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EAST/WEST STEELS FOR REACTOR PRESSURE VESSELS

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INTRODUCTION

This report is in three parts. PART 1 is a comparison of the irradiation behaviour of 'Eastern' and 'Western steels'. PART 2 is on the mechanisms of irradiation embrittlement and Part 3 is on the role of compositional variations on the irradiation sensitivity of pressure vessel steels.

PART 1. COMPARISON OF 'EASTERN' AND 'WESTERN' STEELS

1.1 Introduction

A recent European study [1.1] concluded that for the earlier 'Eastern' and 'Western' steels having deleterious element concentrations above certain levels there was, coincidentally, a similar degradation in mechanical properties during equivalent neutron irradiation. With the identification of and reduction in the concentration of the sensitizing elements then the irradiation sensitivity was reduced and the shift in mechanical properties on irradiation was also reduced. See Figure 1.1

While the key features of this comparison are described below it will be noted that in Figure 1 the neutron fluence has been normalised to $E > 1\text{MeV}$ and the extent of the fluence scale reflects the End Of Life Peak fluences for the Eastern and Western steel Pressure Vessels. The curves are based on the compositions of 'real' steels used in practice, the predictions are from the use of the Russian Code [1.2] for the Eastern steels and from the USNRC Regulatory Guide 1.99 Rev 2 [1.3] for the Western steels.

1.2. REGULATORY CODES AND GUIDES

The US Nuclear Regulatory Commission Guide 1.99 Revision 2 [1.3] to describe irradiation effects in pressure vessel steels states that:

$$RT_{\text{NDT}} = RT_{\text{NDT}}^{\text{initial}} + \Delta RT_{\text{NDT}} + \text{MARGIN} \dots \dots \dots (\text{Equation 1.1})$$

where: RT_{NDT} is the reference temperature for unirradiated material

ΔRT_{NDT} is the increase in this temperature due to irradiation

and, MARGIN is the quantity to be added for conservatism

The value of ΔRT_{NDT} should be calculated by means of the following equation:

$$\Delta RT_{\text{NDT}} = (CF)f^{(0.28-0.010 \log f)} = (CF)(FF)$$

where: f is the fluence in units of 10^{19}n/cm^2 ($E > 1\text{MeV}$) and FF is the Fluence Factor and, CF is the Chemistry Factor from the copper and nickel content and can be derived from the surveillance results or from tables in the Guide.

Using this approach and the appropriate values from published data for the composition of US welds allows the shift in transition temperature to be calculated up to a fluence of $4 \times 10^{23} \text{ n/m}^2$ ($E > 1 \text{ MeV}$). The fluence for use of the Guide limited by the availability of high fluence data underpinning the Guide and the End Of Life fluence of the pressure vessels. The results are shown in Table 1.1 and Figure 1.2 below:

TABLE 1.1: Shift, in $^{\circ}\text{C}$, in transition temperature for selected US RPV welds.

	Cu	Ni	CF($^{\circ}\text{F}$)	Fluence (10^{23} nm^{-2} , $E > 1 \text{ MEV}$)				
				1.0	2.0	3.0	4.0	5.0
CE HiCu, HiNi	0.35	1.0	272	151	180	195	205	212
B&W,HiCu Linde 80	0.35	0.6	212	118	140	152	160	165
B&W,IntCu Linde 80	0.20	0.6	160	89	106	115	121	125
High Cu Lo Ni	0.30	0.1	139	77	92	99	104	108
Lo Cu Hi Ni	0.03	1.0	41	23	27	29	31	32
B&W LoCu Linde 80	0.03	0.6	41	23	27	29	31	32

The Russian Code predictive equation for weld metal irradiated at 270°C is as follows:

$$\Delta T = 800(P+0.07Cu).(f)^{0.33} \dots\dots\dots(\text{Equation 1. 2})$$

The copper and phosphorus values for the critical welds in WWER pressure vessels have been published [1.4]and this allows the Chemistry Factor for Eastern steels to be calculated as in Table 1.2 and plotted in Figure 1.3 below.

TABLE 1.2: Chemistry Factors for WWER 440 weld 4 in reactor plants

PLANT	Copper	Phosphorus	800(P+0.07Cu)
Kola 1	0.15	0.033	34.8
Kola 2	0.15	0.04	40.4
Armenia 1	0.16	0.03	33.0
Armenia 2	No values given		
Novovoronezh 3	0.15	0.031	33.2
Novovoronezh 4	0.17	0.03	33.5
Kozloduy 1	0.12	0.052	48.3
Kosloduy 2	0.18	0.038	40.5
Kosloduy 3	0.20	0.036	40.0
Kosloduy 4	0.04	0.021	19.0
Bohunice 1	0.10	0.043	40.2
Bohunice 2	0.11	0.026	27.0
Greifswald 1	0.10	0.043	40.2
Greifswald 2	0.15	0.036	37.2
Greifswald 3	0.12	0.035	34.7
Greifswald 4	0.16	0.035	37.0

Of course some of these values for deleterious element contents could be modified in the light of additional analysis. But the values given above suffice for the purpose of this paper.

This Chemistry Factor allows the transition temperature shift to be calculated as in Table 1.3 and plotted in Figure 1.3 for different neutron fluences. It is usual for the fluence to be calculated for neutron energies of $E > 0.5 \text{ MeV}$. This fluence can be approximately converted to a neutron energy spectrum of $E > 1 \text{ MeV}$ by using the following relationship:

$$F(E_n > 0.5 \text{ MeV}) / F(E_n > 1 \text{ MeV}) \propto 1.78 \dots\dots\dots(\text{Equation 1.3})$$

TABLE 1.3: Shift in transition temperature for WWER 440 welds covering the range of Chemistry Factors in Table 1.2 for two different neutron energy spectra.

CHEMISTRY FACTOR	FLUENCE (10^{23}nm^{-2})							
	F>1.0MeV	0.1	0.5	1.0	5.0	10	15	20
	F>0.5MeV	0.18	0.89	1.78	8.92	17.8	26.8	35.7
15		18	31	39	67	84	97	106
20		24	41	52	89	113	129	142
30		36	62	78	134	169	193	213
40		49	83	104	179	225	258	284
50		61	104	131	223	282	322	355

These two sets of predictions in Tables 1.1 and 1.3 and shown in Figures 1.2 and 1.3 using the USNRC Guide and the Russian Code and the extreme cases of the 'worst' and 'best' steels in these Tables and Figures are compared in Figure 1.1. Two features are immediately evident. Firstly the irradiation behaviour of the Eastern and Western steels are the same. The older welds show the greatest degradation. The more 'modern' steels, with a reduced concentration of deleterious elements show the expected improvement in sensitivity to irradiation. The second feature is that the End of Life Fluence of the WWER welds are significantly higher than the PWRs partly because of the higher neutron flux incident on the pressure vessel wall in the WWER 440.

It is emphasised that the Western steels, as confirmed by the USNRC guide 1.99 Rev 2, show a marked sensitivity to copper and nickel content (as shown in Equation 1 above). Little sensitivity to phosphorus concentration is observed. On the other hand the Eastern steels are sensitive to phosphorus content and show a significantly lower sensitivity to copper content as shown in the Russian Code (and illustrated in Equation 1.2 above). Yet the degradation on neutron irradiation is the same. This is the first example of a remarkable and unexpected coincidence when comparing these materials. It will be remembered that the data base for the two Guides/Codes has been generated in different countries and there are differences in the mathematical/statistical treatment. However the developments in the production of these steels with regard to improving their irradiation resistance on the basis of reducing the deleterious elements has been effective.

However it is an inescapable conclusion that copper and nickel confer an irradiation sensitivity in the older 'western' steels while phosphorus and copper confer a sensitivity on the older 'eastern' steels. The role of phosphorus and nickel in irradiation embrittlement are then of greater significance in trying to understand the integrity of reactor pressure vessels. These aspects will be discussed in later sections of this paper. However it is stressed here that an unequivocal quantitative description of the embrittlement role of phosphorus is necessary for empirical predictive purposes because it can apparently act in a hardening and non-hardening way.

1.3 NICKEL

Discussion of the role of nickel in irradiation embrittlement, in a comparative exercise such as this, is difficult because of a shortage of surveillance data and comparative irradiations. There are MTR data, see [1.1], which shows that above a certain nickel concentration there is a marked sensitization. Steels with low copper, low phosphorus but with high nickel (1.5-1.9 wt.%) were developed for the WWER 1000 reactor pressure vessels. Unfortunately there has been little published data from WWER 1000 surveillance specimens, because of difficulties in

fluence estimation. However from the limited data there is a marked irradiation sensitivity within the operational fluence.

1.4 ANNEALING IRRADIATION DAMAGE

There has been much work on the recovery annealing response of pressure vessel steels. Of direct technological significance is that substantial recovery (>75%) of the unirradiated properties occurs under modest conditions of temperature and time (450-500C for about a week). The second remarkable coincidence is that these annealing conditions prevail for both Eastern and Western steels. There has been a tendency for US data to be generated at lower temperatures than the Russian/Eastern data. It is thought that the reasons for this slightly different emphasis has been the cautious approach in the US towards annealing and the possibility of higher thermal stresses during annealing the comparatively bigger PWR pressure vessel. However the anneals on the Midland PWRPV have reduced these concerns and it would seem that slightly higher annealing temperatures are now possible [1.4]. Fifteen operating WWER pressure vessels have now been annealed and the conditions have been supported by much experimental work. Besides establishing the annealing conditions it has been found that the residual embrittlement after annealing is defined by the phosphorus content of the steel and not on the neutron fluence. However in the high nickel content WWER 1000 steels the nickel concentration dominates the residual shift. In these particular steels the specimens with very high (~2.4%) nickel had a low phosphorus but a high sensitivity to neutron irradiation. Because of this variation the causal effect could not be readily distinguished.

1.5 IRRADIATION DAMAGE EFFECTS

It is assumed that any difference in the irradiation shift predicted by the different trend equations is more of a reflection of the differences in the predictive equations and their particular unique databases than in any other fundamental differences. The many common factors which are used to describe the cause of change in mechanical properties can be simply shown in the following way for the components of matrix hardening (ΔRT_{matrix}), precipitate hardening (ΔRT_{ppt}) and segregation effects (ΔRT_{seg}) causing the change in mechanical properties.

$$\Delta RT_{NDT} = \Delta RT_{matrix} + \Delta RT_{ppt} + \Delta RT_{seg} \dots\dots\dots(\text{Equation 1.4})$$

<ul style="list-style-type: none"> • point defect clusters • microvoids • dislocation loops or clusters (stabilised by nitrogen) • carbon • fluence dependence • nitrogen effects (low dose, low temperature) • fluence rate effect. etc 	<ul style="list-style-type: none"> • dissolved copper • Cu+Ni, Mn • phosphorus as phosphides • etc. - irradiation enhanced saturation - saturation effects - fluence rate effects 	<ul style="list-style-type: none"> • phosphorus • etc
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Pavinich et al [1.4] have described the factors causing the degradation in mechanical properties on neutron irradiation as being caused by:

- defect production from displacement cascades (vacancies, interstitials, dislocation loops, vacancy clusters, vacancy-interstitial pairs)
- formation of ultrafine copper rich precipitates
- ultrafine phosphide formation
- ultrafine carbide formation
- temper embrittlement

They generally considered that the first two processes were the most important for irradiation embrittlement.

It is also important to note that Russian workers [1.6] [1.7] concluded that the for WWER vessels irradiated at temperatures of 250-270°C the most likely effect of irradiation is the interaction of phosphorus directly with radiation defects and dislocations

So, four possible component parts of the trend equation to empirically describe irradiation effects include the copper, phosphorus, nickel content and neutron fluence. Neither the USNRC Guide or the Russian Code includes all three compositional elements.

1.6 CONCLUSIONS

Irradiation degrades the mechanical properties of PWR and WWER steels. Because of crucial differences in the deleterious element concentration the steels cannot be directly compared. However the Russian Code and USNRC Guide have been developed for each of these two categories of pressure vessel materials. Predictions can therefore be based on these approaches. But the arguments are circular in the sense that predictions are only possible by the interpolation of the data base upon which the code and guide are based.

For the earlier steels there is a coincidentally similar degradation in mechanical properties. For later steels which have have been improved by reducing the concentration of the deleterious elements identified in the Code and Guide. The exception to this statement is the enhanced irradiation sensitive behaviour of WWER 1000 steels where phosphorus and copper were reduced but the nickel was increased to obtain desirable unirradiated start-of-life properties.

The peak neutron fluence in WWER pressure vessel steels is significantly higher than for the Western PWRs. The problems of irradiation embrittlement were therefore seen earlier in 'life' than in PWRs.

Annealing to remove irradiation degradation produces the same beneficial effects in all these steels. This has provided the 'technological fix' to the irradiation problem for WWERs. A successful feasibility annealing of the Midland Plant in the US seems to open the possibility of PWR annealing in PWRs. and thereby eliminate irradiation effects as a life limiting feature.

The most significant mechanistic feature of the comparison of Eastern and Western steels is in the behaviour of phosphorus. In the Russian steels it seems to be behaving in the same way as copper in Western steels. This feature has been explained in terms of concentration levels where phosphorus becomes the dominant sensitizing element above about 0.012wt%. The phosphorus levels in Western steels tend to be lower than this level, which explains the lack of sensitivity in Western steels, but the phosphorus levels tend to higher in Eastern steels (up to ~0.05wt%)- hence their sensitivity. With phosphorus being <0.012wt% then copper is the dominant sensitizing element for irradiation embrittlement.

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FIGURE 1.1: Predicted shift in the transition temperature versus neutron fluence ($E > 1\text{MeV}$) for an appropriate range of Chemistry Factors encompassing the compositions of 'real' Eastern and Western steels. Note that the curves for Western steels are truncated at a fluence of $\sim 4 \times 10^{23} \text{ n/m}^2$ which is the limit of the database underpinning the USNRC Reg Guide 1.99 Rev2. The results for the Eastern steels are plotted up to the 'End-of-Life' peak weld fluence for the WWER-440 reactors.

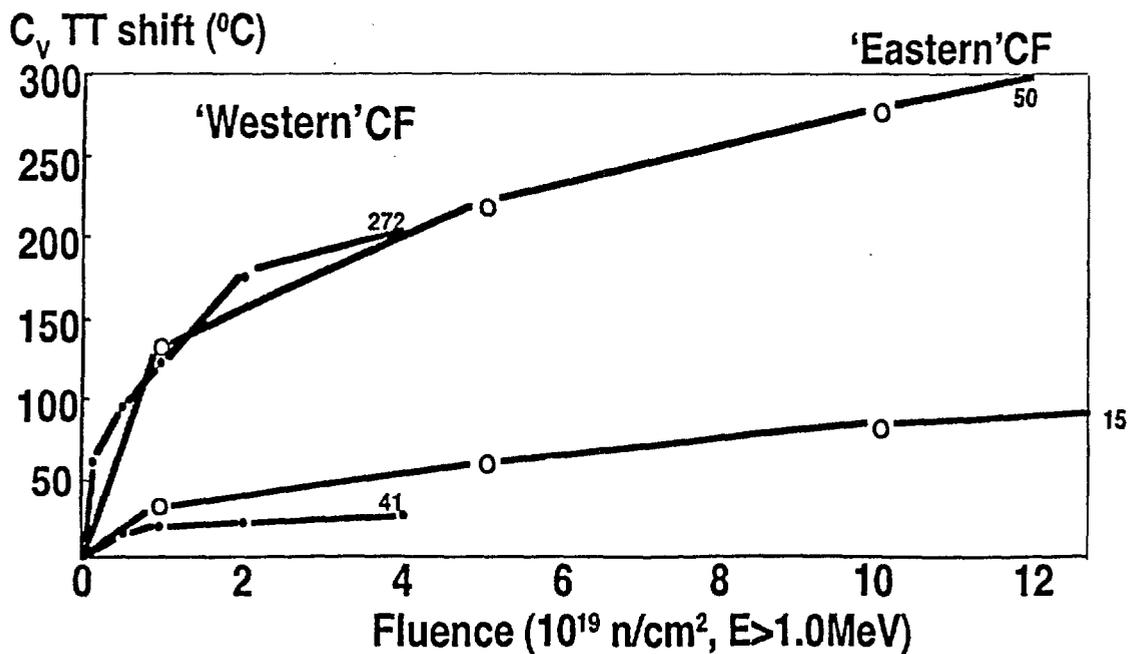


FIGURE 1.2: Shift in transition temperature of US welds encompassing a range of Chemistry factors for 'real' welds and using the USNRC Reg Guide 1.99 Rev 2.

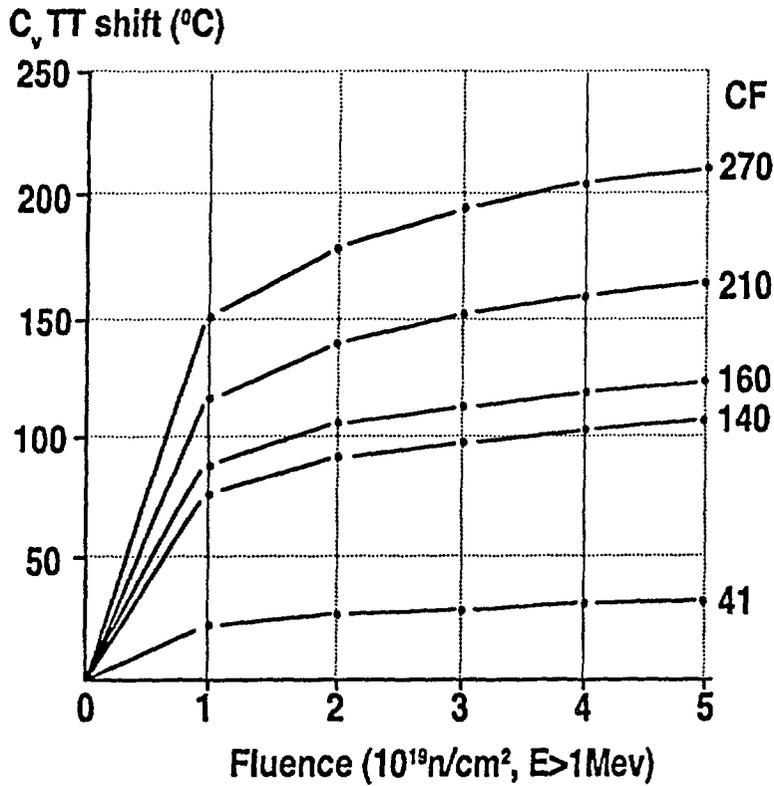
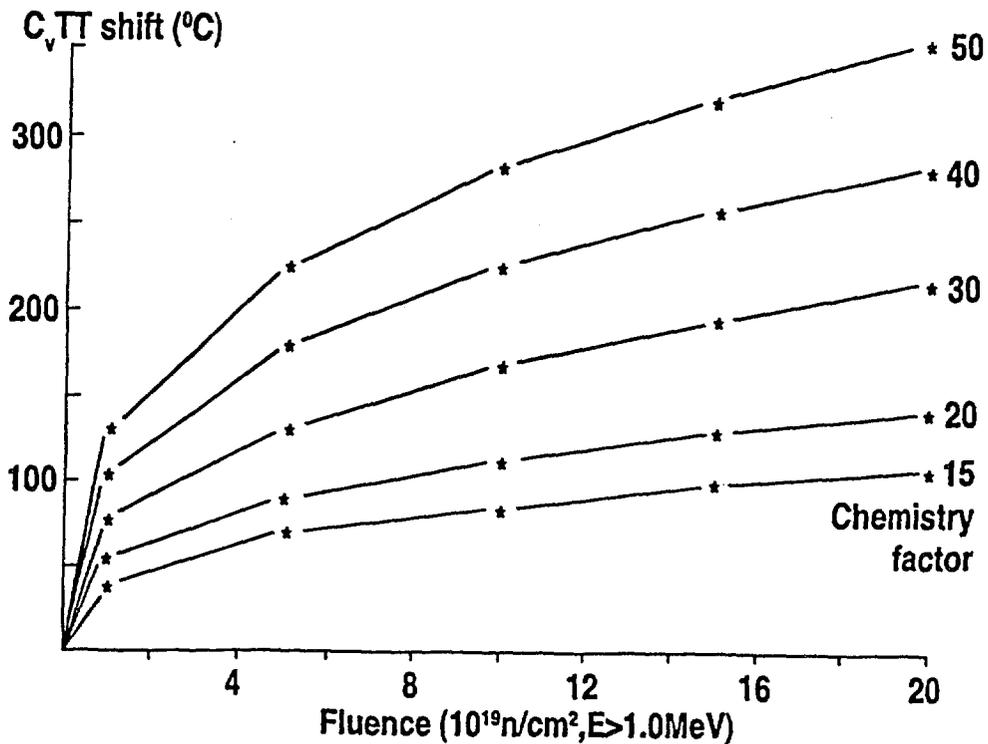


FIGURE 1.3: Predicted shift in transition temperature for WWER Number 4 welds for the range of Chemistry factors of interest in 'real' materials plotted as a function of neutron fluence with E > 1 MeV.



PART 2. MECHANISMS OF IRRADIATION EMBRITTLEMENT IN WESTERN STEELS

2.1 INTRODUCTION

The discussion in Part 1 has highlighted that in both Eastern and Western steels that there is a clear dependence of the change in mechanical properties on the composition of the steels with copper, phosphorus and nickel levels being of central importance. In the case of Western steels significant mechanistic understanding underpins the compositional, fluence and flux dependence which appears in the trend curves. The purpose of this section is to briefly summarise the status of understanding of these mechanisms.

The physical understanding of the embrittlement mechanisms requires an atomistic description of the processes occurring as a result of the damage that the flux of fast neutrons creates in the steel. Indeed, microstructural evolution in RPV steels is dominated by the interaction of the radiation induced point defects with either themselves or with the impurities and residual alloying elements in the steel. This leads to not only point defect clustering but also a complex interaction between defects and solutes. Both vacancies and interstitials are mobile, and their clustering and trapping at sinks (in particular by interstitial impurities such as carbon or nitrogen, and by dislocations) combined with radiation induced segregation of impurities such as copper and phosphorus, leads to a complex microstructure. It is these microstructural and chemical changes at the nanometre scale that control the mechanical properties of irradiated RPV materials.

Three basic micromechanisms of irradiation embrittlement have been identified and agreed world-wide to control RPV embrittlement in Western steels [see for example Phythian and English, [2.1] and Odette [2.2]]:

1. Matrix damage due to radiation produced point defect clusters and dislocation loops;
2. Irradiation enhanced formation of copper-rich precipitates;
3. Irradiation induced/enhanced grain boundary segregation of embrittling elements such as P.

The operation of the three mechanisms leads to a shift in the ductile to brittle transition temperature, ΔT_{40J} , i.e.

$$\Delta T_{40J, \text{total}} = \Delta T_{40J, \text{Cu}} + \Delta T_{40J, \text{Matrix}} + \Delta T_{40J, \text{GB}}$$

However, the segregation of P to a grain boundary leads to a change in the fracture stress but not the yield stress, $\Delta \sigma_y$, thus

$$\Delta \sigma_{y, \text{total}} = \Delta \sigma_{y, \text{Cu}} + \Delta \sigma_{y, \text{Matrix}}$$

This demonstrates that for mechanistic investigations the measurement of the yield stress as well as the change in fracture properties is important. As shown in Part 1, Regulatory Guides and Codes focus on the shift in a reference fracture toughness curve which is indicated by a shift in the ΔT_{RTNDT} or ΔT_{40J} .

2.2. MECHANISMS OF MATRIX DAMAGE

The term 'matrix damage' comprises (i) the agglomerates of intrinsic defects, such as self-interstitial clusters and interstitial-type dislocation loops as well as vacancy-rich regions, microvoids and vacancy-type dislocation loops and (ii) mixed agglomerates of solute atoms and intrinsic defects. Although knowledge of the type, strength, size and concentration of irradiation-induced matrix defects is still quite incomplete, at least for complex commercial steels, impurity contents are known to play an important role for the growth of matrix defects. Impurity elements can not only stabilize dislocation loops (such as interstitial Nitrogen in irradiated mild steel [2.3] but also vacancy solute interactions, as highlighted by recent modelling studies, Odette [2.4].

There is as yet no direct evidence for the nature of the matrix defects, but there has been indirect evidence of their nature and importance. Positron Annihilation techniques can be used to directly monitor the electron density and momentum fluctuations in the microstructure resulting from vacancies, vacancy clusters, interfaces, dislocations etc. Both Doppler broadening and lifetime measurements have been applied to irradiated and unirradiated RPV steels and model alloys. In general no unambiguous observations have been made of significant populations of vacancy clusters (say containing > 30 vacancies) in steels irradiated at 250°C and above. For example Dai et al [2.5] in a study of one of the surveillance sample specimens from the CHOOZ A reactor and electron irradiated Fe-Cu alloys concluded that there was no evidence of vacancy clusters with > single vacancies. Brauer in a comprehensive study of 15LH-15Kh2MFA base metal and 10WM-10KhMFT weld metal [2.6] concluded that such clusters could only be detected in RPV steels that had been irradiated at lower temperatures 92°C-156°C. At higher temperatures no such clusters were observed and the changes in the positron signal was interpreted in terms of the formation of irradiation-induced precipitates. Brauer and Eichorn [2.7] did conclude that there was evidence of vacancy clusters having ≥ 15 vacancies in irradiated Fe-Cu alloys.

In C-Mn steels the matrix damage is thought to be dominated by the formation of dislocation loops or clusters, and there is indirect evidence that their formation is sensitive to the levels of free nitrogen which acts to stabilise the damage clusters. Barton et al [2.8] suggested that the source of the difference in hardening behaviour of three C-Mn steels which exhibited differences in hardening behaviour was their nitrogen content or, more specifically, their dissolved (free) nitrogen content. Subsequent work confirmed the source of this dependence to be dissolved (free) nitrogen (Little and Harries [2.9, 2.10]), which during irradiation was thought to stabilise or strengthen irradiation produced defects, particularly interstitials. It was demonstrated by internal friction and strain-ageing studies that the quantity of free nitrogen was highest (~200ppm) in En2 and virtually zero in the aluminium grain-size controlled steel, with the silicon-killed steel being intermediate (~100ppm). This scaled directly with their irradiation hardening capacity.

Recent studies [2.4, 2.11] suggest that the nature of the defect clusters will depend on the steel, the irradiation conditions, particularly at high fluxes, and the irradiation temperature. The major development has been characterising the matrix defect term as being due to two components; firstly, stable matrix defects (SMD) and secondly, unstable matrix defects (UMD). The unstable matrix defects have been identified in irradiations in Materials Test Reactors, where high dose rates were employed, through undertaking post-irradiation

annealing studies [2.11] which resulted in identifying a component of the damage which was unstable at the irradiation temperature.

It has been found that matrix damage develops continuously during irradiation in the dose, dose rate and temperature range of interest, giving rise to a hardening which, at low dose rates, is dependent on the square root of the irradiation dose, but is independent of dose rate, see for example Jones and Williams [2.12].

2.3. MECHANISMS INVOLVED IN THE FORMATION OF IRRADIATION-INDUCED PRECIPITATION

2.3.1 Influence of Copper

A most important contribution to the degradation of mechanical properties stems from irradiation-assisted redistribution's of solute. In particular, Cu has been identified to undergo irradiation-enhanced precipitation from the solid solution of RPV steels. Under both thermal ageing and irradiation it has been possible to examine its precipitation from solid solution. Initially, this occurs as coherent bcc precipitates producing efficient pinning sites inhibiting dislocation motion. This pinning is thought to occur as a result of the modulus difference between the coherent precipitate and the surrounding matrix (Russell and Brown [2.13]). In thermally aged material the coherent bcc precipitates continue to grow upto about 6 nm diameter, before they become incoherent, resulting in a decrease in hardness (overaged condition). The transformation from bcc to fcc is achieved via an intermediate martensitic stage, where a 9R structure (fcc with a stacking fault every fourth layer) is produced. This then transforms to fcc at sizes of about 15nm and continued growth of the fcc precipitate results in a lenticular precipitate that obeys the Kurdjomov-Sachs relationship with the alpha iron matrix [2.14].

Irradiation of copper containing model alloys results in the formation of small coherent b.c.c. precipitates that grow up to approximately 4 nm in size without reaching the overaged stage and that act as efficient dislocation obstacles. Under irradiation the precipitates have not been observed to overage; instead they remain at ~4 nm diameter in simple alloy systems (similar in size to those at the peak hardness condition in thermally aged material). In commercial type steels they are generally smaller with typically ~2nm diameter.

The absence of overageing during irradiation leads to the conclusion that hardening increases with time or dose, and rises to a plateau rather than a peak, the plateau level corresponding to $\Delta\sigma_{Cu}^{max}$. The level of the plateau depends on the available copper (see below) and the rate at which the plateau is reached depends on dose rate and alloy composition.

Elements, such as sulphur, reduce the amount of copper available for precipitation during irradiation by forming copper sulphide during fabrication. This is particularly important in welds. Furthermore, it is known that copper may be precipitated during the final heat treatment. For high (above about 0.25-0.3wt%) copper materials copper is precipitated during the final post-weld heat treatment (PWHT) [2.15]. For example, at 607°C, a typical mean post-weld heat treatment temperature, only about 0.28wt% copper is soluble. Early indications from use of such techniques suggest that the PWHT employed by different vessel fabricators could have a major influence of the amount of copper which is soluble and available for precipitation.

2.3.1 Influence of other solutes on irradiation-enhanced copper precipitation

The mechanistic understanding of the compositional dependence of elements other than copper, in trend curves such as Reg Guide 1.99 revision 2 has focused on the micro-alloying of the copper rich precipitates rather than the impact of the alloying elements on the initial microstructure or the matrix damage. Evidence from various independent studies using techniques such as FEGSTEM, AP-FIM and SANS has confirmed the small precipitates to be alloyed with Mn and Ni and there is some evidence from AP-FIM of silicon being associated with copper precipitates. Clearly these alloy additions permit the remaining copper in solution to precipitate out, giving rise to an increase in hardness above that expected from a simple estimate of the volume fraction of copper available for precipitation from bulk chemical analysis. Such alloying may change the elastic modulus of the precipitate from the value typical of bcc copper, this in-turn will modify the pinning strength of the precipitate.

The role of nickel is complex and poorly understood. A clue to an important mechanism lies in the fact that copper rich precipitates have been found to be rich in Mn and Ni. Such compositions are consistent with thermodynamic calculations of the Fe-Cu-Mn-Ni quaternary [2.4]. Calculations suggest that nucleation rates will increase rapidly with decreasing copper, but are enhanced by Mn and Ni. These are described as manganese nickel rich precipitates (MNP) in contrast to the copper rich precipitates (CRP). For example Odette [2.4] calculated that at 260°C, reductions from 0.2 to 0.075% Cu, lower the nucleation rate by a factor of 5×10^4 for a 0.75%Ni alloy compared to a factor of 100 for a 1.5% Ni alloy. This leads to the possibility of delayed nucleation of MNP, which shows that MNP's in the high nickel alloy give a rapid increase to the yield strength increment, but only after a pronounced nucleation phase. The results suggest that the eventual hardening may be dominated by MNP's. The primary evidence for MNP's arises from SANS studies which show a precipitate volume fraction which is in excess of the available volume fraction of copper.

There is strong evidence that phosphorus hardens steels during irradiation. There are examples in both A533B and Russian CrMoV RPV steels. SANS shows evidence for P-rich clusters in the matrix [2.16]. Atom probe data also shows evidence of P-rich clusters within the grains, as well as P segregation to grain boundaries and particle interfaces [2.17]. The importance of P clusters decreases with increasing Cu content. It is believed that in high Cu steels phosphides are less important as P becomes incorporated in the copper clusters.

2.4. IRRADIATION-ENHANCED SEGREGATION OF SOLUTES TO GRAIN BOUNDARIES

While the contributions from matrix damage and precipitation give rise to obstacles impeding the motion of dislocations (barrier hardening), irradiation-induced grain boundary segregation of elements like P may influence the intergranular cohesion strength and may therefore act directly on fracture properties. The corresponding *non-hardening embrittlement* may then be due to a change in failure mode from trans- to intergranular fracture. While the detrimental role of P in causing temper embrittlement of the grain boundaries in ferritic-martensitic steels is well documented [2.18], less is known about the irradiation conditions (dose, dose rate and temperature) promoting irradiation-enhanced segregation, and through this the promotion of inter-granular embrittlement [2.19, 2.29, 2.21]. Some observations have been made demonstrating an increase in grain boundary phosphorus during irradiation [2.19].

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PART 3. THE ROLE OF COMPOSITIONAL VARIATIONS ON THE IRRADIATION SENSITIVITY OF PRESSURE VESSEL STEELS

The most obvious reason of the distinction of the trend curves for RPV steels of “Eastern” and “Western” types is the difference in the alloying systems and contents of deleterious impurities:

- Steels of “Western” type are characterised by the relatively low concentration of chromium (~0.1-0.14 wt. %), while in “Eastern” RPV steels the contents of chromium reaches 2-3%.
- If the contents of nickel in “Western” steels of A302 type (~0.18 %) approximately corresponds to the contents of a nickel in “Eastern” WWER-440 steels (0.1 - 0.4 % - 15Kh2MFA), the contents of a nickel in WWER-1000 steels (up to 1.9 % in welds) considerably surpasses the contents of a nickel in “Western” RPV steels alloyed by a nickel: ~0.40-0.70 % (on the average ~ 0.62 %) and ~0.40-1.00 % (on the average ~ 0.75 %) for A533 and A508 steels, respectively.
- In Russian type steels the relative content of phosphorus is higher and relative content of copper is lower than in “Western” steels:

$$Cp/Ccu \times 10 \approx (0.021/0.10) \times 10 \approx 2 \text{ and } (0.011/0.16) \times 10 \approx 0.7$$

for WWER-440 welds and A302B steels, respectively, and

$$Cp/Ccu \times 10 \approx (0.009/0.05) \times 10 \approx 1.8 \text{ and } \approx (0.007/0.15) \times 10 \approx 0.5$$

Analyses of the radiation sensitivity of RPV steels have shown that for “Western” type steels (with the typical ratios of contents of the deleterious impurities) the most deleterious impurity is copper. For Russian type steels been used in manufacturing RPV WWER-440 more strong influence on radiation embrittlement has phosphorus. In U.S. Regulatory Guide 1.99, Rev2 the effect of phosphorus on radiation embrittlement is not taken into account at all. For WWER-1000 welds it is difficult to overestimate the nickel effect.

Comparing radiation stability of various “Western” and “Eastern” RPV steels it is necessary to notice that they differ not by only contents of the essential alloying elements and residual impurities, but also by irradiation conditions:

- the radiation capacity (neutron flux) on “Western” type RPVs is at 5-10 times lower than on the appropriate class “Eastern” RPVs and, respectively, approximately the same ratio is between the end-of-life fluences of “Western” and “Eastern” RPV steels.
- The larger diameter of “Western” RPV in comparison with “Eastern” ones and, respectively, the larger water gap makes the neutron spectrum more ‘harder’ for “Western” RPV.

If the first factor can result in the different importance of various stages of irradiation, the second can bring to definite difference of radiation embrittlement mechanisms for “Western” and “Eastern” RPV steels.

The vast majority of the research on “Western” and “Eastern” RPV steels, carried out to the present time, shows synergism of the radiation responses caused by the presence of copper, phosphorus and nickel. Influence of copper, phosphorus and nickel on irradiation induced DBTT shift with fixing two from the three metallurgical variables under consideration for “Eastern” RPV steels is shown in Figs. Rf-1, Rf-2 and Rf-3, respectively.

Most studies aimed at revealing the nature of the effect of the metallurgical factors on radiation embrittlement of RPV steels are devoted to copper. It is acknowledged that the mechanism of copper effect on radiation embrittlement consists in hardening steel by radiation enhanced production of copper rich precipitates from supersaturated solid solution of copper in α -Fe. However size and volume fraction of these copper rich precipitates depends on contents in steel the other elements.

Phosphorus is known to be surface-active element and its segregation was revealed virtually on all interfaces in irradiated RPV steels. The phosphorus segregation on a precipitate/matrix interface can:

- interlock growth of precipitates;
- change the mechanism of interaction of dislocations with the obstacle;
- alter the critical size of transition of radiation produced precipitates from coherent to noncoherent state.

Therefore the phosphorus effect on radiation embrittlement can be attributed as to segregation decreasing cohesion of grain boundaries and affecting the resistance to failure, for instance, on Rice-Thomson's model, as to their influence on hardening of solid solution produced various precipitates.

In the certain extent the conception of radiation-induced grain boundary embrittlement was confirmed for "Eastern" steels. The presence of the certain correlation of the kinetics of grain boundary phosphorus segregation with radiation embrittlement rate was shown. The occurrence of intergranular failure mode in fracture surfaces of Charpy specimens of irradiated RPV steels and growth of the regions of intergranular failure with damage dose was revealed. Moreover, the radiation-induced change of grain boundary phosphorus segregation in RPV steels was revealed by direct experimental methods.

While the importance of the contribution of radiation induced grain boundary segregation to radiation embrittlement, i.e. the degradation mechanism not related to hardening, the primal contribution in radiation embrittlement attributes to hardening mechanisms. The influence of phosphorus on hardening of RPV steels was shown (Fig. Rf-4). To check the hypothesis of indirect influence of phosphorus on irradiation induced hardening of RPV steels, an irradiation of a special WWER-440 weld with elevated phosphorus content was performed. The weld was fabricated in laboratory conditions on special experimental technology and featured by high purity on the microstructural features such as unmetal and carbide precipitates (electron-microscopy examinations have revealed in this weld not typically low density of such defects) and rather low content of copper. This weld is designated as "A".

The trend curve specified for WWER-440 welds, rather correctly describes their radiation response. It is as follows:

$$\Delta TT_F = A_F F^{1/3}, \quad (1a)$$

where A_F is "radiation embrittlement coefficient":

$$A_F = 800 (C_P + 0.07 C_{Cu}). \quad (1b)$$

where C_i ($i = Cu$ or P) is content of elements in weight %; F is the fast neutron fluence in terms of 10^{22} n·m⁻² ($E > 0.5$ MeV). The experimental data on radiation embrittlement of two surveillance WWER-440 welds in comparison with appropriate trend curves (1) are shown in Fig. Rf-5. The experimentally measured radiation response of weld "A" is shown in Fig. Rf-6 versus the normative evaluation (1). Such a difference in the values of calculated and experimental DBTT shifts can be attributed merely only to the mentioned above features of the manufacturing technology of this weld, i.e. to high purity of the weld on unmetal inclusions and carbides (as it has already been mentioned above, the electron-microscopy study revealed in this weld extremely low density of those features).

Together with weld "A" the weld designated as "B" was irradiated. The weld "B" was manufactured under standard factory technology. Electron-microscopy examinations carried out revealed that weld "B" has microstructure (density and volume fraction of precipitates) characteristic for WWER-440 RPV steels. The radiation response of this weld is well described by trend curve (1), and considerably surpasses the radiation response of weld "A" (DBTT shift for weld "A" was measured three times less than for weld "B"), though the chemistry factor (Eq. 1b) for this material is lower.

Thus, the basic effect of phosphorus on radiation stability of "Eastern" RPV steels at initial stage of irradiation or with the accelerated irradiation can be attributed to its segregation on intragranular interfaces. As to segregation of phosphorus on high angular borders of prior austenitic grains, such mechanism of radiation embrittlement likely requires rather long exposure and cannot result in significant effects in low nickel steels of WWER-440 after one or two years of irradiation.

In WWER-1000 steels the role of grain boundary segregations can be higher than in RPV steels WWER-440, since nickel is known to rather essentially effect processes of phosphorus adsorption on interfaces. Phosphorus contents in RPV steels of WWER-1000 been in operation, are rather low and varies approximately within 0.006 - 0.012 %. In this case influence of phosphorus on radiation sensitivity of RPV steels can become background and the variation of phosphorus content can not result in visible change in the radiation response. It can hamper interpretation of the experimental data.

For finding out the nickel effect on radiation embrittlement of WWER-1000 steel there were basically investigated four weld metals with the same contents of the deleterious residual impurities (0.007%P, 0.06%Cu) and different nickel contents (1^w - 1.28%Ni, 2^w - 1.6%Ni, 4^w - 1.68%Ni and 3^w - 2.45%Ni). Variations of radiation-induced ductile-to-brittle transition temperature (DBTT) shift with fast neutrons fluence for the weld under consideration are shown in Fig. Rf-7a. Statistical analysis of the data in Fig. Rf-7a showed that the dependence of ΔTT_F on fast neutron fluence is close to linear at fluence higher than $\sim 3 \times 10^{23}$ n·m⁻². Consideration of the radiation behavior of three base metals with the same phosphorus and copper contents (0.012%P, 0.1%Cu) and different nickel contents (3^b - 1.3%Ni, 1^b - 1.4%Ni and 2^b - 2%Ni) showed that the general tendency of radiation embrittlement of the welds and base metals were the same.

The materials under investigation exhibited significant yield stress increase at high fluence region (Fig. Rf-8a). As seen from Fig. Rf-8a), $R_{p0.2}$ and R_m increase from fluence of $\sim 3 \times 10^{23}$ n·m⁻² ($E > 0.5$ MeV) and the damage dose dependences of $R_{p0.2}$ and R_m show pronounced drop at the first stage of irradiation for all the represented steels. At the same time DBTT shows uninterrupted increase with damage dose (Figs. Rf-3 and Rf-7). Ductility (A_5 and A_m) of these steels decreases continuously as well (Fig. Rf-8b). The substantial reduction in USE and ductility of the steels (Fig. Rf-8b) brings out that irradiation induced precipitate hardening. The indicated linear dependence of ΔTT_F on damage dose is extremely strong to be explained in the frame of the existing precipitation hardening models.

Among the most important characteristics of the annealing efficiency is the degree of transition temperature recovery determined by

$$\xi = \frac{TT_F - TT_a}{TT_F - TT_0} \times 100\% \quad (2)$$

Here TT_0 , TT_F and TT_a are the transition temperatures in unirradiated, irradiated and annealed conditions, respectively. As can be seen in Fig. Rf-10, the annealing effectiveness of WWER-1000 type steel increases with increasing annealing temperature.

The results of tensile tests of steels after post-irradiation heat treatment exhibited fairly high level of recovery (Fig. Rf-9). Yield stress of the weld 4^w in unirradiated condition was 549 ± 17 MPa. 400°C post-irradiation anneal of this weld produced complete recovery of yield stress. The USE was observed to be completely recovered after the 400°C post-irradiation anneal as well. Increasing annealing temperature resulted in over-recovery of the USE and tensile properties, i.e. increasing the USE higher and decreasing $R_{p0.2}$ and R_m lower than in unirradiated condition. The complete yield stress and USE restoration were not followed by complete DBTT recovery (Fig. Rf-10). Residual DBTT shift up to 80°C was observed after the 460°C anneal.

The indicated low level of DBTT recovery of irradiated WWER-1000 type steel is obviously connected with presence of nickel in the steel. As can be seen in Fig. Rf-11 recovery of WWER-440 type steel with nickel content ~ 0.2 wt.% is substantially higher. In average, 80% recovery was achieved for WWER-440 and WWER-1000 steels at $\sim 420^\circ\text{C}$ and $\sim 470^\circ\text{C}$, respectively.

It is interesting to note, that the post-irradiation annealing efficiency of "Western" steels of A533B type and WWER-440 RPV steels almost coincide (Fig. Rf-11). It is quite possible that there is some threshold nickel content, below which the influence of nickel content becomes negligible. Though, it seems plausible (in much the same way as reasoning made above for the case of influence of low phosphorus contents with elevated nickel

contents) that with nickel contents below some threshold value its influence on radiation behavior of RPV steels can become background and variation of its content can negligibly change the radiation response.

An investigation of the composition effect on the post-irradiation anneal recovery was hampered by deficiency of the data. For the annealing temperatures of 400 and 490°C there are as few as four and three experimental points, respectively. However, it may be assumed that nickel is one of the factors affecting the residual level of DBTT shift after the 460°C post-irradiation anneal (Fig. Rf-12). Comparison of DBTT recovery for steels with close nickel contents exhibited decreasing DBTT recovery with increasing phosphorus contents.

The $R_{p0.2}$ and R_m drops (Fig. Rf-8a) can partially be attributed to the reduction in dislocation density of WWER type forging metal due to irradiation from 10 to $1 \times 10^{13} \text{ m}^{-2}$. However, the dose dependence of $R_{p0.2}$ and R_m for 2^w weld display the drop as well. Therefore, that feature may apparently be attributed to incomplete stabilization of microstructure (probably, due to bainitic phase lock - stabilization - by nickel) by the pre-irradiation heat treatment.

An investigation of the high temper effect on the tensile properties was carried out for a base metal with chemical composition typical for WWER-1000 steel: 1.08%Ni, 0.008%P, 0.15%Cu and 0.18%C. An austenitization of the steel was as follows: 1250°C/10h and 890°C/6h. An air cooling followed the austenitization. The observed decrease in yield stress (650°C/10h - 678MPa, 30h - 627MPa, 100h - 516MPa) and ultimate tensile stress (10h - 767MPa, 30h - 719MPa, 100h - 625MPa) with the 650°C temper is due to decreasing carbon content in solid solution.

It may be supposed that the presence of nickel in steel results in stabilization of carbon in α -Fe lattice followed by incomplete stabilization of microstructure. The latter leads to the rejection of carbon from α -Fe lattice under irradiation, bringing its concentration to the thermodynamic equilibrium value. This mechanism has to cause decreasing yield stress as a result of reducing tetragonality of α -Fe. The one can be responsible for the over-restoration of tensile properties caused by the 460-490°C post-irradiation anneal (that did not accompanied by complete restoration of the ductility) as well (Fig. Rf-12). That is irradiation gives rise to decreasing carbon in solid solution and in this regard acts like the 650°C high temper described above.

Conclusions.

(1) Nickel, copper and phosphorus are the elements rendering the most essential influence on behavior RPV steels under irradiation and subsequent thermal annealing. For each type of steels the contributions of these elements in radiation embrittlement depend on the chemical composition of material, the irradiation conditions and add up not additive.

(2) For WWER-440 RPV steels, in which nickel content does not exceed 0.3 %, the main affecting factors are phosphorus and copper. For WWER-1000 RPV welds, in which nickel contents generally exceed 1.5 %, the role of nickel in radiation embrittlement is determinative. The influence of phosphorus and copper contents for those welds is minimized mainly by sharp reduction of their contents in steels ($C_P \leq \sim 0.010 \%$, $C_{Cu} \leq \sim 0.08 \%$).

(3) In "Western" type steels main influencing elements are nickel and copper. The secondary role of phosphorus in radiation embrittlement of "Western" RPV steels not in the last turn is caused by its lower relative contents in comparison with "Eastern" steels.

(4) The mechanisms of effect of copper, phosphorus and nickel contents on irradiation sensitivity of "Eastern" and "Western" steels seem to be similar. Some distinction between the observed radiation effects is apparently caused by the difference in the irradiation conditions and ratios of the contents in them of the above mentioned elements.

(5) For "Eastern" RPV steels the dependence of the recovery degree of irradiated steels due to post-irradiation thermal annealing is obviously depend on phosphorus contents and the influence of nickel contents on this process is detectable.

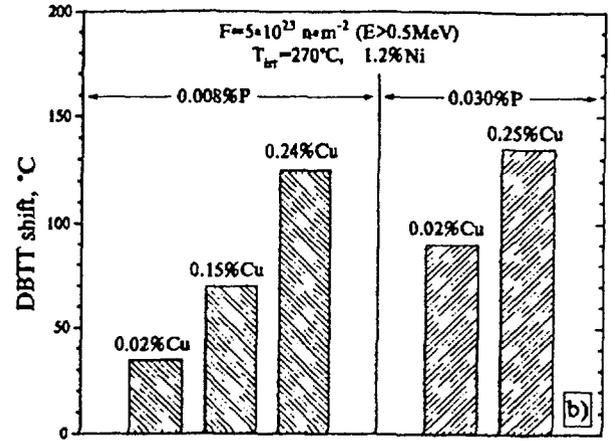
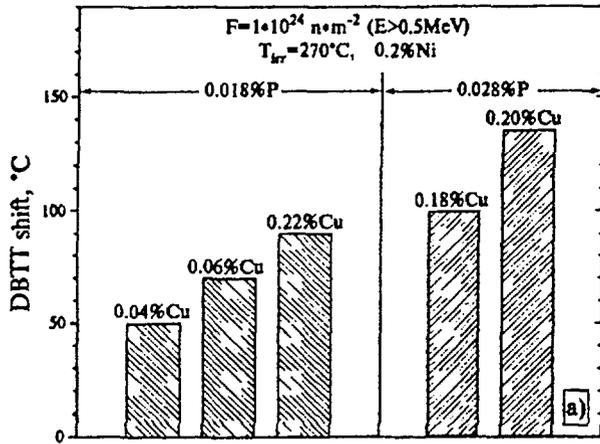


Fig. Rf-1. Effect of copper content on radiation response of WWER type RPV steels.

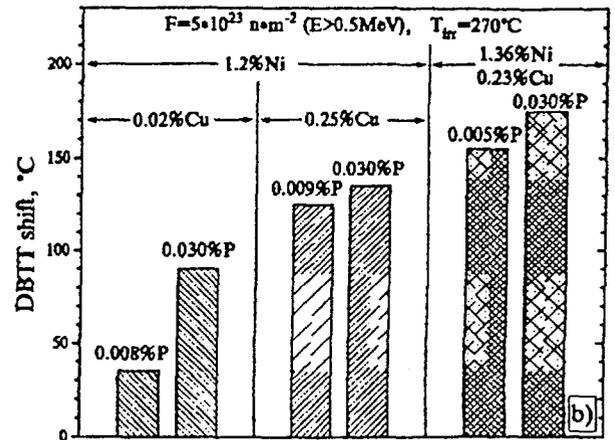
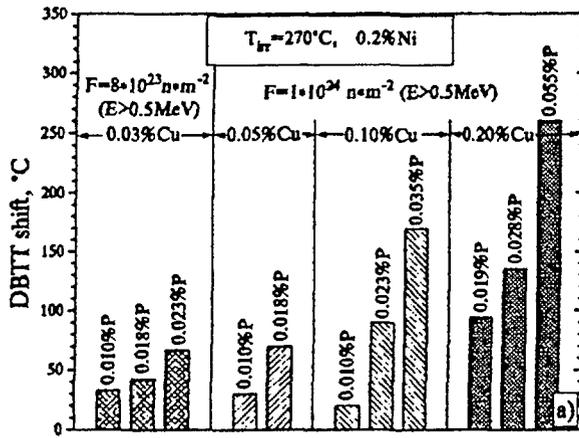


Fig. Rf-2. Effect of phosphorus content on radiation response of WWER type RPV steels.

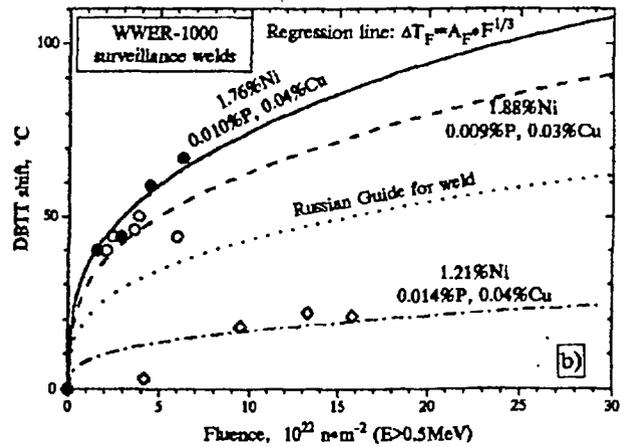
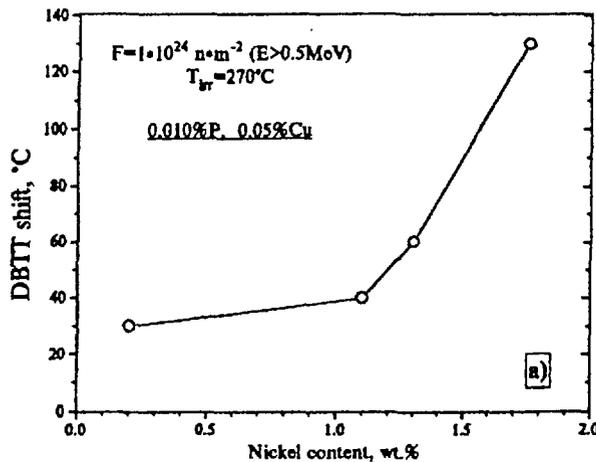


Fig. Rf-3. Effect of nickel content on radiation response of WWER type RPV steels.

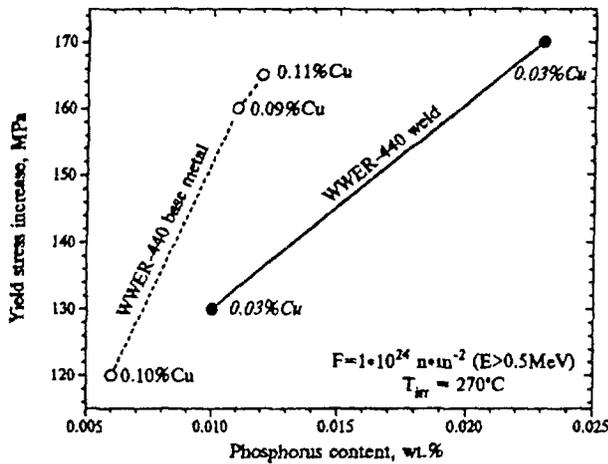


Fig. Rf-4. Effect of phosphorus content on irradiation induced yield stress increase in WWER-440 RPV steels.

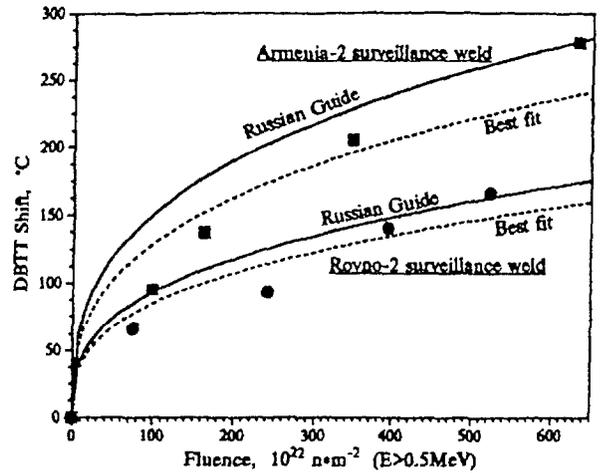


Fig. Rf-5. Radiation embrittlement of WWER-440 surveillance welds in comparison with the one predicted by Russian Guide.

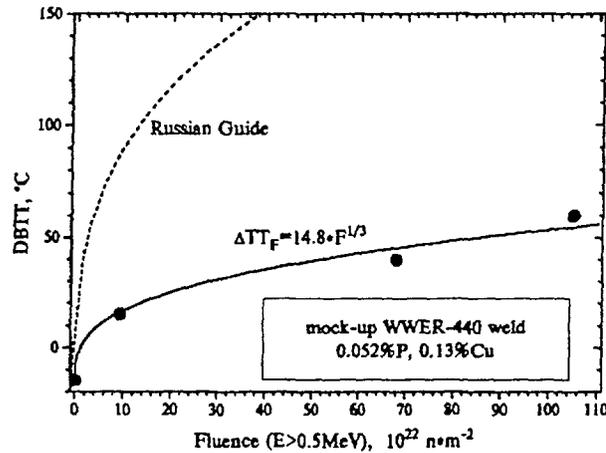


Fig. Rf-6. Radiation embrittlement of a WWER-440 weld with high purity on the microstructural features such as unmetal precipitates and carbides.

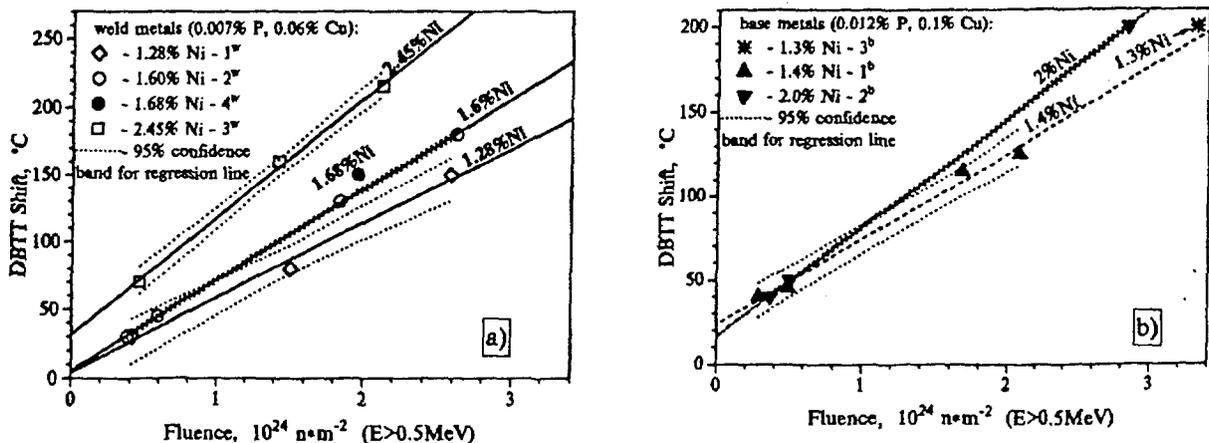


Fig. Rf-7. Fluence dependence of DBTT shift for weld and base metals.

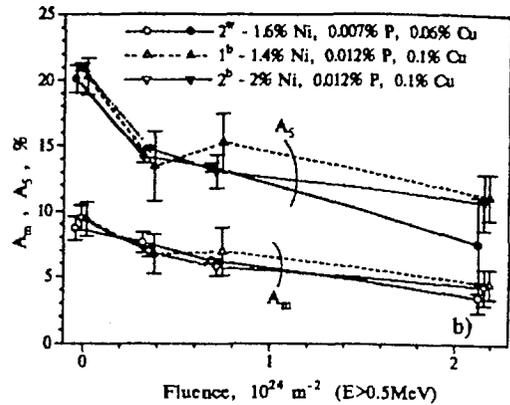
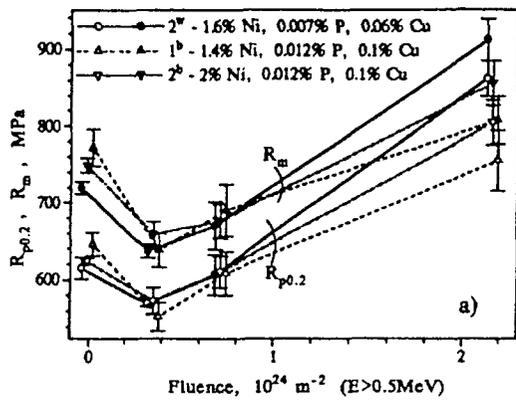


Fig. Rf-8. Tensile properties as a function of fluence for weld and base metals:
 a) Yield stress - open symbols, ultimate tensile stress - closed symbols;
 b) Uniform deformation - open symbols, elongation - closed symbols.

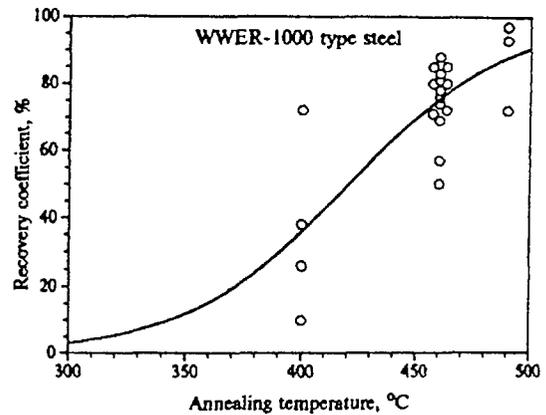
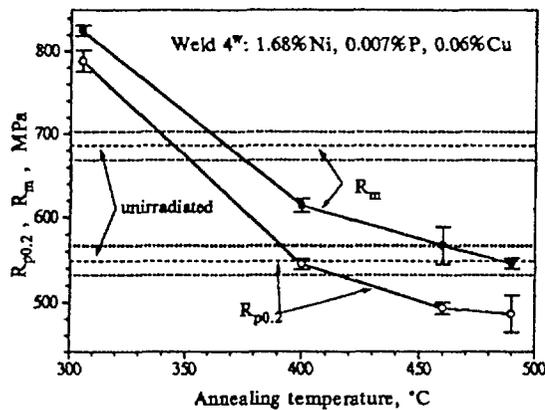


Fig. Rf-9. Dependence of tensile properties of irradiated weld 4^w on annealing temperature.

Fig. Rf-10. Dependence of DBTT recovery of irradiated WWER-1000 type steel on annealing temperature.

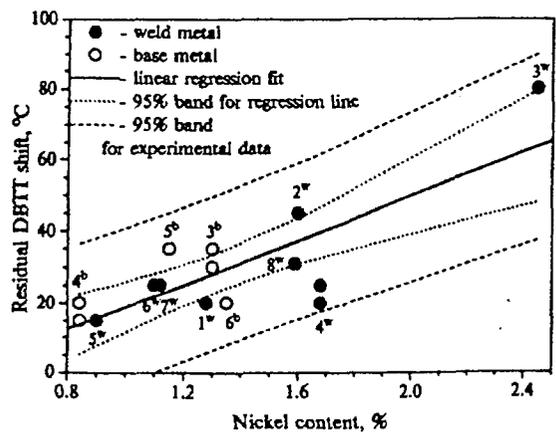
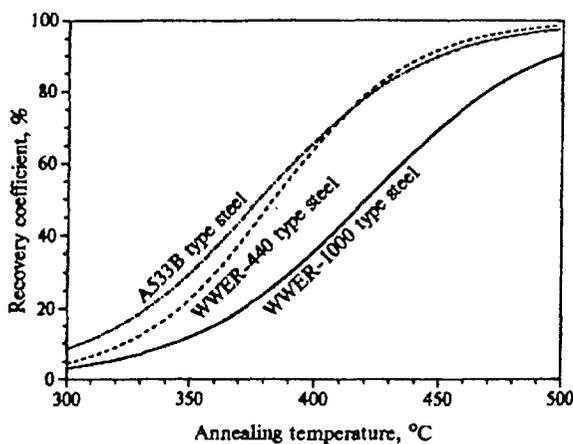


Fig. Rf-11. Comparison of the post-irradiation annealing effectiveness for steels of different types.

Fig. Rf-12. Dependence of the residual DBTT shift on nickel content.