Effect of Y–Ce Complex Modification on Thermal Fatigue Behavior of High Cr Cast Hot Working Die Steels

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The effect of Y–Ce complex modification on the thermal fatigue (TF) behavior of cast hot working die steels was investigated and the mechanism of Y–Ce action was discussed. The experimental result showed that TF behavior of the steel modified by Y–Ce complex modification under thermal cycling temperatures of 650–25°C was over 1.5 times than that of the unmodified, which is likely due to the enhancing of the resistance to oxidation. At the same time, after the Y–Ce complex modification, impact toughness was also increased by nearly 200%, which is mainly attributed to the great improvement of the morphology and distribution of inclusions and the reduction of their amount.

KEY WORDS: Y–Ce complex modification; cast hot working dies steels; thermal fatigue.

1. Introduction

The hot working dies play an important role in manufacturing industry and are called as “black gold” because of their high cost and complicated process. However, hot working dies are easy to cause TF crack as a result of frequent hot and cold shock during the service.1–3) It has been indicated by much research that TF cracks not only reduce the life of hot working die, but also initiate other fractures. Therefore, TF is a main failure, as far as the hot working dies are concerned. In general, TF damage is characterized by a network of cracks on the material surface and the propagation of these cracks could result in material failure.4)

At present, more research has been carried out on TF behavior of forged hot working die steels; however, less research work has been done for effect of rare earth (RE) on TF behavior of high Cr cast hot working die steels, and especially the effect of Y–Ce complex modification on the TF behavior of high Cr cast hot working die steels has yet not been reported in the open literatures. Y, as a reactive element, can greatly improve the high temperature oxidation resistance of both iron and nickel alloys, which contributes to enhancing the TF behavior.5–7) It is also included in the literature8) that when the residual Ce content reaches 0.02%, no obvious changes in strength and hardness are found, while fracture toughness is increased.

And therefore, in the present study, the effect of Y–Ce modification on TF behavior of cast hot working die steels was studied and the mechanism of Y–Ce action was also discussed.

2. Experiment Procedure

The chemical composition of the high Cr cast hot working die steel is shown in Table 1. The steel was melted in a 50 kg medium frequency induction furnace by using a non-oxidation method. After being deoxidized at 1 600°C by aluminum, the steel melt was poured off into the ladle where Y–Ce complex modifiers grinded into powder and Al to deoxidize were placed in advance. All the samples, which was obtained at the bottom position of Y-type castings, were treated with the uniform heat treatment process, i.e. Austenizing at 1 050–1 080°C for 1 h, oil quenched, followed by tempering at 560–590°C for 3 h and air cooled.

The TF samples with a preformed notch of 6×0.18 mm showed in Fig. 1 were machined, grinded and polished in order to minimize the effect of surface nicks on TF. The TF test was carried out in a self-constricted TF test device showed in Fig. 2. The concrete process is as follows: the TF

| Table 1. The chemical composition of the cast hot working die steels (wt%). |
|-----------------|-----|-----|-----|-----|-----|-----|-----|-----|-----|
|                 | C   | Cr  | Si  | V   | Ni  | Mn  | S   | Y   | Ce  | Fe  |
| Unmodified      | 0.3–0.4 | 12–13 | 1.0–1.5 | 0.3–1.0 | 0.8–2.0 | 0.2–0.5 | <0.02 | 0.00 | 0.00 | Bal. |
| Modified        | 0.3–0.4 | 12–13 | 1.0–1.5 | 0.3–1.0 | 0.8–2.0 | 0.2–0.5 | <0.02 | 0.01 | 0.03 | Bal. |
samples uniformly suspended from a disk were heated to 650°C in an electric resistance furnace and then cooled in water for 2 s to 25°C.

The impact samples without notch were machined to a gage size of 55×10×7 mm³ and polished as smooth as possible so that there is the least micro crack leading to the stress concentration. The impact toughness tests were carried out at room temperature, with a comparison to GS344M steel under the uniform condition.

Microstructure, inclusions and TF crack of the steels were investigated by means of Olympus optical microscopy (PMG, Japan) and scanning electron microscopy (SEM) (Model JSM-5310, America) equipped with energy dispersive spectral (EDS) (Model Link-ISIS, Britain).

3. Result and Discussion

3.1. Effect of Y–Ce Complex Modification on TF Crack Propagation and Hardness

There exists great difference between unmodified and Y–Ce complex modified steels in the TF crack propagation. The typical SEM micrographs of crack and surface chap of the unmodified and modified steels are shown in Fig. 3. It can be found that after 2 000 cycles the crack was longer and wider and the chap was more severe in the unmodified steel than in the Y–Ce modified steel. Main crack length and changing of hardness during thermal cycle are shown in Figs. 4 and 5, respectively. Evidently, crack propagation rate is two times faster in the unmodified steel than in the modified steel. Decrements of hardness are 10 HRC in the modified and 14 HRC in the unmodified steels after 2 000 cycles, respectively, which shows that the modified steel has better resistance to soften.

3.2. Effect of Y–Ce Complex Modification on Inclusions

Generally speaking, TF crack preferentially initiates at the stress concentration of the inclusions (such as FeS shown in Fig. 6) and propagates along the grain boundary. Therefore, the amount and morphology of inclusions at the boundary have a great effect on TF. Figure 7 offers the comparison of morphology, distribution and amount of inclusions of the unmodified and modified steels. It is easy to draw a conclusion that, by Y–Ce modification, the morphology and distribution of inclusions are improved, and
furthermore, the amount is also decreased. In evidence, after modified, inclusions look smaller with a shape of ellipse or sphere and are distributed more uniformly. Compared with Mn and Fe, REs have stronger appetency for S and O and are more prone to react with them to form RE oxide or sulphide, as seen in Table 2. Some brittle sulphide and oxide such as FeS, MnS and FeO, whose expanding coefficients are far different from the matrix, which will result in big thermal stress during thermal cycling, are modified into round and fine RE sulfide and oxide. Figure 8 shows Y sulphide in the microstructure by Y–Ce modification. In addition, by addition of Y–Ce inoculant, these RE sulphide and oxide have similar expanding coefficients to the matrix, as shown in Table 2, which reduces the chance of inclusions becoming crack initiation.

3.3. Effect of Y–Ce Complex Modification on High Temperature Oxidation Ability

Into the bargain, TF crack propagation has close relation with the oxidation at front of crack. The oxidation induces tiny cracks around the oxide, and consequently these cracks get wider and longer with increasing of thermal cycles. Then oxygen invades these cracks and makes them be oxidized further. After the Y–Ce modification, there is higher Cr content in the crack, as seen in Table 3, which offers

| Compounds | Expanding coefficients (10⁻⁶/K) | ΔG (J/mol) |
|-----------|---------------------------------|------------|
| Ce₂O₃     | /                               | -171.16    |
| CeS₂      | 12.3                            | -78.99     |
| CeS       | 12.3                            | -72.05     |
| FeS       | /                               | -17.98     |
| MnS       | /                               | /          |
| Steel     | 11.0-13.0                       | /          |
more chance of forming Cr oxide that is thicker than other oxide. These Cr oxides can prevent grain boundary being oxidized further because of their higher density, and so that resist or delay crack to propagate.10,11) According to the reference, 12) REs have been employed to protect steels and other metallic alloys against oxidation and corrosion. RE is well known to have lower melting points, larger atomic radii and acts as stronger super-cooling ingredient. Their partition coefficients are far less than 1. Through solute distribution during solidification, RE concentrates along the grain boundary. These REs, especially Y can enhance diffusion rate of Cr from the matrix to the crack, and thus accelerate the formation of Cr2O3.13) Furthermore, these RE oxide such as Y2O3 distribute in the interface between the matrix and oxide film, which makes oxidation film have better adhesion to the matrix and delays the crack being oxidized further.6,13–16)

3.4. Effect Y–Ce Complex Modification on Impact Toughness

By addition of Y–Ce complex modification, the impact toughness is apparently increased and is 2.5 times higher than that of the unmodified steel, as seen in the Table 4. In general, The value of the impact toughness is mainly relative to the distribution, morphology, size and amount of inclusions at the grain boundaries of the high Cr cast hot working die steel since the inclusion can easily cause crack initiation and hasten its propagation. It is easy to draw a conclusion from Fig. 9 that, by Y–Ce modification, the morphology and distribution of inclusions at the grain boundaries are improved, and furthermore, the size and amount is also decreased, so that there are much fewer chances for the crack to initiate and propagate in the modified steel than in the unmodified steel. Therefore, the impact toughness is greatly enhanced by Y–Ce complex modification.

4. Conclusion

(1) After the steel was modified by Y–Ce complex modification, the Cr content was increased so that the resistance to oxidation was enhanced, which made the propagation of TF cracks much slower and cracks much shorter. Finally, TF behavior of the Y–Ce modified steels under thermal cycling temperatures of 650~25°C was increased by 150% than that of the unmodified.

(2) After modified, evidently, the distribution of inclusions was improved; their shape was modified from bar or block shape to ball shape; besides the size and amount of inclusions was decreased.

(3) After the Y–Ce complex modification, impact toughness was also increased by nearly 200%, which is

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**Table 3.** Distribution of Cr, Fe and O in the modified and unmodified steels (atom%).

| Condition       | Metal matrix | Crack |
|-----------------|--------------|-------|
|                 | Cr  | Fe  | O   | Cr | Fe  | O   |
| Unmodified steel| 10.45 | 82.22 | 7.33 | 14.26 | 54.45 | 31.29 |
| Modified steel  | 9.55  | 85.20 | 5.25 | 21.25 | 35.37 | 43.38 |

**Table 4.** Impact toughness of the unmodified and modified steels (J/cm²).

| Condition      | Impact toughness |
|----------------|------------------|
| Unmodified steel | 72               |
| Y and Ce modification steel | 270             |
| GS344M          | 371              |

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Fig. 8. Spherical Y oxide and sulfides: (a) SEM and (b) EDS.

Fig. 9. Inclusions at the grain boundaries in the as-cast structure: (a) unmodified and (b) Y–Ce modified.
mainly attributed to the great improvement of the morphology and distribution of inclusions and the reduction of their amount. Besides, decrement of hardness after 2,000 cycles was also reduced by about 30% because of Y–Ce complex modification.

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