Original Article

Effect of delta ferrites on the anisotropy of impact toughness in martensitic heat-resistant steel

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ABSTRACT

To avoid brittle failure of the final-stage turbine blades, it is necessary to understand the anisotropy mechanism in martensitic heat-resistant steel 10Cr12Ni3Mo2VN. This study focused on the effect of delta ferrites on the anisotropy of impact toughness by investigating the relationship between the microstructures and the anisotropy of impact toughness. It was mainly interested in the effect of banded delta ferrites on the transverse impact toughness of experimental steel after quenching and tempering. It was found that banded delta ferrites cause banded brittle cracks and induce tempered martensite matrix to fracture in quasi-cleavage mode, which leads to the embrittlement in transverse specimens and the anisotropy of impact toughness. The embrittlement caused by banded delta ferrites is unrelated to other precipitates such as M23C6-type carbides or MX-type precipitates. In addition, by removing the banded delta ferrites, it can eliminate the anisotropy of impact toughness in the experimental steel. It was also found that conventional heat treatment could not improve the isotropy of impact toughness since it has little influence on the content of banded delta ferrites. As suggested, the use of upsetting-stretching forging strategy promises a great of improvement of isotropy of impact toughness as it can remarkably reduce the amount of banded delta ferrites.

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1. Introduction

The final-stage turbine blade is one of the most significant sectors in the ultra-super critical power units. Due to its high strength and excellent performance in resistance to brittle failure and corrosion, the 9–12%Cr martensitic heat-resistant steel has been widely used as a final-stage turbine blade material [1–4]. However, martensitic heat-resistant steels are susceptible to embrittlement by various causes, such as temper embrittlement and aging embrittlement. To avoid brittle failure of turbine blades, there is a strong demand for understanding the fracture toughness in martensitic heat-resistant steels [5,6]. Besides, high isotropy of mechanical properties is also required to martensitic heat-resistant steels used for large final-stage turbine blades of ultra-super critical power units.
The purpose of this study was to understand the anisotropy mechanism of mechanical properties in martensitic heat-resistant steels. In this paper, the anisotropy of impact toughness of 10Cr12Ni3Mo2VN steel was investigated. This steel is a typical martensitic heat-resistant steel that is used for making the final-stage turbine blades. But it exhibits serious anisotropy of mechanical properties. The transverse impact toughness is always lower than the longitudinal impact toughness in forging bars after a heat treatment. According to a preliminary investigation, it was found that the anisotropy of impact toughness in 10Cr12Ni3Mo2VN steel can be related to the content of banded delta ferrites. Therefore, the effect of delta ferrites on the anisotropy of impact toughness is the major focus in this study.

2. Experimental materials and methods

2.1. Sample preparation

The investigated 10Cr12Ni3Mo2VN steels Nos.1-4 were cut from experimental forging bars, which were produced by different forging processes (as shown in Fig. 1) from electro slag remelting ingots. Their chemical compositions include: C 0.09, Si 0.20, Mn 0.82, P 0.011, S 0.002, Cr 11.82, Ni 2.60, V 0.34, Mo 1.75, N 0.033, and Fe balance (in mass percentage). Steel sample preparation was followed as: (1) the sample Steel No.1 was prepared by stretching; (2) the sample Steel No.2 was prepared by upsetting-stretching; (3) the sample Steel No.3 was prepared by upsetting-stretching and stretching; and (4) the sample Steel No.4 was prepared by thrice upsetting-stretching and stretching. To investigate the anisotropic properties, specimens were machined from forging bars in longitudinal and transverse directions, as shown in Fig. 2. All specimens underwent quenching and tempering processes prior to any tests. The impact tests were carried out using the standard Charpy V-notch impact tester at room temperature (20 °C). The impact energy was determined based on the collected test data.

Since those specimens were quenched and tempered, it is of great interest to investigate the effect of heat treatment on the anisotropy of mechanical properties. Table 1 shows the specimen heat treatment. The sample Steel No.1 was further divided into six groups of specimens in order to investigate the temperature effect. For instance, specimen S-1 was quenched after austenitizing for 45 min at 1010 °C and then tempered for 120 min at 660 °C, specimen S-II was quenched after austenitizing for 45 min at 1040 °C and then tempered for 120 min at 200 °C, and so on. The rest of the steel samples were quenched after austenitizing for 45 min at 1040 °C and then tempered for 120 min at 660 °C.

2.2. Tests and characterization

The delta ferrites were investigated by using a ZEISS-AXIOSCOPE A1 optical microscopy (OM). Specimens (after heat treatment) were first ground and polished, and then electrolytic etched in a solution of 20 g NaOH and 100 mL H2O. The boundaries of delta ferrites were able to be clearly seen after the electrolytic etch while the microstructure of the matrix was not displayed. An FEI-QUANTA250 scanning electron microscopy (SEM) was used to characterize the fracture surface of the impact specimens. In addition, a high-resolution FEI-QUANTAFEG450 field emission SEM (FESEM) was used to characterize the microstructure. The specimens were first ground and polished and subsequently etched in a solution (5 g CuSO4, 70 mL HCl, and 100 mL H2O) for FESEM microstructure characterization. A JEM-2100HR transmission electron microscope (TEM) was used to perform TEM analyses of the precipitates on carbon extraction replicas. An X-ray energy dispersive spectroscopy (EDS) was used to analyze the composition of the precipitates on carbon extraction replicas. To
begin{table}
\centering
\begin{tabular}{|c|c|c|c|}
\hline
Sample steel no. entry & Specimen no. entry & Austenitizing & Tempering \\
& & Temperature (°C) & Time (min) \\
\hline
1 & S-I & 1010 & 660 \\
& S-II & 1040 & 200 \\
& S-III & 1100 & 630 \\
& S-IV & 1040 & 660 \\
& S-V & 1100 & 690 \\
& S-VI & 1100 & 660 \\
2 & & & \\
3 & & & \\
4 & & & \\
\hline
\end{tabular}
\caption{Heat treatment for the experimental steels.}
\end{table}

prepare the carbon extraction duplicates, specimens were firstly prepared as for the FESEM investigation followed by a process for depositing a carbon film on the etched surface. After that, the carbon film was removed using a solution containing 5 g CuSO₄, 70 mL HCl, and 100 mL H₂O.

3. Results
3.1. Mechanical properties

Fig. 3 presents the impact toughness of steel samples. The ratio of transverse to longitudinal impact toughness (Ratio: T/L) is the parameter showing anisotropy. The value of such ratio is within a range from 0% to 100%. The smaller number indicates stronger anisotropy and vice versa. Keep in mind that specimen S-IV represents the sample Steel No.1 in this study. From Fig. 3, it can tell that impact toughness in transverse direction is much lower than the one in longitudinal direction in the Steel No.1, indicating a strong anisotropy of impact toughness. The anisotropy of impact toughness was also observed in samples Steel No.2 and No.3. But it becomes weak as compared. However, there is almost no anisotropy in Steel No.4, for which the ratio T/L is 100%. In Fig. 4, the effect of heat treatment on anisotropy in Steel No.1 is presented, showing that (1) the impact toughness changed little under different austenitizing temperatures (in Fig. 4a) and (2) the transverse as well as longitudinal impact toughness significantly increased with tempering temperature (in Fig. 4b).

It is worth noting that the ratios of T/L remain the same no matter how the transverse or longitudinal impact toughness changed, which suggests that the heat treatment of quenching and tempering has little influence on the anisotropy of impact toughness.

Table 2 shows the mechanical properties of Steel No.1 (specimen S-IV) after a heat treatment. It can be seen that the anisotropy in both elongation and reduction of area are very weak. The ratios T/L are almost 100% for both tensile strength and yield strength, indicating there is almost no anisotropy in strength. However, the ratio becomes 58.5% for impact energy, suggesting that the experimental steel is mainly susceptible to anisotropy of impact energy. Hereby, the anisotropy of impact toughness is necessary to be thoroughly investigated in order to improved fracture toughness in martensitic heat-resistant steels.

![Fig. 3 – The impact toughness of Steels Nos.1–4 after quenching and tempering.](image)

![Fig. 4 – The influence of quenching and tempering on the anisotropy of impact toughness in Steel No.1.](image)
Table 2 – The mechanical properties of Steel No.1 (specimen S-IV) after heat treatment.

<table>
<thead>
<tr>
<th>Direction</th>
<th>Tensile strength (MPa)</th>
<th>Yield strength (σ0.2) (MPa)</th>
<th>Elongation (%)</th>
<th>Reduction of area (%)</th>
<th>Impact energy (J)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Longitudinal</td>
<td>1026.5</td>
<td>837.4</td>
<td>17.6</td>
<td>61.2</td>
<td>140.8</td>
</tr>
<tr>
<td>Transverse</td>
<td>1025.9</td>
<td>840.6</td>
<td>16.7</td>
<td>57.6</td>
<td>82.4</td>
</tr>
<tr>
<td>Ratio: T/L</td>
<td>99.9%</td>
<td>100.4%</td>
<td>95.1%</td>
<td>94.2%</td>
<td>58.5%</td>
</tr>
</tbody>
</table>

Fig. 5 – SEM fractograph of fractured longitudinal (a) and transverse (b) impact specimens in Steel No.1 after quenching and tempering.

Fig. 7 – SEM fractograph of fractured transverse impact specimen in Steel No.1 tempered at 200°C.

Fig. 8 – SEM fractograph of fractured transverse impact specimen in Steel No.4 after quenching and tempering.

3.2. Fractograph of Charpy impact specimens

The impact fractures were examined to investigate the anisotropy mechanism of impact toughness. From Fig. 5 it can be seen that the impact fracture surface was a mixture of quasi-cleavage fractures and dimples in Steel No.1 (specimen S-IV). The fracture appearance of longitudinal specimens (in Fig. 5a) is very different from the transverse specimens (in Fig. 5b). The fracture in longitudinal specimens consists of more dimples and less quasi-cleavage fractures; while in transverse specimens, the fracture consists of more quasi-cleavage fractures and less dimples. Most interestingly, banded cracks were observed in transverse specimens. Some of them appear as transgranular cracks. What’s more, clear boundaries can be observed within the banded cracks, as shown in Fig. 6. Internal cracks were also observed in some banded cracks, as show in Fig. 5b and Fig. 6. The size of banded cracks was measured with length of 100–1000 μm and width of 5–25 μm. Furtherly, more quasi-cleavage fractures were observed around the banded brittle cracks, as shown in Fig. 5b. After quenching and tempering at 200°C, the specimens of steel No.1 was fractured primarily in quasi-cleavage mode, as shown in Fig. 7, in which banded cracks were also observed. It is worth noting that, as shown in Fig. 8, no banded fracture was observed in the transverse specimens of steel No.4. As discussed in the previous section, steel No.4 did not show an anisotropy in impact toughness. Hence, we can suggest that the existence of banded cracks may be a signal of anisotropy of impact toughness.

3.3. Microstructures and precipitates

It has been well known that mechanical properties of steel are determined by its microstructure. To understand the anisotropy mechanism, microstructures of the experimental steels after quenching and tempering were characterized in axial direction of forging bars. In Fig. 9, the metallographic
images show that the matrixes of all samples consist of typical temper martensite laths. Besides, some delta ferrites were observed in steel samples from No.1 to No.3 that were quenched after austenitizing at 1040 °C, as shown in Fig. 9a–c. The morphology of the delta ferrites varies a lot across samples. Long-banded delta ferrites were observed in steel samples No.1 and No.3. Only short-banded delta ferrites were observed in the sample No.2. The size of long-banded delta ferrites in Steel No.1 were measured with length of 30–800 μm and width of 5–15 μm. The size of delta ferrites is similar to that of the banded cracks observed in fractured transverse impact specimens. The volume content of delta ferrites was measured as well by using an ImageTool software. The volume content was less than 1% in Steel No.1 as measured. No other banded microstructure was observed besides the banded delta ferrites. However, as shown in Fig. 9d, no delta ferrites or any other banded microstructure were observed in Steel No.4, which might suggest that the delta ferrites contribute to the anisotropy of impact toughness.

Fig. 10 shows the FESEM micrograph of Steel No.1 (specimen S-IV). It can be seen that both grain boundaries and precipitates exist within banded delta ferrites. The morphologies of the precipitates are very different within delta ferrites and tempered martensite matrix, as shown in Fig. 10b. Numerous spherical precipitates formed within the tempered martensite matrix and at the boundaries between matrix and delta ferrites. Lots of finer precipitates and a small number of spherical precipitates formed within the delta ferrites. The type of precipitate can be determined by its diffraction pattern and chemical composition using TEM and EDS. The TEM micrographs and diffraction patterns of these precipitates are shown in Fig. 11. The TEM micrographs show that the finer precipitates formed within delta ferrites are acicular (in Fig. 11b). The EDS analytical results are shown in Fig. 12. Both the structure and chemical composition prove that the spherical precipitates are M23C6-type carbides and Cr-rich. And the finer acicular precipitates formed within delta ferrites are the MX-type and V-rich.

From Fig. 13a no precipitates were observed in Steel No.1 quenched after austenitizing for 45 min at 1040 °C. Also no precipitates were observed in Steel No.1 after quenching and tempering for 120 min at 200 °C, as shown in Fig. 13b. The boundaries between the prior austenite grains and the martensite laths are relatively distinct after quenching and tempering for 120 min at 200 °C. While lots of M23C6-type carbides and MX-type precipitates formed in the specimens.
within the group of sample Steel No.1 after quenching and tempering for 120 min at 630 °C and 690 °C respectively, as shown in Fig. 13c and d. And there seem to be less precipitates after tempering at 630 °C compared with 660 °C. Furtherly, there seem to be more precipitates after tempering at 690 °C compared with 660 °C.

Fig. 14 shows the micrographs of delta ferrites in the specimens within the group of sample Steel No.1 which were quenched after austenitizing for 45 min at 1010 °C and 1070 °C.

4. Discussion

As noted above, strong anisotropy of impact toughness was observed in the experimental sample Steel No.1 after quenching and tempering. Much lower impact toughness exists in transverse direction but higher impact toughness in longitudinal direction. According to the SEM fractograph of the fractured Charpy impact specimens in Steel No.1 (specimen S-IV), the fracture in longitudinal specimens was primarily in dimple mode, while in transverse specimens the fracture was much more complicated. It was in a mixing of dimples, quasi-cleavage fractures, and banded brittle cracks. By comparing the morphologies of the banded brittle cracks and banded delta ferrites, it can be inferred from Figs. 6 and 10 that the banded brittle cracks formed in banded delta ferrites. Obviously, the banded brittle cracks are harmful to the resistance of impact. In the other hand, the results of impact tests and OM characterization showed a strong relationship between

Fig. 12 – EDS spectra of precipitates in Steel No.1 after quenching and tempering at 660 °C. (a) Spherical precipitates at the boundary between tempered martensite matrix and delta ferrite. (b) Acicular precipitates within delta ferrite.

Fig. 13 – The FESEM micrographs of steel No.1 after quenching (a) and tempering for 120 min at 200 °C (b), 630 °C (c) and 690 °C (d).

Fig. 14 – The OM micrographs of delta ferrites in Steel No.1 quenched after austenitizing for 45 min at 1010 °C (a) and 1070 °C (b).

The OM micrographs at different temperatures suggest that austenitizing temperature at 1010–1070 °C has little influence on the delta ferrites in the experimental steel.
the anisotropy of impact toughness and the banded delta ferrites. By looking at the content of banded delta ferrites, the sample Steel No.1 contains the highest amount. Interestingly, according to the discussion on impact toughness, the sample Steel No.1 has the strongest anisotropy. Also it was found that the less amount of banded delta ferrites in Steel No.3 leads to weak anisotropy. So does the Steel No.2. But there is no anisotropy as the amount of banded delta ferrites reduces to almost zero in Steel No. 4. In conclusion, the anisotropy of impact toughness in the experimental steel should be caused by banded delta ferrites.

It was also found that the brittleness of steel samples was attributed to the banded brittle cracks. SEM fractographs show that more quasi-cleavage fractures existed in the transverse fractured specimens. Most of them were observed around the banded brittle cracks. That indicates the banded delta ferrites induced tempered martensite matrix to fracture in quasi-cleavage mode, which is also known as brittle mode. While no banded cracks formed in longitudinal specimens because banded delta ferrites are distributed along the axial direction within forging bars. This is the reason why banded delta ferrites cause embrittlement in transverse specimens and lead to anisotropy of impact toughness.

Martensitic heat-resistant steels incline to form delta ferrite, which is a non-equilibrium phase at room temperature and always known as a harmful phase to the steel performance [7,8]. Up to now, there are lots of studies about delta ferrites in martensitic chrome steels [9–12]. The results of the literatures [9,10] show that delta ferrites remarkably reduce the low-temperature toughness but have little effect on impact toughness at room temperature. The literature [11,12] mentions that the influence of delta ferrites on mechanical properties in martensitic chromium steels has a strong relationship with concomitant precipitates. The delta ferrites improve the toughness of martensitic chromium steels when there is no concomitant carbide. But delta ferrites will reduce the impact resistance when M23C6-type carbides formed on the boundaries between delta ferrites and matrix. In addition, these studies show that delta ferrites have little influence on mechanical properties of martensitic heat-resistant steels when the volume content of delta ferrites is less than 2%. However, in this study, the experimental results show that a small amount of banded delta ferrites (less than 1% in volume content) can markedly reduce the transverse impact toughness in the experimental steel.

Both FESEM and TEM micrographs show that lots of spherical M23C6-type carbides precipitates formed at the boundaries between tempered martensite matrix and delta ferrites, as well as lots of finer acicular MX-type precipitates formed within delta ferrites in sample Steel No.1 after tempering for 120 min at 630–690 °C. And the number of precipitates increased with temper temperature. While no M23C6-type carbide and MX-type precipitate were observed after tempering for 120 min at 200 °C. Due to the different degrees of precipitation of precipitates and recovery of quenched martensite under different temperatures, the impact toughness varied with temper temperatures [6]. For instance, the quenched martensite is difficult to be effectively recovered after a low-temperature tempering at 200 °C, so the impact toughness is much lower after tempering at 200 °C. But the impact test results show that temper temperature has little influence on the anisotropy of impact toughness. Banded brittle cracks caused by banded delta ferrites were also observed in sample Steel No.1 after tempering at 200 °C, in which no M23C6-type carbide and MX-type precipitate were observed within delta ferrites. That indicates the embrittlement caused by banded delta ferrites is unrelated to other precipitates such as M23C6-type carbides or MX-type precipitates. That is different to the conclusion from previous studies.

We think that the effect of banded delta ferrites on the transverse impact toughness may be attributed to the lower strength and lower shear deformation resistance of delta ferrites and the stress concentration during deformation. The low strength of delta ferrites is attributed to their lower carbon content, which caused smaller lattice distortion and lower resistance against dislocation movement [9]. The strength of delta ferrites is difficult to be tested due to the microscale size of delta ferrites. The microhardness of delta ferrites and tempered martensite matrix were measured as about 310HV and 350HV respectively for sample Steel No.1 after tempering for 120 min at 660 °C. It is worth noting that strength is always proportional to harden in steel. As a result, the strength of delta ferrites is lower than tempered martensite matrix. The difference in microstructure and strength between delta ferrites and tempered martensite matrix would cause stress concentration during deformation. Stress concentration is always favorable to crack formation and propagation [13]. Besides, cracks tend to developed in the phase with lowered deformation resistance. Therefore, delta ferrites promote the formation and propagation of cracks. Furthermore, they lead the tempered martensite matrix to fracture in brittle mode, resulting in the embrittlement in transverse specimens.

The results obtained in this study show that, to increase the isotropy of impact toughness in the experimental steel, it is necessary to control the amount of banded delta ferrites. However, delta ferrites are difficult to be removed by conventional quenching and tempering [9,14,15]. The metallographic images obtained in this study also show that austenitizing at 1010–1070 °C has little influence on the delta ferrites. That is the reason why austenitizing temperature has little influence on the anisotropy of impact toughness in the experimental steel. But the metallographic results show that upsetting-stretching has a significant influence on the amount of delta ferrites. The content of delta ferrites is highest in sample Steel No.1. But it is markedly reduced in Steel No.3. And there is almost no delta ferrite in Steel No.4. The relationship between the amount of delta ferrite and sample preparation methods indicates upsetting-stretching is helpful to eliminate delta ferrites in the experimental steel.

Furthermore, the reason why the anisotropy of plasticity is much lower than that of impact toughness in steel No.1 is still not clear. Further tests are required to analyze the mechanism. The future research will be focused on this project topic.

5. Conclusions

From the study in the effect of delta ferrites on the anisotropy of impact toughness in martensitic heat-resistant steel, it is concluded as follows: (1) The anisotropy of impact toughness
in the martensitic heat-resistant steel 10Cr12Ni3Mo2VN after quenching and tempering is caused by banded delta ferrites. A small amount of banded delta ferrites can markedly decrease the transverse impact toughness. (2) Banded delta ferrites cause banded brittle cracks and induce tempered martensite matrix to fracture in quasi-cleavage mode due to stress concentration. That leads to the embrittlement in transverse specimens. The embrittlement caused by banded delta ferrites is unrelated to other precipitates such as M23C6-type carbides or MX-type precipitates. (3) The key way to increase the isotropy of impact toughness in the experimental steel is to remove the banded delta ferrites. Conventional quenching and tempering have little influence on the anisotropy of impact toughness. Upsetting-stretching is helpful to eliminate the delta ferrites.

**Conflicts of interest**

The authors declare no conflicts of interest.

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