Use of the semi-mechanistic analytical model to analyze radiation embrittlement of model alloys; Cu and P effects

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Background

General agreement on basic mechanism of radiation embrittlement exists for primary embrittlement of steels and welds based on three major contributions to damage: direct matrix damage, precipitation (mainly Cu) and element segregation (mainly P). In spite of this fact the models for analysis of radiation data are mainly based on statistical correlation of large d-base data. In this paper a model based on key mechanisms is proposed.

The advantages of the proposed semi-mechanistic model, when compared to non-mechanistic models, is that it allows improved fitting of data and permits the visualization of the relative contribution of the various damage components.

A set of model alloys with parametric variation of Cu, P and Ni content have been irradiated in High Flux Reactor (HFR) Petten [1] and tested, the results are published [2, 3 and 4]. A second set of such model alloys have been also irradiated in Kola NPP at higher fluence and recently the data have become available.

The low Ni model alloys results are studied in details in this paper showing the application of the semi-mechanistic model capabilities and potential for application to commercial steles and welds; in particular for VVER-440 type materials.

Key embrittlement mechanisms

The key embrittlement mechanism taking place during irradiation of RPV steels and welds, which are considered in this paper, is summarized in Table 1.

Table 1 – Embrittlement mechanisms considered

Embrittlement mechanism	*Remarks*
Direct matrix damage	**Due to neutron bombardment**
Precipitation hardening the matrix	**Cu is the leading element**
Segregation	**P is a recognized segregating element**

Direct matrix damage due to neutron bombardment can be assumed to be simply root square dependent on fluence for a given material and a given temperature. At higher irradiation temperatures the rate of damage is considered to be decreasing due to increased atoms mobility.
During direct matrix damage formation, Copper, together with other elements, is known to lead precipitation mechanism of nano-precipitates also inducing matrix hardening and embrittlement. Such mechanism continues until saturation depending on available amount of precipitants, Cu concentration in particular.
In addition, other elements, like P, can segregate, in grain (and or through diffusion processes at grain boundary) also in combination to matrix damage or attracted into the Cu-type precipitates. Diffusion of segregates plays also a role making this mechanism rather difficult to understand in detail.
In the following, the analytical model based on the above mentioned key mechanisms is reviewed.

Semi-mechanistic model
The effect of the various embrittlement parameters is considered to be additive to the total damage expressed in terms of ΔT_{shift}. Matrix damage contribution, assumed to be square root dependent on fluence, is then described simply as follows:

$$\Delta T_{shif\_matrix} = \left[a * \Phi^{n} \right]$$

where:	ΔT_{shift}	is the transition temperature shift component
	Φ	is the neutron fluence
	a	is model fitting parameter
	n	is the exponent (normally ½)

The parameter is **a** constant for a given material and a given irradiation temperature, while decreases with increasing irradiation temperature.
In addition to direct matrix damage, during the primary embrittlement, Copper, together with other elements, is known to lead precipitation mechanism of nano-precipitates also inducing matrix hardening and embrittlement. Such precipitation mechanism continues until saturation depending on available amount of precipitants, Cu concentration in particular. The contribution to the total transition temperature shift can be described as:

$$\Delta T_{shift\_Cu\_precipitation} = b1 * \left[1 - e^{-\Phi/\Phi_{sat}} \right]$$

where:	ΔT_{shift}	is the transition temperature shift component
	b1	is a model fitting parameter, representing the maximum saturation value of the shift due to precipitation
	Φ_{sat}	is a model fitting parameter, representing the fluence at which saturation effects begin

Subsequently other segregates can be formed both proportionally to the matrix damage and attracted into the Cu precipitates. Diffusion of segregates plays also a role. A simple model to describe generally this additional contribution is proposed in the following. The proposed model is based on a 'logistic' shape type of function describing a process of gradual increase then a rapid saturation of the process:

$$\Delta T_{shift\_P\_segregation} = c1 * [1/2 + 1/2 * Tangh(\frac{\Phi - \Phi_{start}}{c2})]$$

where:

	ΔT_{shift}	is the transition temperature shift component
	c1	is a model fitting parameter, representing the maximum saturation value of the shift due to segregation
	Φ_{start}	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

Based on the above mentions partial effects, the total effect in term of transition temperature shift is:

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

An example of primary radiation embrittlement calculated with the proposed model is given in figure 1.

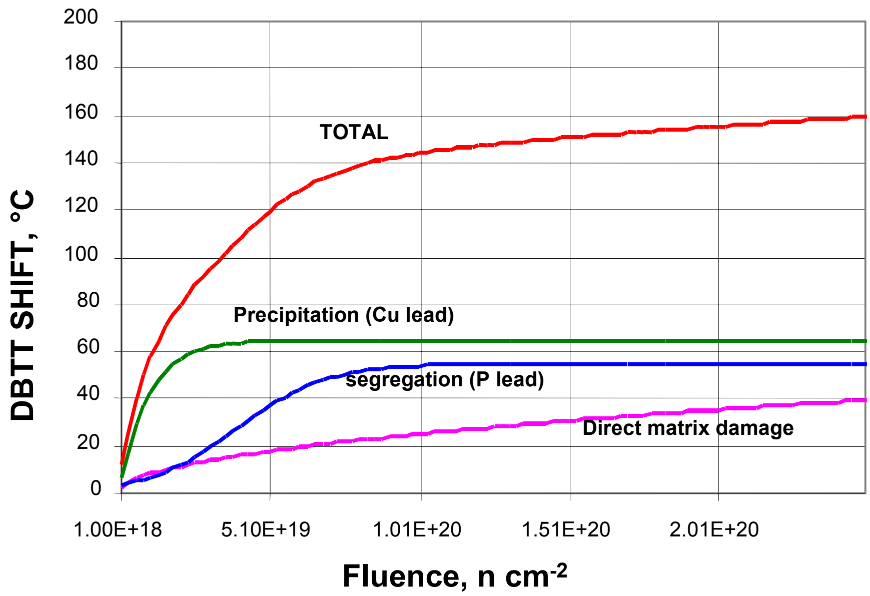

Figure 1 - Example of primary radiation embrittlement calculated with proposed model (Eq.1)

The relative contribution of the various damage components is also visualized in Figure 1. In total, a maximum of 6 parameters are required for the proposed model:

$$a, b1, \Phi_{sat}, c1, c2, \Phi_{start}.$$

Some parameters (Φ_{sat}, Φ_{start} and c2) can be derived and fixed in first instance depending on the general behavior of the data set to be analyzed making the fitting easier. The most important parameters are: a, b1 and c1. Parameter b1 if the model is correct will be depending mainly on Cu content while c1 mainly on P content.

The proposed model is suited in particular for analyzing data sets not really showing a simple power-type function like it happens in real surveillance data sets.
The other great advantages of the proposed semi-mechanistic model, when compared to non-mechanistic models, is that it allows better verification of hypothesis on mechanisms relative importance at the difference embrittlement phase. In particular, hypothesis of the peculiar behavior of re-embrittlement after annealing of high P steels, like some VVER-440 high P welds, can be better analyzed. What is in fact observed in the mentioned steels [4] is that the embrittlement kinetic after annealing is different from the kinetics after annealing: the embrittlement seems to start with a certain delay and increases rapidly afterwards. Such behavior is supported by micro structural investigations indicating that during annealing P does massively re-solute back and is almost fully available for the re-embrittlement (some will not re-solute back and a fraction might reach grain boundary). Cu does not re-solute back the same way and would thus contribute marginally to re-embrittlement. The hypothesis that P is leading re-embrittlement after annealing is also supported by available data on VVER-440. In fact, the transition temperature shift is mainly strongly correlated by P content and not with Cu content.

Using the proposed model it is possible to predict the behavior difference of the re-embrittlement in comparison with the primary embrittlement. In fact assuming that P is the leading element for re-embrittlement and that Cu has marginal effect, we can simply suppress the Cu term during the re-embrittlement after annealing. The behavior obtained, see Figure 2, reproduce qualitative well the behavior shown by VVER-440 high P welds.

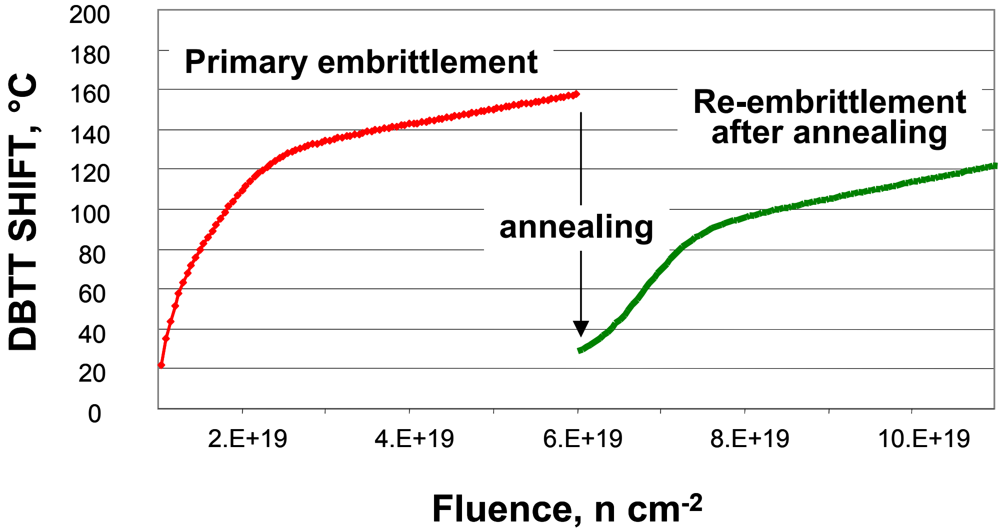

Figure 2 - Example of primary radiation embrittlement and re-embrittlement calculated with proposed model (Eq.1)

Model applied to model alloys data

The proposed model is tested on available data of model alloys. A set of model alloys with parametric variation of Cu, P and Ni content have been irradiated in HFR Petten [1] and tested. The material composition, full description and the obtained results are given in [2 and 3].

A second set of such model alloys have been also irradiated in Kola NPP at higher fluence and recently the data have become available.

In particular the low Nickel sets are analysed in this paper; such sets, even if quantitatively different, demonstrated to be qualitatively a good representation of VVER-440 materials [5]. Both irradiations were done at 270 °C and at very similar fluence rate to minimize rate effects: ~$2X10^{12}$ n cm^{-2}.

The obtained fluence at the HFR and Kola were respectively ~6.9 and ~ 71 10^{18} n cm^{-2}.

The shifts obtained at the HFR ranged from few degrees for very clean alloys to up to more than 250 ºC for alloys with very high combined contents of Cu and P.

The shift obtained in Kola, in spite of the much higher fluence, were just slightly higher than those obtained at HFR.

The proposed semi-mechanistic model has been tested and tuned using the set of data, 22 data sets in total. The data on alloys with low P contents have been analyzed before in order to single out Cu effect and related parameters first; see for example Figure 3.

Subsequently, the additional effect of P has been analyzed considering the alloys containing P at different Cu contents. The segregation parameters have been optimized to fit the data, see Figure 4.

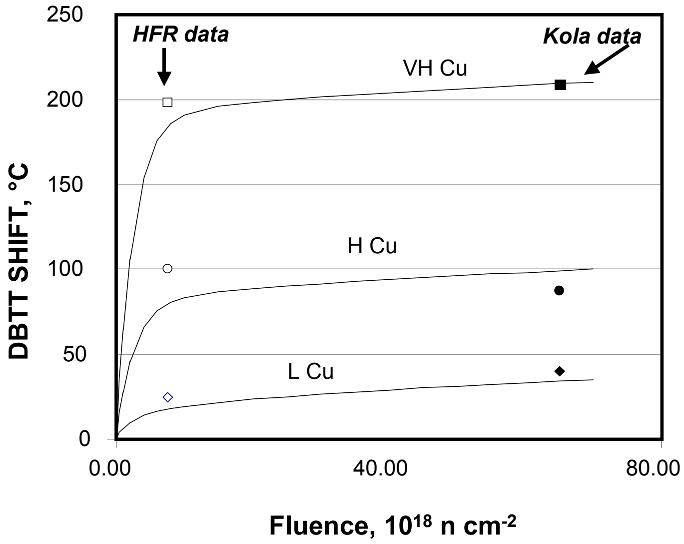

Figure 3 –Model tuning on P free alloys

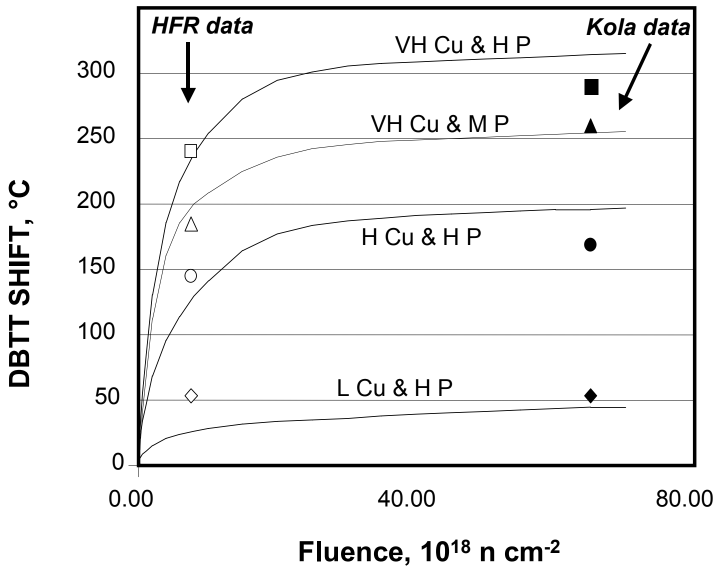

Figure 4 – Model tuning on P rich alloys; additional effect of P

The proposed model can be optimized to fit the complete data set of Ni-free alloys at both fluencies. The model parameters for precipitation and segregation, as expected, are in direct relation with the Cu and P contents respectively. The observed relationship is simply linear reinforcing the confidence of the validity of the proposed model, see Figure

5. The overall capability of the model to predict the behavior of the 11 model alloys at the two fluencies is summarized in Figure 6. The fitting could be further improved by improving regression using weighting factors for a few data points with larger uncertainties that others, but for the scope of this work the results are more than satisfactory and real improvement will be booked by producing new sets of data at lower fluence, below the HFR fluence actual value.

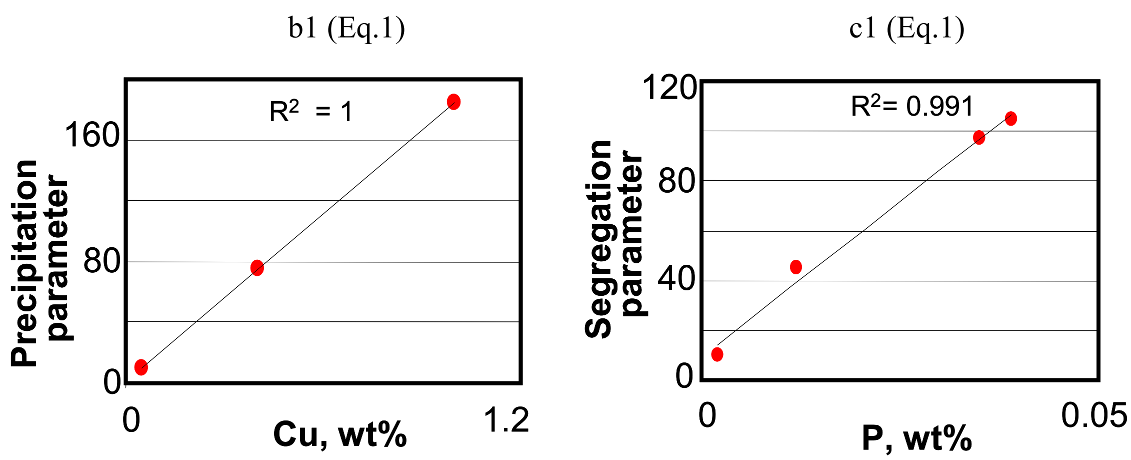

Figure 5 – Model parameters; linearly related to Cu and P contents

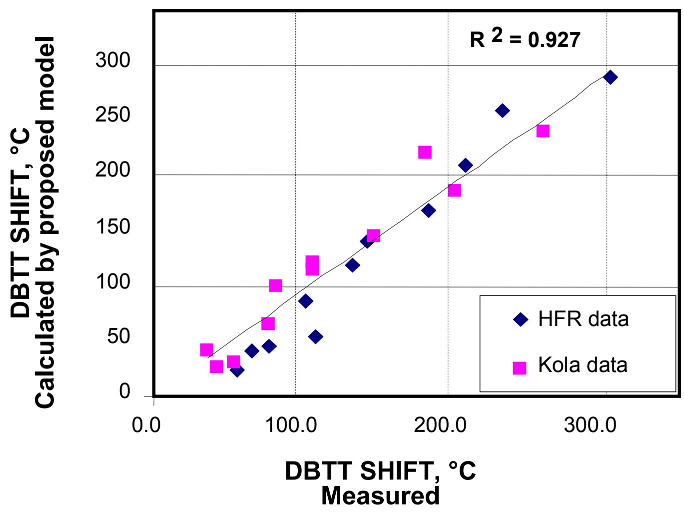

Figure 6 – Model prediction (Eq.1) versus measured DBTT shifts (for all alloys and two fluencies)

Conclusions

The basic mechanisms of radiation embrittlement for primary embrittlement of steels and welds are considered to be: direct matrix damage, precipitation (mainly Cu) and element segregation (mainly P). The effect of the various embrittlement parameters is considered to be additive to the total damage expressed in terms of ΔT_{shift}.

In fact, in addition to direct matrix damage, during the primary embrittlement, Copper, together with other elements, is known to lead precipitation mechanism of nano-precipitates also inducing matrix hardening and embrittlement. Such precipitation mechanism continues until saturation depending on available amount of precipitants, Cu concentration in particular. Subsequently other segregates can be formed both proportionally to the matrix damage and attracted into the Cu precipitates. Diffusion of segregates plays also a role. A simple model to describe generally this additional contribution is proposed based on a 'logistic' shape type of function describing a process of gradual increase then a rapid saturation.

The advantages of the proposed semi-mechanistic model, when compared to non-mechanistic models, is that: it allows improved fitting of data, it is suited in particular for analyzing data sets not really showing a power-type function like it happens in real surveillance data sets, it permits the visualization of the relative contribution of the various damage component and it permits better verification of hypothesis on mechanisms relative importance at the difference embrittlement phases; in particular the behavior of re-embrittlement after annealing; supporting the hypothesis that P is leading re-embrittlement after annealing. Finally it makes possible to understand and predict the behavior difference of the re-embrittlement in comparison with the primary embrittlement; assuming that Cu has marginal effect compared to P.

The proposed model has been tested in this paper on a large set of data on Ni-free model alloys irradiated at the same temperature and at two very different fluencies; the data have been obtained at the HFR Petten (The Netherlands), and in Kola NPP, Russia.

The results show the potential of the proposed model to analyze the behavior and fitting the qualified set of data of Ni-free model alloys. Since such model alloys are qualitatively very similar to VVER-440 materials [6], and the model can explain re-embrittlement differences when compared to primary embrittlement, the proposed model has high potential for application to commercial VVER steels and welds [7-8].

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