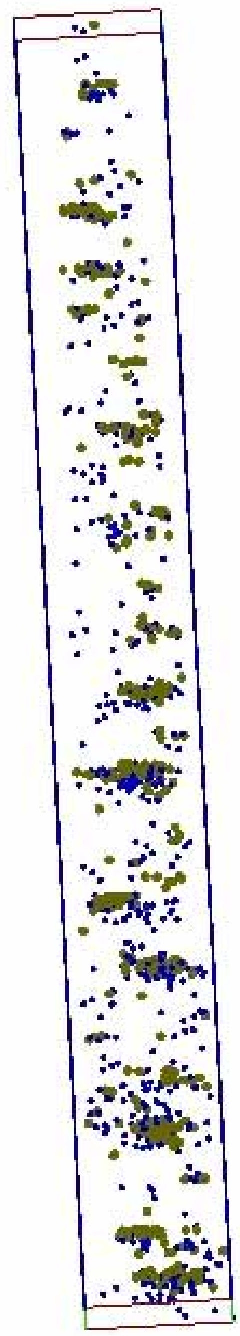
EO04: Heat treatment: 31 min in air @ 980°C + 90 min in air @ 760°C; **Test condition: 500°C** (Charpy impact test)

Radioactivity of the samples

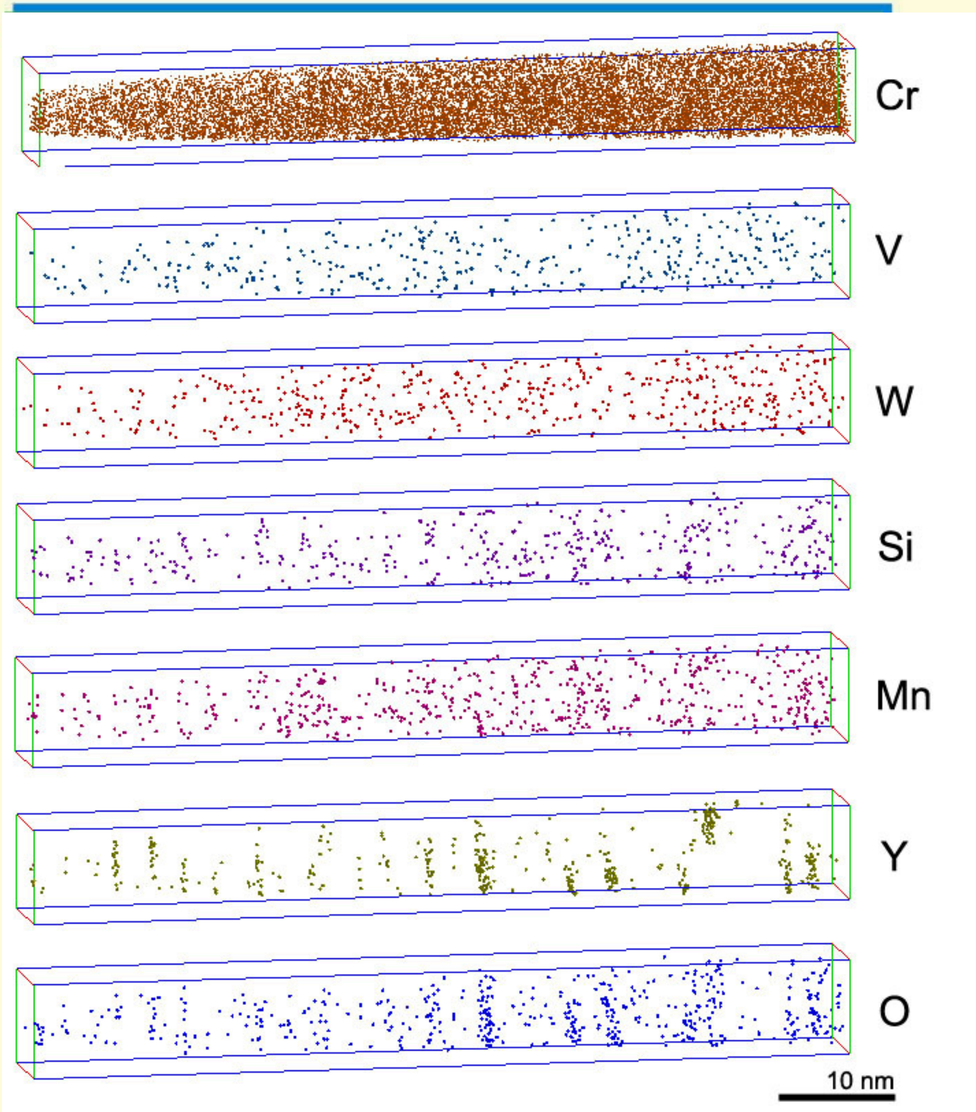
Radioisotope	Radioactivity of irradiated EUROFER, Bq/g	Total radioactivity of Charpy specimen, Ci
Mn-54	2.5×10^9	0.032
Fe-55	2.4×10^9	0.068
Co-60	1.8×10^5	0.000017
	Total	~ 0.1

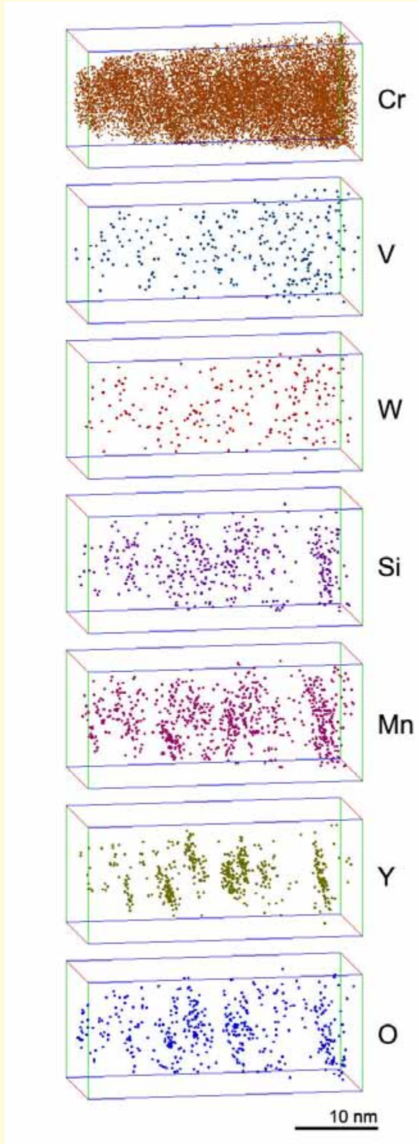
Reconstructed volume of irradiated ODS EUROFER (EO01)



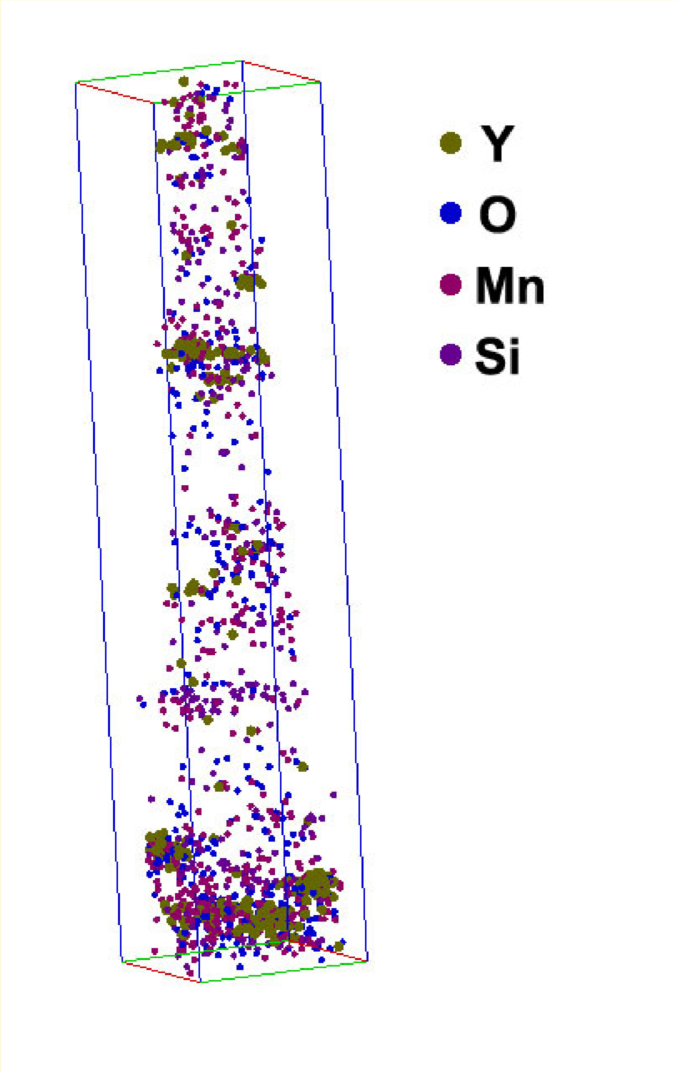


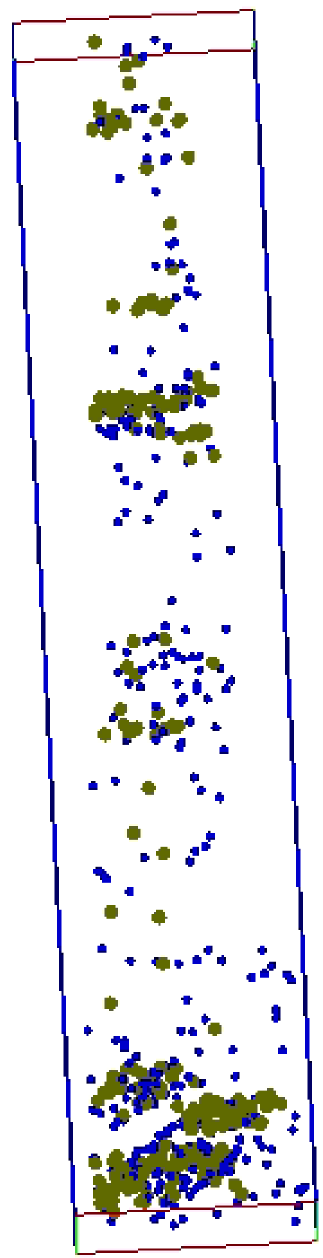
Atom maps of irradiated ODS EUROFER (EO01)



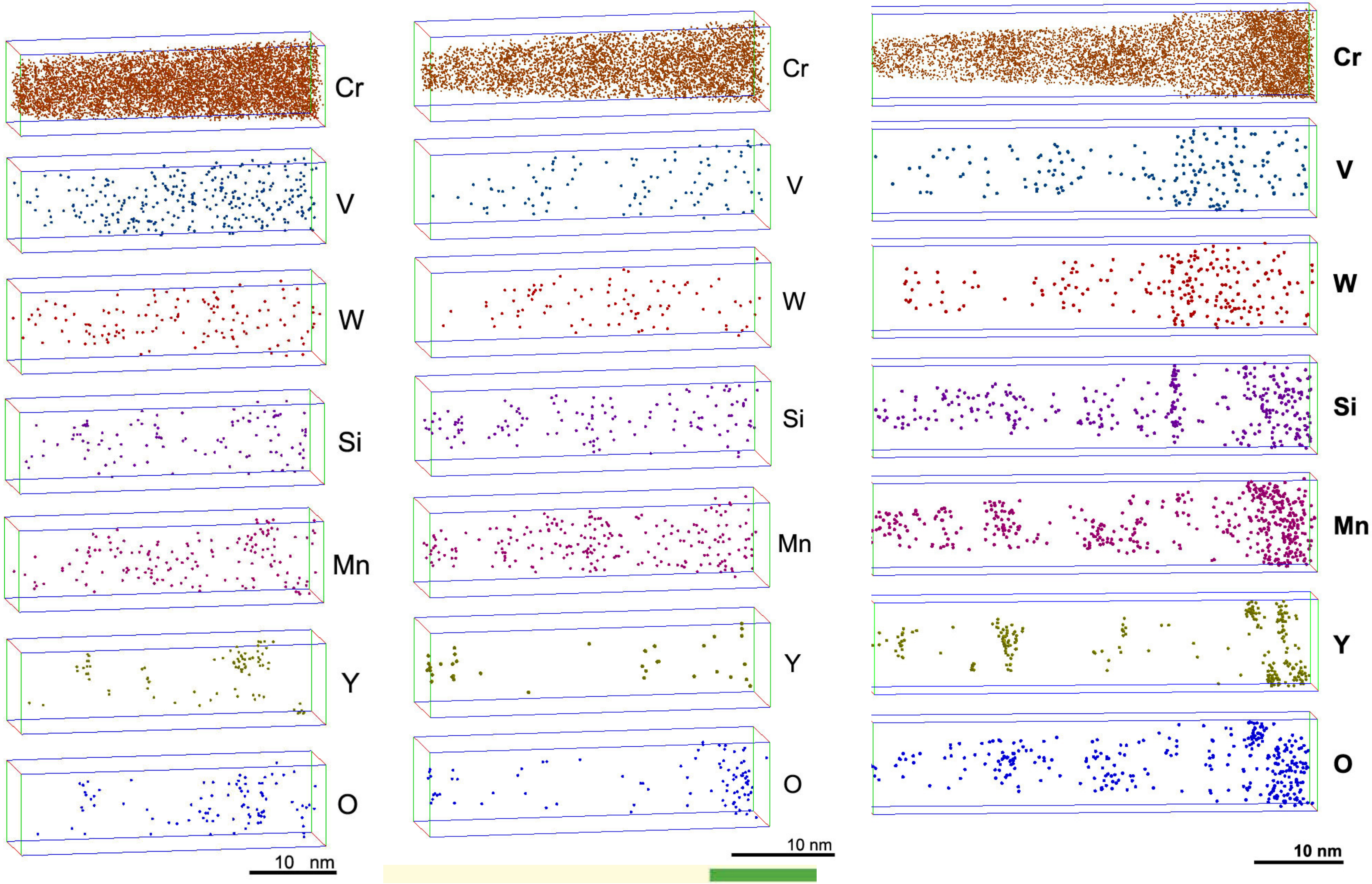


Reconstructed volume of irradiated ODS EUROFER (E004)

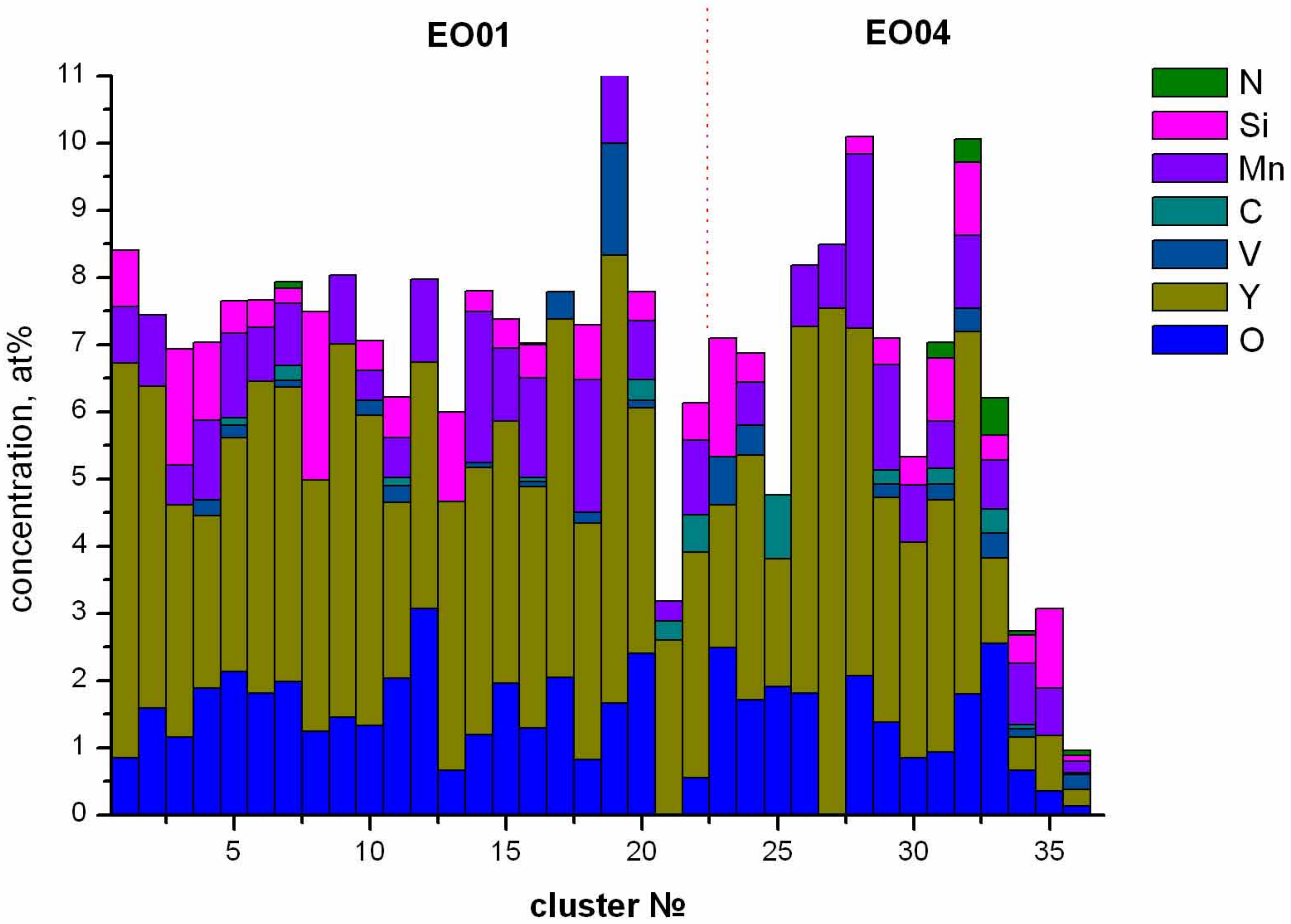




Atom maps of the irradiated ODS EUROFER (EO04)



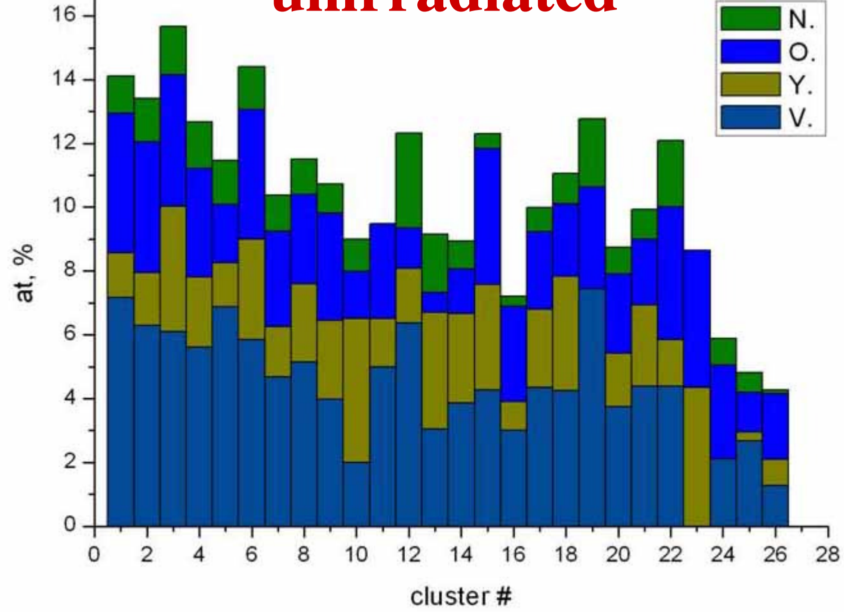
Composition of Y-O-clusters observed in irradiated specimens



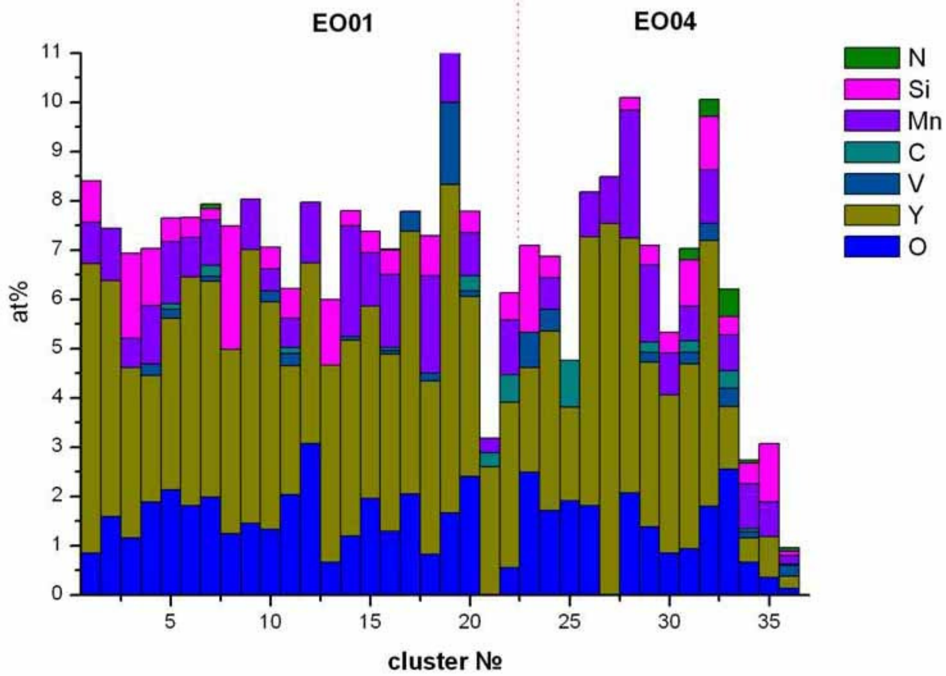
Comparison of clusters in unirradiated and irradiated ODS EUROFER

Cluster composition

unirradiated



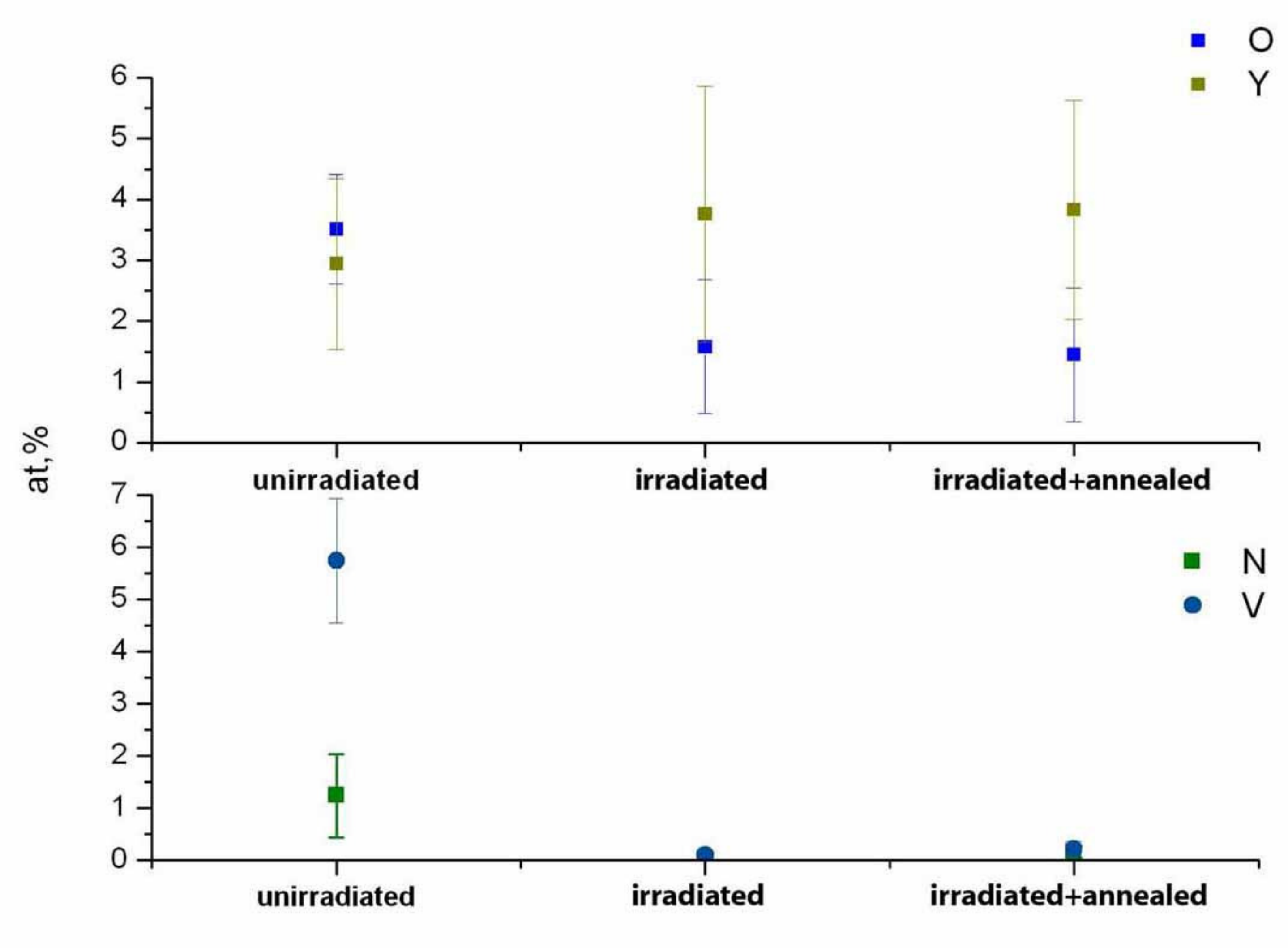
irradiated



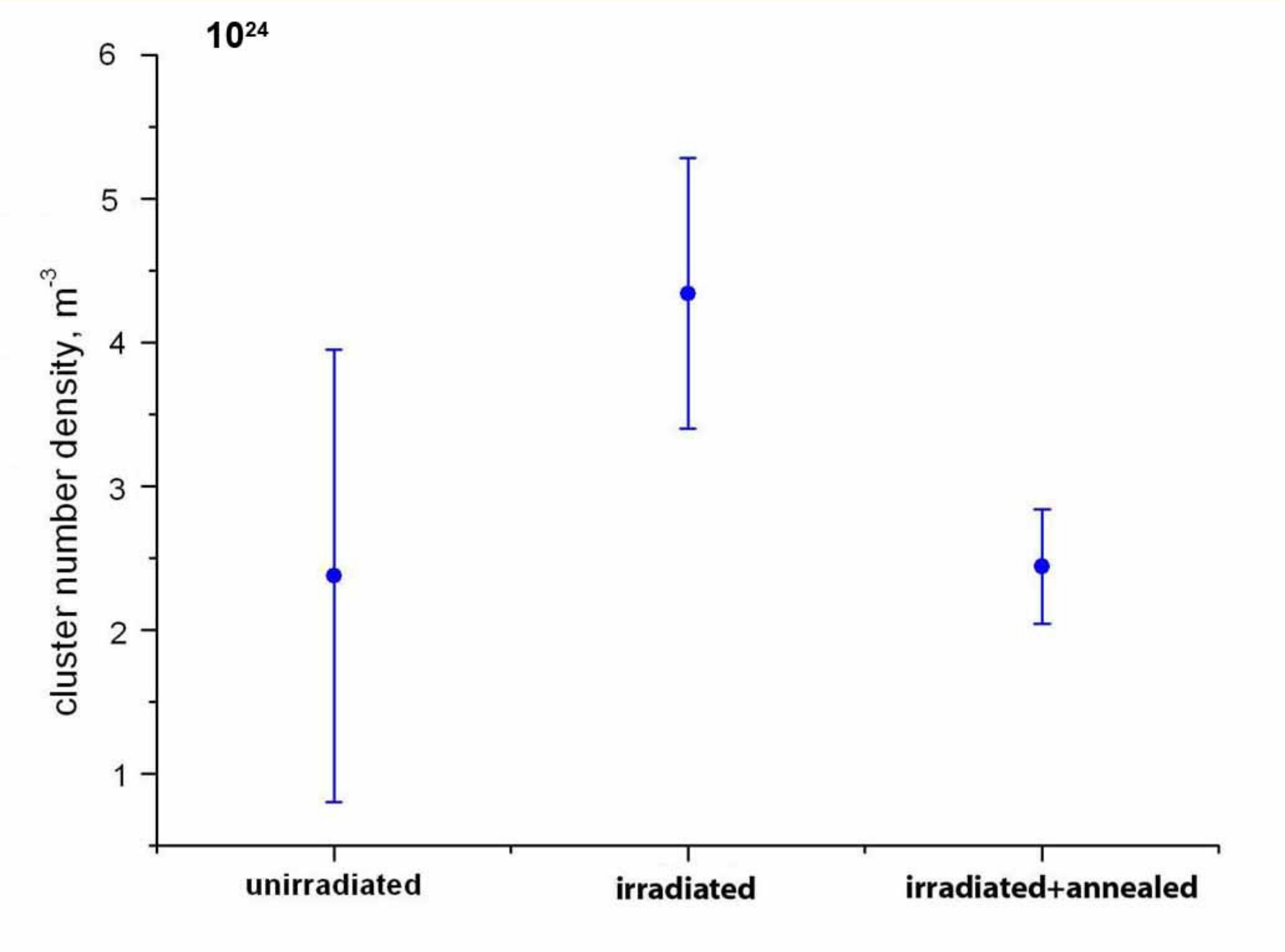
The main difference between irradiated and unirradiated states is in nanocluster composition. In unirradiated state they are enriched in V, Y, O and N, whereas after neutron irradiation up to 32 dpa V and N left clusters and concentration of Y, Cr and Mn increased.

Comparison of clusters in unirradiated and irradiated ODS EUROFER

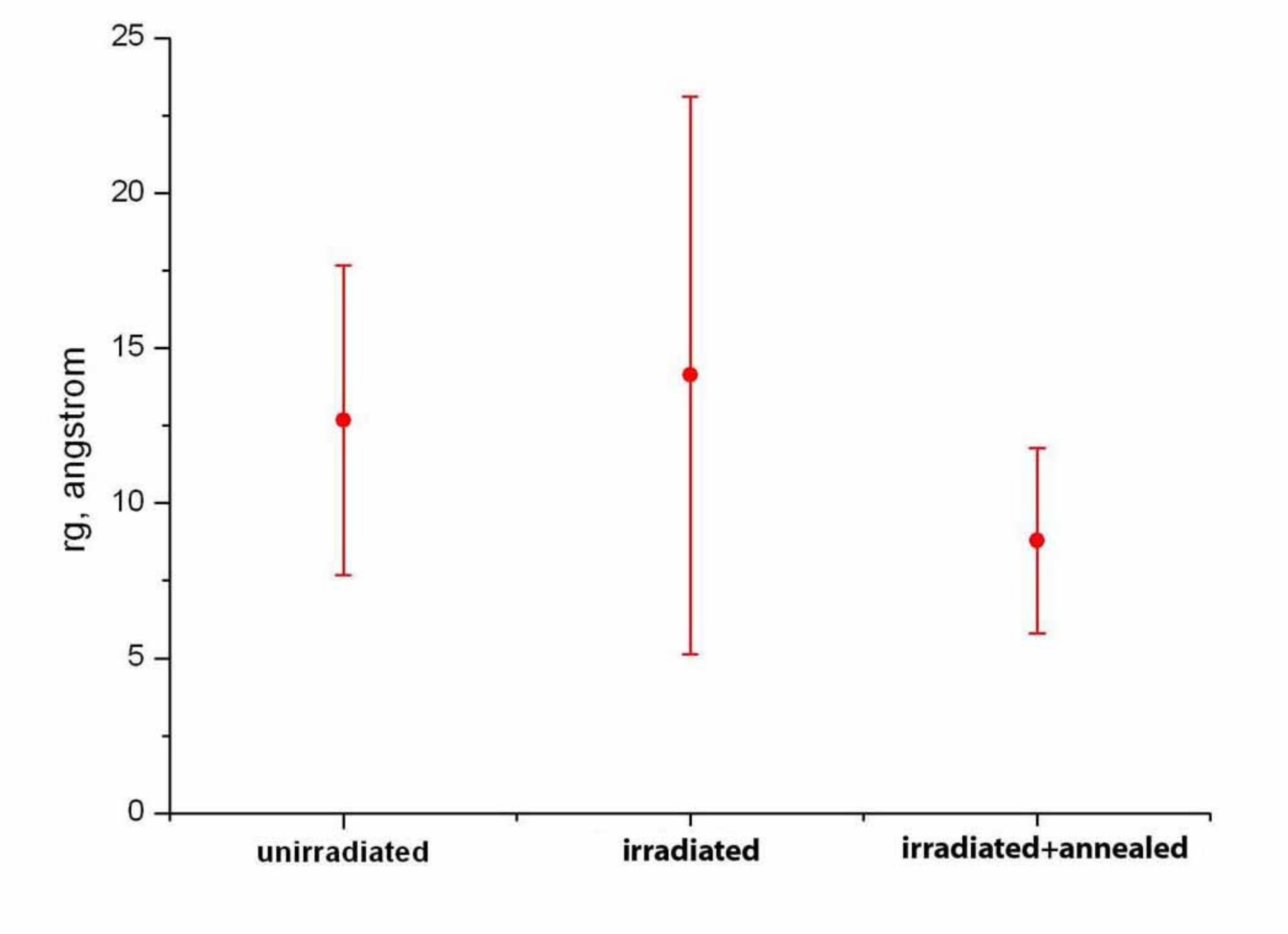
Cluster composition: Y, O, V, N concentrations



Clusters in unirradiated and irradiated ODS EUROFER. Number density



Clusters in unirradiated and irradiated ODS EUROFER. Cluster size

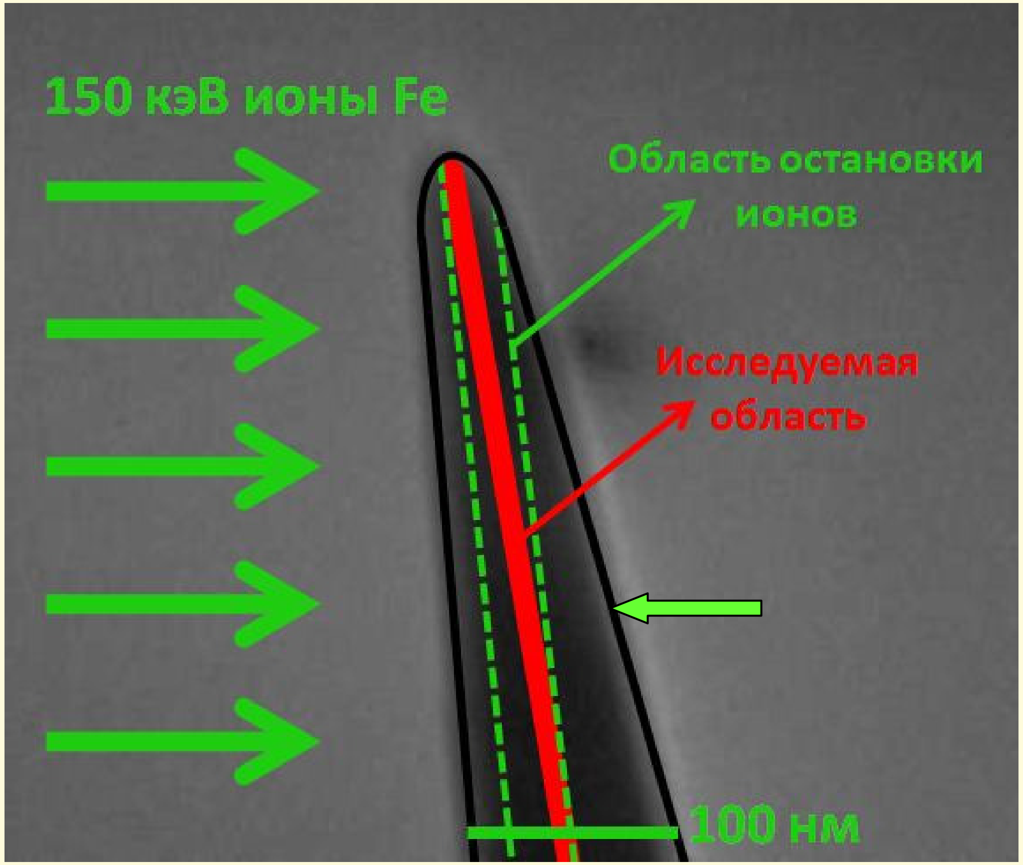


Comparison of material local chemical composition in un- and irradiated states

- **Tomographic atom probe data of irradiated ODS Eurofer indicates that after irradiation nanoscale clusters are still presented in matrix at high number density ~ 10^{24} m^{-3}. Number density of nanoscale clusters increased in two times after irradiation up to 32 dpa.**
- **Cluster composition changed under irradiation: V (and N) leaved nanoscale clusters and dissolved in matrix. Mn segregated on the clusters, concentration of Cr increased in the clusters.**
- **Concentrations of Y and O increase in matrix after irradiation. Increase in manganese in the irradiated specimens was observed.**
- **All elements mentioned above were mostly allocated in oxide particles (with sizes more than 10 nm) in unirradiated material. Thus, the data shown indicate that oxide particles, that were not seen in this tomographic atom probe investigation, are not stable under irradiation and dissolve.**

Heavy ion simulation of radiation damage in structural materials

Scheme of the atom probe specimen irradiation experiment



Atom probe sample TEM

Conclusions

- ODS Eurofer steel have been characterised by means of TAP.
- The evolution of the nano-structure of the steel under irradiation was shown.
- Further investigations are necessary to understand the development of the nano-structure during the different production steps and the influence on the material properties.
- This could be helpful to optimise the micro/nano structure in order to further improve the material properties.
- The change of micro/nano structure during irradiation is also a crucial point.

Annex 11: Zeman's presentation on Materials for Innovative Reactors

PRIMAVERA Workshop

OVERVIEW OF MATERIALS FOR INNOVATIVE REACTORS

IE-JRC-EC, Petten (NL), 15 March 2011

Andrej Zeman

NAPC / Physics section

IAEA

International Atomic Energy Agency

Outline

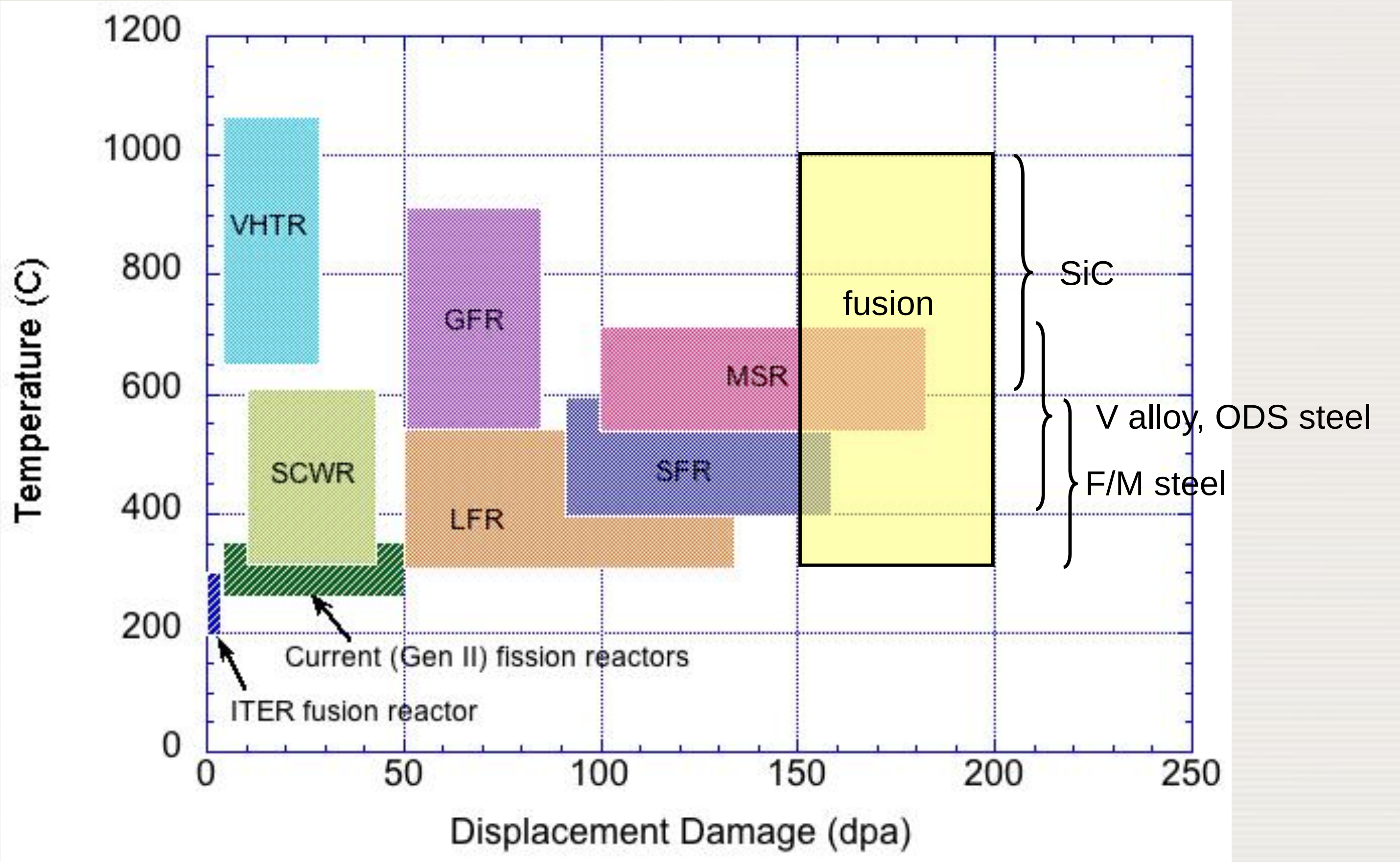
Overview

Activities

Coordinated research

Overview

Temperature windows and radiation damage



IAEA CS Meeting, 3 Sep 2010, INTEC, KAERI, Daejeon, Republic of Korea

Overview

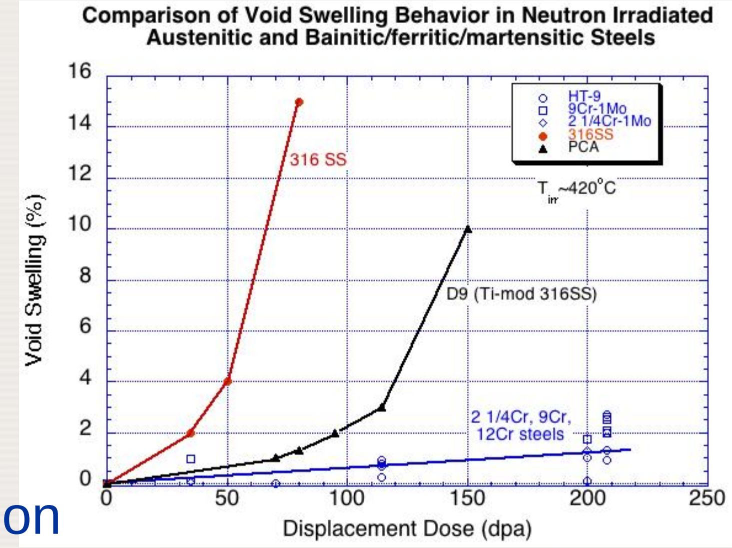
System	Coolant	Pressure (MPa)	T_{in}/T_{out} (°C)	Neutron spectrum, Maximum Dose (dpa)	Fuel	Cladding	Structural Materials	
							In-core	Out-of-core
Pressurized water reactor -PWR	Water – single phase	16	290/320	Thermal, ~80	UO_2 (or MOX)	Zirconium alloy	Stainless steels, nickel-based alloys	Stainless steels, nickel-based alloys
Boiling water reactor - BWR	Water – two phase	7	280/288	Thermal, ~7	UO_2 (or MOX)	Zircaloy	Stainless steels, nickel-based alloys	Stainless steels, nickel-based alloys
Supercritical water cooled reactor - SCWR	Supercritical water	25	290/600	Thermal, ~30 Fast, ~70	UO_2	F-M (12Cr, 9Cr, etc.) (Fe-35Ni-25Cr-0.3Ti) Incoloy 800, ODS Inconel 690, 625, & 718	Same as cladding options, plus low swelling stainless steels	F-M, low-alloys steels
Very high temperature reactor - VHTR	Helium	7	600/1000	Thermal, <20	UO_2 UCO	SiC or ZrC coating and surrounding graphite	Graphites PyC, SiC, ZrC Vessel: F-M	Ni-based superalloys 32Ni-25Cr-20Fe-12.5W-0.05C Ni-23Cr-18W-0.2C F-M w/ thermal barriers, low-alloy steels
Gas fast reactor - GFR	Helium, supercritical CO_2	7	450/850	Fast, 80	MC	Ceramic	Refractory metals and alloys, Ceramics, ODS Vessel: F-M	Ni-based superalloys 32Ni-25Cr-20Fe-12.5W-0.05C Ni-23Cr-18W-0.2C F-M w/ therm barriers
Sodium fast reactor - SFR	Sodium	0.1	370/550	Fast, 200	MOX or U-Pu-Zr or MC or MN	F-M or F-M ODS	F-M ducts 316SS grid plate	Ferritics, austenitics
Lead fast reactor - LFR	Lead or Lead-busmith	0.1	600/800	Fast, 150	MN	High-Si F-M, ODS, ceramics, or refractory alloys		High-Si austenitics, ceramics, or refractory alloys
Molten salt reactor - MSR	Molten salt, for example: FLiNaK	0.1	700/1000	Thermal, 200	Salt	Not applicable	Ceramics, refractory metals, High-Mo, Ni-based alloys (e.g., INOR-8), graphite, Hastelloy N	High-Mo, Ni-based alloys (e.g., INOR-8)

Overview

FAST REACTORS
fuel and core-structural materials, several "technological" issues

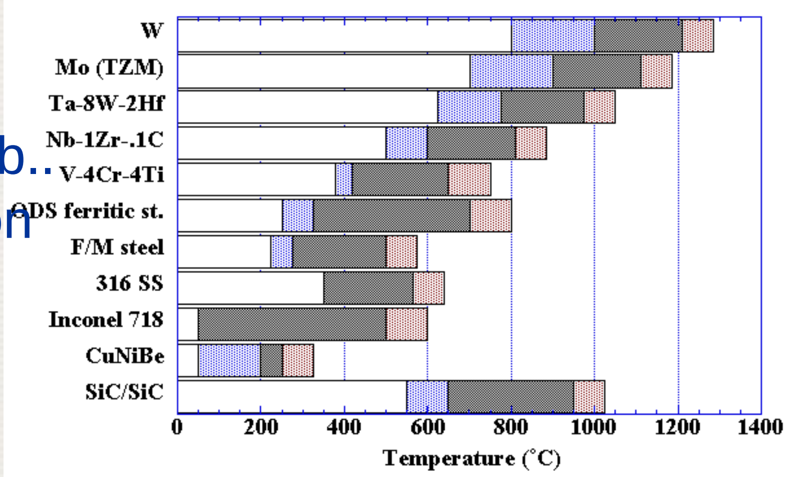
(1) Low deformation

- ➢ Swelling, Irradiation Creep
- ➢ Thermal creep
- ➢ Fabricability & Weldability



(2) Mechanical prop. before and after irradiation
toughness, DBTT,…

- ➢ Embrittlement under irradiation
- ➢ Behaviour in coolant media (Na Pb..)
- ➢ Fuel Cladding Chemical Interaction
  Reprocessing
- ➢ Stability at high temperature
  Phase transformation

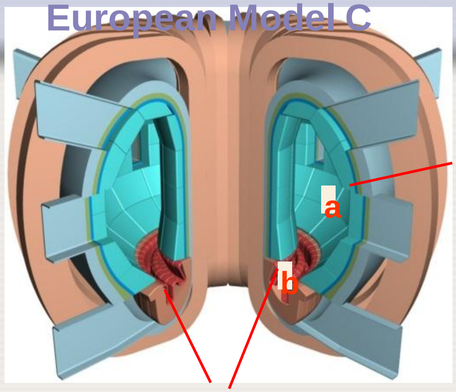


Overview

FUSION: 9% - 14% Cr reduced activation ODS steels are candidate materials for structural applications in advanced future fusion reactors

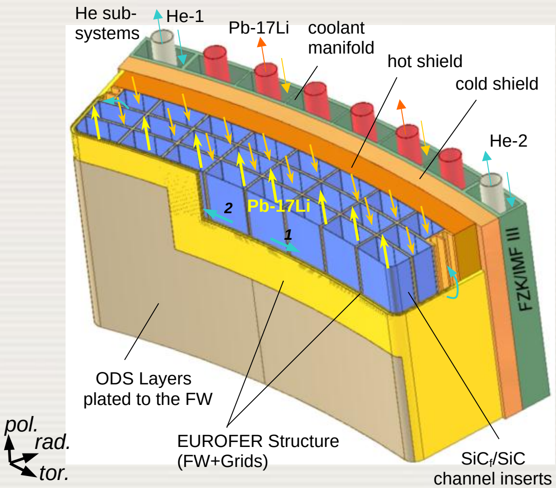
(1) Good irradiation properties: high swelling resistance, no HT He-embrittlement .
(2) Good thermo-physical properties: high thermal conductivity, low thermal expansion
(3) Fast decay of radioactive inventory: recycling, storage within reasonable time scale, low level waste ~ 100 years
(4) Operational temperature window, Blanket: ~ 250– 550°C (EUROFER); ~ 650°C (ODS-EUROFER), Divertor: ~ 600°C – 700°C (ODS RAFM/RAF steel)

Power Plant Conceptual Studies European Model C



176 blanket modules (a) (5-6 yrs. lifetime)

48 divertor plates (b) (1-2 yrs. lifetime)



"Dual Coolant" He-PbLi LM Blanket Design T_{max} ≥ 650° C, 80-150 dpa in DEMO

IAEA Experts Meeting, 3 Sep 2010, INTEC, KAERI, Daejeon, Republic of Korea

IAEA

Activities

Series of Experts meeting held during last 2 years, advice form senior specialists on new coordinated research project, specifically CIAE/ China, CEA / France, IGCAR/ India, JAEA/ Japan, JRC / EC), Bochvar Institute/ Russia), ORNL and INL/ USA.

Two particular areas recommended:

(i) high performance materials capable of operation over a wide range of elevated temperatures and high dpa levels, primarily advanced ferritic/martensitic steels ODS grades.

(ii) structural design criteria, with particular emphasis on creep-fatigue interactions. This is not resolved even for well known materials, such as austenitic stainless steel type 316L(N). It becomes even more challenging for martensitic steels that show cyclic softening.

IAEA

Coordinated research (new)

New IAEA CRP on Benchmarking of advanced materials pre-selected for innovative nuclear reactors (jointly NA-NE) should address critical review of structural materials pre-selected for innovative reactor systems (focus on FR technology), stimulation of further technological improvements in area of advanced structural materials

- Response to MS demand in R&D of SM via coordinated assessment of key parameters and technological limits
- Performance testing of materials pre-selected for primary components of new innovative reactor systems.
- Assessment of candidate materials for critical core structural components (reactor vessel, internals and fuel cladding); harmonisation of analysis, consideration of samples miniaturisation, round robin, etc.).
- Methodology for testing of selected materials from the radiation stability, ageing other degradation mechanism point of view.

Coordinated research (new)

It is expected that coordinated research project should address following issues:

- Production process and availability (low and high Cr), mechanical milling, alloying and extrusion process in order to achieve the best possible performance, both fission and fusion applications.
- Heat treatment and mechanical properties
- Mechanical and microstructural characterisation (creep, strength, tensile properties, weldability and/or joining procedures, size and distribution of oxide particles)
- Test matrix – fabrication of samples to be distributed as well as list of parameters to be evaluated in the framework of CRP (mechanical as well as microstrctural).

IAEA

Coordinated research (on-going)

IAEA CRP on Accelerator Simulation and Theoretical Modelling of Radiation Effects (jointly NA-NE)

Deals with several issues related to the proton and ion beam irradiation in order to achieve very high radiation damage, project aims to facilitate following issues:

(1) Better understanding of radiation effects and mechanisms of material damage and basic physics of accelerator irradiation under specific conditions,

(2) Improvement of knowledge and data for the present and new generation of structural materials,

(3) Contribution to developmental of theoretical models for radiation degradation mechanism and

(4) Fostering of advanced and innovative technologies by support of round robin testing, collaboration and networking.


Coordinated Research Activities Website - Windows Internet Explorer
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Thank you for your attention

email: a.zeman@iaea.org

Annex 12:
Kryukov’s presentation on Vanadium Alloyed Low Nickel Steel

Petten, 14-15 March, 2011

PRIMAVERA Seminar

Vanadium alloyed low nickel steel for future reactors

A. Kryukov, L. Debarberis, P. Hähner, F. Gillemot and F.Oszvald

EC-JRC Petten – Institute of Energy
AEKI, Budapest, Hungary

Vanadium alloyed low nickel steel

- WWER RPV are in operation more than 50 years

- Response to radiation is very well understood and predicted

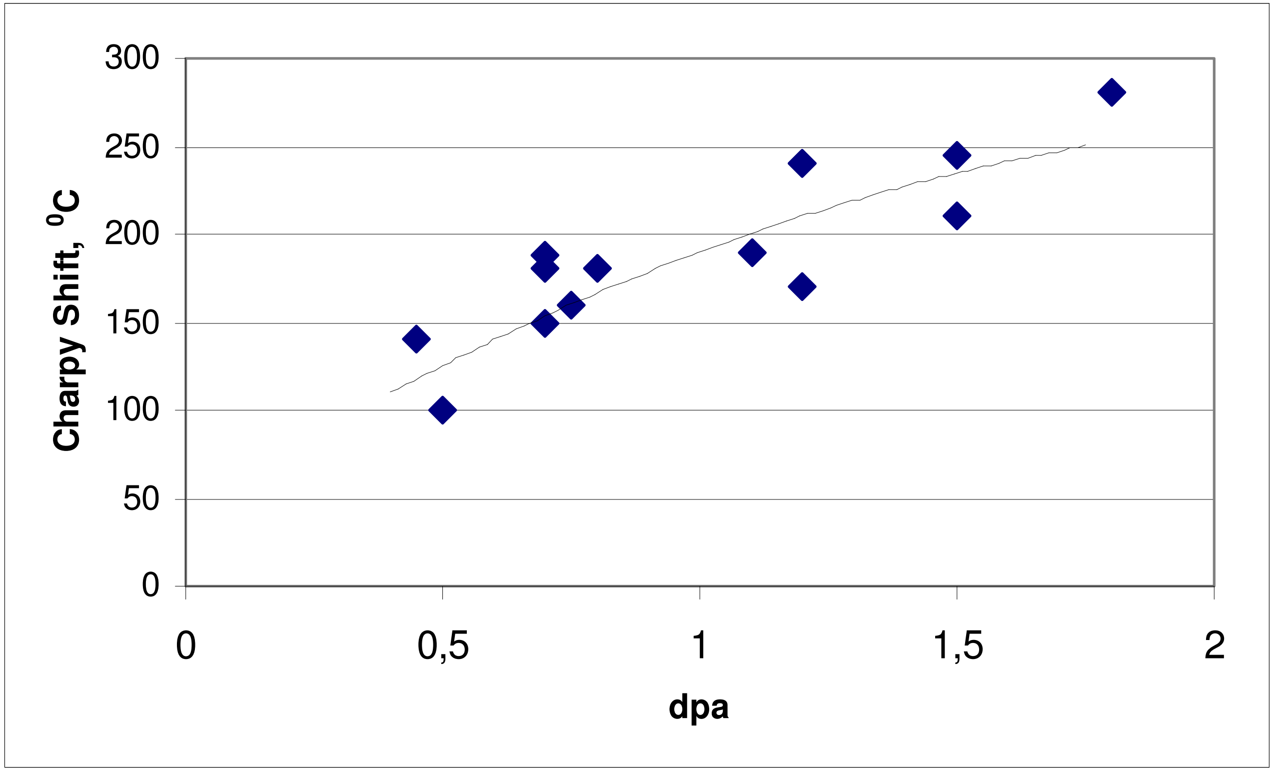
- 3 major contributions and their synergisms:
  - copper rich radiation induced nano-precipitates
  - phosphorus segregation at different internal surfaces
  - basic damage of the material matrix

- High radiation stability of WWER-440 steel with low P and Cu

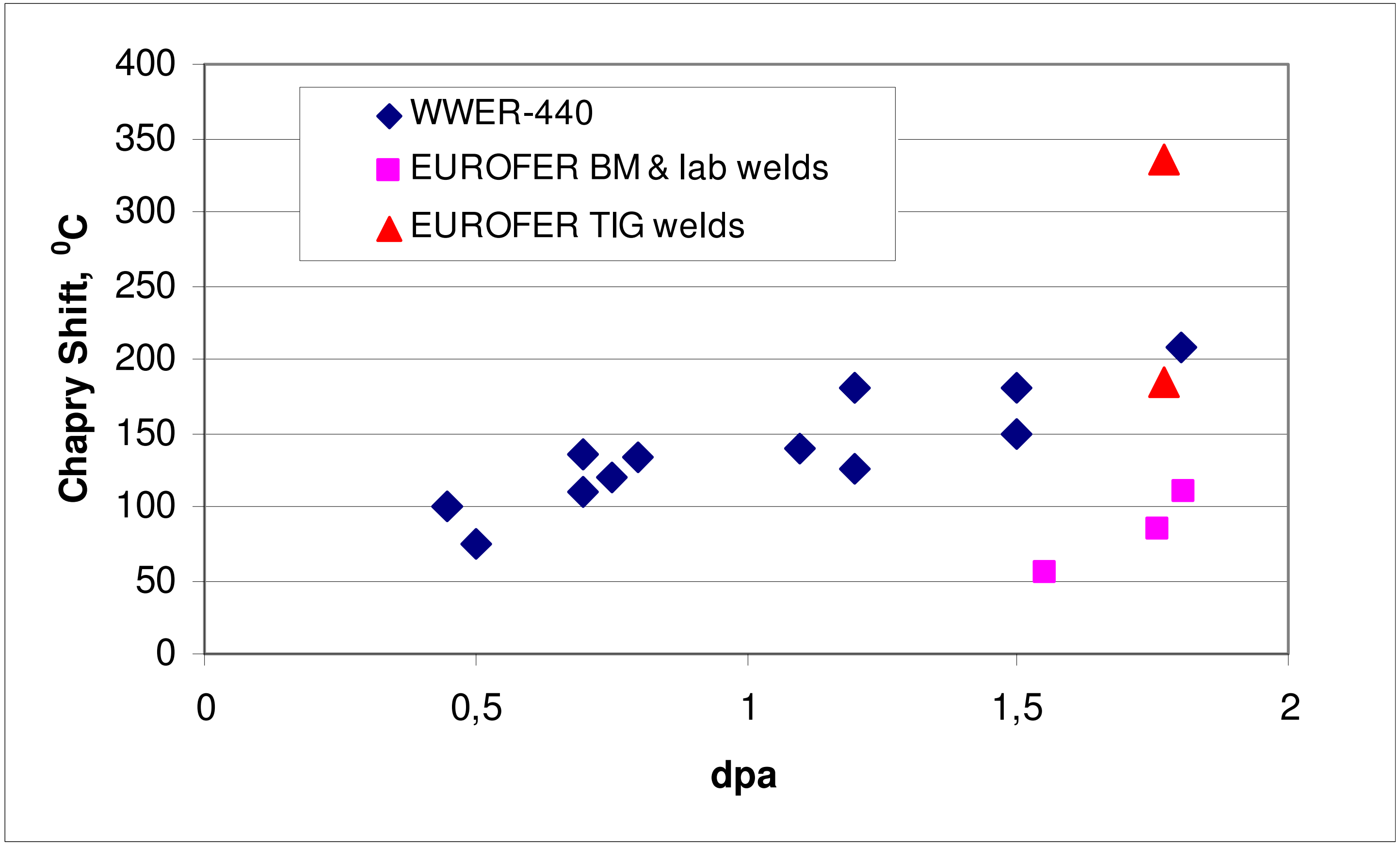
Structural materials for Generation 4 NPPs (GEN IV).

- Special ferritic-martensitic steels
- high temperatures up to 700 ºC
- high neutron dose influence
- EUROFER material data obtained by NRG and other laboratories

Trend of WWER-440 irradiation damage data at 270 ºC

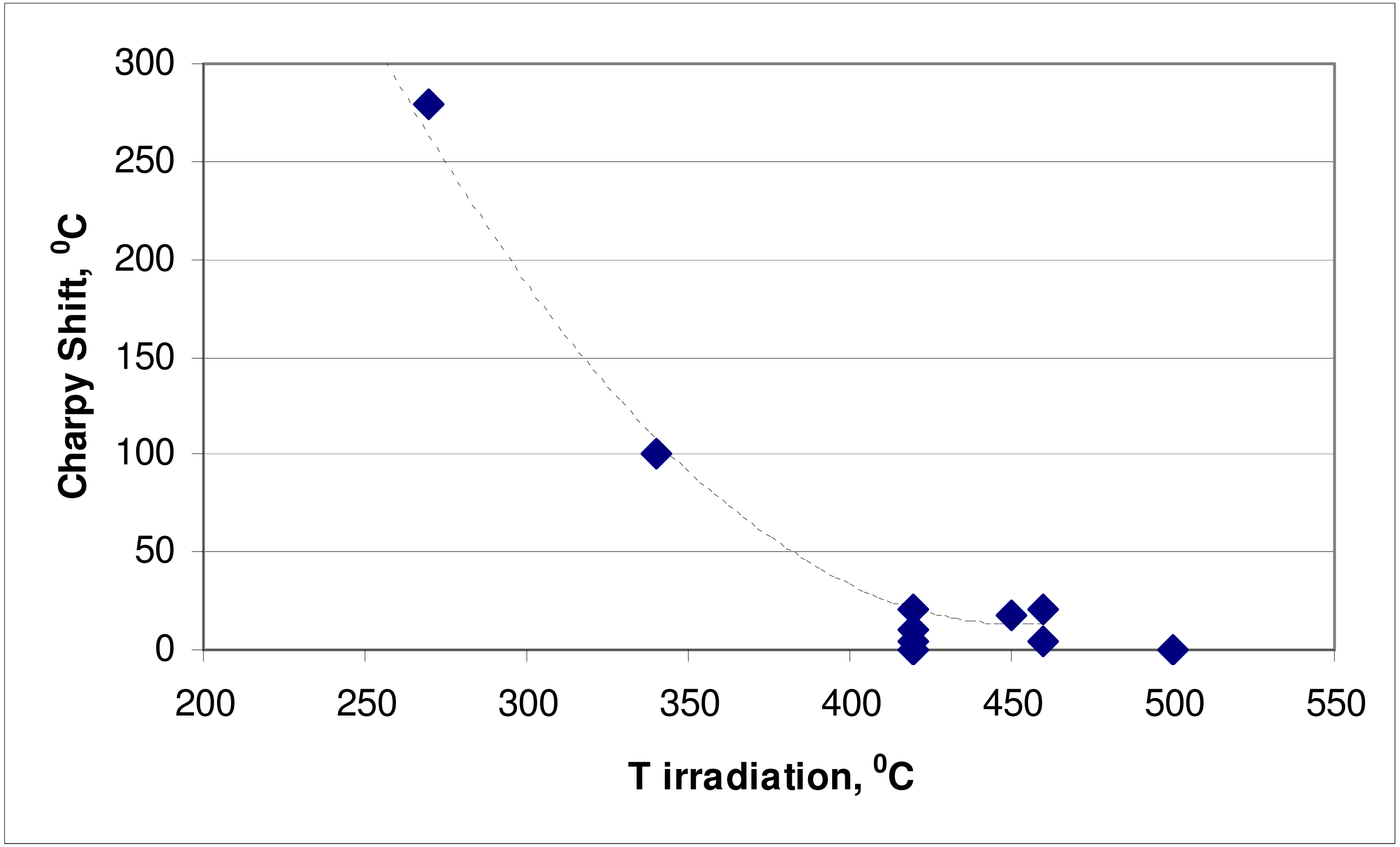


WWER-440 and EUROFER data at 300 ºC.

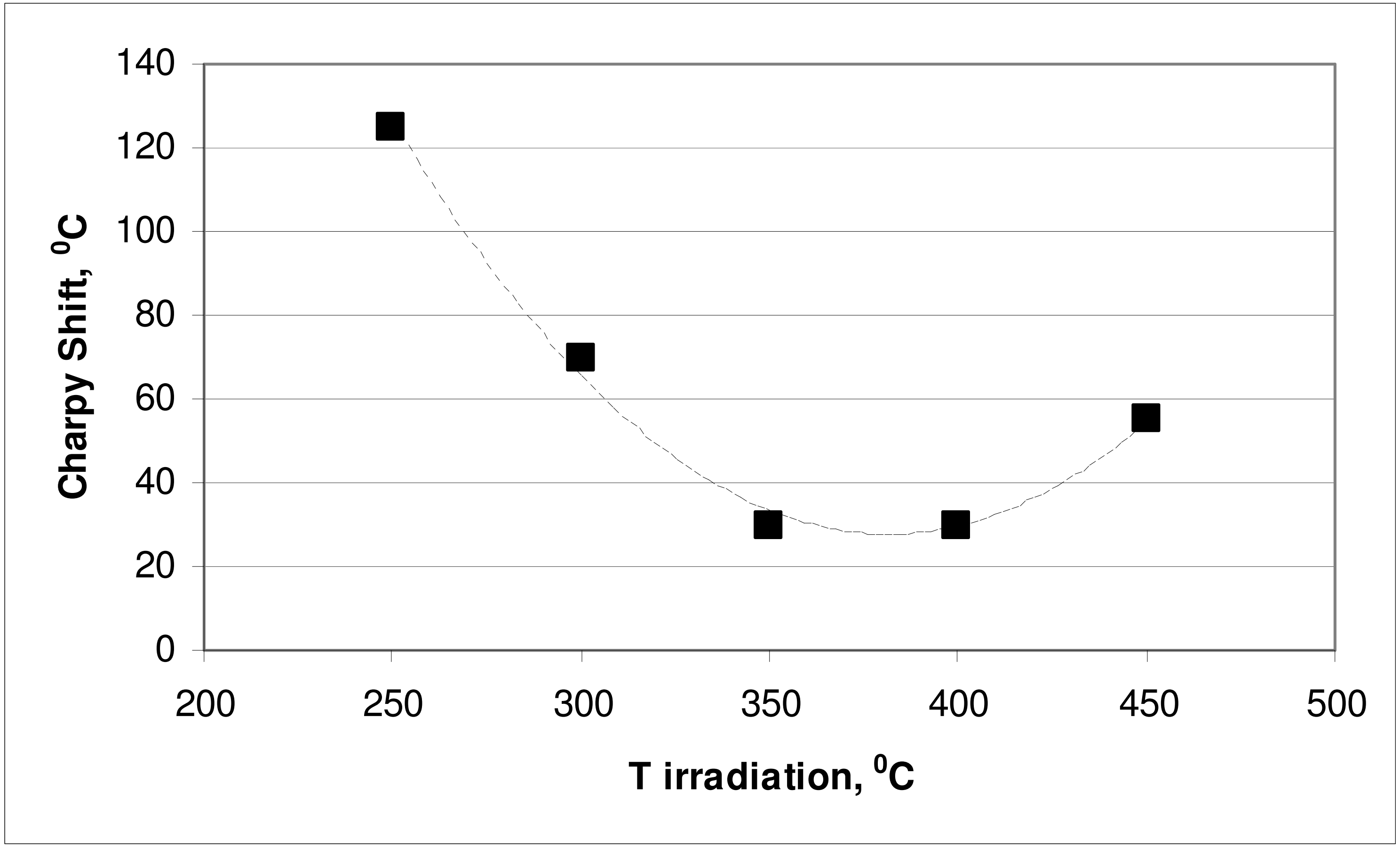


EUROFER data from “E. Lucon et al, Fusion Engineering and Design, 2008”

Available WWER-440 data at higher temperatures



LA12TaLC Reduced Activation steel; damage vs temperature



A.Alamo et al, Jornal of Nuclear Materials, 2000

Conclusions

- Low alloyed steels have been developed and are extensively used as RPV materials since decades
- base metal and welds of WWER-440 (2CrMoV) with low content of impurities have very high radiation stability
- WWER-440 steel presents acceptable radiation stability at least up to a neutron dose of 2 dpa at irradiation temperature 270 ºC
- At irradiation temperatures above 400 ºC the Tk shift is very small

Conclusions (2)

- comparison between 2CrMoV and ferritic-martensitic steels:

  - for the neutron doses of 1.5-2 dpa at 300 ºC the Tk shifts for WWER steel and EUROFER welds are comparable

  - At 350-560 ºC the radiation embrittlement level of both WWER and ferritic-martensitic steel is low

- Further studies will be required to qualify the material for GEN IV applications.

European Commission

EUR 24881 EN – Joint Research Centre – Institute for Energy
Title: Proceedings of the PRIMAVERA International Workshop on Re-embrittlement after Annealing of Reactor Pressure Vessel Steels
Author(s): A. Ballesteros, C. Bruynooghe, P. Haehner
Luxembourg: Publications Office of the European Union
2011 – 253 pp. – 21x 29.7 cm
EUR – Scientific and Technical Research series – ISSN 1018-5593
ISBN: 978-92-79-20666-5
doi:10.2790/34573

Abstract

The International PRIMAVERA Workshop on "Re-embrittlement after Annealing of Reactor Pressure Vessel Steels" took place at JRC-IE Petten, Netherlands, in March 2011, and was organized together by the POS and MATTINO Actions of the SPNR and SFNR Units of JRC-IE. The main purpose of the workshop was to present the results of the PRIMAVERA project, which is currently in its final phase, to identify and discuss open issues in the topics covered by the project (annealing and re-embrittlement after annealing), and to propose additional investigations to address the identified open questions. A second objective of the workshop was to explore the possibilities of cooperation among the IAEA, JRC and the rest of the PRIMAVERA partners on research in advance materials and their behaviour under neutron irradiation, as materials from future reactors (e.g., Gen IV reactors) will be exposed to high neutron fluence and high temperature.

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