JMEPEG (2007) 16:80–85
DOI: 10.1007/s11665-006-9012-0

1059-9495/$19.00

Influence of Prior Austenite Grain Size on the Degree of Temper Embrittlement in Cr-Mo Steel

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(*Submitted April 19, 2006; in revised form May 11, 2006*)

Reversible temper embrittlement has been frequently observed in many different low alloy steels serving at high temperature, e.g. order of 500 °C. This type of embrittlement can change the brittle transgranular fracture mode to intergranular decohesion with subsequent change in fracture stress and fracture toughness. The present paper deals with the influence of the prior austenite grain size and isothermal aging time on the degree of embrittlement of 2.25Cr-1Mo steel, which is very popular for its use in power generating and other petrochemical industries. In this research work, the specimens of 2.25Cr-1Mo steel were treated in three different austenitizing temperatures along with different isothermal embrittling time periods. Then the induced degree of embrittlement was characterized by the fracture stress values at −196 °C and area fraction of intergranular failure. The outcome of the experimental results shows that the increase in austenite grain size and/or isothermal embrittling time severely weakens the grain boundary cohesive strength leading to brittle intergranular failures and thus to a greater degree of temper embrittlement.

Keywords grain boundary length, intergranular fracture, isothermal aging, prior austenite grain size, temper embrittlement

1. Introduction

In the case of 2.25Cr-1Mo steel, it has been found that the brittle fracture behavior can be changed from its typical transgranular cleavage fracture to intergranular decohesion, if the impurity element segregation level at prior austenite grain (PAG) boundaries exceeds a certain critical value (Ref 1-3). As for brittle fast fracture, impurity element segregation, due to classical temper embrittlement, can also change the fracture mode in fatigue failure and enhance the crack growth rate (Ref 1, 4-6). As a result, impurity element segregation at microstructural sites plays an important role to control the fracture toughness and fatigue life of many components. It has also been mentioned that the degree of segregation depends on embrittlement temperature, holding time, fluctuation in temperature during exposure and so on. Several investigators (Ref 1, 7-9) have shown that PAG size is also a very important factor for the degree of embrittlement.

Nowadays, environmental pollution is a worldwide concern. As a result, auto body makers are trying to make light-weight cars to reduce fuel consumption and CO_2 emissions. Moreover, many countries are looking for high earthquake-resistance materials. Availability of high strength steels might give the possible solution for the prevailing demands. As a result, steel producers are trying to produce various grades of high strength steels. One of the ways to increase the strength is to refine the grain size of the steel. Many countries are now producing ultra-fine grained steels using conventional processing facilities without adding expensive alloying elements (Ref 10, 11). Fine-grained steels provide not only higher strength, but also reduce temper embrittlement-related deterioration in toughness. They also provide better fatigue lives (Ref 12, 13). In this present work, the influence of PAG size on fracture stress values and degree of temper embrittlement of 2.25Cr-1Mo steel has been studied by observing the proportion of intergranular fracture in the SEM and measuring the microscopic fracture stress (σ_F) values at low temperature.

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2. Experimental

2.1 Material

The material used in this study is a commercial grade of 2.25Cr-1Mo-pressure vessel steel. Table 1 shows the chemical composition of the steel used in this study.

2.2 Heat Treatment

In this work three groups of samples were austenitized, respectively, at 1250, 1100 and 950 °C temperatures for 2 h and quenched in oil. After quenching, tempering heat treatment (HT) was carried out by heating the specimens of all groups for 2 h at 650 °C followed by oil quenching. Then one-third of the samples from each austenitizing group were kept at quenched and tempered condition i.e., in unembrittled condition. One third of the specimens were aged at 520 °C for 100 h and air-cooled. The remaining specimens were also aged at 520 °C but for 200 h and cooled in still air. Table 2 gives a clear idea of the detailed HT conditions and codes to be used throughout the whole text.

2.3 Metallography

Specimens from all HT conditions were cut for metallographic observation. They were prepared following the standard techniques. In order to reveal the PAG boundaries, metallographic specimens from all conditions (unembrittled and embrittled) were etched in aqueous picric acid solution in boiling state. After that, micrographs of the samples of each of the HT conditions were taken at different magnifications, and using these micrographs grain sizes of the specimens austenitized at three different temperatures were determined by linear intercept technique.

2.4 Measurement of Fracture Stress (σ_F)

After performing mechanical tests at −196 °C, the loads required for fracture of all the test samples were obtained and converted to the actual fracture stress values. Using Griffiths and Owen's (Ref 9) analysis of stress intensification, σ_{11}/σ_y, as a function of σ_{nom}/σ_y, the values of σ_{nom} were obtained for various specimens from the equation:

$$\sigma_{nom} = \frac{6M}{B(W-a)^2} \qquad \text{(Eq 1)}$$

where *B* is the specimen thickness, *W* is the specimen width, *a* is the notch depth and *M* is the applied bending moment.

Then σ_{11} (max) at fracture was obtained from the knowledge of σ_y (yield stress) and the fracture load of the notched bend specimen. This stress has been taken to be the microscopic fracture stress, σ_F i.e.:

$$\sigma_F = \sigma_{11}(\max) \qquad \text{(Eq 2)}$$

where σ_{11} (max) is the maximum principal tensile stress below the notch root (see also Ref 9).

2.5 Fractography

After mechanical tests at −196 °C, specimens were cut behind the fracture surfaces to provide samples suitable for the scanning electron microscope (SEM). The fracture surfaces of all specimens were then carefully observed and photographed in the SEM.

3. Results

3.1 Metallographic Observation

For all groups, tempered martensitic structures were observed, which can be found elsewhere (Ref 1, 14, 15). The PAG sizes of three different austenitizing groups are presented in Table 3 (for detail see also Ref 14, 15).

3.2 Fracture Behaviors

In the unembrittled condition, samples from all austenitizing groups exhibited completely transgranular cleavage failure (Fig. 1). But the fractographic observations of the embrittled samples demonstrated the existence of two distinct regimes (mixed mode of fracture) on fracture surfaces characterized by different dominant fractographic features. Figures 2 and 3 exhibit the typical mixed mode of fracture surfaces for samples of LQTE200 and HQTE200, respectively. The fracture behavior in the first regime is of transgranular type where the fracture path advanced through the transgranular cleavage plane. The second regime consists of intergranular failure where weak regions of grain boundary assisted the fracture process. The SEM fractographs of HQTE200 (Fig. 3) clearly shows the presence of dominant intergranular fracture features along with some transgranular cleavage fracture (small proportion). With increase in the PAG and embrittlement time periods, the proportions of IGF have been found to increase (Fig. 4, 5). An important observation is that if the PAG size is reduced to 10 μm, the proportions of IGF would be (from the extrapolation), respectively, about 4% and 12% after 100 and 200 h of TE (Fig. 4).

3.2.1 Fracture Stress Values. Experimental results exhibit that coarser PAG size resulted in lower fracture stress values (Fig. 6). Similar to PAG sizes, higher embrittlement time periods and %IGF also decreased the fracture stress values (Fig. 7, 8). An interesting observation is that the deterioration in toughness values were found to increase with increase in the PAG sizes and this was observed for both embrittlement periods (Fig. 9, 10).

Table 1 Chemical composition (in wt.%) of the 2.25Cr-1Mo steel

C	Si	S	P	Mn	Ni	Cr	Mo	Cu
0.15	0.22	0.023	0.013	0.51	0.11	2.27	0.91	0.16

Table 3 PAG sizes of different groups

Group code	HQ	MQ	LQ
Austenite grain size, μm	155	120	25

Table 2 Details of HT cycles

HT conditions	HT codes	Group code
1250 °C/2 h/OQ + 650 °C/2 h/OQ	HQT	HQ
1250 °C/2 h/OQ + 650 °C/2 h/OQ + 520 °C/100 h/Air cooling	HQTE100	
1250 °C/2 h/OQ + 650 °C/2 h/OQ + 520 °C/200 h/Air cooling	HQTE200	
1100 °C/2 h/OQ + 650 °C/2 h/OQ	MQT	MQ
1100 °C/2 h/OQ + 650 °C/2 h/OQ + 520 °C/100 h/Air cooling	MQTE100	
1100 °C/2 h/OQ + 650 °C/2 h/OQ + 520 °C/200 h/Air cooling	MQTE200	
950 °C/2 h/OQ + 650 °C/2 h/OQ	LQT	LQ
950 °C/2 h/OQ + 650 °C/2 h/OQ + 520 °C/100 h/Air cooling	LQTE100	
950 °C/2 h/OQ + 650 °C/2 h/OQ + 520 °C/200 h/Air cooling	LQTE200	

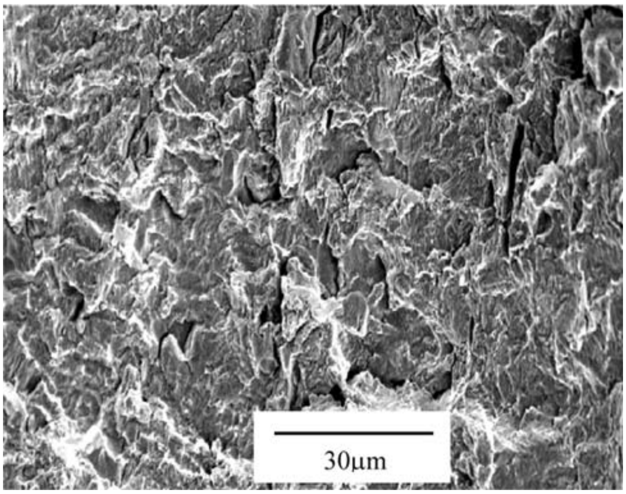

Fig. 1 Transgranular cleavage fracture on LQ specimen before temper embrittlement

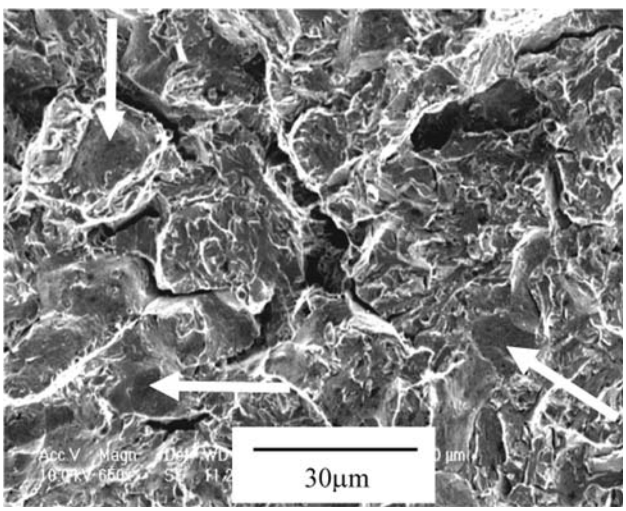

Fig. 2 Fractograph on LQTE200 specimen showing the mixed mode of fracture (transgranular cleavage and intergranular decohesion marked by arrows)

4. Discussion

The main observations that will be discussed are:

1. TE changed the fracture behavior from almost completely transgranular cleavage fracture mode of unembrittled steel to a mixed mode of fracture (Fig. 1-3).
2. The proportions of IGF increased with increase in both PAG size and TE time period (Fig. 4, 5).
3. σ_F values decreased with increase in the PAG size, TE time period and %IGF (Fig. 6-8).
4. Coarser PAG significantly increased the rate of toughness deterioration, Fig. 9 and 10, whereas grain refinement could result in a much delayed TE effect (Fig. 4).

Let us consider the change of fracture morphology. In general, the brittle fracture mode of ferritic steels is transgranular cleavage (Fig. 1). During reversible temper embrittlement, preferential segregation of certain residual impurity elements

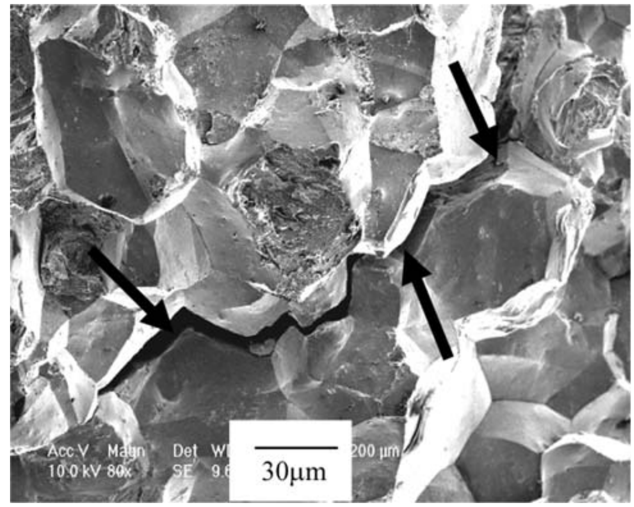

Fig. 3 Fracture features on HQTE200 specimen. Very sharp and deep secondary intergranular fracture (marked by arrows) can be seen on the fracture surfaces

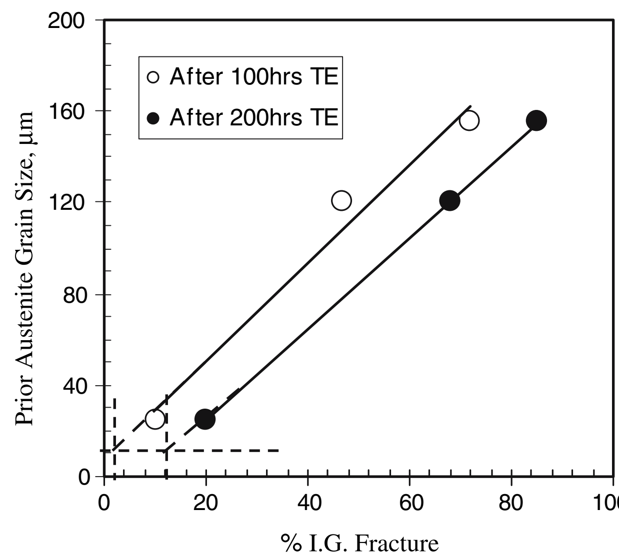

Fig. 4 Effect of PAG on the proportions of intergranular fractures

and/or alloying elements take place to the PAG boundary and/or carbide-matrix interfaces, which has been investigated in detail (Ref 1-3, 5, 15). In this present HT condition, P has been found to segregate at grain boundaries (Fig. 11). For the same steel, under reversible TE condition, Faulkner et al. (Ref 16) also found P to be the main segregating element. This type of segregation reduces the intergranular cohesive strength of the steel. Before TE, the intergranular cohesive strength remains higher than the strength of the transgranular cleavage plane, which has been shown in the schematic diagram in Fig. 12. So, the brittle fracture in ferritic steel in the unembrittled condition is transgranular cleavage type. During TE, P starts to segregate at various microstructural sites such as grain boundaries and carbide-matrix interfaces. Gradually the intergranular cohesive strength reduces and approaches to that of the cleavage plane (Fig. 12b). With exposure time, the degree of segregated P coverage at some grain boundaries becomes to such a level that causes the intergranular cohesive strength lower than the

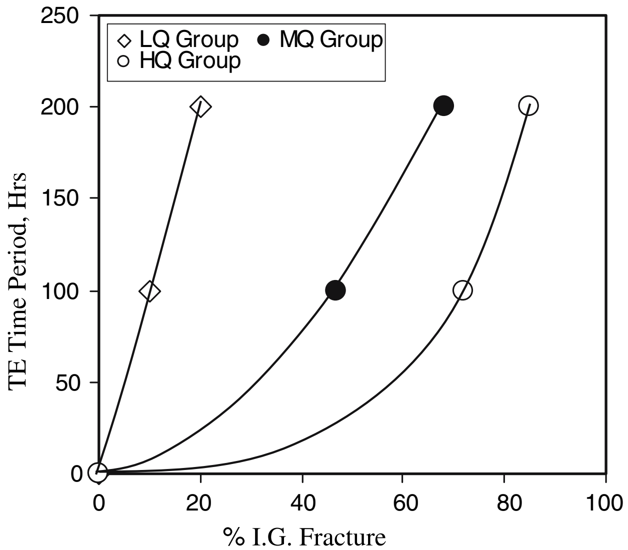

Fig. 5 Effect of temper embrittlement time on the proportions of intergranular fractures

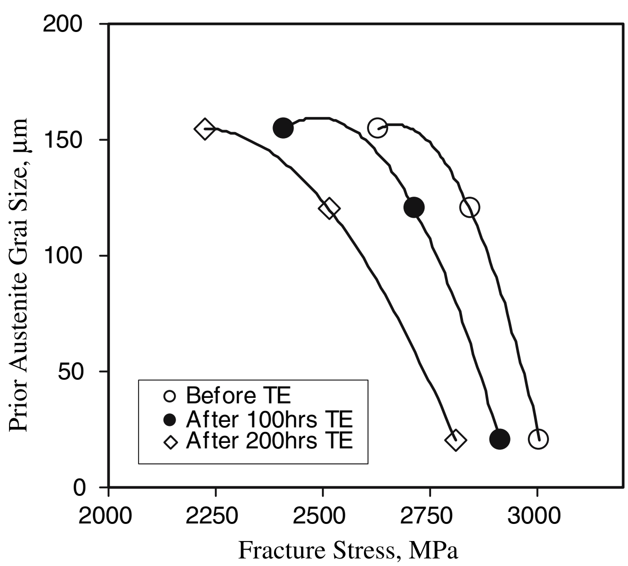

Fig. 6 Variations of fracture stress values with PAG sizes

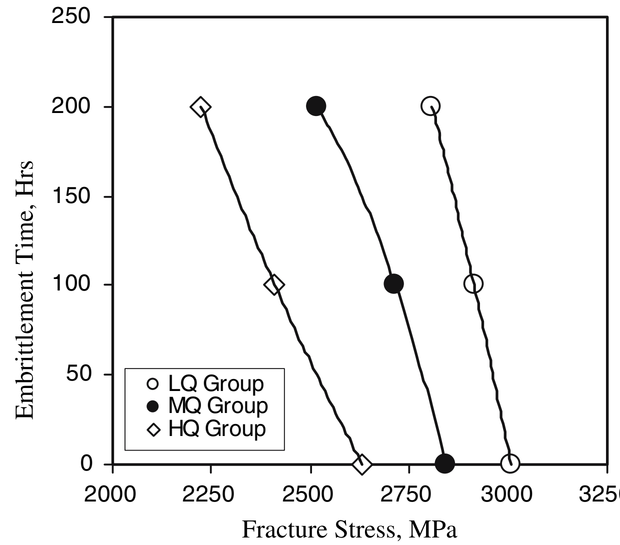

Fig. 7 Effect of embrittlement time on the fracture stress values

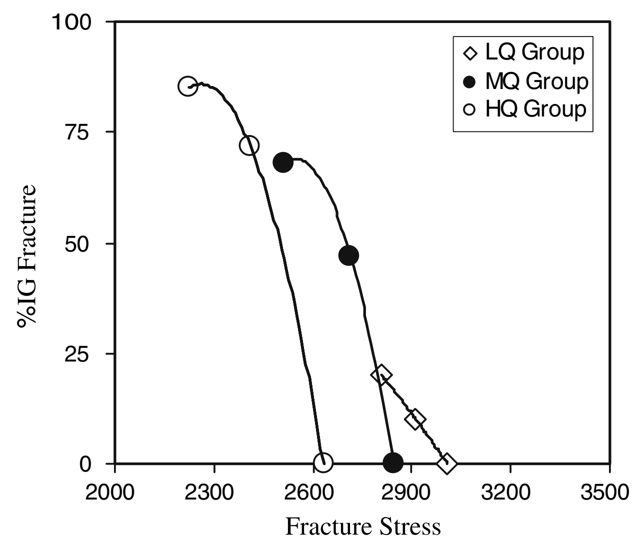

Fig. 8 Effect of %IGF on the fracture stress values

strength of the cleavage plane. In this situation, these grain boundaries exhibit intergranular decohesion type of brittle fracture rather than the usual transgranular cleavage fracture and thus the fracture mode starts to change (Fig. 2, 3). With time, segregation levels on other grain boundaries that are comparatively less favorable for segregation, also cross the critical level required for intergranular decohesion. As a result, the proportions of intergranular fractures on the fracture surfaces of specimens under all groups increased (Fig. 5).

Figure 4 shows the relationship between grain size and intergranular failure as a function of embrittling time. This figure exhibits that coarser PAG size causes higher proportion of intergranular fracture after a similar period of TE. It is true that if the PAG size is large (e.g. 155 μm of HQ group) then there will be comparatively smaller number of grains in per unit volume of metal compared to that of smaller grain size (e.g. 120 or 25 μm). Smaller number of grains means shorter will be the total grain boundary length. As a result, all the samples from HQ group have significantly shorter grain boundary length or smaller grain boundary surface area than those of similarly treated samples from other groups. If we assume, at least for simplicity, that an identical amount of impurity element segregation takes place within identical period of embrittling treatment, the segregation of harmful species might occur heavily along the available grain boundaries of the samples from HQ group. The segregation of deleterious elements reduced the grain boundary cohesive strength level equal to or lower than a level of cleavage fracture strength more readily causing the sites to fail in an intergranular fashion. These weak regions subsequently assisted in both initiating and propagating fracture with much lower applied stress than that was actually required for cleavage fracture. On the reverse, the average grain diameter of LQ group was only 25 μm and hence specimens of this group could accommodate a fairly large number of grains and grain boundary surface area within any identical volume of metal. In such a situation, concentration of harmful P segre-

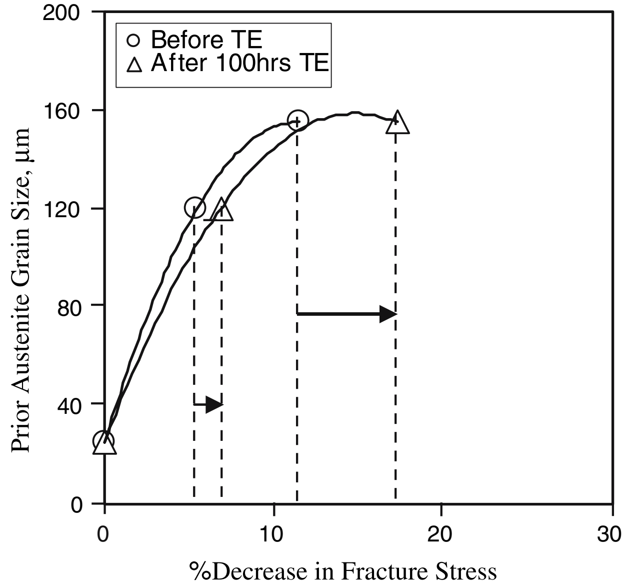

Fig. 9 Effect of PAG sizes on the decrease in fracture stress values after 100 h of TE

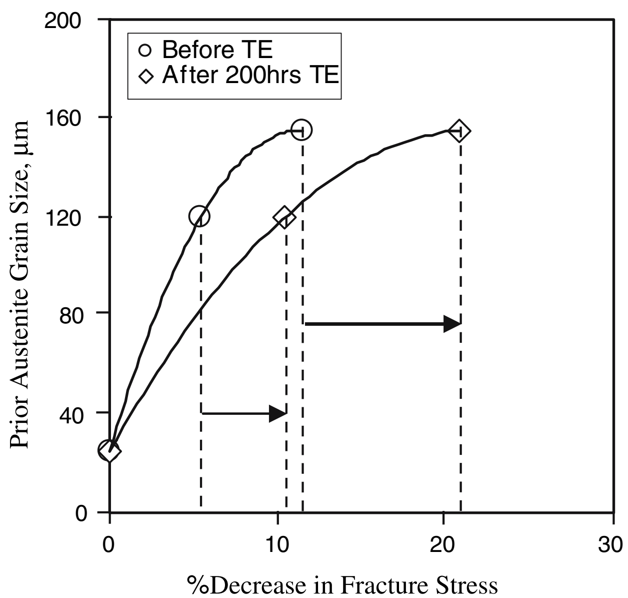

Fig. 10 Effect of PAG sizes on the decrease in fracture stress values after 200 h of TE

gation at grain boundaries will be much lower than that of the HQ group. At this situation, only highly favorable sites experience critical level of segregation to cause intergranular decohesion. So, the specimens of LQ groups exhibited IGF to be the lowest. Following the same rule, MQ group produced IGF to be in between HQ and LQ groups. Experimental results are also very similar to that of the theoretical assumption (Fig. 4). For any embrittlement time, similar trend to result IGF is observed (Fig. 5). In this situation, if the PAG is reduced to less than 10 μm (note: to achieve higher strength steel producers are producing many commercial steels of 1-2 μm grain sizes), then the proportion of IGF will be drastically reduced, which might have no or insignificant effect on fracture stress or fracture toughness values, even after a long time of

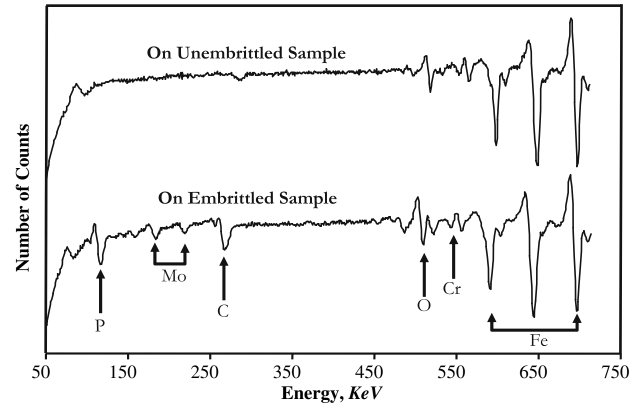

Fig. 11 Typical AES differential spectra taken from transgranular cleavage fracture of unembrittled sample and intergranular facet of embrittled sample of MQ group

exposure at TE temperature. In such case, one would get double benefits from fine grained steel; at first higher strength and second, very delayed deterioration in toughness due to TE that eventually provide longer life of steel products susceptible to TE under service.

Many investigators have mentioned that (Ref 1, 5, 17) the fracture toughness decreases with increase in the proportion of IGF. Conducting experiment on a large numbers of samples with varying amount of IGF, Islam et al. (Ref 5) showed the relationship between fracture toughness and %IGF, which has been reproduced in Fig. 13. In the present investigation, similar results are obtained (Fig. 8). The reason is that during TE impurity element segregation takes place by means diffusion, which is a slow process and time dependent. At the initial stage of embrittlement, only the favorable sites (e.g. very high-angled grain boundaries) experience sufficiently high level of segregation to cause intergranular fracture. With more TE, these grain boundaries experience more segregation causing further reduction in fracture stress. In the mean time, impurity element segregation to some other grain boundaries, which were seemed to be comparatively less favorable segregating sites during the initial stage of TE, also crosses the critical level and causes IGF. So, with TE time, the %IGF increases and it became more dominating fracture mode with subsequently more decrease in the fracture stress values (Fig. 7, 8).

Another very important observation could be made by observing Fig. 9 and 10. These figures show the rate of embrittlement in terms of percentage decrease in fracture stress values due to increase in grain size. From these figures it is evident that as the PAG size increased the rate of decrease in fracture stress also increased and this has been found true for both TE time periods. This observation reveals that coarser austenite grains becomes more susceptible to embrittlement. Very sharp secondary intergranular cracks present in Fig. 3 also support this. Considering LQ group as a reference, the percentage decrease of fracture stress value for HQT, HQTE100 and HQTE200 are, respectively, 12.47%, 17.26% and 20.83%, which are, respectively, 5.45%, 6.83% and 10.43% for MQT, MQTE100 and MQTE200 specimens (Fig. 9, 10). Hence, it is very much clear that all of the specimens austenitized at higher temperature (HQ group) showed greater decrease in fracture stress values and they are more susceptible to the embrittling treatment, although specimens from both groups (HQ and MQ) had received same type of embrittling treatment. The percentage

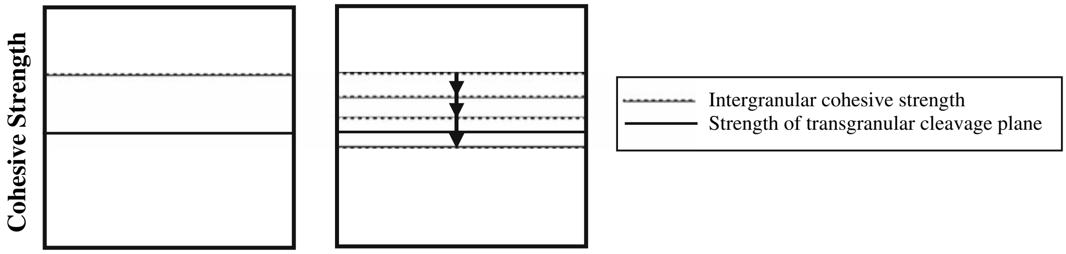

Fig. 12 Schematic diagram showing the changes in the intergranular cohesive strength with grain boundary segregation level

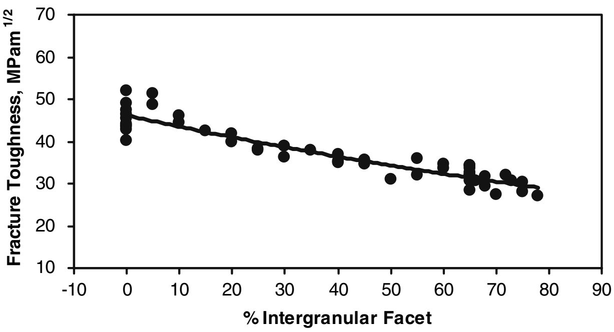

Fig. 13 Variations of fracture toughness with IGF (after Ref 5)

decrease in σ_F values for HQTE100 (embrittled at 520 °C for 100 h) is 17.26%, whereas the heavily embrittled sample of MQTE200 (embrittled at 520 °C for 200 h) showed this value to be 10.43%. So, it can be concluded that, as the PAG size increases the rate of embrittlement also increases. The reason behind this result is that specimens in HQ group have shorter grain boundary length or smaller grain boundary surface area. So, within a short TE period, most favorable grain boundaries experience critical level of segregation and cause intergranular decohesion type of fracture well before other groups.

5. Conclusions

1. Temper embrittlement changes the fracture mode from transgranular cleavage to a mixed mode of fracture and with embrittlement time intergranular fracture gradually becomes more dominating. With increase in PAG size and temper embrittlement time period, the percentage of intergranular fracture increases and the fracture stress value decreases.
2. Gradual increase in the PAG sizes also causes a gradual increase in the severity of degree of embrittlement. Coarse PAG size provides shorter grain boundary length or surface area of grains per unit volume to accommodate the segregating harmful species, which is thought to be responsible for the higher rate of embrittlement effect in this steel.
3. The harmful effect of P segregation on the toughness of the same steel could be very insignificant, even after a very long time of service in the range of embrittling temperature, if the steel is quenched from the temperature with PAG size of 10 µm or less.

Acknowledgments

The authors are greatly indebted to Bangladesh University of Engineering and Technology (BUET) for providing fund to carry out the research and also to the head of the Materials and Metallurgical Engineering Department for providing Lab facilities.

References

1. M.A. Islam, "Intergranular Fracture in 2.25Cr−1Mo Steel at Low Temperature," Ph.D. Thesis, The University of Birmingham, UK, 2001
2. M.A. Islam, P. Bowen, and J.F. Knott, Grain Boundary Fracture Processes in Quenched and Tempered Structural Steels, *Proceedings of a Workshop Held at Birmingham University, UK* (16-17 Sep., 1999), Published by 10M Communications Ltd., 1 Carlton House Terrace, London SW1Y 5DB, Year of First Publication is 2001, p 55–72
3. M.A. Islam, M. Novovic, P. Bowen, and J.F. Knott, Effect of Phosphorus Segregation on Fracture Properties of 2.25Cr−1Mo Pressure Vessel Steel, *J. Mater. Eng. Perform.*, 2003, **12**(3), p 244–248
4. K. Nishioka and J.F. Knott, *Effects of Environment on the Occurrence of Intergranular Facets During Fatigue Crack Propagation in 9Cr−*1Mo Steel, Mech. Engr. Publications, London, 1990 241–254
5. M.A. Islam, J.F. Knott, and P. Bowen, Critical Level of Intergranular Fracture to Affect the Toughness of Embrittled 2.25Cr−1Mo Steels, *J. Mater. Eng. Perform.*, October 2004, **13**(5), in press
6. M.A. Islam, P. Bowen, and J.F. Knott, Intergranular Fracture on Fatigue Fracture Surface of 2.25 Cr−1 Mo Steel at Room Temperature in Air, *J. Mater. Eng. Perform.*, 2006, **14**(1), p 28–36
7. S.A. Khan and M.A. Islam, Temper Embrittlement in Cr-Mo Low Alloy Steel, *Proceedings of SPPM2004*, Sponsored by TMS, Organized and Published by the Materials and Metallurgical Engineering Dept., Bangladesh University of Engineering and Technology, Dhaka, Bangladesh, Year of Publication 2004, p 182–192
8. J.H. Bulloch and D. Crowe, Embrittlement Observed in Cr-Mo Turbine Bolts After Service, *Theor. Appl. Fract. Mech.*, 1998, **29**, p 59–61
9. J.R. Griffiths and D.R.J. Owen, An Elastic-Plastic Stress Analysis for a Notched Bar in Plane Strain Condition, *J. Mech. Phys. Solids.*, 1971, **19**, p 419–431
10. Annual Report 2004, Steel Research Centre (SRC), National Institute for Materials Science (NIMS), Japan
11. M. Wakida, Y. Adachi, S. Shimokawa, and Y. Tomota, Ultrafine TRIP-Aided Multi-Phases Steels, *CAMP-ISIJ*, 2005, **18**, p 613
12. J. Anderson, The Influence of Grain Size Variation on Metal Fatigue, *Int. J. Fatigue*, 2005, **27**, p 847–852
13. K. Kobayashi, K. Yamaguchi, M. Hayakawa, and M. Kimura, Grain Size Effect on High-Temperature Properties of Alloy718, *Mater. Lett.*, 2005, **59**, p 383–386
14. M.A. Islam and S.A. Khan, Characterization of the Influence of Prior Austenite Grain Size on Reversible Temper Embrittlement in Cr-Mo Low Alloy Steel, *Proceedings of ICAMT2004* Held in Malaysia, 11–13 May 2004, Published by Research Centre, International Islami University Malaysia, 2004, p 1084–1091 (Also accepted for publication in the *J. Mater. Process. Technol.*, Elsevier Science Ltd)
15. S.A. Khan, Observation of Embrittlement in Cr-Mo Steels," Masters Thesis, Bangladesh University of Engineering and Technology, Dhaka, 2004
16. R. G. Faulkner, S. H. Song, and P. E. J. Flewitt, Combined Quenching and Tempering Induced Phosphorus Segregation to Grain Boundaries in 2.25Cr−1Mo Steel, *Mater. Sci. Technol.*, 1996, **12**, p 818–822
17. C. Naudin, J.M. Frund, and A. Pineau, Intergranular Fracture Stress and Phosphorus Grain Boundary Segregation of a Mn-Ni-Mo Steel, *Scripta Mater.*, 1999, **40**, p 1013–1019