1. Introduction

Ni–Cr–Mo–V steels are known for their high hardenability, strength and toughness properties and are widely used for manufacturing of various armaments, turbine rotors and several heavy-duty components. The manufacturing processes, alloying technology, and heat treatment are the prime governing factors for the development of suitable microstructures, which can impart desired combination of high strength and good toughness properties in these steels. Quenching and tempering are well-established means to strengthen these steels, which are achieved mainly due to precipitation of fine alloy carbides during tempering. The highest strength level in alloy steels of this type can be obtained by martensite structure in untempered condition; this structure, however, is rarely used in direct applications due to its associated high internal stresses developed during the martensitic transformation, which severely impairs ductility and toughness of the material. The process of tempering is able to considerably reduce these stresses without changing the basic features of the martensitic structure.

V-added AISI 4335 steel is one of the commercial grades of alloy steels under this category, which is able to provide desired combinations of strength, ductility and toughness for use in several applications. But one of the limitations of this steel is its embrittlement, which occurs during tempering in certain temperature ranges. Studies on the microstructure and the mechanical properties of V-added AISI 4335 steel subjected to different tempering conditions are, therefore, essential to avoid embrittlement in this steel. Numerous investigations have been carried out to understand the effect of microstructure on the temper embrittlement phenomena. There exists a series of attempts to detect the temper embrittlement regime of these alloy steels using variation of impact toughness with tempering temperature. Current design concepts necessitate database on fracture toughness for this engineering component, however, literature related to temper embrittlement phenomenon with respect to the variation of fracture toughness with tempering temperature do not exist to the best knowledge of the authors. An attempt has been made, therefore, in this investigation to make a comparative assessment on the temper embrittlement phenomenon of a V-added AISI 4335 steel as determined by its fracture toughness and impact toughness in a wide range of tempering temperatures.

2. Experimental

2.1. Material

A V-added AISI 4335 steel was obtained as courtesy of Metal and Steel Factory, Ishapure, India. The chemical composition of the steel has been reported in Table 1. The steel was produced in an electric arc furnace and was sub-

The structure–property relations of V-added AISI 4335 steel forgings tempered at different temperatures have been examined to delineate the effect of tempering on their ductility and toughness characteristics. The experimental work involved characterization of the microstructures and determination of hardness, tensile properties, impact toughness and plane strain fracture toughness of a series of hardened and tempered samples. The tempering treatments were carried out at eight different temperatures in the range of 633–833 K. The obtained results have shown that hardness and strength decrease in a monotonic fashion with tempering temperature while impact toughness and ductility increase with increasing tempering temperature with an inflection around 753 K. Analyses of the results highlight that the variations of impact toughness and ductility with tempering temperature possess the potential to directly reveal the embrittlement temperature range. It has been also found here that the embrittlement temperature range can be delineated from the variation in the rate of change of fracture toughness with tempering temperature. These observations have been discussed considering the energy absorbed by the initiation and growth of cracks during fracture of a specimen by tensile, impact and fracture toughness tests.

KEY WORDS: temper embrittlement; impact toughness; fracture toughness; tensile properties; AISI 4335 steel; martensite.

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jected to secondary refining in a ladle furnace having vacuum degassing facility, followed by pouring into ingot moulds of approximately 400 mm inner diameter. Next, the steel was subjected to electro-slag re-melting (ESR) and was solidified in the form of a cylindrical ingot of approximately 650 mm diameter. The ESR slug (i.e. the ingot produced after ESR) was subjected to diffusion annealing for homogenization and anti-flaking treatment in the temperature range of 593–1 123 K for 170–180 h prior to forging. The forging was done at 1 423 K with forge-finish temperature of 1 123 K followed by controlled cooling to ambient temperature. These forgings were first machined to hollow cylinders with outer and inner diameters of 270 and 105 mm, respectively. Specimen blanks of approximately 100 mm thick were cut from the end of the machined hollow cylindrical forgings using a circular band saw. Eight blanks of this type were subjected to heat treatment for preparation of suitable specimens for different studies.

2.2. Heat Treatment

The as-received specimen blanks were subjected to heat treatment, which consisted of homogenizing, hardening and tempering in the sequence as shown in Fig. 1. Homogenization of the specimen blanks was carried out at 1 173 K for 6 h followed by air cooling. Hardening treatment was done by heating the homogenized specimens to 1 143 K, soaking at that temperature for 6 h followed by water (kept for 5 min) and then oil quenching (kept at ambient temperature of 300 K for 90 min). The hardened blanks were tempered at eight different temperatures of 633, 673, 713, 753, 773, 793, 813 and 833 K for 6 h duration followed by water quenching. Specimens for various tests were cut from heat treated blanks using computerized numerically controlled (CNC) machine while the notches for the specimens used for fracture toughness tests were cut by an electrical discharge machine (EDM) operated using wire.

2.3. Inclusion Characterization

Hardened samples of dimension 10×10×20 mm³ were used for inclusion characterization. The samples were ground and polished up to 0.25 µm finish using diamond paste to reveal the inclusions. Optical photographs of several inclusions were compared with standard inclusion charts to evaluate the inclusion rating as per ASTM Standard E45. The volume fraction of the inclusions was determined by the point counting technique as per Japanese Industrial Standards JIS 0555 using 20×20 grid at a magnification of ×400 on 60 fields of observations. Chemical compositions of the inclusions were determined using EDX analysis (attached to SEM) on several inclusions observed on fracture surfaces of specimens, as shown in Fig. 2.

2.4. Microstructural Characterization

Samples, ground and polished as described earlier, were etched with 2% nital to reveal the microstructure. The microstructures of the specimens were examined using both optical and scanning electron microscopes. A typical microstructure is shown in Fig. 3.
2.5. Conventional Mechanical Tests

Hardness values of the hardened and tempered samples were measured by a Brinell Hardness Tester using a load of 29.4 kN (3 000 kgf) following ASTM Standard E 10.11) Tensile tests were done using cylindrical specimens of 10 mm diameter and 50 mm gauge length with a Universal Testing Machine as per ASTM Standard E 8M-04.12) These tests were done with a strain rate of $3 \times 10^{-3}$ s$^{-1}$ at room temperature of 298 K. Impact tests were carried out at 293 K and at 223 K using standard Charpy V-notched specimens following ASTM Standard E 23.13)

2.6. Determination of Fracture Toughness

Fracture toughness tests were carried out using 25 mm thick Compact tension, C(T), specimens with C-R orientation having dimensions and orientation nomenclature as per the ASTM standard E 399.14) The machined specimens were first subjected to fatigue pre-cracking to obtain initial crack length ($a$) corresponding to $a/W = 0.5$ prior to fracture toughness tests, where $W$ (= 50 mm) is the width of the specimen. Pre-cracking was carried out at a stress ratio of $R = 0.1$ using a frequency of 3 Hz, with maximum and minimum loads of 66 and 6.6 kN respectively. These loads were reduced in three steps and in the final step the maximum and minimum loads for each cycle were 33 and 3.3 kN respectively. Fracture toughness tests were carried out using a crosshead velocity of 0.003 mm/s at room temperature. A clip gauge (with a travel of 10 mm) was attached to the mouth of the specimen to monitor the crack mouth opening displacement (CMOD) during the fracture toughness tests. The load vs. CMOD plot for each specimen was recorded for subsequent analysis to estimate their fracture toughness values. The lengths of the machined and the fatigue pre-cracked regions were measured (using three point method) on fracture surfaces of the broken C(T) specimens after the tests. The configuration of a typical pre-cracked C(T) specimen and its fracture surfaces after breaking are shown in Fig. 4. The details of specimen dimensions, initial crack length and maximum load encountered for each test are reported in Table 2. The fatigue pre-cracking and the fracture toughness tests were done using a servo hydraulic INSTRON Machine (1343 series) of ±250 kN load capacity.

3. Results and Discussion

The selected steel was found to contain 0.019 vol% inclusion and its inclusion rating as per ASTM standard E 459) indicated only type A (sulphide) of thin-0.5 and type D (oxide) of thin-1.0 sizes. The effect of tempering temperature on the evolution of different microstructures and their mechanical properties are discussed, hereafter, in separate sub sections.

3.1. Effect of Tempering Temperature on Microstructural Changes

The observed microstructures of the differently heat treated specimens are almost similar in nature. A typical scanning electron micrograph of a tempered (at 833 K) sample is shown in Fig. 3. The microstructure shows plate (lenticular) type$^{15–17}$ martensite. Careful observations indicate that the inter-plate boundaries of the tempered microstructures were relatively deeply etched compared to that of the quenched specimen; this might be attributed to the precipitation of various carbides at the inter-plate boundaries during tempering, such as $\varepsilon, \eta$-carbide, as well as cementite.

3.2. Effect of Tempering Temperature on Hardness and Tensile Properties

The mechanical properties such as hardness, yield strength (YS), tensile strength (TS), reduction of area and elongation have been measured as a function of tempering temperature and the results are summarized in Fig. 5. The results in Fig. 5(a) show that hardness decreases monotonously with increasing tempering temperature, similar to the observations of Lee et al.$^{13}$ and Leskovsek et al.$^{19}$ for AISI 4340 steel and H11 tool steel respectively. The varia-
tions of TS and YS with tempering temperature in Fig. 5(b) indicate that these properties also decrease with the increase in tempering temperature, analogous to the results of Salemi and Zadeh.\textsuperscript{20} It is noticed, however, that the difference in the magnitudes of TS and YS initially increases with increasing tempering temperature, followed by gradual decrease, indicating the maximum in the range of 713 K and 753 K. Considering the difference between TS and YS as extent of work hardening, one can infer that increasing the tempering temperature results in lower work hardening capacity. This can be explained by following Salemi et al.\textsuperscript{20} who pointed out the effect of tempering on the dislocation density; the higher the tempering temperature, the lower is the dislocation density, and hence lower is the extent of work hardening. The variations of %elongation and %reduction in area with tempering temperature are illustrated in Fig. 5(c). This figure shows that both %elongation and %reduction in area increase continuously beyond the tempering temperature of 753 K. But a trend of decrease in %elongation and %reduction in area is observed near 673 K and 753 K. The hardness and tensile behaviour of the investigated V-added AISI 4335 steel are thus found to be similar with the conventional tempering behaviour of quenched steels.\textsuperscript{15,18}

3.3. Effect of Tempering Temperature on Impact Toughness

The results of impact toughness tests conducted at 293 K and 223 K are depicted as variation of impact toughness vs. tempering temperature in Fig. 6. The results in Fig. 6 indicate that impact energy (both at 293 K and 223 K) initially increases with increasing tempering temperature, followed by gradual decrease, indicating the maximum in the range of 713 K and 753 K. The observed drop in impact energy at 753 K is attributed to temper embrittlement phenomenon. Temper embrittlement is known to take place in commercial alloy steels which contain tramp or impurity elements.\textsuperscript{18,21,22} This phenomenon is usually attributed to the result of segregation of tramp elements like P, As, Sb, Sn, at grain boundaries, when tempered in the range of 723–873 K and is often referred as two stage temper embrittlement\textsuperscript{5} or reversible temper embrittlement.\textsuperscript{21} This phenomenon results in lower cohesive strength of the grain boundaries with subsequent degradation of impact toughness.

3.4. Effect of Tempering Temperature on Fracture Toughness

The equivalent fracture toughness values ($K_{IC}$) of the specimens have been calculated using the standard expression (equation A4.1 of reference 14) given in ASTM E 399-05.\textsuperscript{14} Using the estimated $K_{IC}$ values and the yield strength values of the steel, heat treated at different conditions, the critical thickness\textsuperscript{14} required for plane strain fracture toughness ($K_{f}$) have been estimated and are shown in Table 2. It is noted that except for the steel tempered at 833 K, all the estimated $K_{IC}$ values can be considered as $K_{f}$. The results obtained from fracture toughness tests of the differently heat treated specimens of the investigated steel are depicted in Fig. 7. The results in Fig. 7 indicate that fracture toughness increases continuously with increase in tempering temperature without revealing any temper embrittle-
ment regime like the variation of impact toughness with tempering temperature as shown in Fig. 6. However, it is interesting to note that the temper embrittled zone corresponding to that in Fig. 6 can be delineated from the variation in the temperature-derivative of fracture toughness \([d(K_{IC})/dT] \) vs. tempering temperature \([T_T]\), as illustrated in Fig. 7. The curve of \([d(K_{IC})/dT] \) vs. \([T_T]\) indicates distinct transition exhibiting a peak in the temperature range of 723 to 823 K. One may note that the peak position of \([d(K_{IC})/dT] \) vs. \([T_T]\) is at \(\approx 773 \) K while the minimum observed in the impact toughness vs. temperature was at \(\approx 753 \) K. These results thus assist to infer that while impact toughness directly indicates the most severe embrittlement temperature, variation of temperature-derivative of fracture toughness with tempering temperature can highlight the temper embrittlement in an indirect manner.

The best combination of properties i.e. hardness, strength and specifically toughness for the selected steel is obtained by tempering at and above 823 K. At 833 K, the combination of mechanical properties obtained is as follows. Hardness: 410 BHN, yield strength: 1 310 MPa, tensile strength: 1 383 MPa, impact toughness: 43 J/cm\(^2\) (at room temperature), and 40 J/cm\(^2\) (at 223 K) and fracture toughness: 133.8 MPa\(\cdot\)m. These properties are best suited for heavy-duty service applications. Hence, tempering temperature at or just above 823 K is recommended to avoid any type of temper embrittlement in order to achieve better combination of mechanical properties.

3.5. Effect of Tempering Temperature on Fracture Behaviour

Scanning electron micrographs of the fracture surfaces of the broken impact specimens, heat treated at different tempering temperatures, have been examined to understand the fracture behaviour of the selected steel as a function of tempering temperature. Typical SEM images are shown in Fig. 8. The fracture surface of the as-quenched sample exhibits primarily quasi-cleavage features with a few microvoids and intergranular facets as shown in Fig. 8(a). The fracture surfaces of specimens tempered at 633, 673 and 713 K exhibit similar features like that shown in Fig. 8(a), but with minor variations in the number of voids or intergranular facets. The fractograph of the sample tempered at 753 K is illustrated in Fig. 8(b), specifically to reveal any possible difference in the fracture features at the temper embrittled regime. Figure 8(b) exhibits significantly larger amount of intergranular facets apart from quasi-cleavage domains and is mixed with a few voids. Fracture features of quenched sample and those of tempered samples up to tempering temperature of 753 K are similar in nature but with variation in their amounts. In addition the fracture surfaces of the samples tempered at 753 K are found to contain distinct secondary cracks (Fig. 9). The samples tempered at \(\approx 793 \) K exhibit primarily dimple fracture, with dimple sizes varying with the tempering temperature. A typical fracture surface of a specimen tempered at 833 K is shown in Fig. 8(c). The observed variation of the dimple size with increasing tempering temperature has not been quantitatively examined but the observations are in accordance with a few earlier reports. It is well established that the void nucleation in steel primarily occurs either by fracture of particle or by decohesion of particle–matrix interface. With increase in tempering temperature, the precipitated fine carbide particles coalesce and grow in size. This reduces the microvoid initiation sites, causing effective increase in their inter-particle spacing, and as a consequence results in the increase in the dimple size.

The nature of variation of impact toughness and fracture
toughness with tempering temperature can be corroborated to a significant extent with the fractographic features shown in Fig. 8. It may be noted from Fig. 6 and Fig. 7 that the sharp drop in impact toughness occurs at 753 K while the fracture toughness derivative with tempering temperature indicates the peak at 773 K. The initiation of the drop in impact toughness occurs at 713 K while the initiation of the upward trend for the peak in the fracture toughness derivative plot occurs at around 730 K. On the other hand, the regime beyond the peak of fracture toughness derivative plot and that beyond the trough of the impact toughness plot are both at 813 K. Thus the nature of impact toughness and that of the fracture toughness derivative plot with tempering temperature appear to provide identical information about the tempered embrittled regime for the selected steels within the present results.

The fractographs in Figs. 8(a), 8(b) and 8(c) depict fracture features corresponding to “prior embrittlement regime (as quenched),” “embrittlement regime (at 753 K)” and “post embrittlement regime (at 833 K)” respectively. In the tempered embrittled regime, initiation of cracking primarily occurs through grain boundaries and one finds its evidence in Fig. 8(b) through larger amount of cleavage facets and secondary cracks. At the post embrittled regime, initiation of cracks occurs both at grain boundaries as well as at carbide particles; but these initiated cracks get the opportunity to grow and coalesce leading to formation of dimples, as has been observed in Fig. 8(c). The as-quenched structure having the high internal stresses results in quasi-cleavage fracture showing only a few dimples of smaller sizes. It is thus interesting to note even from qualitative assessment of the fractographs that their associated features illustrate the inherent fracture micro-mechanism corresponding to the embrittled and its prior and post states in a distinguished way. It would be interesting to direct investigations for the correlation of quantitative fractographic parameters with the variation of toughness around the temper embrittled regime.

The V content of the steel influences the microstructure through the precipitation of vanadium carbide above 773 K. This carbide-precipitation occurs at post embrittled regime and the precipitation occurs throughout the microstructure without any specific preference for grain boundary precipitation. Since the precipitation occurs beyond the temper embrittled zone, these assists to initiate void formation and subsequently facilitates growth and coalescence of the voids to lead to dimple fracture. The precipitation of vanadium carbide is necessarily associated with carbon depletion of the matrix which further assists the growth of the micro-voids.

4. Conclusions

Microstructural features, hardness, tensile properties, impact toughness, fracture toughness and fracture behaviour of a V-added AISI 4335 steel have been investigated as a function of tempering temperature in order to achieve the suitable heat treatment for engineering applications with respect to their fracture toughness. It is observed that hardness and strength decrease whereas fracture toughness increases with increase in tempering temperature. Ductility gradually increases with increasing tempering temperature exhibiting slight drops near 673 K and 753 K. Impact toughness increases with increasing tempering temperature showing sharp decrease near 753 K, which is attributed to the temper embrittlement phenomenon. The variation of fracture toughness with tempering temperature does not directly indicate the temper embrittlement phenomenon, as depicted by the impact toughness vs. temperature plot. However, it has been shown for the first time that the rate of variation of fracture toughness with tempering temperature (i.e. temperature-derivative of fracture toughness) assists to reveal the temper embrittled zone. The present results indicate that the best combination of hardness, strength and toughness for the selected steel would be achieved only when the steel is tempered above 833 K.

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