DETECTION OF EMBRITTLEMENT IN Cr-Mo PRESSURE VESSEL STEELS

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Cr-Mo reactor pressure vessel steels have a potential for temper embrittlement that leads to toughness degradation and a reduction of the critical flaw size for brittle fracture. A vessel with adequate toughness when originally constructed may therefore embrittle during service and such changes result in pressure restrictions during start-up and shut-down. A survey of the literature shows composition to be the main controlling parameter for embrittlement hydrogen attack, in-particular the presence of residual impurity elements, such as P, and the presence of elements, such as Mo, which nullify the effect of impurity segregation. This paper describes a microstructural characterisation route which allows the suceptibility of Cr-Mo vessels to embrittlement to be examined.

INTRODUCTION

Low carbon, low alloy Cr -Mo ferritic steels are widely used in the petroleum refining and petrochemical industry for hydro-processing units such as hydro desulphurising and hydro-cracking reactors operating at temperatures in the range 350 to 580°C and pressures up to 28MPa(1). The most widely used material for the main walls of these vessels is 2¼Cr1Mo steel steel(2). The potential problems that can affect the performance of low alloy steels used in refinery plant are: (a) temper embrittlement, (b)hydrogen embrittlement, (c)hydrogen attack, (d)creep embrittlement and(e)loss of cladding integrity.

TEMPER EMBRITTLEMENT

Low carbon Cr -Mo steels, in particular 2¼Cr1Mo steel may be susceptible to temper embrittlement (TE). This can result in a significant increase in the fracture appearance transition temperature (FATT), a loss of toughness, and a reduction in the critical flaw size for brittle fracture(3). The phenomenon of TE in Cr-Mo steels and the effect on material properties has been reviewed by a number of authors(4,5). TE is caused by the diffusion and segregation of tramp elements to grain boundaries(6,7,8). The degree of in-service embrittlement (ie. the magnitude

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of ΔFATT) depends on the composition, starting microstructure and properties(9). Increases in the ductile to brittle transition temperature of up to 150°C have been observed(10). An example of toughness degradation in 2¼Cr1Mo steel is illustrated in Figure 1 for a hydro-desulphurisation unit after seven years of service.

The effect of microstructure on TE is not clear cut and has been reviewed by Viswanathan(14) and Moss and Kelly(11). However, there are many correlations between TE and composition(12,13). These relate the TE susceptibility to the presence of impurity elements such as P, Sn and As and have been reported as being poor for weld metals but acceptable for plate material(5). For commercial Cr-Mo steels, 2¼Cr1Mo steel in particular, the J factor correlation {J = (Mn + Si) x (P + Sn) 10^4 (wt%)} has been found to be the most satisfactory in predicting both FATT prior to service and the change in FATT as a result of service, eg. (3). Figure 2 shows the relationship between the J factor and FATT for 1¼Cr ½Mo and 2¼Cr 1Mo steel., it is evident that higher values of J lead to larger FATT, particularly for 'brittle condition' 2¼Cr 1Mo steel. Figures 3(a) and (b) show ΔFATT data from isothermal and step-cooling studies, aiming to simulate in service embrittlement, for a variety of different product forms, grain sizes and heat treatments(14). The composition of the steel, the cooling rate during the initial heat treatment and the time and temperature of any subsequent tempering or stress relieving determines the type of carbides that are present in the virgin material(15,16,17,18). With increasing tempering time or time in service iron rich cementite (Fe_3C) and chromium rich M_7C_3 tend to be replaced by the more stable, molybdenum rich M_2C(19). This change in carbide type removes Mo from solution where it would scavenge P and also increases the availability of Cr , thus altering the resistance of the alloy to TE. The toughness is therefore dependent on changes in carbide type that may occur during service(20,21).

HYDROGEN EMBRITTLEMENT AND HYDROGEN ATTACK

The stress intensity for crack propagation ($K_{I(H)}$) decreases more significantly as a result of HE than it does for TE which has significant implications for temper embrittled vessels and the situation has been reviewed by Erwin and Kerr(2). If both TE and HE are present the interaction between the two causes a further reduction of threshold stress intensity(22,23) The correlation between K_{IC}, $K_{I(H)}$ and FATT is shown schematically in Figure 4(24). At both high and low degrees of embrittlement K_{IC} and $K_{I(H)}$ approach each other while in the intermediate range of TE major interactive effects are observed.

Hydrogen attack (HA) is a decarburisation process in which dissolved hydrogen reacts with carbon to form methane bubbles which may link-up to form fissures and cracks which cause an appreciable and irreversible decrease in the mechanical strength, ductility and toughness. The effect of HA may cause blistering and crack formation(25). Tempering and PWHT have pronounced effects on susceptibility to attack and an extended heat treatment leads to more stable carbides and hence greater resistance to HA(26). The formation of stable

cabides is in contrast to a structure that is resistant to TE and HE because stable carbides lock up elements such as Mo which impede impurity segregation.

EXAMINATION OF THE EXTENT OF EMBRITTLEMENT

Clearly the most reliable way to determine the degree of TE is by carrying out mechanical testing such as impact or fracture toughness tests, the methods by which an analysis would be performed are detailed in the abundant literature (eg. 27 and 28). Unfortunately such methods require the removal of material from the component being investigated which may not be possible and so indirect methods involving non-destructive investigations must be used. The information concering embrittlement that can be derived by correlation from indirect tests is described below.

Hardness. TE normally results from prolonged service at temperatures in the range 350 to 540°C. At the lower end of this range (450°C and below) the effect on hardness of the period in service will be minimal even after 100,000 hours or more. Hence in service hardness is no real guide to the existence of temper embrittlement. However, hardness can indicate whether or not the material is in a heat treat condition that would render it susceptible to TE, eg. a low hardness, which is associated with the pre-service heat treatment rather than the period in service, may indicate that excessive tempering has been carried out and that the material will be potential susceptible to TE.

Microstructure and Chemical Analysis. The effect of 'coarse' microstructure it is relatively small and much less important than the composition of the material and hence simple microstructural examination is unlikely to be a reliable indication of TE. However, transmission electron microscopy (TEM) and X-ray analysis can identify the type(s) of carbides present in the steel(29,30) and hence permit an estimate of the possible extent of TE. Chemical analysis of the steel allows a J factor to be calculated for the particular steel. The X-ray analysis of extracted carbides, together with a chemical analysis of the supernatant electrolyte, allows the amount of Mo remaining in solution in the ferrite to be estimated and from this the extent of the potential scavenging effect for P. The latter can be determined by extracting the carbides from drillings of the material and then chemically analysing the supernatant electrolyte after the extraction is complete. X-ray diffraction patterns from the extracted carbides will indicate the types of carbide present in the material and permit a quantitative determination of the relative amounts of each type. For 2¼Cr1Mo steels there are 5 possible carbide types, M_2C, M_3C, M_6C, M_7C_3 and $M_{23}C_6$, and these can readily be distinguished by their almost unique Fe/Cr /Mo ratios, which can be readily determined using microprobe analysis. The Mo content of the carbides M_3C, M_7C_3 and $M_{23}C_6$ is relatively low and hence, if these carbides predominate in the microstructure, there will be a significant amount of Mo still left in solution in the ferrite. On the other hand, the formation of significant amounts of Mo bearing carbides will leave little Mo available to scavenge embrittling elements like P.

Example A. In this first case replicas and one gram of drillings were taken from a 2¼Cr1Mo hydro-treater vessel. Energy dispersive X-ray analysis of extraction replicas in the electron microscope revealed that the large majority of the carbides were $M_{23}C_6$ with the remainder consisting of very fine M_2C. X-ray diffraction of electrolytically extracted carbides showed lines from both the carbides $M_{23}C_6$ and M_2C, but the intensity of the lines indicated that the amount of M_2C present in the carbide mixture was no more than about 5%. Hence the carbides in the steel could be taken to consist of about 95% $M_{23}C_6$ and 5% M_2C. Because the carbon content of the steel is 0.12 wt%, the $M_{23}C_6$ should contain an amount of Mo equivalent to about 0.23 wt%, whilst the M_2C should contain the equivalent of 0.07wt%. Hence the total amount of Mo incorporated in the carbide is estimated to be 0.3 wt%, leaving 0.7 wt% in solution in the ferrite. The conclusion is that steel (A) should not be susceptible to TE.

Example B. In this case the analysis of carbides in replicas taken from a 2¼Cr1Mo vessel examined by TEM indicated that, in addition to $M_{23}C_6$, there were significant quantities of M_2C and M_7C_3. The X-ray diffraction analysis of carbides extracted from drillings showed that approximately 50% of the carbide mixture was $M_{23}C_6$, 28% was M_7C_3, 19% was M_2C, and there was a small amount (~3%) of M_6C. The carbon content of the steel was 0.13 wt% and if it is assumed that the carbon is divided between the carbides in the ratio of their relative abundance in the carbide mixture then the amounts (wt%) of Mo in each of the carbides are as follows:-

$M_{23}C_6$	M_7C_3	M_3C	M_2C	Total Mo
0.1196	0.0612	0.2766	0.0693	0.5267

This would leave only 0.4733 wt% of Mo in solution in the ferrite. Chemical analysis of the supernatant electrolyte used for the carbide extraction gave 0.517 wt% Mo - a figure which agrees extremely well with the estimate derived from the composition and relative abundance of the carbides. The relatively small amount of Mo remaining in the ferrite, coupled with the metallographic observation that the prior austenite grain boundaries were decorated with an almost continuous string of large carbides, indicated that the material would be very susceptible to TE and that if embrittlement had occurred in service it was likely to be severe.

DISCUSSION

The use of chemical analysis of the supernatant electrolyte from the carbide extraction process gives the amount of Mo in solution directly. Additional information gained by the examination of replicas by TEM and by the X-ray diffraction analysis of the extracted carbides includes:-

1. confirmation of the chemical analysis result, as the example B above illustrates.
2. confirmation that the electrolytic carbide extraction process has not dissolved any of the carbides via analysis of the carbide composition and a qualitative estimate of the relative abundance of the carbide types is an independent .
3. additional qualitative evidence about the possible degree of TE.

Suppose the steel is known to have been tempered at a relatively high temperature (eg. 700°C or higher) then, according to Baker and Nutting(18), any M_2C particles in the microstructure should be relatively coarse. Long periods of service at temperatures in the embrittlement range of 350 to 540°C, on the other hand, will result in the precipitation of the fine M_2C needles characteristic of this temperature range. Hence the presence of fine M_2C needles in the microstructure would suggest that the material has been in the temperature range likely to cause embrittlement. By estimating the amount of Mo removed from solution by the pre-service heat treatment, and also from the composition and relative abundance of the larger carbides, the susceptibility of the material to TE prior to being put into service can be determined. For example, steel B showed some relatively coarse M_2C carbides, and a small amount of M_6C, both of which are characteristic of a high temperature heat treatment (> 700°C in this case). Also present were relatively coarse particles of $M_{23}C_6$ and M_7C_3, and some very fine needles of M_2C. The $M_{23}C_6$ and M_7C_3 would also have resulted from the initial tempering treatment, since the service temperature had never been above 450-500°C, and the Baker-Nutting diagram indicates that neither of these carbides should appear below 550-600°C even after 100,000 hours. Hence it is reasonable to conclude that all of the $M_{23}C_6$, M_7C_3, M_6C and most of the M_2C (the coarser particles of M_2C) would have been present before the material went in to service. The observation of numerous fine M_2C needles, primarily in the proeutectoid ferrite, is a strong indication that the material has spent a long period of service at a relatively low temperature around 400°C - a temperature favourable for TE. The microstructural and carbide X-ray diffraction evidence therefore suggest that the material is suffering from TE. The chemical analysis of the supernatant electrolyte merely showed that the material was a candidate for TE because a considerable amount of Mo had been removed from solid solution, and was therefore not available to scavenge P, by itself chemical analysis could not determine whether or not the material was embrittled.

CONCLUSIONS

1 Embrittlement of Cr-Mo steels can occur during initial tempering, PWHT, stress relief heat treatment and during service. Large increases in the fracture appearance transition temperature (large ΔFATT) have been recorded. The consequences of such considerable reductions of fracture toughness is the need for changes in start-up and shut-down procedures to avoid catastrophic failure and subsequent economic penalties through lost production.

2 Temper embrittlement (TE) can result from the formation of Mo containing carbides. The precipitation of such carbides reduces the free Mo content in solution which would otherwise be available to scavenge embrittling impurity elements such as P. Hydrogen embrittlement (HE) can lead to a considerable further reduction of toughness beyond that of the unembrittled condition. Hydrogen attack (HA) results from the decomposition of carbides due to

temperature and the presence of hydrogen and is reduced by heat treatments which produce stable carbides.

3 A number of non-destructive microstructural characterisation processes are required in combination to indicate material susceptibility to embrittlement or HA and degree of TE. These include (1) transmission electron microscopy (TEM), (2) X-ray analysis of carbides and (3) chemical analysis of matrix and X-ray natant and carbide residues.

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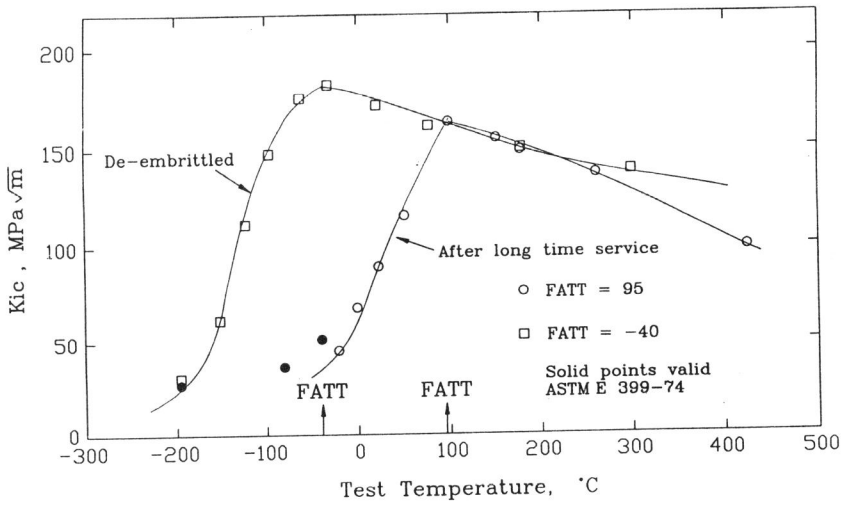

Figure 1. Effect of long term service (7 years) on the fracture toughness of a 2¼Cr1Mo steel taken from a hydro-desulphuriser unit, after Ref. (5)

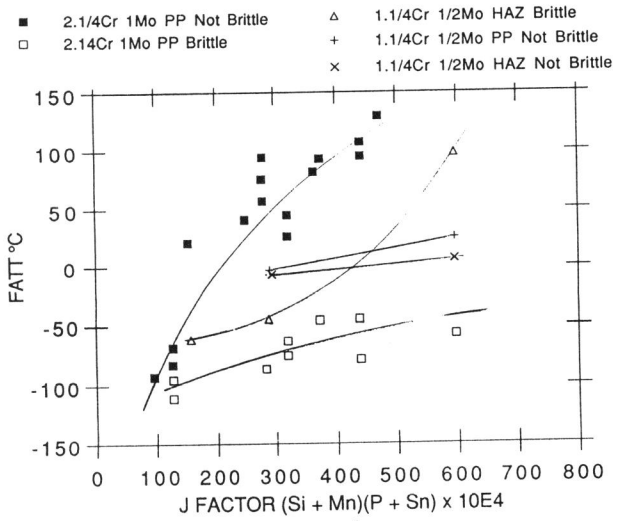

Figure 2. FATT vs J Factor for two Cr-Mo steels; after Refs. (3,13)

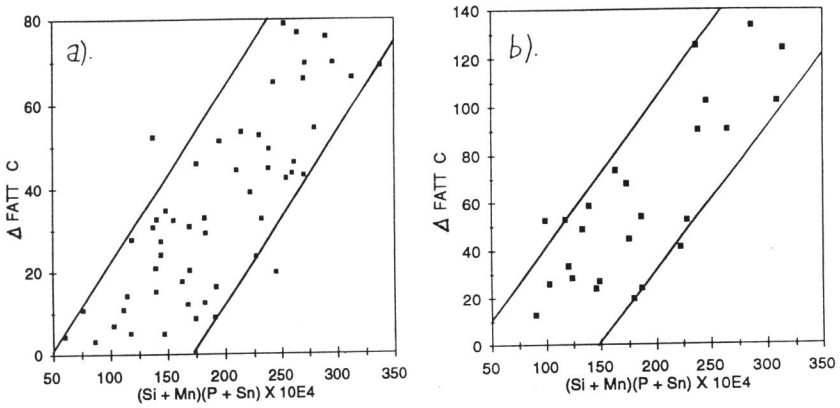

Figure 3. Correlation between ΔFATT and J Factor for a). isothermal and b). step cooling studies, after Refs. (5, 14)

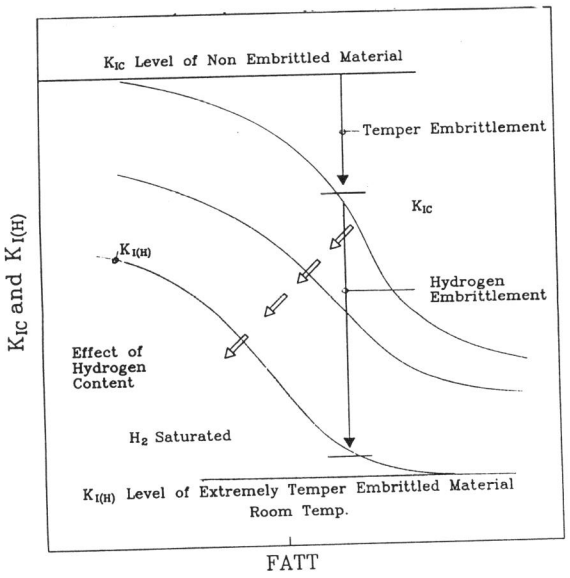

Figure 4. Schematic illustration of the correlation between K_{IC}, $K_{I(H)}$ and FATT. Taken from Ref (24)