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Effect of Phosphorus Segregation on Fracture Properties of 2.25Cr-1Mo Pressure Vessel Steel

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Phosphorus is a very common trace element that can segregate at prior austenite grain boundaries and/or carbide/matrix interfaces of low alloy steels at high temperature (e.g., order of 500 °C) and adversely affect the fracture properties. This paper investigates segregation of P during reversible temper embrittlement (96 h at 520 °C) of quenched and fully tempered 2.25Cr-1Mo steel by Auger electron spectroscopy and describes the segregation mechanism. This paper also describes the effect of P segregation on fracture resistance and fracture mode of unembrittled steels, respectively, by fracture toughness testing over a temperature range of −196 °C to 20 °C and fractography in scanning electron microscopes. During temper embrittlement phosphorus segregation has been attributed due to the mechanism of "carbide rejection". This segregation caused a reduction in fracture toughness values of the quenched and tempered steels at all test temperatures and an increase in the transition temperature. Phosphorus segregation also changed the brittle fracture micromechanism of quenched and fully tempered samples from one of transgranular cleavage to a mixed mode of fracture (transgranular cleavage and intergranular decohesion). The micromechanism of fracture at temperatures from the upper shelf, however, remained almost unchanged.

Keywords carbide rejection, cleavage, fracture toughness, intergranular decohesion, transition temperature

1. Introduction

The steel of composition 2.25Cr1-Mo-0.15C is widely used for the manufacture of large components (e.g., pressure vessel in petrochemical and power industries) due to its good combination of strength and toughness over a wide range of temperatures.[1-3] However, the fracture properties of this steel under service especially at temperatures of ~500 °C can be adversely affected by the segregation of the trace impurity elements to microstructural sites such as prior austenite grain boundaries and/or carbide/matrix interfaces.[4] In this regard, phosphorus is a very common element, which can cause an increase in the ductile/brittle transition temperature, a change in the fracture behavior, and a reduction in the fracture toughness values. This paper examines the mechanism of P segregation under the present heat treatment condition and its effect on the ductile-brittle transition temperature and fracture properties of this steel.

2. Experimental Procedures

All tests were performed on a commercial grade of 2.25Cr-1Mo steel plate of the composition given in Table 1. Single edge notch bend (SENB) test pieces of dimensions 10 × 15 × 70 mm^3 were machined and encapsulated in silica glass tubes under an inert atmosphere. All test pieces were austenitized for 2 h at 1100 °C in a furnace with a temperature control ±4 °C and were then quenched in oil. All quenched specimens were given the protective coating "Berkatekt" (Indestructible Paint Ltd., Birmingham, UK) and tempered for 2 h at 650 °C and then oil quenched (QT condition). Half of these quenched and tempered (QT) specimens were aged at 520 °C for 96 h to induce embrittlement. Specimens of this group are marked as QTE condition.

Using a Vibrophore (Roell Amsler, Berlin, Germany) fatigue precracks were grown at room temperature according to BS7448[5] at a constant R ratio (where R is defined as P_{min}/P_{max}) of 0.1. The specimens were in their final heat treated and machined condition. Using three point bending, fracture toughness testing of the precracked specimens was carried out at different temperatures using a 200 kN capacity servo controlled universal testing machine (ESH Testing, Ltd., Brierly Hill, UK) at a nominal stress intensity factor rate of ~100 MPa $\sqrt{m}$/minute under displacement control. For all heat treatment conditions, fracture toughness test was carried out from room temperature to liquid nitrogen temperature (−196 °C). The fracture surfaces of all samples were examined in a JEOL 6300 (JEOL USA, Inc., Peabody, MA) scanning electron microscope (SEM) and photographed.

Using the broken fracture toughness samples, cylindrical specimens with a central notch (Fig. 1) were prepared for Auger electron spectroscopy (AES) to analyze segregated elements at grain boundaries. For this, specimens were cooled by liquid nitrogen and fractured by hammering in the chamber under high vacuum. Immediately after fracture, analysis was carried out as quickly as possible to avoid possible contamination in the vacuum.

3. Results and Discussion

3.1. Fractography and AES Analysis

From Fig. 2, it is clear that 96 h embrittlement changed the brittle fracture mode of the quenched and tempered specimens

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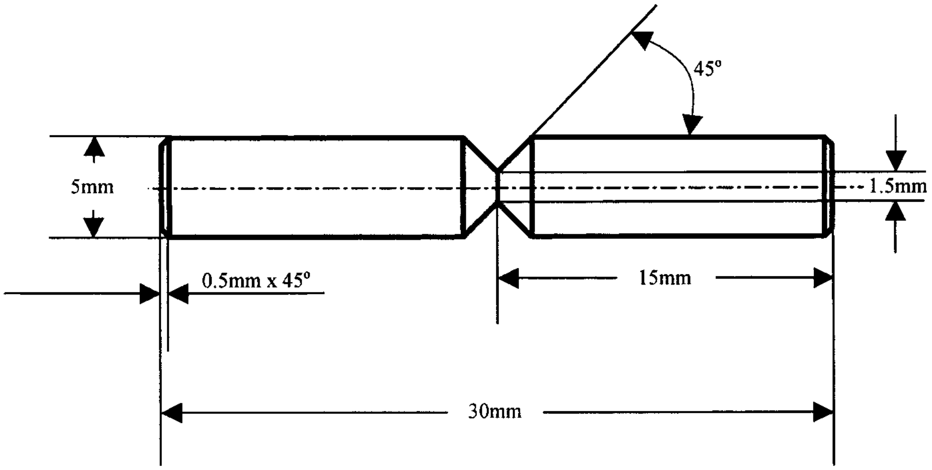

Fig. 1 AES specimen geometry

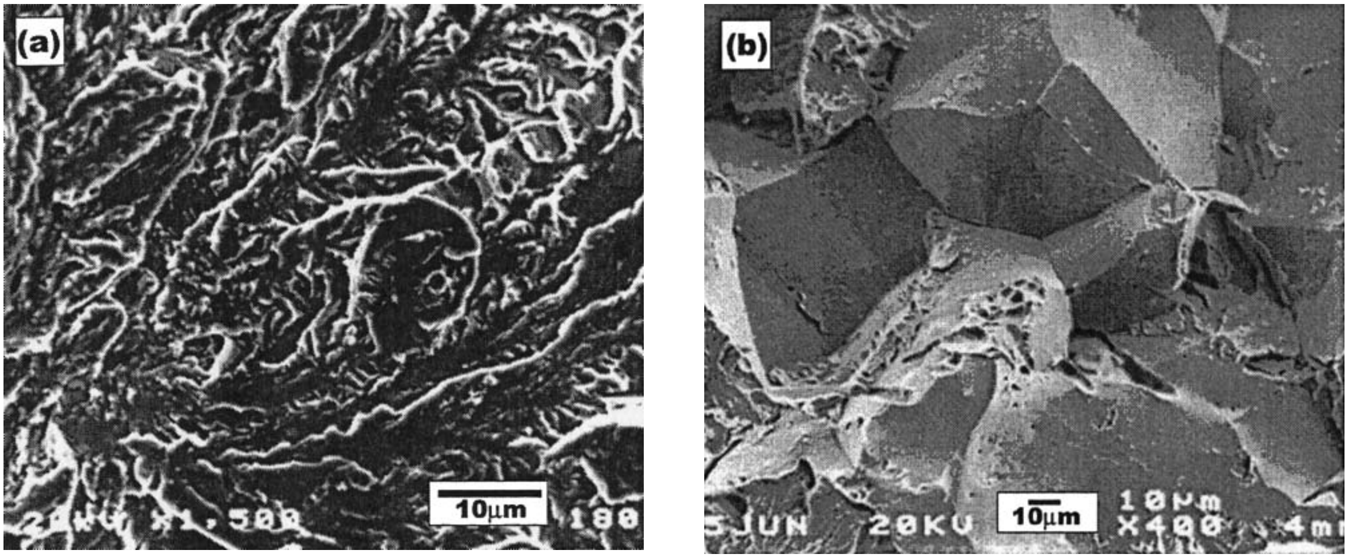

Fig. 2 SEM showing the brittle fracture modes of **(a)** quenched and tempered condition and **(b)** quenched, tempered, and embrittled condition

Table 1 Chemical Composition (in wt.%) of the 2.25Cr-1Mo Steel

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

from transgranular cleavage to intergranular decohesion. As can be seen from the AES spectra in Fig. 3 the intergranular facet of embrittled specimens clearly exhibited P peak whereas it is absent on transgranular cleavage facets of the quenched and tempered specimens. Embrittlement treatment did not change any significant parameter (e.g., hardness, yield stress, ultimate tensile strength) except the impurity element (here P) segregation level at grain boundaries.[6] So, the change in the brittle fracture mode from transgranular cleavage to mixed mode of fracture (transgranular cleavage and intergranular decohesion) is due to this P segregation.

3.2. Mechanism of Phosphorus Segregation

In the as-quenched steel, most of the alloying elements and impurity elements remain dissolved in the matrix. The interaction energy between phosphorus and Mo with respect to solvent iron is very high. As a result, the role of Mo in this steel is to scavenge P atoms and tie them up within grains in the form of Mo-P clusters (Fig. 4a). However, Mo is a strong carbide former.[7] If dissolved Mo is allowed to precipitate as carbide, it will not be available to scavenge P.

It is well documented that quenched steel is always tem-

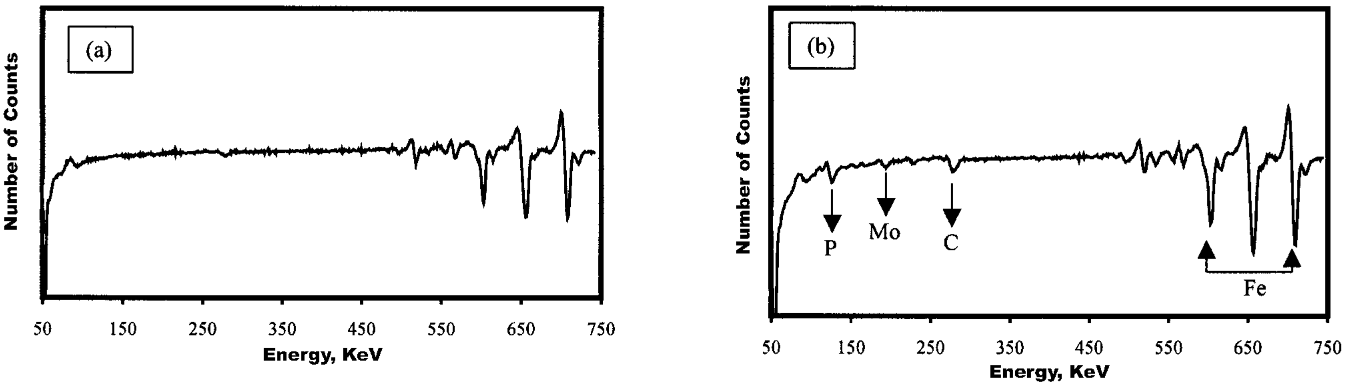

Fig. 3 Auger electron spectra on **(a)** transgranular cleavage facet of quenched and tempered specimen and **(b)** intergranular facet of quenched, tempered, and embrittled specimen

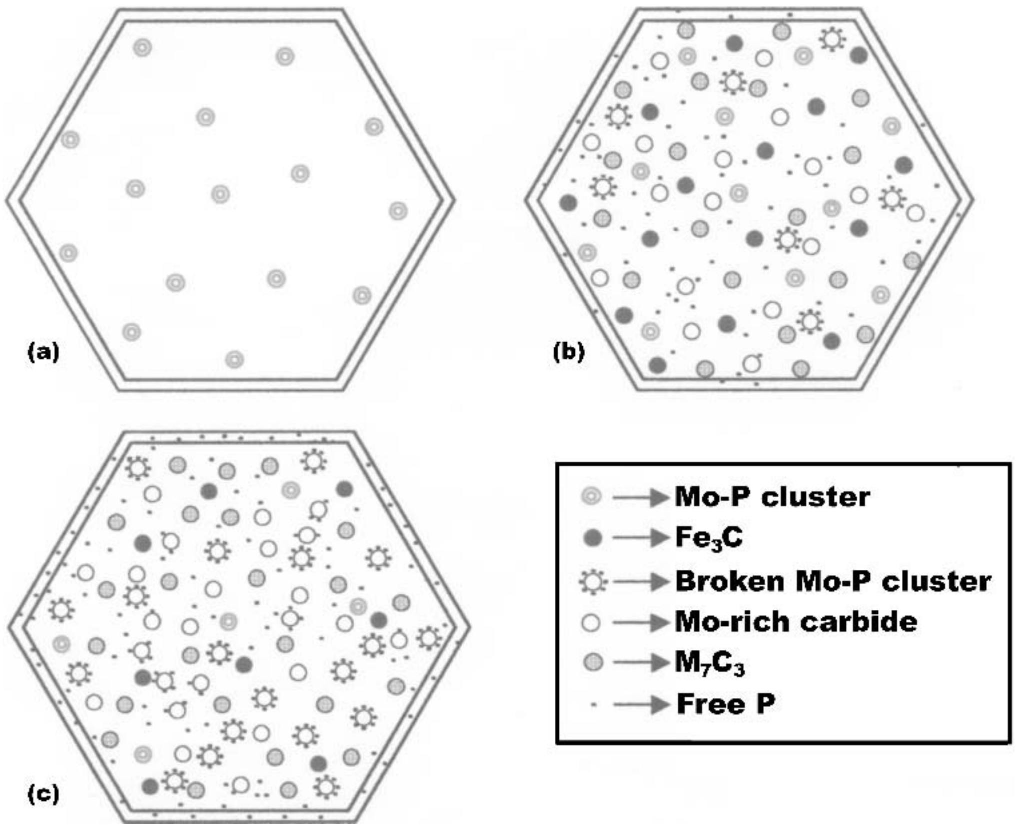

Fig. 4 Schematic representation showing the kinetics of P segregation under different heat treatment conditions **(a)** as-quenched, **(b)** QT, and **(c)** QTE conditions

pered to reduce internal stress and to achieve a good combination of mechanical properties. During tempering of this 2.25Cr-1Mo steel, different types of alloy carbides are formed depending on the tempering temperature and time. In this investigation, for unembrittled condition (QT), specimens were quenched after austenitizing at 1100 °C for 2 h and were then tempered at 650 °C for 2 h. The possible carbides present in this heat treatment condition are M_3C, M_2C, and M_7C_3, which are respectively iron, chromium, and molybdenum enriched carbides.[8-10] With formation of Mo-rich carbides (M_2C), P atoms become released in the matrix by splitting-up of Mo-P clusters. These released P atoms do not segregate at grain boundaries selectively, because above 600 °C there is no thermodynamic (strain energy) driving force for P atoms to migrate preferentially to grain boundaries. In this situation, released P atoms remain randomly distributed both at grain boundaries and within grains (Fig. 4b). Although some of the released phosphorus atoms may stay at grain boundaries due to their random distribution, they cannot reduce the intergranular-work-of-fracture below the transgranular cleavage-work-of-fracture. So, the brittle fracture mode of unembrittled steel is transgranular cleavage.

When these unembrittled (quenched and fully tempered condition) specimens are exposed at temperatures of ~500 °C the materials experience the following effects:

1) P atoms, released during tempering at 650 °C due to formation of Mo-rich carbides, tend to migrate to grain boundaries due to differences between strain energies of grains and grain boundaries.
2) A gradual replacement of M_3C by M_2C takes place and more P atoms get released in the matrix as a result of carbide rejection.[1,11,12] With aging time, the released P atoms also migrate to grain boundaries (Fig. 4c).

So, with aging time the grain boundary P coverage increases. The segregation of P atoms at grain boundaries decreases the intergranular cohesive strength and changes the fracture mode from typical transgranular cleavage to intergranular decohesion.

3.3. Fracture Toughness Values

The fracture toughness values obtained for both heat treatment conditions has been plotted as a function of test temperatures in Fig. 5. From this figure, it is evident that 96 h exposure at 520 °C decreased the fracture toughness values of quenched and tempered steels at all test temperatures. The brittle fracture mode of unembrittled ferritic steel is transgranular cleavage, because intergranular cohesive strength of this condition is higher than the strength of the cleavage plane. When this unembrittled steel was exposed at 520 °C, P segregation took place that reduced the intergranular cohesive strength. After 96 h of exposure the segregation level of some grain boundaries was so that it caused the intergranular cohesive strength lower than the cleavage strength. Therefore, the brittle fracture of these grain boundaries followed the intergranular path rather than the cleavage plane and thus the fracture mode was changed from transgranular cleavage to intergranular decohesion. The grain boundaries, where the P segregation level could not change intergranular cohesive strength below the cleavage strength level, failed by transgranular cleavage manner, because the cleavage plane was still weaker than the segregated grain boundaries. Consequently, the brittle fracture mode of embrittled steels became mixed. The grain boundary cohesive strength controls the fracture toughness of embrittled steels. As a result, embrittled steels exhibited lower fracture toughness values in the lower shelf region (Fig. 5).

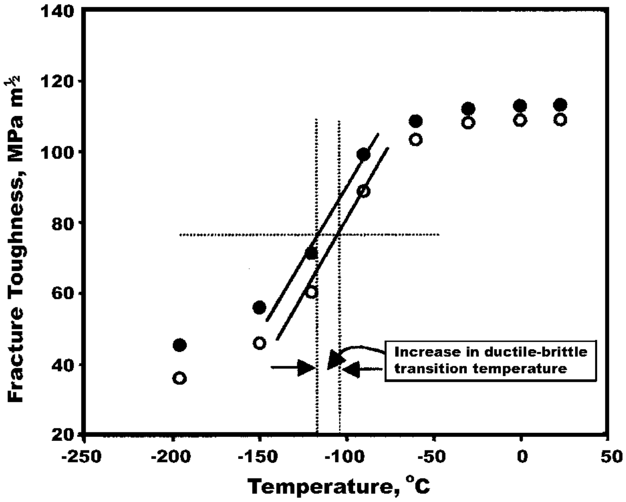

Fig. 5 Fracture toughness as a function of test temperatures. Note: Filled and empty circles denote the fracture toughness values of QT and QTE specimens, respectively.

In the upper shelf region, the fracture mode is ductile microvoid coalescence for both heat treatment conditions. Even

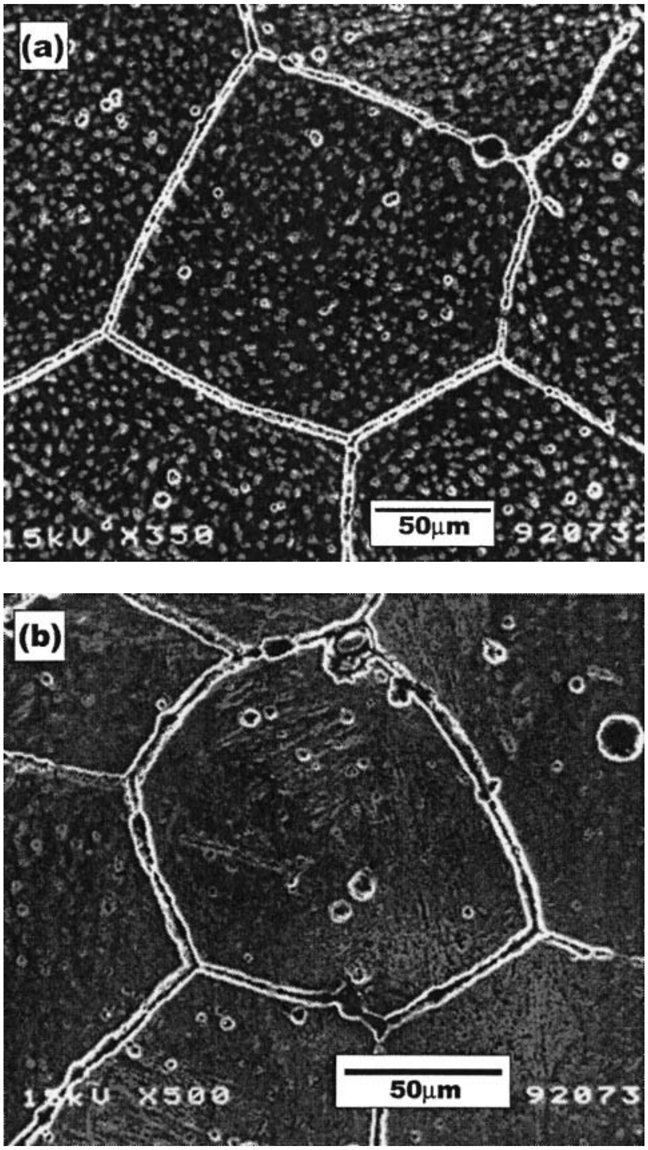

Fig. 6 SEM micrographs on polished and etched steels: **(a)** QTE condition and **(b)** QT condition. Note: Significant corrosion attack (grooving) at both grain boundaries and carbide/matrix interfaces is observed for etched QTE specimens, whereas carbide matrix interfaces of QT specimen are almost unaffected even though the etching time for this condition was double that for QTE condition.

though, the fracture mode is the same, the embrittled condition exhibited slightly lower fracture toughness than that for the unembrittled condition. The reason is that embrittling heat treatment allows trace impurity elements to segregate not only to grain boundaries but also to carbide/matrix interfaces.[13,14] The evidence is clear from the corrosion attack at both grain boundaries and carbide/matrix interfaces for QTE specimen during etching in saturated picric acid solution, whereas the carbide matrix interfaces of QT specimen is almost unaffected (Fig. 6). This type of segregation weakens carbide/matrix bonding and enables the interfaces to fail at lower strains. For ductile microvoid coalescence type failure, the fracture usually initiates from relatively coarse inclusions, but the final failure is controlled by closely spaced carbide particles. So, the embrittled specimens also showed lower fracture toughness values in the upper shelf region compared with that of the unembrittled specimens due to relatively weaker P segregated carbide/matrix interfaces.

4. Conclusions

- Exposure of quenched and fully tempered 2.25Cr-1Mo steel at 520 °C for 96 h changed the brittle fracture mode of the steel from transgranular cleavage to intergranular decohesion, and increased the ductile-brittle transition temperature of the unembrittled specimen by ~20 °C.
- Auger electron spectroscopy confirmed P to be segregated at grain boundaries due to exposure of quenched and fully tempered 2.25Cr-1Mo steels at 520 °C P. This has been found to be the basic cause for the observed change in fracture mode and decrease in the fracture toughness values.
- Experimental results suggest that P segregation took place during aging and plausibly by carbide rejection.

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