Effect of Heat Treatment Conditions on Shape Control of Large-sized Elongated MnS Inclusions in Resulfurized Free-cutting Steels

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Effect of heat treatment conditions on shape evolution of large-sized elongated MnS inclusions in resulfurized free-cutting rolled steel has been investigated using confocal scanning laser microscope and Si₂Mo resistance furnace. The results show that the heating rate, soaking temperature and soaking time impose significant effects upon shape profiles of elongated MnS. The split of slender MnS was observed in continuous heating with heating rate in the range of 0.5–2 K/s. In addition, split degree of MnS indicated a negative relation with the rise of heating rate. As a result, separation of elongated MnS was not observed at the heating rate of 6 K/s. During soaking experiments, there was no remarkable shape change for MnS at temperature lower than 1073 K. While the elongated MnS split up and spheroidized obviously at 1473 K. Correspondingly, number density of inclusions increased while mean length reduced as the soaking time increased from 1 h to 4 h at 1473 K. Significant shape change from slender to spindle-like or spherical was identified only when the soaking time exceeds 3 h or 4 h. Based on the Gibbs Thompson relation and the obtained experimental results, mechanism of shape evolution of MnS inclusions was discussed and morphology evolution of MnS was divided into three major steps: (1) first, the shrinkage occurred in the longitudinal direction at the beginning of heating process, (2) expansion and contraction in radial direction followed after the shrinkage which caused the split of slender MnS; (3) eventually, the spherical particles emerged from the split parts.

KEY WORDS: large-sized elongated MnS inclusions; in-situ observation; resulfurized free-cutting steel.

1. Introduction

MnS is a common type of non-metallic inclusions in steel, which is of good deformability during rolling. As elongated MnS inclusions along rolling direction often cause poor transverse toughness and stress corrosion cracking of medium plates, they are commonly considered to be harmful thus are removed as impurities. However, different from most steel products, some steel grades such as free cutting steel, hot forging steel, etc. must contain certain amount of MnS inclusions so as to have good machinability. For getting better property of the steel, MnS inclusions must be strictly controlled to be small, uniformly distributed, and shaped like spindles or spheres.

Shape and size variation of MnS inclusions by heat treatment have been discussed in the previous reports. Flowers⁽¹⁾ first studied MnS inclusion in Fe-3%Si alloy with respect to texture formation. After that, Gnanamuthu⁽²⁾ concerned with different types of MnS and found all MnS inclusions finally changed to polyhedron after long time soaking. Murty^(3–5) found there were three stages for the evolution of elongated type II and III MnS in high sulfur steel: (1) cylinderization (2) ovulation (3) coarsening. Then Mcfarland⁽⁶⁾ paid attention to the spheroidization of type II MnS with the homogenization.

Nishida⁽⁷⁾ focused on MnS inclusions in low sulfur rolled steel and found these particles started to spherize at 873 K. We also have lately investigated the behavior of MnS inclusions in hot forging casting steel through various heat treatments.^(8,9) However, direct observation on the shape change of elongated MnS in solid steel have not been reported yet.

In present study, confocal scanning laser microscope (CSLM) was first used to in-situ observe the shape evolution of large-sized elongated MnS inclusions in resulfurized free-cutting steels. The effects of heating rate, soaking temperature and soaking time on shape control of large-sized elongated MnS were systematically investigated with methods of in-situ observation by CSLM and iso-thermal treatments in electrical resistance furnace. And the mechanism why these large-sized elongated MnS could break up during heating was also analyzed. The research can provide a theoretical guidance for the design of thermal parameters in heat treatment of resulfurized free-cutting steels.

2. Experimental Procedures

Steel materials used in the experiments were commercial rolled steels of resulfurized free-cutting steel. Major chemical

compositions (mass%) are determined as Carbon of 0.086, Silicon less than 0.01, Manganese of 1.02 and Sulfur of 0.32.

A typical confocal scanning laser microscope (VL2000DX-SVF17SP) was used for in-situ observation of shape evolution of large-sized elongated MnS inclusions during heating. The samples were 7.5 mm in diameter, 4 mm in height and mirror polished before the experiments. In the in-situ observation, the sample was continuously heated to desired temperature at an even rate in an alumina crucible under high purity Ar atmosphere. Two series of experiments were carried out to elucidate the effects of heating rate and soaking temperature on the evolution of MnS, respectively. In heating rate experiments, the samples were heated at the rate of 0.5 K/s, 1 K/s, 2 K/s, 6 K/s and 10 K/s, respectively to 1463 K. In soaking temperature experiments, the sample was heated to 873 K, 1073 K, 1273 K and 1473 K at a rate of 6 K/s and held for 300 seconds, respectively. After the experiments, characteristics like composition and shape of MnS inclusions were analyzed by SEM (JSM-6480LV).

Experiments were carried out in a vertical type Si₂Mo resistance furnace to find the influence of soaking time on MnS. In each experiment, the furnace was first heated to 1473 K under Ar atmosphere. Then a sample with a thickness of 1.2 mm was hanged by a steel wire from the top cover and set at the even temperature zone of the furnace. After soaked for a predetermined period of time, the sample was quickly dropped into the ice water. The soaking time was controlled to be 1 h, 2 h, 3 h and 4 h, respectively. All the obtained samples were mounted and mirror polished. Size characters of MnS inclusions in about 20 mm² in each

sample were analyzed by optical microscope (LEICA DM6000).

3. Results

3.1. Non-metallic Inclusions in Rolled Steel

Initial morphology, composition and distribution of inclusions in rolled materials were shown in Fig. 1. Inclusions were mainly MnS of slender shape (Length/Width>3), elongated along the rolling direction. Lengths of 8735 non-metallic inclusions in 20.46 mm² were measured (see Table 1). It was found that large-sized inclusions are abundant, with a density of 15.06/mm² for MnS larger than 40 μm.

3.2. In-situ Observation

Figure 2 showed the shape evolution of slender MnS at the heating rate of 0.5 K/s. The original size of the MnS was about 86.3 μm in length and 91.3 in aspect ratio. Division of MnS was observed in the continuous heating. When temperature rose to about 1073 K, single MnS inclusions began to divide into two particles. At 1373 K, there are nine split particles. As the temperature increased, lengths of split MnS reduced, and shapes changed to spindles. The aspect ratios of initial MnS and split MnS particles at different temperatures were shown in Fig. 3.

Table 1. Number density of MnS inclusions at different length distributions.

Distribution, μm	5–20	20–40	40–60	60–80	80–100	>100
Density, /mm ²	344.87	67.01	10.46	2.69	1.08	0.83

Fig. 1. Morphology and composition of typical inclusions in steel (a) SEM image (b) EDS result (c) OM image.

Fig. 2. Shape evolution of large-sized elongated MnS inclusion at the heating rate of 0.5 K/s.

After the heating, MnS inclusions were observed by SEM. Two types of divisions were identified: (1) For type A division, the gap between two split MnS inclusions was fully filled with Fe atoms, as shown in Fig. 4(a). (2) For type B division, the gap was void from the picture in Fig. 4(b). Both types of divisions for MnS can be observed in the above in-situ observation experiment at 1463 K, as shown by Fig. 4(c). It's found that type A division occurred twice for MnS at 1463 K. Meanwhile, type B division happened twelve times. And total 15 split particles formed eventually.

From the above analysis, we knew that large-sized elongated MnS divided into 15 particles at 1463 K. In order to get detailed information on shape evolution of MnS, the length and the width of each split MnS were analysed. And the length and the width of initial slender MnS in corresponding positions were also measured. First, intervals were divided according to the length of split MnS at 1463 K, as shown in Fig. 5(a). Then, same intervals were made for original slender MnS at 292 K, as shown in Fig. 5(b). Lastly, the length and the width of MnS in each interval were analyzed, as shown in Figs. 5(c) 5(d).

Figures 5(c) 5(d) showed that the length and the width of MnS changed significantly. For the length in the same interval, MnS at 1463 K were smaller than the ones at 292 K. For the width, some were larger at 1463 K, the others are bigger at 292 K. It's indicated that shape variations of MnS inclusions were as follows: (1) The shrinkage occurred in length direction (axial contraction). (2) Expansion and contraction happened in radial direction, which finally caused the break-up of slender MnS. Numerical simulation of shape evolution for a rod has been done by Nichol *et al.*^{10,11} It's found that for the rod ($L/D=7.19$), the length

recedes toward each other. Simultaneously, Bulges near the two ends and necking in the middle occur, which finally form two egg-shaped particles. Shape evolution observed in present study is basically in agreement with Nichol.

3.3. Effect of Heating Rate

In order to investigate the effect of heating rate on shape evolution of large-sized elongated MnS, samples were heated at 1 K/s, 2 K/s, 6 K/s and 10 K/s respectively. The maximum temperature was 1463 K, at which slender MnS in casting slab had been observed to split in our previous work.¹² Besides, 1463 K is still in the proper temperature range for heat treatment in actual production process. Images were listed only at 300 K, 1073 K and 1463 K for each heating rate (See Fig. 6). Investigated MnS inclusions were indicated by arrows. Images at 0.5 K/s were shown in Fig. 2. It's found that MnS split remarkably at 0.5 K/s and 1 K/s. When the heating rate increased to 2 K/s, splitting degree reduced. There were no obvious changes for MnS at 6 K/s and 10 K/s.

Figure 7 showed aspect ratios and the number of split MnS at different heating rates. When the heating rate decreased from 2 K/s to 0.5 K/s, the number of split MnS increased from 4 to 14 and corresponding aspect ratios sharply reduced.

Shape changes of MnS could be indicated by the change rate of mean aspect ratio (CR for short), which was calculated by Eq. (1). As shown in Fig. 8, the change rate of mean aspect ratio reduced with an increasing of heating rate. It's

Fig. 3. Aspect ratios of MnS at different temperatures.

Fig. 5. Same intervals in images of 1463 K and 292 K and size characters of MnS in each interval (a) Interval-division of split MnS in the field of 1463 K (b) Same intervals divided in the field of 292 K (c) Length of MnS in each interval (d) Width of MnS in each interval.

Fig. 4. SEM images of typical MnS after heating and enlarged photo of split MnS at 1463 K in in-situ observation experiment.

Fig. 6. In-situ observation of shape evolution of large-sized elongated MnS at different heating rate.

Fig. 7. Aspect ratios and the number of split MnS vs heating rate.

Fig. 8. Change rate of mean aspect ratio of MnS vs heating rate.

found that rapid heating is not beneficial to the break-up of large-sized elongated MnS.

$$CR = \frac{(L/W)_0 - (\overline{L/W})}{(L/W)_0} \dots\dots\dots (1)$$

Where CR means change rate of mean aspect ratio, L is length, W is width, $(L/W)_0$ is initial aspect ratio of the inclusion, $\overline{L/W}$ is mean aspect ratio of split inclusions.

Fig. 9. In-situ observation of shape evolution of large-sized elongated MnS at different soaking temperature.

3.4. Effect of Soaking Temperature

In this part of experiments, soaking time and heating rate were chosen intentionally. From above experiments, it had been known that the heating rate of 6 K/s had slight effect on slender MnS during continuous heating process. Therefore, this heating rate was chosen to investigate the effect of soaking temperature on shape change of MnS while favored diminishing interference of heating rate. Influence of phase transformation on MnS was also taken into account by varied soaking temperatures at 873 K (α -Fe), 1 073 K (α + γ), 1 273 K (γ -Fe) and 1 473 K (γ -Fe), respectively, as diffusion coefficient of Mn and S atoms in α -Fe is higher than in γ -Fe at the same temperature.^{13,14} In view of soaking time, it had been found that 300 s was enough for the separation of elongated MnS and longer soaking time may affect the diffusions of Mn and S in turn which is not good to diminish effect of soaking time here. Hence, a soaking time of about 300 s was chosen.

Figure 9 showed MnS inclusions at 300 K and at desired temperatures for 300 s. Sizes characters of original MnS particles were similar in four experiments. Their lengths were 83.65, 85.49, 108.74 and 119.76 μ m, respectively and widths were 2.32, 1.66, 2.80 and 3.67 μ m, respectively. Aspect ratios of split MnS at desired temperatures were shown in Fig. 10. At 873 K and 1 073 K, MnS could not break up. When soaking temperature rose to 1 273 K, initial single MnS split to five particles. However, aspect ratios of the two of these five split MnS were still large, which were 24.79 and 22.33. At 1 473 K, the number of splitting MnS increased to six and aspect ratios reduced.

Shape change of MnS can be indicated by the change rate

Fig. 10. Aspect ratios of split MnS vs soaking temperature.

Fig. 11. Change rate of mean aspect ratio of MnS vs soaking temperature.

of mean aspect ratio, which was calculated by Eq. (1). As shown in Fig. 11, the change rate of mean aspect ratio increased with rising soaking temperature. It's found that in the soaking temperature range of 873–1473 K, high temperature is beneficial to the break-up of large-sized elongated MnS.

3.5. Effect of Soaking Time

As seen in Fig. 12, soaking time had a great effect on shape evolution of MnS. With the soaking time of 1 h or 2 h, most inclusions were still in slender shape. The significant shape change from slender to spherical is identified only when the soaking time reached 3 h or 4 h, with the number of MnS smaller than 5 μm sharply increased. However, there were still some coarse MnS in large-size which could not break up. Even after 4 hour's soaking, the splitting of these extreme coarse ones had not been observed yet.

The number of small-sized MnS (<5 μm) and large-sized ones (>80 μm) with soaking time was shown in Fig. 13. It's found that as soaking time increased from 0 hour to 4 hour, the number density of large-sized MnS decreased from 1.91/mm² to 0.46/mm². Meanwhile the number density of small-sized MnS increased dramatically from 1322/mm² to 5206/mm². The splitting behavior was very notable.

Shape change of MnS was characterized by the change of mean length, as shown in Fig. 14. It's found that mean length reduced from 5.47 μm to 0.67 μm with the soaking time increased from 0 hour to 4 hour. It's concluded that soaking time had a great effect on both size and morphology

Fig. 12. Typical images of MnS at different soaking time.

Fig. 13. Number density of MnS vs soaking time.

changes for large-sized slender MnS.

3.6. Evolution Mechanisms of Inclusions

The shape evolution of an elongated MnS changing to a single spherical particle or splitting to two particles is discussed. Schematic diagrams are listed in Fig. 15.

Shape changes of elongated MnS are caused by surface diffusion of Mn atoms and S atoms.⁵⁾ Chemical potential on the surface of MnS is obtained by Gibbs-Thompson relation.

$$\mu = \mu_0 + \Omega \gamma K \dots \dots \dots (2)$$

Fig. 14. Mean lengths of MnS vs soaking time.

Fig. 15. Schematic diagrams of shape evolution for elongated MnS.

Where μ_0 represents the chemical potential of a flat surface, Ω is the molecular volume, γ is the surface tension and K is the total curvature of the surface at the point of interest.

Point E is at the flat surface and point F is at the surface with the curvature radius of R_F ($K_E < K_F$). According to Gibbs-Thompson relation, chemical potential at point E is lower than chemical potential at point F. Because of the potential difference, Mn atoms and S atoms at point F diffuse to point E. Macroscopic reflection is the contraction in length direction. If the length is small, the contraction directly leads to the formation of the spindle, as shown in Fig. 15(a-1). If the length is large, the two ends bulge. There is no time for atoms to diffuse to the center, so it is still flat in the middle part, as shown in Fig. 15(b-1).

Point H is at the flat floor and point E is at the bulge, in Fig. 15(b-1). μ_H is smaller than μ_E . So atoms diffuse from point E to point H at the rate of V_1 . At the same time, the tendency of spheroidization makes Mn and S atoms diffuse from point H to point E at the rate of V_2 . (I) When $V_1 > V_2$, atoms fill the center part quickly, forming single spindle. (II) When $V_1 < V_2$, Mn and S atoms in the center diffuse to two bulges, as shown in Fig. 15(b-2). Then, it splits and spheroidizes into two distinct particles, as shown in Fig. 15(b-3). In our experiment, many MnS shaped like the ones in Fig. 15 were observed (see Fig. 16).

In order to clarify the diffusion mechanism, mathematical deduction combined with experimental results are carried out.

From the above explanation, it's known that slender MnS can change into two bulges due to the chemical potential difference, as shown in Fig. 17. As a result, change in the

Fig. 16. Shape evolution for slender MnS observed in present study.

Fig. 17. Schematic diagrams of split process for MnS inclusion.

distance between the centers of two bulges (ΔL) satisfies the following geometric relationship.

$$\frac{\Delta L}{L} = \frac{[(r + \rho) \cos \theta] - r}{r} \quad (3)$$

Where, L is the distance between centers of the two bulges, ΔL is the change in the distance between the two centers, r means the radius of MnS inclusion and ρ is the radius of the neck.

If θ is small enough, $\cos \theta$ approximately equals to one.

$$\rho = r(1 - \cos \theta) = 2r \sin^2 \frac{\theta}{2} \approx \frac{x^2}{2r} \quad (4)$$

Combined Eq. (3) with Eqs. (4), (5) was obtained.

$$\frac{\Delta L}{L} = \frac{x^2}{4r^2} \quad (5)$$

Mass transfer in present study is assumed to be controlled by diffusion alone. Kuczynski has derived diffusion-controlled kinetic equation for stable neck growth.¹⁵⁾

$$\left(\frac{x}{r}\right)^n = F(T) \times T^{-m} \times t \quad (6)$$

Where $F(T)$ is the function of temperature. m and n are constants, which are only relevant to diffusion type.

Introducing Eqs. (5) to (6), (7) can be obtained as follows:

$$\frac{\Delta L}{L} = \frac{1}{4} \times \left(F(T) \times T^{-m} \times t\right)^{\frac{2}{n}} \quad (7)$$

Logarithmic equation on both sides, it's obtained

$$\lg\left(\frac{\Delta L}{L}\right) = \lg\frac{1}{4} + \frac{2}{n} \lg\left[F(T) \times T^{-m}\right] + \frac{2}{n} \lg\frac{t}{4} \quad (8)$$

From Eq. (8), it's known that $\lg(\Delta L/L)$ shows a linear correlation with $\lg(t/4)$ at a fixed temperature.

Fig. 18. $\lg(\Delta L/L)$ vs $\lg(\text{time}/4)$.

Relation between the measured logarithm of $(\Delta L/L)$ and $(t/4)$ in soaking experiments at 1273 K in section 3.4 is given as Fig. 18, as indicated by solid circles. It could be seen that simple linear relation existed between the two with a slope of about -0.302 , whose absolute value is 0.302 .

So $n=7$ is derived from Eq. (8). According to Kuczynski's research,¹⁵⁾ it indicated that surface diffusion was the main diffusion type for shape change of elongated MnS.

4. Conclusions

(1) In-situ observation experiments showed that large-sized elongated MnS could split up and spheroidize at high temperature.

(2) The combined in-situ experiments and theoretical analysis indicated that shape evolution of elongated large-sized MnS were (1) axial contraction (2) expansion and contraction in radial direction (3) spheroidization.

(3) Heating rate has a great effect on shape variation of slender MnS. With heating rate rose from 0.5 to 2 K/s, the

number of split MnS decreased and the maximum aspect ratio increased. When heating rate exceeded 6 K/s, slender MnS kept unchanged. Slow heating rate would facilitate the shape control of large-sized elongated MnS.

(4) Regarding soaking temperature, the break-up of slender MnS didn't occur until 1273 K. When reached 1473 K, the splitting degree was more remarkable than at 1273 K. It's indicated that high soaking temperature is beneficial to obtain spindle-like MnS with small sizes.

(5) For soaking time, when extended from 0 h to 4 h, the number density of MnS larger than $80 \mu\text{m}$ decreased from $1.91/\text{mm}^2$ to $0.46/\text{mm}^2$, while that of MnS smaller than $5 \mu\text{m}$ increased from $1322/\text{mm}^2$ to $6913/\text{mm}^2$. The obvious shape change from slender to spherical was identified only when the soaking time exceeds 3 h. It's indicated that soaking at 1473 K for 3 h or 4 h is good for shape and size control of large-sized slender MnS.

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