On Modeling of Thermal Embrittlement in PWR Steels using the Local Approach to Fracture

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Abstract Experiments on Charpy and CT specimens were carried out on one heat of A533B steel under two conditions: (i) as received, and (ii) thermally aged (450°C – 5000h). A shift of the ductile to brittle transition temperature (DBTT) was measured after aging. In both cases SEM observations showed that fracture occurred both by intergranular and transgranular cleavage fracture modes when the materials were tested at sufficiently low temperature. Detailed examinations revealed that intergranular fracture was associated with micro-segregated zones, enriched in carbon and phosphorus. A recent model developed by the authors for predicting the fracture toughness of inhomogeneous materials was applied to describe the large scatter related to the bimodal failure modes observed in both conditions and the DBTT shift after aging. It is shown that thermal aging produces a slight decrease of the critical cleavage stress (due to the crossing of grain boundaries embrittled by phosphorus segregation) and a larger decrease of the critical intergranular fracture stress. The McLean-Guttmann- Militzer model is used to predict the kinetics of segregation during aging. An attempt is made to show how these results can be used to model DBBT variations under in-service conditions.

Keywords Ductile to brittle transition, intergranular, phosphorus segregation

1. Introduction

It is often noticed the presence of segregated zones (S.Z) in large components used for the fabrication of pressurized water reactors (PWR) (see e.g. [1, 2]. These SZs are linked to the solidification process of large ingots. They are enriched in the alloying elements (Mn, Ni, Mo, C, etc.) present in the steel. They are also enriched in impurities, such as P which may segregate at grain boundaries during aging. These local microstructural modifications can generate a bimodal fracture process (cleavage and intergranular fracture), as shown elsewhere [2].

Brittle (cleavage and intergranular) fracture in homogeneous ferritic (or bainitic) steels has been investigated by many authors, for a review see e.g. [3]. The seminal work by Beremin [4] has shown that in a homogeneous material the fracture toughness, K_{IC} obeys a size effect given by $K_{IC}^4 B =$ constant, where B is the thickness of the specimen, while the scatter in test results can be described by a Weibull law. The probability of failure can be expressed as:

$$P_r = 1 - \exp\left[-\frac{K_{IC}^4 B \sigma_o^{m-4} C_{m,n}}{V_o \sigma_u^m} \right] \quad (1)$$

Where σ_o is the yield strength of the material, m is the Weibull shape factor, $C_{m,n}$ is a parameter depending both on material work-hardening exponent, n, and the Weibull shape factor, m (see [5] for detailed values of C_{mn}.) V_o is a representative volume and σ_u is the Weibull scale factor. Recently it has been shown how Eq.1 must be modified in the presence of inhomogeneities leading to local intergranular fracture [2].

The main aim of the present study is the application of these recent modifications of the original

Beremin model to predict the variation of fracture toughness with temperature. One heat of 18 MND5 grade steel (type A533B) was used for this purpose. The material (a 100mm thick hot-rolled plate) was tested in the as-received condition and after aging at 450°C for 5000 hours. This aging heat treatment was introduced to reinforce the segregation of phosphorus at grain boundaries and to decrease the grain boundary fracture resistance. The McLean [6]–Guttmann [7] theories for impurity intergranular segregation was used to calculate the grain boundary enrichment in phosphorus and in carbon under isothermal conditions. These theoretical values were compared to experimental values determined by Auger spectrometry. The interaction between C and P atoms was adjusted from this comparison. Therefore the approach developed in the present study contributes to an improvement in the prediction of the shift in DBTT with thermal aging.

2. Material and experimental procedures

The composition of the investigated steel is (in weight %): C = 0.192, Mn = 1.44, Ni = 0.683, Mo = 0.473, Cr = 0.194, Si = 0.249, S = 0.0053, P = 0.010. It was received as a thick plate (100 mm) produced for simulating welding operations. This material was used in the past for the manufacturing of steam generator secondary pressure vessel, and is very close to plates used in the past for pressurizer vessels. The material was given the conventional heat-treatments applied to PWR components, including the final stress-relieving heat-treatment (615°C-Air cooling at ~ 30°C /hour). The prior austenite grain size was between 20 and 30 μm. The yield strength determined at RT was 490 MPa.

The microstructure of the material is shown in Fig.1. Segregated zones (SZ) aligned along the rolling direction (L) and distant of about 0.2 mm in the short-transverse (ST) directions are observed in Fig.1a. This is the consequence of micro-segregations of alloying elements during solidification, deformed by the rolling process. The dark zones are much harder than the matrix (~ 300 HV instead of ~ 210 HV) (Fig.1b). They are enriched in all alloying elements (C, Mn, Mo, Si) and in P as revealed by microprobe analysis (Fig.1b). The surface fraction covered by these segregated zones is about 10%. SEM and Auger spectrometry were used to examine the fracture surfaces and to determine the amount of phosphorus segregated along the grain boundaries.

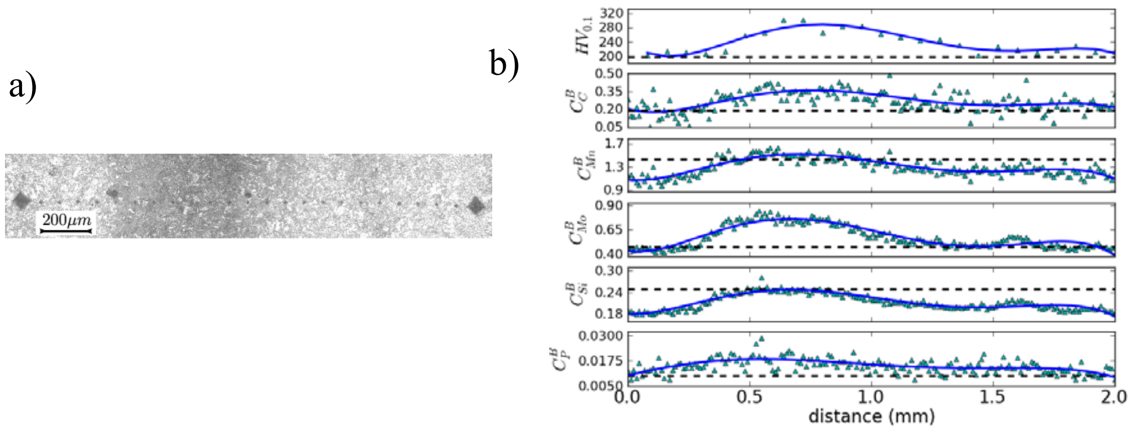

Figure 1. a) Optical micrograph showing two segregated zones aligned along the rolling direction; b) Microprobe analysis across one segregated zone showing the bulk concentration C^B in carbon, manganese, molybdenum, silicon and phosphorus. The variations of micro-hardness (100g) are also shown.

3. Results – Mechanical tests and fractography

The results obtained on Charpy specimens and on CT specimens, tested along the T (transverse) – L orientation are reported in Fig. 2. A shift of the ductile to brittle transition temperature (DBTT) measured at 41J appears in Fig. 2a when comparing the as-received and the aged conditions. This shift is of about 39°C. Similarly the fracture toughness determined on CT_{20} specimens is lowered by aging (Fig. 2b and c). In these figures we have also reported the probabilities to fracture for 5%, 63% and 95% determined from the master curve (MC) analysis [8, 9]. The temperature T_o at which K_{JC} = 100MPa m$^{1/2}$ is shifted from – 124°C in the as-received condition to – 91°C in the aged condition. The scatter in the aged material is much wider than in the as-received material. In particular it is noticed that the MC analysis is unable to describe this large scatter.

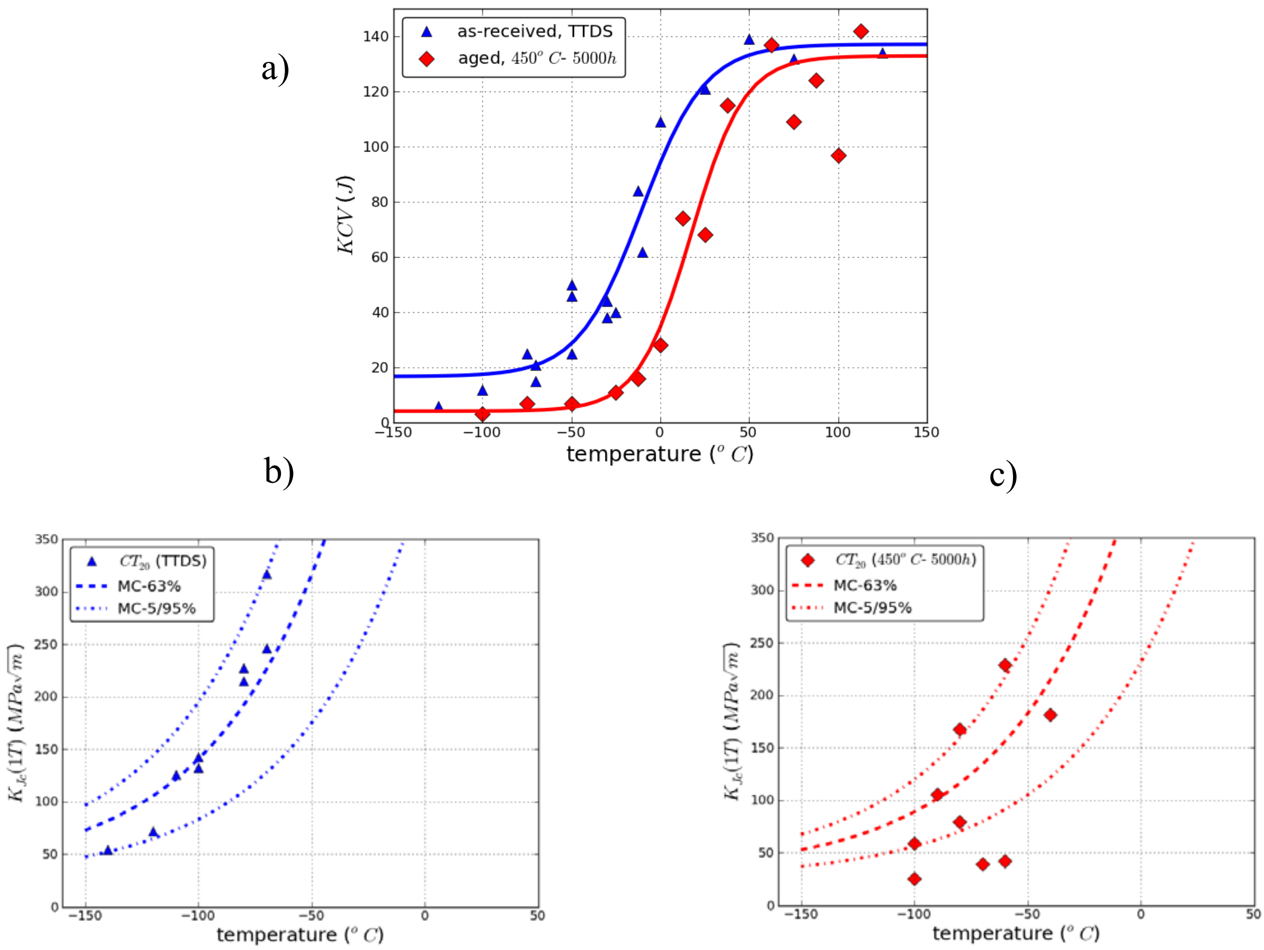

Figure 2. a) Charpy tests in as-received and aged (450°C – 5000 h) conditions; b) Fracture toughness, K_{JC} (thickness) determined on CT 20 mm thick specimens as a function of temperature in the as-received material; c) Fracture toughness K_{JC} on CT20 mm thick specimens in the aged (450°C – 5000 h) condition. The probabilities P_r = 5%, 63%, 95% determined from the Master Curve (MC) are also drawn.

Fracture surface examination of Charpy and CT specimens tested at relatively low temperature showed the presence of elongated zones aligned along the L direction (Fig. 3a) in which the fracture mode was intergranular (Fig. 3c). This local intergranular fracture mode was observed in both conditions. These zones correspond to the SZ evidenced in Fig. 1a. They contained very often MnS inclusions (Fig. 3b) and were surrounded by cleavage facets as observed in Fig. 3b. This observation is thus similar to previous examinations on a segregated PWR material (see Fig. 1 in [2]). The ratio of intergranular/transgranular cleavage fracture was similar in both conditions.

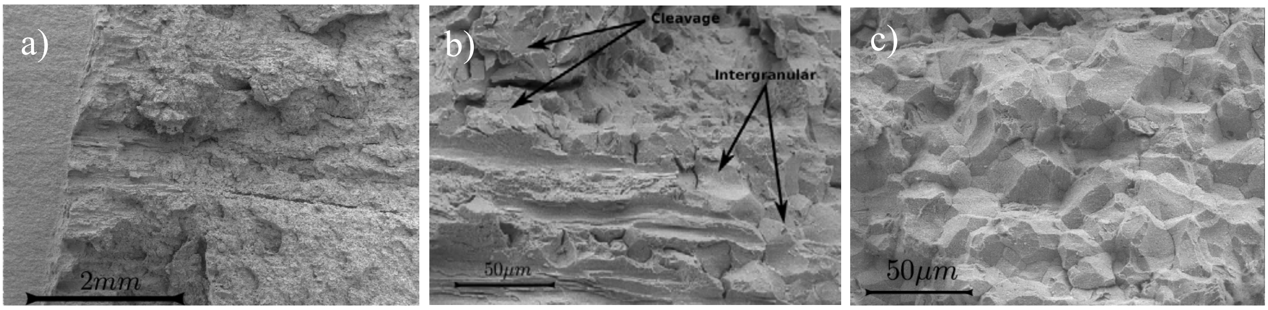

Figure 3. SEM observations: a) and b) As received material; c) Aged (450°C – 5000 h) condition.

4. Intergranular segregation – Results and theoretical considerations

Auger spectrometry measurements showed that the phosphorus concentration (atomic %) at grain boundaries increased significantly between the as-received condition $\left(C_p^{gb} = 12.5 \pm 6\%\right)$ and the aged condition $\left(C_p^{gb} = 23 \pm 9\%\right)$. The grain boundary concentration in carbon tended to decrease with aging ($C_c^{gb} = 37 \pm 14\%$ in the as-received condition compared to $C_c^{gb} = 28 \pm 10\%$ in the aged condition). Full details about these measurements can be found elsewhere [10]. Intergranular P phosphorus segregation was shown to occur during cooling after the stress-relieving heat treatment. The relatively low cooling rate (~ 30°C/h below 615°C) thus produces temper-embrittlement effect in the segregated zones enriched in phosphorus.

The theory of isothermal intergranular segregation has been developed by McLean [6] in his pioneering work. This theory was extended by Guttmann [7] to account for the interaction of an impurity element (here P) with other elements, in particular carbon atoms. A comprehensive review of these theories can found in the recent book of Lejcek [11]. The grain boundary concentration at equilibrium, $C^{gb,eq}$ in a system containing N elements in solid solution C^B can be written as:

$$\frac{C_i^{gb,eq}}{1-\Sigma_{j=o}^{N} C_j^{gb,eq}} = \frac{C_i^B}{1-\Sigma_{j=o}^{N} C_j^B} \exp\left[-\frac{\Delta G^{seg}}{\mathrm{R}T}\right] \tag{1}$$

The segregation energy ΔG_i^{seg} is expressed as:

$$\Delta G^{seg} = \Delta G_i^o + \Delta G_i^E = \Delta H_i^o - T\Delta S_i^o + \Delta G_i^E \tag{2}$$

where ΔG_i^E represents the deviation from an ideal system due to the presence of elements other than the impurity, i.

In a binary system, such as Fe-C or Fe-P, the kinetics of segregation $C^{gb}(t)$ is given by [6]:

$$C^{gb}(t) = C^{gb,eq}(T_2) - C_o(\alpha_2 - \alpha_1)\exp\left[\frac{4Dt}{\alpha_2^2\delta^2}\right] erfc\left[\frac{2\sqrt{Dt}}{\alpha_2\delta}\right] \quad (3)$$

where $C^{gb,eq}$ is the concentration at equilibrium of the impurity, at temperature T_2, given by Eq. 1, $Co = C^B$ (t = 0) is the impurity concentration in the matrix which is assumed to be constant, $\alpha_1 = C^{gb,eq}(T_1) / C_o$ with T_1 the temperature from which the material is cooled down, $\alpha_2 = C^{gb,eq}(T_2) / C_o$, D the coefficient of diffusion of the impurity at T_2, t the time and δ, the thickness of the grain boundary.

In a ternary system, Guttmann [7] assumed that ΔG_i^{seg} can be expressed as:

$$\Delta G_i^{seg} = \Delta G_i^o - 2\alpha_{ii} C_i^{gb} + \alpha_{ij} C_j^{gb} \quad (4)$$

where the coefficients α_{ii} and α_{ij} describe the interaction between the elements segregating at grain boundaries (α_{ii} > O or α_{ij} < O correspond to a repulsive interaction which is the situation met with C and P).

The solution for the kinetics of segregation for non-isothermal conditions can be derived from Militzer's work [12].

All terms in Eqs. 1-4 have been determined in the literature:
$d = 8 10^{-10}$ m

$$D_p = 0.25\exp\left(-\frac{200\,000}{\mathrm{R}T}\right) \ (\mathrm{cm^2 s^{-1}}) \quad [13, 14] \quad (5)$$

$$D_C = 0.003\exp\left(\frac{76000}{\mathrm{R}T}\right) \ (cm^2 s^{-1}) \quad [15] \quad (6)$$

$$\Delta G_p^o = 64273 - 23.7T\,(\mathrm{J\,mol^{-1}}) \quad [13] \quad (7)$$

$$\Delta G_c^o = 16752 + 40.9T\,(\mathrm{J\,mol^{-1}}) \quad [13] \quad (8)$$

$$\alpha_{cc} = 4000\,\mathrm{J\,mole^{-1}}; \quad \alpha_{pp} = 1500\,\mathrm{J\,mole^{-1}}; \quad \alpha_{cp} = -4500\,\mathrm{J\,mole^{-1}} \quad [10, 16] \quad (9)$$

The McLean-Guttmann-Militzer model has been applied to our steel with T_1= 888 K, C_C^B = 80 ppm (Wt %) and C_P^B = 150 ppm (Wt %) for predicting the C and P grain boundary concentration in the as-received condition (t = 0) and during aging at 450°C. Full details can be found elsewhere [10]. The results are compared to experimental measurements in Fig. 4 where it is observed that in the as-received condition (t = 0), phosphorus and carbon atoms are already segregated. Carbon atoms desegregate during aging while phosphorus concentration is increasing. This results from the repulsive interaction between C and P atoms (Eq. 9). The calculated values are in good agreement with the experimental values.

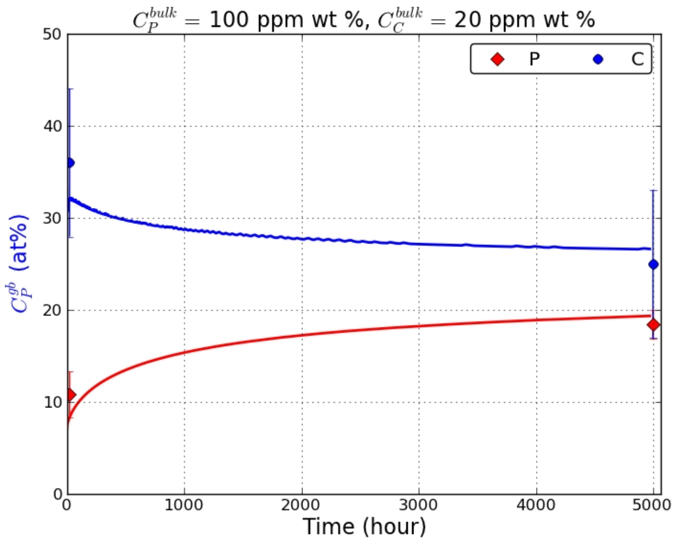

Figure 4. Phosphorus (P) and carbon (C) concentration at grain boundaries (expressed in atomic %) a function of aging time at 450°C. Experimental results and calculated curves.

5. Prediction of fracture toughness – Influence of impurity segregation

It has been shown that the fracture mode of our material in the DBTT regime was bimodal: transgranular cleavage and intergranular. A recent model has been proposed for this situation [2]. However this model includes a number of parameters (Weibull shape factors, critical cleavage and intergranular fracture stress, σ_u) which have to be discussed first. This is related to the fact that aging produces a variation in the concentration of impurities (C and P) segregated along the grain boundaries. It is well to remember that C atoms produce a strengthening effect of the grain boundaries while P atoms have an opposite effect [17].

It has been shown previously that the intergranular fracture stress decreases linearly with C_p^{gb} [18, 19] as soon as the grain boundary concentration in P is larger than about 10 at %. These results can be used to predict the variation of the fracture toughness with aging using the kinetics models developed in the preceding section.

The cleavage fracture stress is also dependent on the grain boundary composition as explained below. This effect is related to the crossing of grain boundaries by cleavage cracks, which has already been studied in some detail by Qiao [20, 21]. This crossing depends on the misorientation between two adjacent grains, as depictured in Fig. 5 where the tilt, ϕ, and the twist, ψ, components between two grains are defined. The tilt component produces only a deviation of the crack front. The twist component produces a segmentation of the crack front and the formation of ridges, as observed in Fig. 6a and as schematically depictured in Fig. 6b. Complete crossing of the grain boundary by the cleavage crack in grain 1 necessitates in these conditions that the intergranular “triangles” are also broken. The = global? cleavage stress is thus also dependent on the local composition of the grain boundaries.

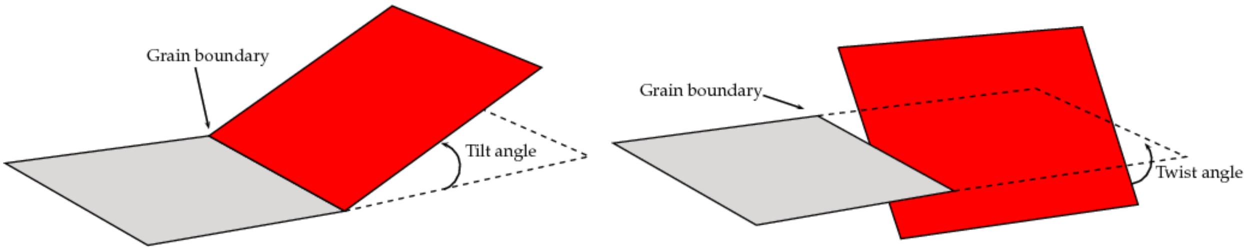

Figure 5. Notations for tilt and twist grain boundaries.

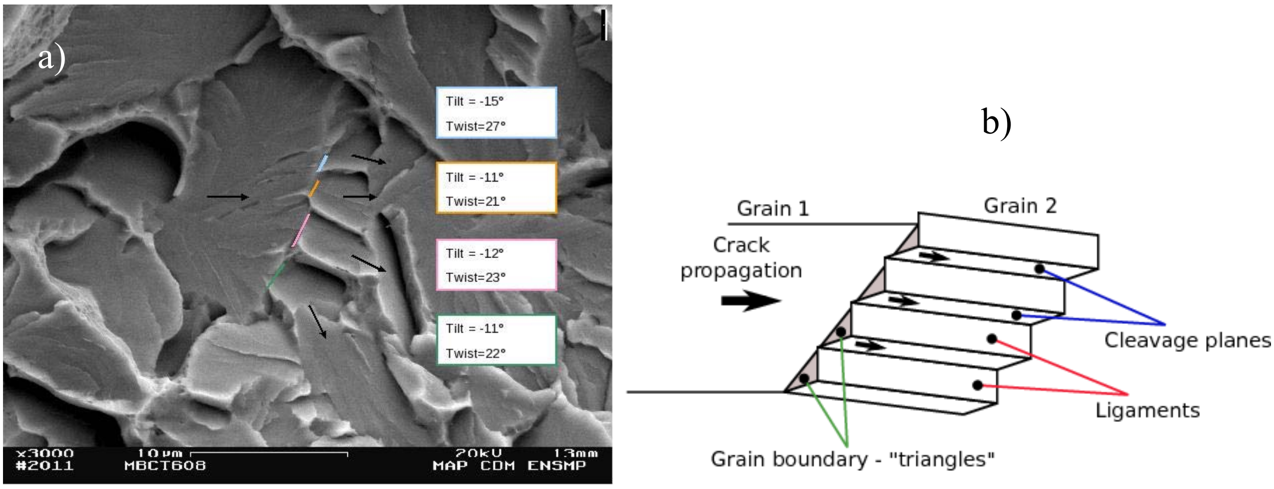

Figure 6. a) SEM observations showing the formation of bifurcations when a cleavage crack crosses a grain boundary. Four ridges are formed. The values of the tilt and twist angles determined by quantitative stereoscopy are given; b) Sketch.

A model was developed to analyze this phenomenon of crossing of twisted grain boundary cleavage cracks. It is out of the scope of the present paper to describe in detail this model which is schematically shown in Fig. 7. The grain boundary crossing process includes four steps. The cleavage crack in grain 1 is approaching the grain boundary in step 1. Cleavage microcracks are assumed to nucleate on (001) planes in grain 2 (step 2). These microcracks propagate in the second grain and break the “triangles” remaining along the grain boundary and which belong to the grain boundary itself (step 3). This generates a perturbed crack front which is still attached to the grain boundary by remaining ligaments. In step 4 the perturbed crack front propagates and leads to final fracture. The model is based on an energy balance between the driving energy corresponding to the strain energy release rate of the perturbed crack and the dissipated energy. This energy includes three contributions: (i) the cleavage surface energy on the facets of the second grain, (ii) the intergranular energy of the "triangles", and (iii) the energy spent in breaking the remaining ligaments. This model predicts that the number of segmentations along a given grain boundary is an increasing function of ψ, as observed experimentally [10] and that the = global ? cleavage stress is also increasing with ψ.

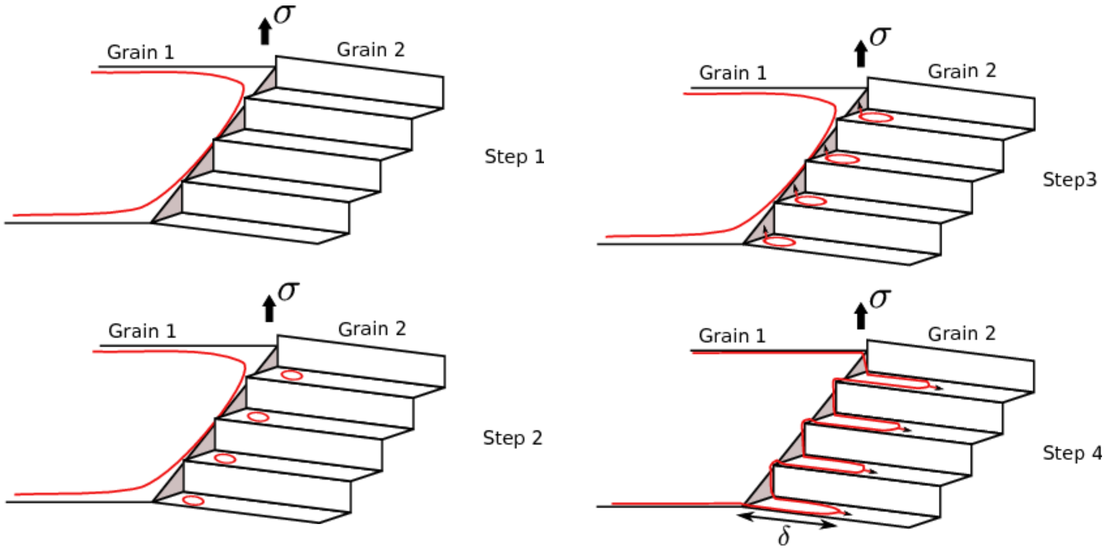

Figure 7. The four steps for a cleavage crack to cross a twisted grain boundary.

This model of grain boundary crossing has been used to identify the parameters introduced in the Beremin-type model for predicting the fracture toughness of inhomogeneous materials [2] in which two modes of failure (intergranular and cleavage) are competing. The results shown in Fig. 8 were obtained using V_o = (50 µm)^3, $m_B = m_{SZ}$ = 30 (Weibull shape factors for base metal (B) and segregated zones (SZ)) in the as-received and aged conditions), f = 10 % (volume fraction of segregated zones). The critical stresses were taken as:

$$\sigma_u^B = 3300\,MPa\,(as-received),\ \sigma_u^B = 3230\,MPa\,(aged),$$
$$\sigma_u^{SZ} = 3250\,MPa\,(as-received),\ \sigma_u^{SZ} = 2750\,MPa\,(aged)$$

It is thus observed that aging produces a small decrease of the cleavage stress (by about 2%), due to the mechanism for cleavage described in Figs. 6 & 7, and a larger decrease of the intergranular fracture stress in the segregated zones (by about 15%)due to phosphorus intergranular segregation after aging. This value is in good agreement with the measurements carried out on homogeneous material representing the composition of the segregated zones [18].

Fig. 8 shows that the bimodal model for fracture is able to reproduce the observed variations in fracture toughness with temperature in both conditions (as-received and aged). This model accounts also reasonably well for the shift in DBTT with aging (~ 30°C at $K = 100\,MPa\sqrt{m}$ and P_r = 63 %). It accounts also for the increased scatter observed in test results on aged material. This model can also be used for predicting the variation of fracture toughness with longer aging times and lower temperatures typical of those of in-service conditions.

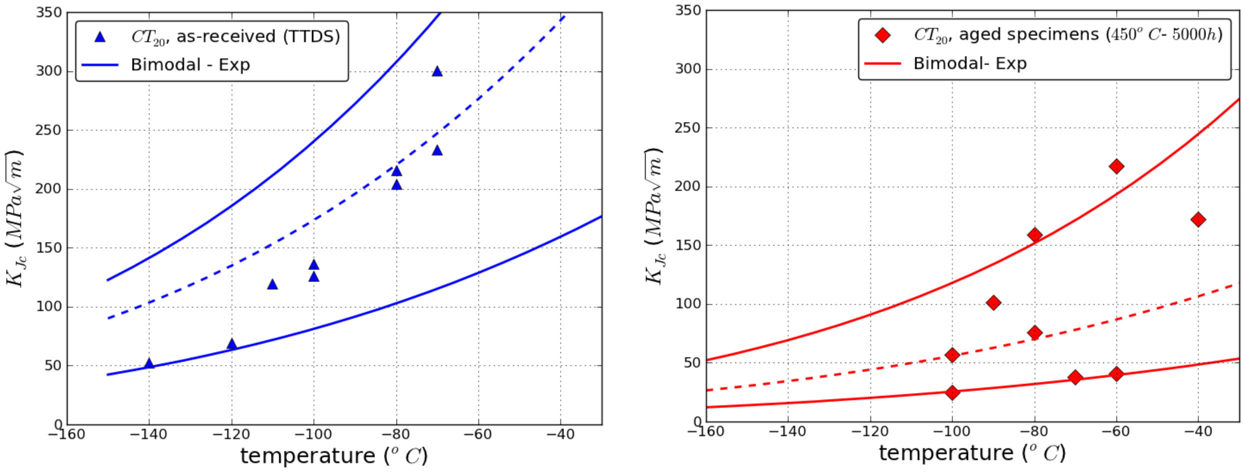

Figure 8. Variation of the fracture toughness with temperature. Experiments and predictions from Beremin-type bimodal model [2]. The calculated values corresponding to failure probabilities of 5%, 63% and 95% are shown.

6. Conclusions

1. Thermal aging of a 18MND5 plate (type A533B) at 450°C for 5000 hours produces a shift of the ductile-to-brittle transition temperature (DBTT) of about 39°C. This shift is not accompanied by a drastic change in fracture modes which remain partly intergranular in the segregated zones and transgranular cleavage in the matrix. The fracture toughness of aged material is much more scattered than that of the as-received material.
2. The slow cooling rate applied during cooling after the stress-relieving heat treatment (~ 30°C/h) generates intergranular phosphorus segregation which is sufficient to provoke intergranular fracture in the segregated zones, even in the as-received conditions.
3. Auger spectrometry measurements showed that during aging at 450°C, phosphorus continues to segregate along the grain boundaries, while carbon concentration at grain boundaries decreases. Both phenomena produce an embrittlement effect of the grain boundaries.
4. A model of intergranular segregation including the interaction between C and P atoms and non-isothermal conditions was identified. The results of this model were used as inputs for the prediction of bimodal fracture toughness of an inhomogeneous material representing the banded structure of the micro-segregated steel. The kinetics is represented using the McLean – Guttmann – Militzer theories.
5. The variations in DBTT and in the scatter of fracture toughness test results induced by aging are correctly predicted using these models of segregation and of fracture toughness.

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