Hydrogen and Temper Embrittlement Effects on Fatigue Fracture Behaviour of 2.25Cr-1.0Mo Nuclear Reactor Pressure Vessel Steel

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Abstract – The Reactor Pressure Vessel known as RPV is an essential element of nuclear power plants. The vessel is a robust container with a thick wall that is designed to endure the internal pressure resulting from the activity of the reactor. This also serves a crucial function in establishing a requisite barrier to prevent the dispersion of radioactive substances into the surrounding environment. When evaluating the functional requirements, high strength low alloy (e.g., 2.25Cr-1Mo) steel is typically a suitable choice for fabricating the vessel. The working environment for the RPV is very harsh. Due to neutron bombardment the steel vessel, especially around reactor core, becomes hard and loses its ductility due to build-up of dislocations. Radiation can cause secondary and tertiary changesin microstructures. The working temperature (order of 300^{o}C) also favours carbide precipitation as well as trace element segregation at various microstructural sites. The situation is further aggravated by the phenomenon known as hydrogen embrittlement (HE). The purpose of this study is to investigate how the classical temper embrittlement (TE) due to segregation of trace elements (like phosphorus and sulphur) alone or in combination with HE embrittlement changes the fatigue crack growth rate and morphologies of the fracture surfaces of 2.25Cr-1.0Mo pressure vessel steel under both pre- and post-thermal exposure conditions. The experimental findings indicate that both HE and TE mechanisms play an important role in augmenting the propagation of fatigue cracks, as well as altering the fracture morphology, which need to be considered in design and fabrication of less susceptible RPV via customizing the chemical compositions and various microstructural features of the steel used.

Keywords: 2.25Cr-1.0Mo steel, Temper embrittlement, Hydrogen embrittlement, Fatigue, Fracture, Crack growth

I. Introduction

Metal fatigue is widely acknowledged as a significant factor contributing to the failure or premature decommissioning of various engineering structures, including the RPV.The selection of steel for the RPV is a critical processas it must meet stringent safety standards and ensure structural integrity. The correlation between the chemical composition and the mechanical characteristics of the material employed for the RPV, as well as its interaction with the operational environment, are intricately interconnected**[1,2]**. Considering all factors, the general trend is to construct the RPV from high strength low alloy (HSLA) steels featuring tempered martensitic or bainitic microstructures **[3]**.The degradation of RPV steel because of hydrogen absorption during service is a commonly observed phenomenon. The originsof hydrogen, in this case, are diverse such as thechemical reactions of corrosion, the breakdown of elevated temperature water, the process of radiolysis of water at high temperatures, etc. The literature sources indicate that the degradation of RPV steel is intensified by the concurrent influence of HE andthermally induced classical TE, in addition to dynamic strain aging and irradiation**[4-8]**.

Individually, both classical TE and HE degrade the mechanical properties of steel. For RPV steel, the work of Zhang and Zhou **[9]**showedthat the higher the TE is, the higher the degree of action of HE. However, they did not quantify individual effects of TE and HE. Guan et al **[10]** measured the combined action of TE and HE in a 3Cr-1.0Mo-1/4V pressure vessel steel. There are lots of varieties of reactors as light water, heavy water, pressurized water, gas cooled, etc. Because of differences in

operating temperatures and availability of species for HE, effects of TE and HE might be different. So, for better understanding of property degradation in RPV of different reactors and their integrity, knowledge on the individual effects of TE and HE on property degradation would be very helpful in proper material selection as well as optimum component design. This investigation is dedicated to comprehend the impact of previous classical TE and HE singly or in combination on fatigue crack growth rate and fractured mode of 2.25Cr-1.0Mo RPV steel.

II. Experimental

II.A. Materials and Heat Treatment

The present study employed a commercial grade 2.25Cr-1.0Mo steel, which was procured from Magnox Ltd, UK. Table 1 displays the chemical composition of the steel in question.

Table 1. Chemical compositions of the steel used (wt%)

C	Si	Mn	P	S	Cr	Mo
0.15	0.22	0.51	0.013	0.023	2.27	0.91
Ni	V	Cu	Al	Co	Nb	Ti
0.11	0.01	0.16	0.03	0.01	0.003	0.004

For this study, the following microstructures were considered:

(1) As-quenched Condition: Oil-quenched microstructures that have been followed two hours austenitizing at 1100°C.
(2) QT Condition: Quenched and tempered (at 650°Cfor 2 hours) microstructures.
(3) QTE Condition: QT condition with TE for 210 hours at 520°C.

II. B. Metallography

The present study involved a comprehensive microstructural analysis of test specimens subjected to varying heat treatment conditions to visualize various microstructural features.

II. C. Fatigue Crack Growth Test

Vibrophore (Walter and Bai, Switzerland), was used for fatigue precracking at 65Hz frequency following BS 7448 **[11]**. This standard allows precracking force less than 60% of the force required to measure the toughness of the material used to avoid any chance of ductile tearing on the fatigue fracture surface. So, load was kept fixed at 6.0kN and fatigue crack growth test was carried in the stress intensity factor range 14-45 MPa(m)$^{1/2}$ on a 200kN Instron tensile testing machine at 1Hz frequency for as-quenched and QT at room temperature (RT) in airemploying sinusoidal waveform. For QTE specimen, test was additionally conducted at 110°C in air. For all cases, crack growth was monitored by direct current potential drop technique.

II.D. Fractography

Fractographic observations of the fatiguefracture surfaces, were conducted on a JEOL 5410 scanning electron microscope (SEM)at 20kV and 0° tilt. The area fractions of IGF were determined through both manual and automated methods utilizing a Quantimet-500 image analyzer software.

III. Results and Discussion

III.A. Microstructures

After austenitizing at 1100°C and quenching in oil, the resulting microstructures were mostly lath martensitic, Fig.1. However, tempering heat treatment (QT condition) changed the as-quenched microstructure to temper martensites having some small carbide particles, Fig.2. A long time (210 hours) TE treatment of QT specimen at 520°C (QTE condition) caused a very minor change in the matrix microstructures, however, a significant change in the size, shape and distribution of carbide particles has been observed (marked by arrows), Fig.3.

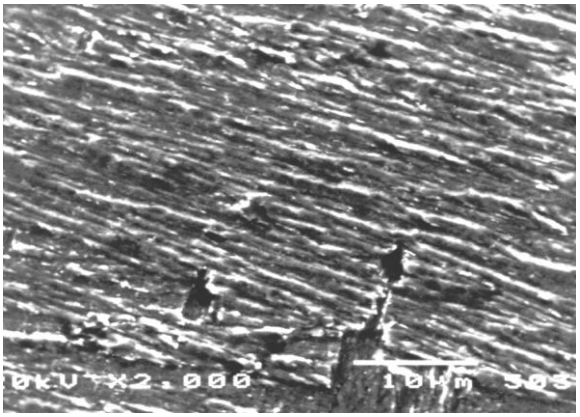

Fig.1. Microstructure of as-quenched specimen showing lath type martensites.

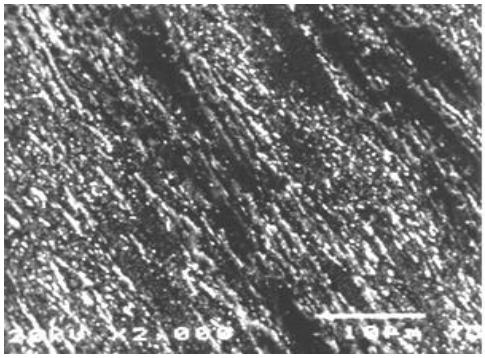

Fig.2. Microstructure of QT sample showing tempered martensite with distributed small carbides.

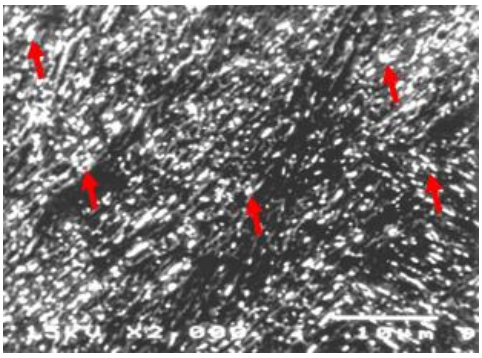

Fig.3. Microstructure of QTE specimen showing tempered martensite with small to large carbide particles (marked by arrows).

SEM photographs (Figs.1-3) revealed that microstructures for all heat treatment (HT) conditions were quite compatible with their HT conditions. Carbide particles on QTE specimen were revealed to be Mo rich, Fig.4. Many research works have been carried on various Cr-Mo steels **[12-14]**. The research results concluded that, TE can cause changes in the chemico-morphology of the carbide particles and that during TE treatment the iron (Fe) rich carbides gradually transform to Mo rich carbides.

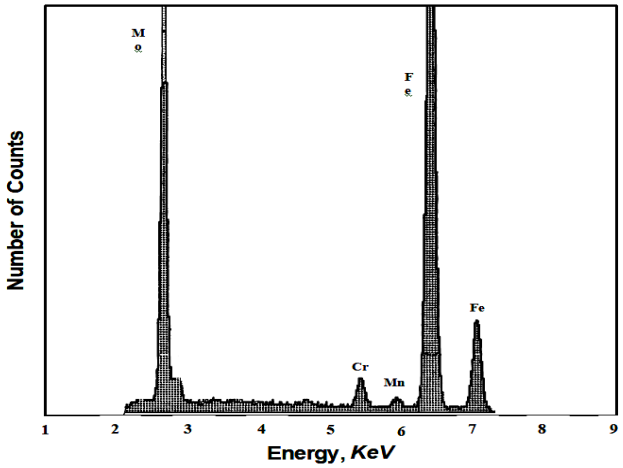

Fig.4. EDS spectra on carbide particles of QTE specimen.

Along with chemico-morphological change in carbide particles, TE also causes trace element segregation at grain boundaries. To identify grain boundary segregation species, Auger Electron Spectroscopy (AES) was carried out on both transgranular (TG) and intergranular (IG) facets (Fig.5) of QTE specimen broken in vacuum chamber at -196°C. AES analysis traced both phosphorus (P) and sulphur (S)on IG facet, Fig.6. However, AES identified no existence of any of these two elements on TG facet. The presence of P and S on IG facet indicates that the grain boundary (GB) cohesion has been decreased due to segregation of these elements that created easy going fracture path over the trangranular cleavage plane. Many researchers have mentioned this trace element segregation at GB due to TE of HSLA steels and that this type segregation encourages intergranular cracking over transgranular one **[5,7,8].**

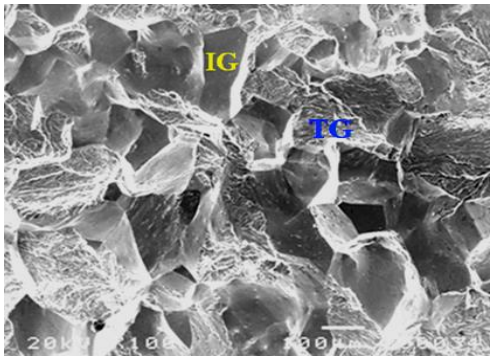

Fig.5. Transgranular (marked by TG) and intergranular (marked by IG)fractures on fracture surface of QTE specimen.

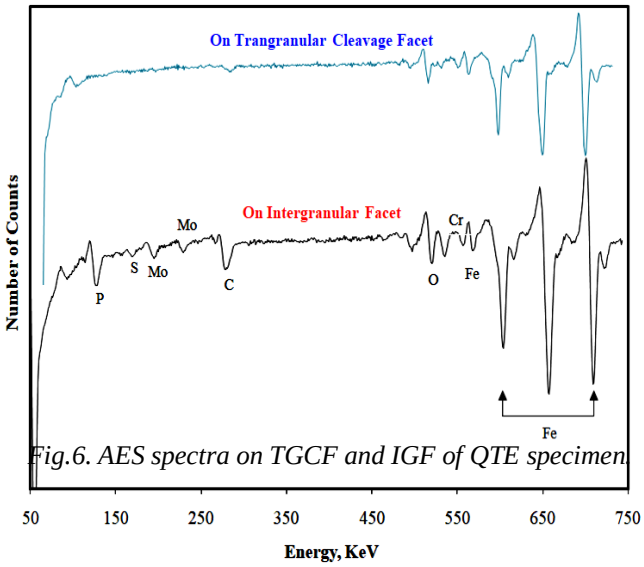

Fig.6. AES spectra on TGCF and IGF of QTE specimen.

Fig.6. AES spectra on TGCF and IGF of QTE specimen.

Fractographs on fatigue fracture surface of various HT conditions are shown in Figs.7-10.Fatigue crack growth tests of as-quenched and QT specimens at RT in air and for QTE specimen at both RT and 110^{o}C in air were performed over the stress intensity (K) range 14-45MPa√m. Throughout this stress intensity range, almost no intergranular fracture (IGF) was observed for as-quenched specimen, Fig.7. Some isolated IGF (maximum ~10%, marked as IG)was found for QT specimen tested at room temperature in air,Fig.8. After 210 hours of classicalTE at 520^{o}C (QTE sample) resulted a drastic change in the proportion of IGF (marked as IG), Fig.9. However, when this QTE sample was tested at 110^{o}C in the same laboratory air no IGF was observed, i.e., the mode was fully TGCF, Fig.10. For QTE condition, IGF was observed across a comprehensive range of K values spanning from 14-35MPa√m (refer to Fig.11). Subsequently, it was also observed that the concentration of IGF increased at first and then declined with elevated levels of K value. At K value of approximately 36MPa√m, the occurrence of IGF was entirely impeded, resulting in completely TGCF, as depicted in Figs. 9 and 11.
Figure 11 also reveals the variation in area fraction of IGF with stress intensity factor. As per Fig.10 (test carried out at 110^{o}C in air), P and S segregation due to TE cannot produce IGF alone without further HE. During cyclic loading crack tip is opened mechanically and H atoms of water vapour enter along grain boundaries. At low K value, crack growth rate is also low. Lower proportion of IGF at low K value is suggesting that on all grain boundaries at the freshly opened crack tip in every cycle was not sufficient. This may be responsible for the lower proportion of IGF at lower range of K. At very high K values, the crack growth rate is also very high. At this situation, the available H at the laboratory air is not sufficient to embrittle GBsahead of the fast growing crack tip in each fatigue increment and change the traditional TGCF to IGF one. Similar observation has also been made by Rao et al **[8]**.

III.C. Role of HE on IGF

Based on the fractographic analysis, it was observed that the fatigue surfaces of the as-quenched specimen did not display any intergranular facets. However, in the case of QT and QTE conditions, the IG facets were found to be present in the maximum proportions of approximately 10% and 45%, respectively. The lack of IGF observed on the fatigue fracture surface at a temperature of 110°C on QTE specimen necessitates further contemplation from a novel perspective. Initially, it is important to contemplate the fundamental distinction in the environmental circumstances. Water vapour or moisture is present at the growing fatigue crack tip when the specimen is at room temperature in air, whereas it is not present in the specimen tested at 110°C. The elevated temperature, surpassing the boiling point of water, resulted in the expulsion of water vapour from the crack tip. Consequently, the crack tip remained consistently arid and devoid of hydrogen source throughout the process of fatigue crack propagation. According to existing arguments **[8,15]**, it is suggested that hydrogen atoms tend to infiltrate into GBs, mainly in the vicinity of the crack tip. It is further posited that the likelihood of this occurrence could be mitigated by subjecting the bulk specimen to high temperatures. The QTE specimen did not exhibit any IGF at a temperature of 110^{o}C, despite having a significant degree of segregation coverage of S and P at the GBs. According to the prevailing viewpoint, the exclusive cause of intergranular fracture cannot be ascribed to the presence of impurity elements solely at the GBs, even high degree of impurity coverage.The occurrence of this phenomenon necessitates the presence of supplementary HE during fatigue fracture under room temperature in an atmospheric environment. The presence of IGF in low alloy steel during fatigue has been linked to the presence of water vapour and is believed to be caused by the generation of atomic hydrogen through chemical reactions by the following reactions.

$$Fe + H_2O = FeOH^+ + H^+ + 2e^-$$
$$H^+ + e^- = H$$

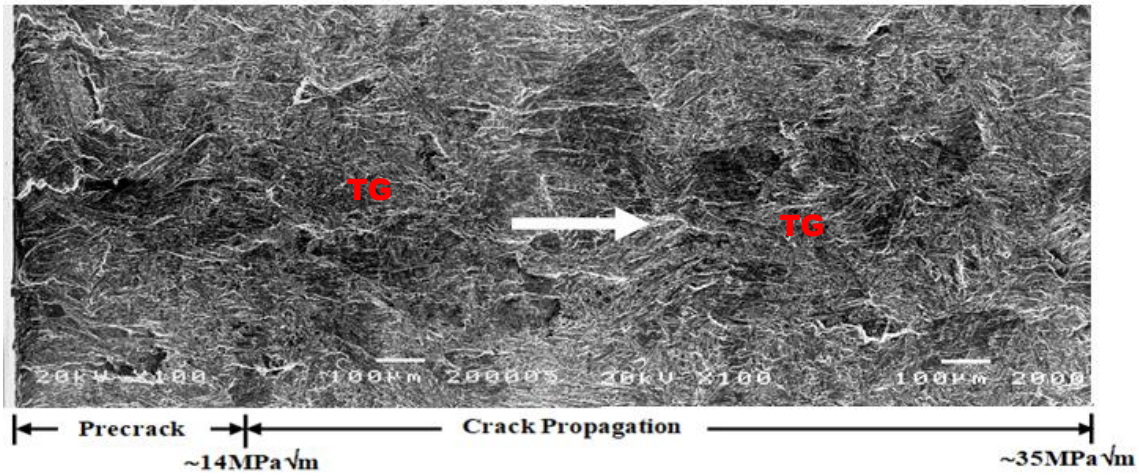

Fig.7. Complete trangranular cleavage type fracture (marked by TG) on fatigue fracture surface on as-quenched specimen at RT in air. Note: Arrow shows crack growth direction.

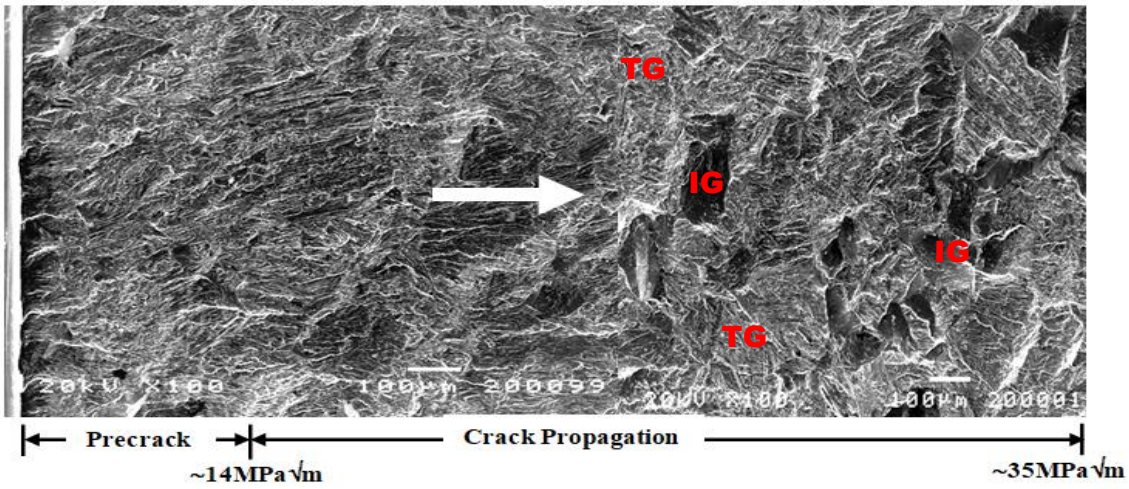

Fig.8. Mixture of trangranular (marked by TG) and intergranular (marked by IG) on fatigue fracture surface on QT specimen at RT in air. Note: Arrow shows crack growth direction.

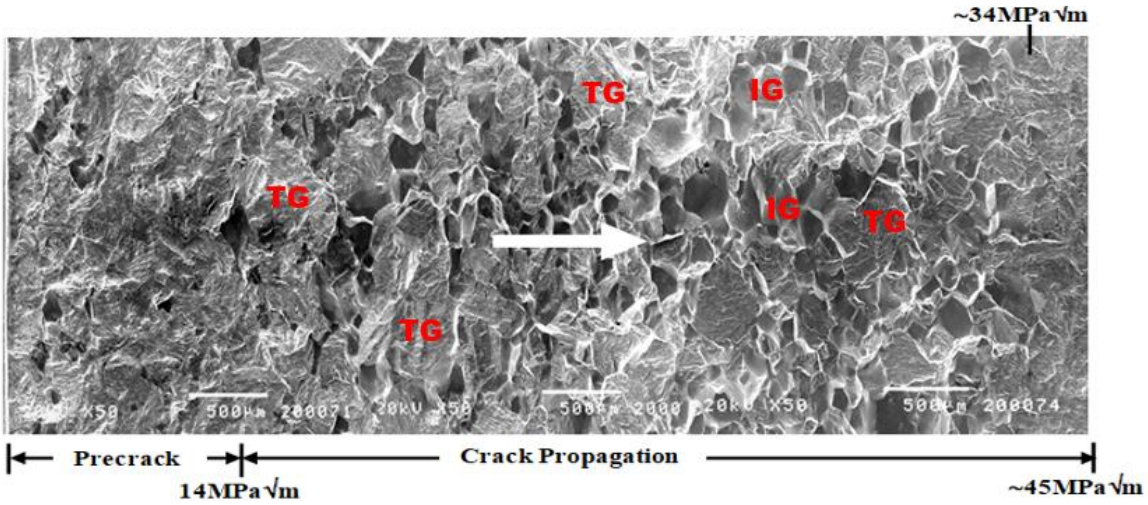

Fig.9. Mixture of trangranular (marked by TG) and intergranular (marked by IG) on fatigue fracture surface on QTE specimen at RT in air. Note: Arrow shows crack growth direction.

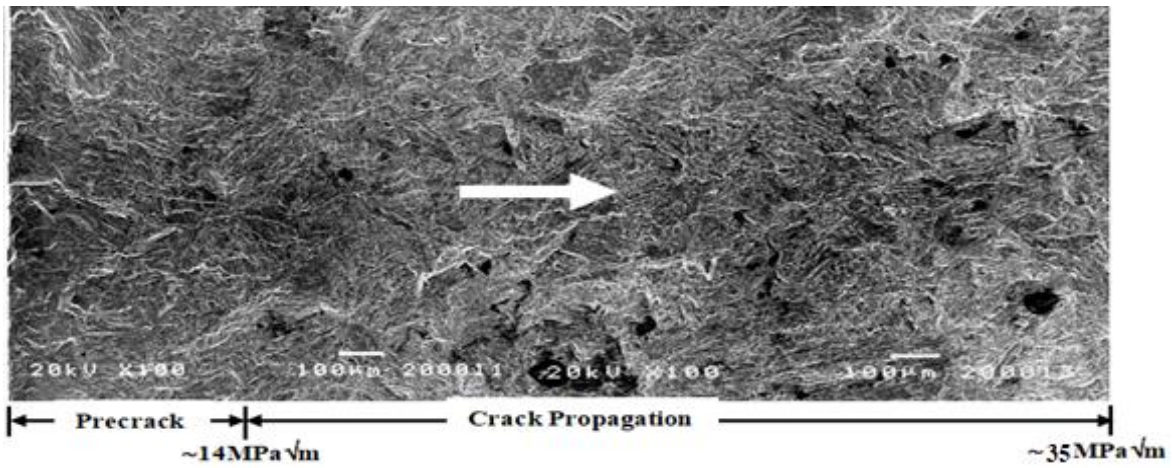

Fig.10. Completely transgranular type fatigue fracture surface on QTE specimen tested at 110°C in air. Note: Arrow shows crack growth direction.

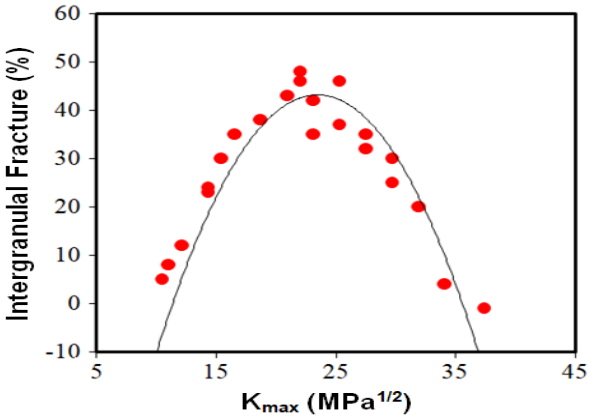

Fig.11: The impact of stress intensity factor on the variation in IGF on fatigue fracture surface of QTE specimen tested at RT in air.

III.D. Embrittlent and Fatigue Crack Growth

The rates of fatigue crack growth under ambient conditions and at 110°C are shown in Fig.12 for the QT and QTE specimens. The presented data indicated that the crack growth rate of the QTE specimen was somewhat elevated due to the occurrence of TE.
Regarding QTE heat treatment conditions, it has been observed that the proportion of IGF present on the fatigue surface is over four times greater than that of the QT condition, Figs.8 and 9. Specifically, the QT condition exhibits approximately 10% IGF, while the QTE condition displays approximately 45% IGF. Nevertheless, the increased percentage of IGF did not significantly impact the fatigue crack propagation rate of the QTE sample. The IGF observed on the fatigue surface is a result of the combined effects ofboth TE and hydrogen-induced grain boundaryembrittlement. The extent of intergranular crack propagation and embrittlement is dependent on the quantity of clean surface area generated during each cycle.

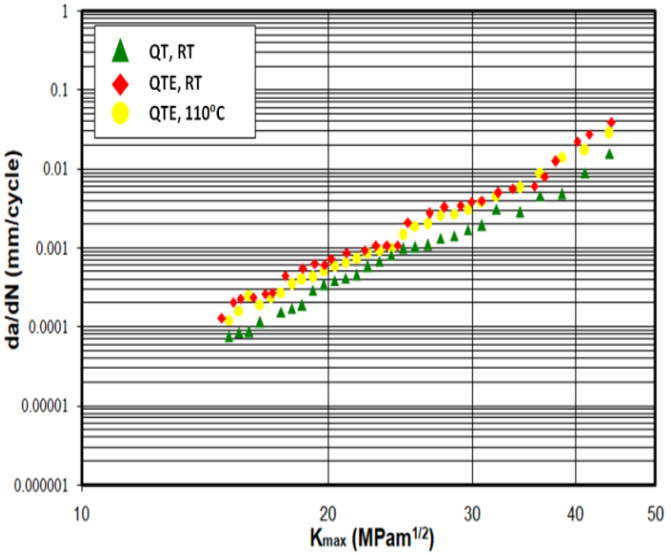

Fig.12. Fatigue crack growth curve of different specimens.

The TE level resulting from isothermal exposure at a temperature of 520°C for a duration of 210 hours is predetermined, while the HE level is immediate. Alvarez and colleagues observed that HE caused a greater rate of fatigue crack growth at a K value of 30 MP√*m* for Cr-Mo **[15]**. The research findings indicate that the fatigue crack growth rate is increased by both TE and HE when considered separately. TE induces the phenomenon of impurity segregation at the interfaces of carbide/matrix and prior austenite grain boundaries. Here, the primary TE elements have been

identified as P and S through the utilization of AES analysis. The segregation at multiple microstructural locations results in a reduction of local bonding strength, thereby facilitating the opening of interfaces at lower strain levels. The QTE specimen exhibits a elevated rate of crack growth in comparison to the QT specimen at RT in an atmospheric air. This observation can plausibly be attributed to a greater degree of grain boundary debilitation caused by the presence of P and S.

According to Figure 12, it can be observed that the rate of crack growth in the QTE specimen is marginally greater at room temperature under atmospheric conditions as compared to that at a temperature of 110^{o}C. The material utilized in this study belongs to the category of high temperature materials. According to reference **[15,16]**, subjecting certain types of materials to a temperature of 110^{o}C results in negligible or insignificant alterations to the tensile properties of the steel. Song et al **[17]** mentioned that, for 2.25Cr-1.0Mo steel, high temperature causes reduction in both tensile and yield strengths, however, it is only significant after 300^{o}C. Considering this, it is arguable that the yield and tensile strengths of the steel at room temperature and 110^{o}Care more or less very similar.Thus, the fatigue crack growth rate is not supposed to be affected by the strength level, as per the available evidence. The sole determinant impacting the fatigue fracture process is the participation of HEeffect. The marginally elevated rate of crack propagation observed in the QTE specimen at ambient temperature can beattributed to the supplementary HE phenomenon, which is not present during the fatigue examination conducted at 110^{o}C.

IV. Conclusions

From the present investigation, the following important observations have been emerged:

1. In the state of being quenched, most alloying elements remain in a solid solution. The fatigue fracture morphology is not affected by any minor TE effect (if there is any) related to grain boundary segregation.
2. Both tempering and TE result in the precipitation of carbides and segregation of impurity elements. The augmentation of impurity element segregation and carbide precipitation during thermal exposure leads to a rise in the quantity of IGF. The transformation of TGCF to IGF cannot be achieved solely through the TE effect and this happening it requires the simultaneous involvement of the HE effect.
3. A fatigue crack growth experiment conducted at a temperature of 110^{o}C results in a desiccated and dehydrogenated growing crack tip. Therefore, HE is not feasible for it to occur.
4. Both TE and HE have a distinct impact on the rate of fatigue crack growth. Nevertheless, it has been discovered that TE is more effective in augmenting the rate of fatigue crack growth in comparison to HE induced in ambient laboratory conditions during fatigue crack growth test.

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Nomenclature	
Symbol	**Meaning**
RPV	Reactor pressure vessel
HE	Hydrogen embrittlement
AES	Auger electron spectroscopy
QT	Quenched and tempered
QTE	Quenched, tempered and embrittled
SEM	Scanning electron microscope
TE	Temper embrittlement
TG	Transgranular
IG	Intergranular
GB	Grain boundary
TGCF	Transgranular cleavage fracture
IGF	Intergranular fracture

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