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Use of a Semi-Mechanistic Analytical Model to Analyze Radiation Embrittlement of Model Alloys: Cu and P Effects

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Применение полумеханистической аналитической модели для анализа радиационного охрупчивания модельных сплавов. Влияние содержания меди и фосфора

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Выполнен анализ основного механизма радиационного охрупчивания сталей и сварных швов с учетом разрушения матрицы материала, осаждения и выделения химических элементов. Предложена модель разрушения матрицы вследствие нейтронной бомбардировки, что позволяет достаточно точно описать для 11 модельных сплавов процессы первичного и вторичного охрупчивания после плановой термообработки (отпуск). Особенностью модели является возможность объяснения отличий между процессами охрупчивания до и после отпуска сплавов с малым (или нулевым) содержанием никеля, что позоляет использовать ее для анализа поведения материалов, используемых в реакторах ВВЭР, при эксплуатации.

Ключевые слова: радиационное охрупчивание, полумеханистическая аналитическая модель, отпуск.

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, available models for analysis of radiation data are mainly based on statistical correlation of large sets of data. In this paper, a semi-mechanistic model based on key mechanisms is proposed, which 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 and tested [1–4]. A second set of such model alloys has been irradiated in Kola NPP, Russia

The low Ni model alloys results are studied in detail and demonstrate the applicability of the proposed model to commercial steels and welds, in particular, to WWER-440 type materials.

Key Embrittlement Mechanisms. The key embrittlement mechanisms taking place during irradiation of RPV steels and welds are summarized in Table 1 [5].

Table 1

Embrittlement Mechanisms Considered

Embrittlement mechanism	Intrinsic features
Direct matrix damage	Due to neutron bombardment
Matrix precipitation hardening	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 the particular material and temperature. At higher irradiation temperatures the rate of damage is considered to be decreasing due to increased atoms mobility.

During direct matrix damage formation, Cu, among with other elements, is known to lead precipitation mechanism of nano-precipitates also inducing matrix hardening and embrittlement. Such mechanism occurs until saturation depending on available amount of precipitants, Cu concentration in particular.

In addition to matrix damage, other elements, like P, can segregate in grains (and/or through diffusion processes at grain boundaries) or get attracted into the Cu-type precipitates. Diffusion of segregants also takes place making this mechanism rather difficult to understand in detail.

The analytical model based on the above-mentioned key mechanisms is proposed and reviewed below.

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 as follows:

$$\Delta T_{shift(\mathrm{matrix})} = [a\Phi^{n}],$$

where ΔT_{shift} is the transition temperature shift component, Φ is the neutron fluence, a is model fitting parameter, and n is the exponent (normally $n = 1/2$).

The parameter a is constant value for a given material and a given irradiation temperature, which value decreases with incresing irradiation temperature.

The contribution of Cu precipitation to the total transition temperature shift can be described as

$$\Delta T_{shift(\text{Cu precipitation})} = b_1[1 - e^{-\Phi/\Phi_{sat}}],$$

where b_1 is a model fitting parameter, representing the maximum saturation value of the shift due to precipitation, and Φ_{sat} is a model fitting parameter, representing the fluence at which saturation effects begin.

Subsequently other segregants can be formed both proportionally to the matrix damage and attracted into the Cu precipitates. Diffusion of segregants plays also a role. To describe this additional contribution the following simple model is proposed. It is based on a “logistic” shape type of function describing a process of gradual increase followed by a rapid saturation:

$$\Delta T_{shift(\text{P segregation})} = c_1\left[\frac{1}{2} + \frac{1}{2}\tanh\left(\frac{\Phi - \Phi_{start}}{c_2}\right)\right],$$

where c_1 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, and c_2 is a model parameter representing the increase rate of the saturation effect.

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

$$\Delta T_{shift} = a\Phi^n + b_1[1 - e^{-\Phi/\Phi_{sat}}] + c_1\left[\frac{1}{2} + \frac{1}{2}\tanh\left(\frac{\Phi - \Phi_{start}}{c_2}\right)\right]. \qquad (1)$$

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

The relative contribution of the various damage components is also visualized in Fig. 1. In total, a maximum of 6 parameters are required for the proposed model: a, b_1, Φ_{sat}, c_1, c_2, and Φ_{start}.

In order to simplify the fitting, some parameters (Φ_{sat}, Φ_{start}, and c_2) can be derived and fixed in first instance depending on the general behavior of the analyzed data. The most important parameters are: a, b_1, and c_1. Provided the model is correct, parameter b_1 should depend mainly on Cu content, while c_1 mainly on P content.

The proposed model is applicable for analyzing real surveillance data sets, which can not be described by simple power-type functions.

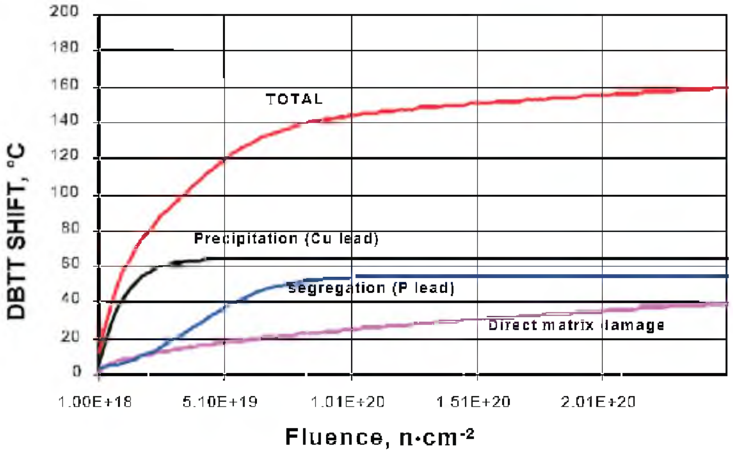


Fig. 1. Example of primary radiation embrittlement calculated with proposed model (Eq. 1).

In particular, the model accounts for the peculiar re-embrittlement behavior after annealing of high P steels, like some WWER-440 high P welds. What is in fact observed in the above steels [4] is that the embrittlement kinetics after annealing is different than before annealing: re-embrittlement starts with a certain delay and then rapidly increases. Such behavior is supported by microstructural investigations indicating that during annealing P does massively re-solute back and is almost fully available for the re-embrittlement, in contrast to Cu, which would thus contribute marginally to re-embrittlement. The hypothesis that P is a leading element of re-embrittlement after annealing is also supported by the available data on WWER-440. In fact, the transition temperature shift is strongly correlated with P content, but not with Cu content.

Application of the proposed model makes it possible to predict the specific re-embrittlement behavior in comparison with the primary embrittlement. In fact, assuming that P is the leading element of re-embrittlement and that Cu has marginal effect, we can simply suppress the Cu term during the re-embrittlement after annealing. The pattern obtained (see Fig. 2) reproduces qualitatively well the behavior shown by WWER-440 high P welds.

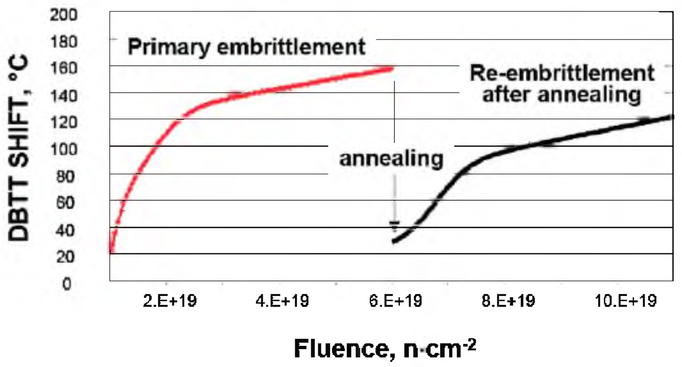


Fig. 2. Example of primary radiation embrittlement and re-embrittlement calculated with proposed model (Eq. 1).

Model Application 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 has been irradiated in HFR Petten and Kola NPP [6].

Both irradiations were executed at 270°C and at very similar fluence rate to minimize rate effects: $\sim 2 \cdot 10^{12}$ $\mathrm{n \cdot cm^{-2}}$. The obtained fluence at the HFR and Kola were respectively $\sim 6.9 \cdot 10^{18}$ and $\sim 71 \cdot 10^{18}$ $\mathrm{n \cdot cm^{-2}}$. The shifts obtained at the HFR ranged from few degrees for very pure alloys to up to more than 250°C for alloys with very high combined contents of Cu and P. The shifts 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 refined using 22 data sets in total. First the data on alloys with low P contents have been analyzed, in order to single out effect of Cu and related parameters; see for example Fig. 3. Subsequently, the additional effect of P have been analyzed for the alloys containing P at different Cu contents. The segregation parameters have been optimized to fit the data (see Fig. 4).

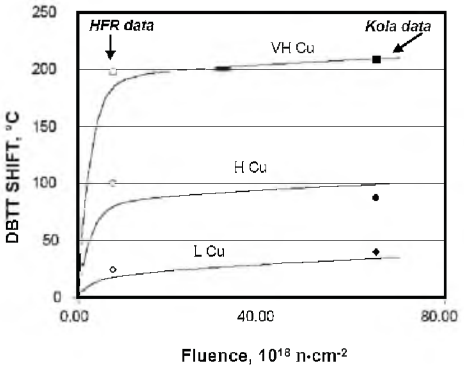


Fig. 3

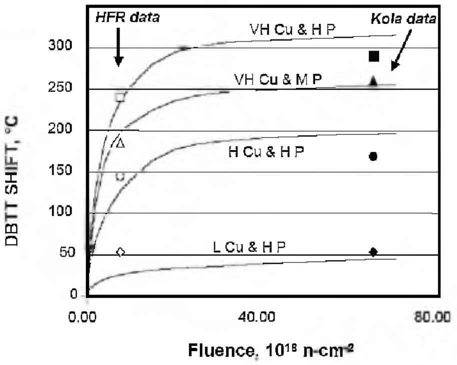
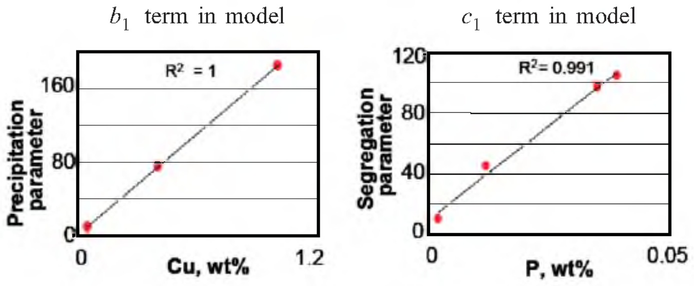


Fig. 4

Fig. 3. Model tuning on P free alloys (VH Cu ~0.9 wt.%; H Cu ~0.4 wt.%; L Cu ~0.05 wt.%).
Fig. 4. Model tuning on P rich alloys; additional effect of P (H P ~0.04 wt.%; M P ~0.01 wt.%).


b_1 term in model

c_1 term in model

Fig. 5. Model parameters linearly related to Cu and P contents.

The proposed model can be optimized to fit the complete data set of Ni-free alloys at both fluences. The model parameters for precipitation and segregation, as expected, are in direct relation with the Cu and P contents, respectively. The

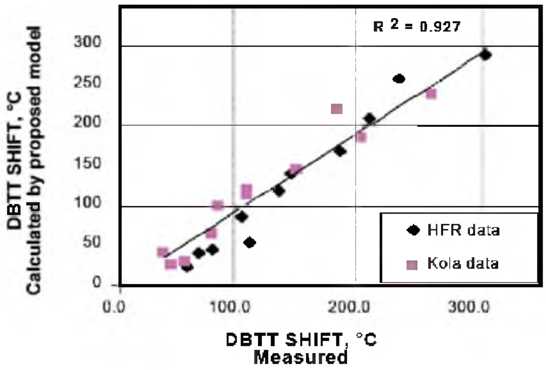


Fig. 6. Model prediction (Eq. 1) versus measured DBTT shifts (for all alloys and two fluences).

observed relationship is simply linear, which confirms validity of the proposed model (see Fig. 5). The overall capability of the model to predict the behavior of the 11 model alloys at the two fluences is summarized in Fig. 6. The fitting could be further improved by using weighting factors for a few data points with lower probabilities than others, but for the scope of this work the results are considered to be satisfactory, and real improvement can be achieved by producing new sets of data at lower fluence, below the HFR fluence actual value [7].

Conclusions. The basic mechanisms of radiation primary embrittlement of steels and welds are 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}.

The proposed model has been tested on a large set of data on Ni-free model alloys irradiated at the same temperature and at two very different fluences obtained at the HFR Petten and Kola NPP.

The model was used to analyze the behavior of Ni-free alloys and fit the qualified data sets qualitatively very similar to WWER-440 materials. The model allowed to describe the re-embrittlement differences when compared to primary embrittlement. It is recommended for application to commercial WWER steels and welds [8–9].

Резюме

Виконано аналіз механізму радіаційного окрихчення сталей та зварних швів з урахуванням руйнування матриці матеріалу, осадження і виділення хімічних елементів. Запропоновано модель руйнування матриці унаслідок нейтронного бомбардування, що дозволяє достатньо точно описати для 11 модельних сплавів процеси первинного і вторинного окрихчення після планової термообробки (відпуск). Особливістю моделі є можливість пояснити відмінності між процесами окрихчення до і після відпуску сплавів із малим (або нульовим) вмістом нікелю, що дозволяє проводити аналіз поведінки матеріалів для реакторів ВВЕР при експлуатації.

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