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## Influence of P and C intergranular segregation during manufacturing and ageing on the fracture toughness of nuclear pressure vessel steels

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### Abstract

Mechanical tests on Charpy and CT specimens of a low alloy MnNiMo steel under two conditions, as received and thermally aged, revealed a shift of the ductile to brittle transition temperature. In this paper, an approach based on the combination of local fracture mechanics and segregation kinetics is proposed in order to describe this shift.

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**Keywords:** Low alloy steels; thermal ageing; fracture; DBTT shift; intergranular; Phosphorus

### 1. Introduction

Heavy components of Pressurised Water Reactor (PWR) are made of low alloy MnNiMo steels. Once these components are welded together a Post Weld Heat Treatment (PWHT) is applied both to relax residual stresses introduced by the welding operations and to temper the fresh martensite or bainite microstructures located in the heat affected zone (HAZ). This PWHT heat treatment is basically composed of a holding time at around 615°C during few hours followed by a slow cooling rate ( $\leq 50^\circ\text{C/h}$ ). These low alloy steels were selected because they demonstrated an excellent compromise between strength, toughness and weldability. Nevertheless they also exhibit a relative sensitivity to thermal ageing, that corresponds to a shift of the ductile to brittle transition temperature after long term exposure at high temperature. This phenomenon is known as 'reversible temper embrittlement' and is tightly linked to the local material chemical composition and in particular to the content in residual impurities such as phosphorus.

Before 1993, most of the shells used to fabricate pressurisers and steam generators were manufactured using rolled and welded plates. This manufacturing process generates characteristic microstructures composed of thin strips of microsegregated material, MSZ, surrounded by base material, BM (i.e having a chemical composition close to that of the selected steel). These micro-segregated strips, revealed by nital etching, exhibit an increase of microhardness

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and a local enrichment in alloying elements and residual impurities such as phosphorus ( $\sim 50\%$ ) compared to the base metal. Measurements performed with a Castaing microprobe are presented in figure 1. Because of the local heterogeneous chemical composition, it is thus suspected that BM and MSZ microstructures will not have the same sensitivity to thermal ageing.

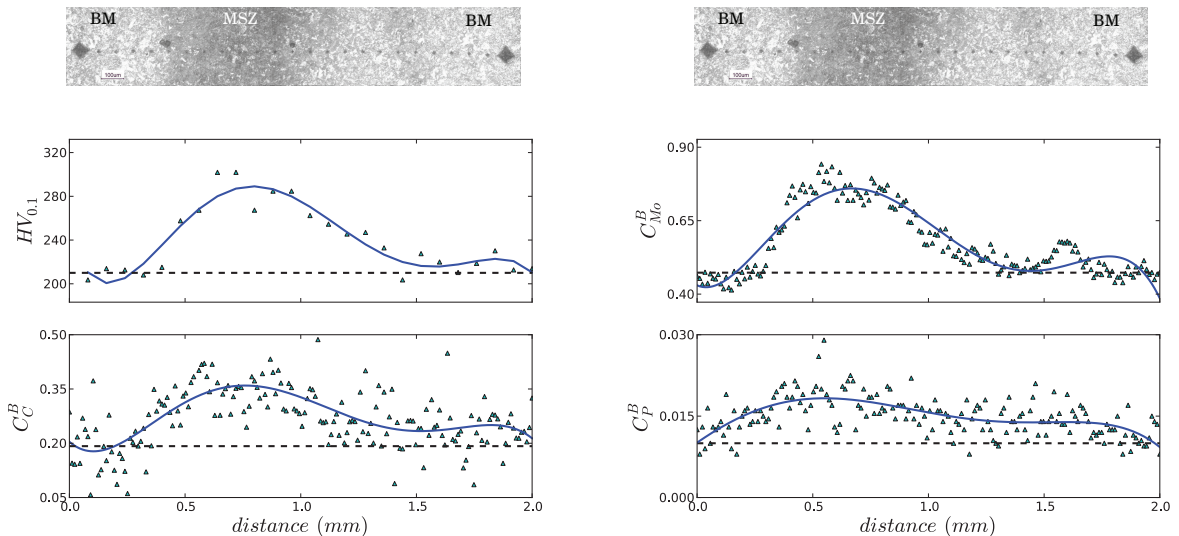


Fig. 1. Measurement of the bulk content in C,P and Mo while crossing a micro-segregated zone (MSZ) and microhardness measurements.

Analysis of fracture surfaces of specimens broken at low temperature, figure 2(a), revealed a bimodal brittle failure: brittle cleavage in BM and brittle intergranular fracture in MSZ after the PWHT heat treatment. This bimodal fracture was also observed after ageing at  $450^{\circ}\text{C}$ . Auger spectrometer analysis, figure 2(b), revealed the presence of P and C on intergranular surfaces. These observations raise two questions:

- What is the role of the PWHT heat treatment on the appearance of intergranular fracture in the non-aged state?
- How to predict the fracture toughness of an heterogeneous material?

Within the frame of the lifetime extension of PWR, problems linked to ageing became of major interest. A number of approaches have been developed to predict the effect of thermal ageing on the DBTT shift. One of these approaches is presented in the first part of this paper. It is shown that this first order model is too conservative and more detailed models are needed to describe the phenomenon. In particular, as the brittle fracture is bimodal (cleavage/intergranular), the modelling of the effect of thermal ageing on the fracture properties relies on the modelling of its impact on the critical cleavage and intergranular stresses. This more sophisticated approach is described in the two following parts.

## 2. Calculating intergranular segregation and DBTT shift - State of the art

The segregation of phosphorus at prior austenitic grain boundaries is mainly responsible of the embrittlement of low alloy steels. In order to describe the DBTT shift induced by thermal ageing and to provide a simple model, Druce et al. (1986) developed an approach based on a single parameter:  $C_{gb}^P$ , the concentration of phosphorus at grain boundaries. To evaluate this parameter, these authors used the segregation theory proposed by McLean (1957) which is based on the thermodynamic of ideal binary  $\{\text{Fe}+\text{X}\}$  systems where X represents an impurity present in the steel.

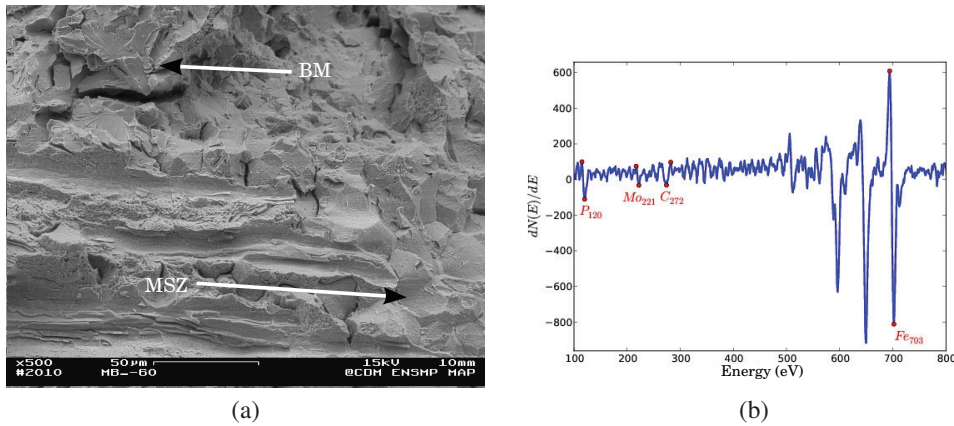


Fig. 2. (a) Representative fracture surface of a CT specimen tested at  $-60^{\circ}\text{C}$  exhibiting intergranular fracture in microsegregated zones (MSZ) and cleavage in base metal (BM). (b) Derivative Auger spectra indicating the presence of C and P on intergranular surfaces.

According to McLean theory,  $C_{gb}^P$ , depends on: the concentration of phosphorus in the bulk,  $C_1$ , the time,  $t$ , and the temperature of ageing,  $T$ . The kinetic of enrichment of grain boundaries in phosphorus is then given by:

$$C_{gb}^P(t) = C_{gb}^P(t \rightarrow \infty) - C_1(\alpha_2 - \alpha_1) \exp\left(\frac{4Dt}{\alpha_2^2 d^2}\right) \operatorname{erfc}\left(\frac{2\sqrt{Dt}}{\alpha_2 d}\right) \quad (1)$$

with  $C_{gb}^P(t \rightarrow \infty)$  given by the Langmuir-McLean equilibrium model:

$$C_{gb}^P(t \rightarrow \infty) = \frac{C_1 \exp\left(\frac{\Delta G^0}{RT}\right)}{1 + C_1 \exp\left(\frac{\Delta G^0}{RT}\right)} \quad (2)$$

The free energy of segregation,  $\Delta G^0$ , and the diffusion coefficient,  $D$ , were determined from measurements of P segregated at grain boundaries by Druce et al. (1986). In eqs 1,2  $R$  is the gaz constant,  $d$  the thickness associated to the grain boundaries arbitrarily chosen equal to  $3 \cdot 10^{-8} \text{cm}$  by McLean,  $\alpha_1$  is the ratio between the initial concentration in P at grain boundaries (i.e prior to ageing), divided by the P bulk content and  $\alpha_2$  is the ratio between the concentration of P at grain boundaries at any time during the ageing treatment divided by the concentration of P in the bulk.

After having performed many ageing heat treatments on a simulated HAZ made of A533B steel, Druce et al. (1986) proposed to relate the concentration in phosphorus at grain boundaries to the shift of the DBTT curve thanks to the following expression:

$$\Delta T K_{80J} = 1300 \times (C_{gb} - 0.065) \quad (3)$$

that was revised later by Druce et al. (1988) after measurements on real HAZ made of A533B:

$$\Delta T K_{80J} = 1080 \times (C_{gb} - 0.065) \quad (4)$$

The number 0.065 that appears in both equations is supposed to represent the initial concentration in P at grain boundaries. It has been determined by Druce et al. (1986, 1988) after Auger spectrometer measurements on a coarse grain HAZ of A533B steel. Joly et al (2013) showed that the application of these relations to the AREVA internal ageing program, composed of HAZ and BM of 18MND5 (French equivalent to A533B) and to the welded metal lead to a large overestimation of the embrittlement compared to that measured experimentally. See results on figure 3 where the observed DBTT shift corresponding to 68 Joules is compared to the shift at 80J predicted from eqs 3, 4. This overestimation can be attributed to the fact that another element has to be considered when calculating the kinetic of segregation. Indeed, as mentioned in the introduction, Auger measurements performed on the material used in this study (18MND5) revealed the presence of C at grain boundary. Guttmann et al. (1982), Erhart and Grabke (1981) showed that C can modify the kinetics of the segregation of P at grain boundaries because it segregates on the same sites. Moreover, following the classification established by Hondros and Seah (1977), carbon and phosphorus have an antagonistic effect: phosphorus decreases the cohesion of grain boundaries while carbon reinforces them.

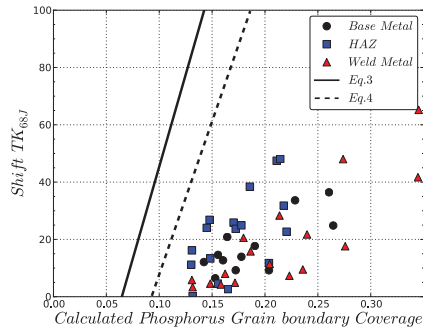


Fig. 3. Prediction of DBTT shift of a 18MND5 steel using Druce et al. (1986) and Druce et al. (1988). Figure from Joly et al (2013)

### 3. Enriched theory of intergranular segregation

Nakata et al. (2006) studied the ageing of a A533B steel and highlighted the competition between P and C. To describe the kinetics of segregation in the ternary system {Fe,C,P} the theory developed by Guttman et al. (1982) was applied. In that theory, the {Fe,C,P} system is no longer ideal and the free energy of segregation of P and C can be written as:

$$\begin{aligned}\Delta G_C &= \Delta G_C^0 - 2\alpha_{CC}C_C^{gb} + \alpha_{CP}C_P^{gb} \\ \Delta G_P &= \Delta G_P^0 - 2\alpha_{PP}C_P^{gb} + \alpha_{CP}C_C^{gb}\end{aligned}\quad (5)$$

where the coefficients  $\alpha_{i,j}$  express the modification of the free energy created by the interaction existing between the element  $i$  and the element  $j$  at the grain boundary. This interaction can be either attractive (leading to an increase of the segregation kinetics) or repulsive (leading to a slow down of the segregation kinetics). The calibration of these interaction coefficients was performed thanks to Erhart and Grabke (1981) work while the calibration of the ideal free energy was performed using Nakata et al. (2006) work. Militzer and Wieting (1986) demonstrated that, in the case of ternary systems with site competition, the kinetics of segregation is given by:

$$\begin{aligned}C_i^{gb}(t) &= C_i^{gb,0} + 2\frac{C_i^{B,0}}{\sqrt{\pi}\delta/2} \sqrt{\int_0^t D_i(t')dt'} - \frac{1}{\sqrt{\pi}\delta/2} \int_0^t \frac{q_i(t')D_i(t')}{\sqrt{\int_0^{t'} D_i(t'')dt''}} dt' \\ D_i(t) &= D_i^0 \exp(-Q_i/RT(t)) \\ q_i(t) &= \frac{C_i^B \exp(-\Delta G_i(t)/RT(t))}{1 + \sum_{j \in I} C_j^B \exp(-\Delta G_j(t)/RT(t))}\end{aligned}\quad (6)$$

These equations can be used under non isothermal conditions. It is observed that before ageing C and P are already segregated on the grain boundaries. This results from the slow cooling rate from 615°C. In our material, it is found that with P=150ppm (representative of MSZ content) the initial P concentration on the grain boundaries is ~13%. Naudin et al. (1999) showed that this concentration is sufficient to initiate intergranular fracture.

Applications of this model to Nakata et al. (2006) and Andrieu (2013) results are presented in figure 4. In figure 4(b), the black dotted line describes the kinetics of segregation that is calculated using McLean model, that is to say without taking into account the competition between C and P at segregation sites. It highlights the fact that considering 18MND5 steel or A533B steel as a binary system leads to an overestimation of the concentration of P at grain boundaries. The competition between P and C atoms is clearly observed. According to the thermodynamical model proposed by Rice and Wang (1988), this modification of the chemical composition leads to a decrease of the grain boundary cohesion and thus to a decrease of the intergranular fracture stress.

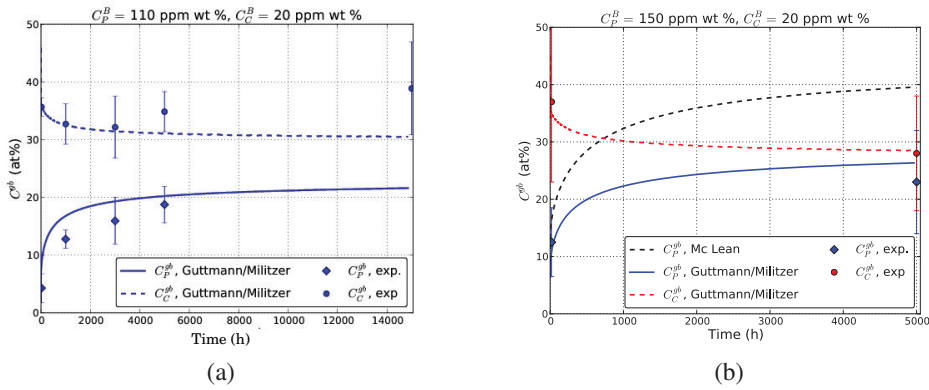


Fig. 4. Application of the Guttman-Militzer segregation model to: (a) Results obtained by Nakata et al. (2006) on a A533B steel containing 110ppm of phosphorus and aged at 450°C a ageing temperature, (b) Results obtained by Andrieu (2013) on a 18MND5 steel containing 90ppm of phosphorus and aged at 450°C.

#### 4. Physically based prediction of DBTT shift

The prediction of the shift in DBTT measured on Charpy impact specimens requires heavy numerical calculations (see e.g. Tanguy et al. (2005)). This is one of the reason why in this study the shift was measured and modelled using fracture toughness CT type specimens (B=20mm). Results are shown in figures 5(a) and (b) where it is noticed that the measured shift at  $K_J = 100MPa \sqrt{m}$  due to ageing (450°C-5000h) is of the order of 40°C which is a value similar to those reported by Joly et al (2013).

As mentionned previously, the material of the present study exhibits a bimodal brittle failure, even before ageing: BM fails by brittle cleavage while MSZ breaks in a brittle intergranular mode. To model the ductile to brittle transition, we decide to use the Beremin model Beremin (1983). This model is based on the weakest link theory and predict the evolution of the probability to fracture with temperature. Andrieu et al. (2012) have shown that for this type of microstructures, exhibiting bimodal brittle fracture, the probability to fracture,  $P_r$ , is given by the relation:

$$P_r = \sum_{i=0}^{B/e} P_i P_r(i) \tag{7}$$

where  $B$  is the thickness of the CT specimen,  $e$ , a distance (for example 50µm),  $P_i$ , the probability that  $i \times e$  mm of MSZ intercept the crack front and  $P_r(i)$  the probability to fracture, given by:

$$P_r(i) = 1 - \exp \left( - \frac{(B - ie)K^4 (\sigma_0^{BM})^{m_{BM}-4} C_{m_{BM}}}{V_0 (\sigma_u^{BM})^{m_{BM}}} - \frac{ie(E_{MSZ}\sigma_0^{MSZ}/E_{BM}\sigma_0^{BM})^2 K^4 (\sigma_0^{MSZ})^{m_{MSZ}-4} C_{m_{MSZ}}}{V_0 (\sigma_u^{MSZ})^{m_{MSZ}}} \right) \tag{8}$$

In this last equation,  $\sigma_0$  denotes the yield stress,  $E$  the Young modulus,  $m$  the Weibull exponent,  $V_0$  an elementary volume and  $\sigma_u$  the Weibull stress that can be related to the critical stress while exponent  $^{BM}$  and  $^{MSZ}$  denote base material or micro-segregated zones. The distribution of MSZ has been determined by image analysis. The initial Weibull parameters have been calibrated in order to describe the results obtained before ageing. Results presented in figure 5(a) show a good description of the measurements in the initial state. Plots obtained for the aged state (450°C-5000h) has been determined only by modifying the Weibull stresses. Naudin et al. (1999) showed that an increase of the concentration of phosphorus of about 11% decreased the intergranular critical stress of by ~ 15%, while the increase of phosphorus has a slight impact on the critical cleavage stress (~ 2.5%). The results are shown in figure 5 where it is observed that the model accounts not only for the shift in the DBTT but also on the increase in scatter observed in the aged condition compared to the initial condition. It is also worth noting that the predicted shift is of the order of 40°C at  $K_J = 100MPa \sqrt{m}$  for large value of  $P_r \sim 95\%$ . This is due to the relative importance of cleavage and intergranular failures modes with the probability to fracture.

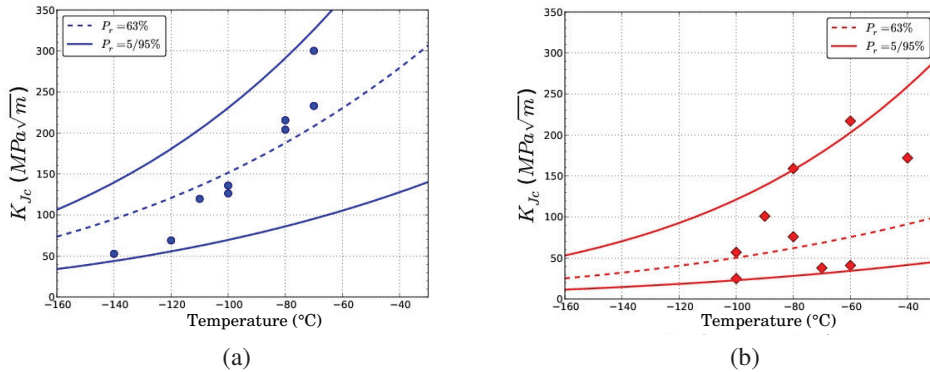


Fig. 5. Prediction of scattering of fracture toughness measurements and of the DBTT shift induced by ageing. Experimental results (a) After PWHT  $\sigma_u^{BM} = 3364$  MPa√m,  $\sigma_u^{MSZ} = 3200$  MPa√m, (b) After PWHT and 5000h-450°C  $\sigma_u^{BM} = 3318$  MPa√m,  $\sigma_u^{MSZ} = 2720$  MPa√m

## 5. Conclusions

It is shown that in a MnNiMo steel used in the fabrication of heavy components and containing micro-segregated zones enriched in impurities (P,C,Mo . . .) the slow cooling rate applied after stress relieving heat treatment generate a mixed mode of failure (cleavage + intergranular) when the material is tested at low temperature. It is possible to calculate the amount of impurities (P,C) segregated along the grain boundaries during the cooling operations followed by thermal ageing at 450°C-5000h, using a model in which repulsive interaction between C and P is taken into account. The shift of DBTT observed after ageing at 450°C can be predicted using a statistical bimodal Beremin theory.

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