Hot Ductility of Sulfur-containing Low Manganese Mild Steels at High Strain Rate

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The hot ductility of low manganese mild steels was investigated at a high strain rate of 22 s\(^{-1}\) to simulate a roughing mill in the hot rolling process for various contents of manganese and sulfur. With all steels, ductility loss occurred in a low temperature range in the austenite region after reheating at 1 573 K. A decrease in the manganese content and an increase in the sulfur content deteriorated hot ductility. A low reheating temperature and a long holding time before tensile deformation improved hot ductility. Tensile strength decreased at reduction-in-area below 40% at a constant temperature, and had no relationship with chemical composition. The brittle fracture surfaces were intergranular fractured ones and were observed at reduction-in-area below 40%. \((\text{Fe},\text{Mn})\text{S} \) precipitates existed in small dimples on the brittle fracture surfaces. The quantities of the precipitated sulfides were calculated by Thermo-Calc, and increased with increasing manganese and sulfur contents. An increase in the manganese content promoted coarse \((\text{Fe},\text{Mn})\text{S} \) at the same temperature. The sizes of the sulfides were also correlated with thermal diffusion at various temperatures and holding times. Hot ductility was understood by the quantity and size of the precipitated sulfides at high reheating temperatures. Embrittlement was accelerated by an increase in the quantity of precipitated sulfides and a decrease in the precipitate size. At low reheating temperatures, improvement of hot ductility was recognized as a result of a decrease in solved sulfur in the reheating process.

KEY WORDS: hot ductility; mild steel; low manganese; sulfide; precipitation; intergranular fracture.

1. Introduction

Hot ductility is an important factor in surface cracking of continuously cast slabs\(^1\) and hot rolled strips. In continuous casting, transverse cracks may develop when a curved strand is straightened, while in hot rolling, surface or edge cracks may occur in first rolling during the rough rolling. Hot ductility is greatly affected by the temperatures and strain rates in these two processes, and the failure mechanisms are also different. In the case of continuous casting, the strain rate is low, at about 10\(^{-4}\) to 10\(^{-3}\) s\(^{-1}\), so the failure is caused by thin-films of ferrite formed at austenite grain boundaries in the temperature range from 1200 to 900 K.\(^2\) The strain concentrates at soft ferrite on the grain boundaries and causes embrittlement. Furthermore, precipitates such as sulfides, carbides, nitrides, etc., on grain boundaries accelerate the formation of voids that deteriorate hot ductility.\(^1\)–\(^9\) When the strain rate increases, the flow stress of ferrite increases relatively more than that of austenite, so the concentration of strain is restrained.\(^4\),\(^10\)

At the roughing mill in hot rolling, the strain rate is higher than 10 s\(^{-1}\). Intergranular embrittlement occurs in a low austenite temperature range from 1500 to 1200 K when the intergranular strength is weakened by segregation or precipitation.\(^1\) Many previous reports described hot ductility with respect to manganese and sulfur contents, and concluded hot ductility improves with increased manganese content and decreased sulfur content.\(^1\)–\(^4\) Furthermore, a decrease in the reheating temperature and an increase in the holding time before deformation also restrain hot ductility loss.\(^1\)–\(^3\) The critical ratio of manganese to sulfur to prevent embrittlement is about 30 when the manganese content is above 0.1 mass%.\(^1\) In this case, \((\text{Fe},\text{Mn})\text{S} \) precipitates or segregated sulfur at the austenite grain boundaries may deteriorate the strength of the austenite grain boundary. When manganese is free, hot ductility is controlled by the sulfur content. The critical content of sulfur to improve ductility is about 0.005 mass%.\(^5\) In this case, embrittlement would be due to segregated sulfur at the austenite grain boundaries. However, there have been few studies of low manganese-containing steels with manganese contents below 0.1 mass%. In commercial mild steels, manganese is eliminated to increase formability, so the manganese content is very low.

This study investigated the hot ductility of sulfur-containing low manganese steels at a high strain rate, and discussed the roles of manganese and heat treatment in increasing hot ductility.

2. Experimental Procedure

The steels used in this investigation were as-cast ingots of low carbon steel with various manganese and sulfur contents. The chemical compositions of steels 1–13 are shown...
in Table 1. The manganese contents vary from 0.06 to 0.30 mass%, and the sulfur contents vary from 0.0008 to 0.0209 mass%. Cylindrical specimens for hot tensile tests were machined from the subsurface of the ingots along the parallel direction to casting. The parallel part of the specimen was 6 mm diameter and had a gauge length of 16 mm.

The process of experiments is illustrated in Fig. 1. Specimens were basically heated at a rate of 5 K/s up to 1573 K (reheating temperature, RHT) and then soaked for 600 s in a vacuum. Subsequently, the specimens were cooled to tensile temperatures (TT) in the range from 1023 to 1473 K at a constant rate of 30 K/s by nitrogen gas. After holding for 300 s (holding time, Ht) at each tensile temperature, the specimens were deformed at a strain rate of 22 s\(^{-1}\) until final fracture occurred. After the fracture, the samples were immediately quenched to room temperature by helium gas. Furthermore, the influence of RHT and Ht on hot ductility were also investigated. RHT was changed from 1573 to 1473 K, and Ht was varied in the range from 60 to 1800 s. Hot ductility was evaluated by reduction-in-area (RA), which was measured by the diameter of the fractured specimens.

The fractured surfaces were observed by scanning electron microscope (SEM) and analyzed by energy-dispersive X-ray spectroscopy (EDS). Precipitates of sulfide in the vicinity of the fractured surfaces were extracted in a methanol solvent containing 4% methyl salicylate, 1% salicylic acid and 1% tetramethylammonium chloride by electrolysis with a constant current of 0.2 mA/mm\(^2\). The sulfur quantity in the extracted precipitates was measured from infrared absorption by the combustion method. Carbon extraction replicas of precipitates were also prepared and observed by transmission electron microscope (TEM).

3. Experimental Results

3.1. Influence of Manganese and Sulfur Contents on Hot Ductility

Figure 2 shows the influence of TT and sulfur content on RA for 0.06 and 0.14–0.16 mass% manganese steels. Here, the RHT is 1573 K, and the Ht is 300 s. As TT decreases, RA decreases until a temperature of 1223 or 123 K is reached, and then increases drastically at 1073 K. This improvement of RA is thought to be caused by transformation of ductile ferrite. Furthermore, as the sulfur content increases, RA decreases in steels with the same manganese content. For the 0.06 mass% manganese steels, the lowest RA is over 40% at sulfur contents below 0.005 mass%, and in contrast, RA is under 15% at sulfur contents above 0.009 mass%. With the 0.14–0.16 mass% manganese steels, the minimum RA is under 20% at sulfur contents above 0.008 mass%. Especially with low manganese and high sulfur content steels, ductility loss starts at high TT. RA becomes 15% at 1423 K with steel 4 (0.06Mn–0.02S), and 28% at 1373 K with steel 7 (0.14Mn–0.014S).

Figure 3 shows the influence of TT and manganese content on RA for 0.005 and 0.008–0.009 mass% sulfur steels. With 0.005 mass% sulfur steels, RA is the largest at above 1373 K for Ht of 300 s. (a) 0.06 mass% manganese steels, ○; steel 1, △; steel 2, ●; steel 3, ▲; steel 4. (b) 0.14–0.16 mass% manganese steels, ○; steel 6, △; steel 7, ●; steel 9.
temperature austenite region, and an increase in manganese content and a decrease in sulfur content improve hot ductility.

3.2. Influence of Reheating Temperature and Holding Time on Hot Ductility

Figure 4 shows the influence of $RHT$ on $RA$ for various manganese containing steels with 0.014–0.017 mass% sulfur. Here, the $TT$ is 1 223 K, and the $Ht$ is 300 s. With the 0.14–0.20 mass% manganese steels, $RA$ is improved gradually with decreasing $RHT$. $RA$ is below 20% at $RHT$ of 1 573 K, and increases to above 70% at $RHT$ of 1 473 K. On the other hand, with the 0.29 mass% manganese steel, $RA$ increases greatly with decreasing $RHT$. Specifically, $RA$ increases from 50 to 85% when $RHT$ decreases from 1 573 to 1 548 K.

Figure 5 shows the influence of $Ht$ on $RA$ for steel 10. Here, the $RHT$ and the $TT$ are 1 573 K and 1 223 K, respectively. When the sample is held for an extended time before tensile deformation, $RA$ rises greatly. Although $RA$ is below 20% until 300 s, $RA$ increases to 70% at $Ht$ of 1 800 s.

Figure 6 shows the relationship between tensile strength ($TS$) and $RA$ in the austenite region for steels 1, 2, 3, 4, 9 and 11. Irrespective of chemical compositions, $TS$ decreases as $RA$ decreases at $RA$ below 40% at each temperature, while it is almost constant at $RA$ above 40%. Furthermore, $TS$ decreases as $TT$ increases. It seems that nductile deformation occurs at $RA$ below 40%.

3.3. Relationship between $RA$ and Fracture Surface

Figure 7 shows SEM images of the fracture surface with various $RA$ in the austenite region. With the specimen with superior ductility of 73% $RA$, the fracture surface is completely covered with large dimples over 50 μm in size, which are considered to be traces of transgranular ductile rupture. On the other hand, with the specimen with 12% $RA$, the fracture surface is predominantly a smooth surface, which is considered to be an intergranular ruptured surface. The fracture surface of the specimen with 34% $RA$ displays a combination of transgranular ductile fracture and intergranular fracture. In this study, intergranular fracture is observed at $RA$ below 40%. It is likely that the decrease in $TS$ in the $RA$ range under 40% corresponds to an increase in the area of the intergranular fractured surface. It is accepted that intergranular fracture occurs when intergranular strength is below transgranular strength. Therefore, it is
conceivable that the appearance of intergranular surface means a decrease in intergranular strength. Generally speaking, surface defects originating from a shortage of hot ductility are said to occur when RA is below 40%. Consequently, the finding in this research supports the idea that nonductile deformation accompanied with intergranular fracture would cause surface defects.

Figure 8 shows minute SEM images of the intergranular rupture surface with different magnifications. The surface is seen to be smooth at low magnification, however, it is uneven with dimples at high magnification. About half of the dimples contain small particles, and the others are empty. The particles were analyzed by EDS. The result is also shown in Fig. 8. S Kα and Mn Kα peaks are clearly recognized in addition to an Fe Kα peak, which includes the peak from the matrix. Furthermore, from the EDS analyses by the carbon extraction replicas, the precipitates were identified as (Fe,Mn)S.

The cause of embrittlement has been proposed to precipitates or segregated sulfur at grain boundaries. In this study, precipitates of (Fe,Mn)S were observed at the nonductile surface, however, it is possible that segregated sulfur also influences hot ductility. So we investigated manganese free steel to eliminate the effect of precipitates. Figure 9 shows the SEM images of the fracture surface of manganese free steel with 0.0095 mass% sulfur when deformed at 1 223 K. Here, RA is zero. Almost half of the area of the fracture surface is concave, and the other area is convex. Precipitates are not observed on either area. The undulation
of the fractured surface would be due to meltdown of FeS. The intergranular fracture surface with precipitates is apparently different from the fracture surface with segregated sulfur. Therefore, it can be seen that the decrease in hot ductility in the austenite region in low manganese steels is attribute to precipitates of (Fe,Mn)S.

Figure 10 shows the predicted mechanism of the decrease in hot ductility caused by precipitates. Sulfur is segregated in grain boundaries, so sulfides precipitate at the grain boundaries, and a precipitation free zone (PFZ) is formed around the grain boundaries. When stress is applied, strain concentrates around the grain boundaries, because the PFZ is soft. Therefore, when stress increases, microvoids are formed on precipitates in the grain boundaries. When the voids coalesce, intergranular nonductile rupture occurs.

3.4. Precipitation of Sulfides

Sulfides are considered to be the cause of deterioration of hot ductility by providing the starting point for voids. Figure 11 shows the relationship between the quantity of precipitated sulfur (PS) and RA. Here, the RHT, the TT and the Ht are 1 573 K, 1 223 K and 300 s, respectively. PS was calculated by Thermo-Calc, and is controlled by the sulfur content at 1 223 K. RA decreases with increasing PS at a constant manganese constant. Furthermore, RA decreases with decreasing manganese content at a constant PS. This means RA is determined not only by PS but also by the manganese content.

Therefore, we will consider the influence of manganese on precipitation of sulfides. We investigated in detail samples with different manganese contents, namely, steels 3 and 9, which have similar PS in spite of different RA. Steel 9 has a higher manganese content and higher RA than steel 3. Next, the quantities of sulfur and manganese in the precipitates which were extracted from the vicinity of the fracture surface were analyzed. Here, the quantity of iron in the precipitates is difficult to evaluate because many precipitates of cementite, Fe3C, were included in the extracted precipitates.

In low manganese steel 3 (0.06 mass% Mn), the amounts of precipitated sulfur and manganese are 32 and 12 mass ppm, respectively. In the high manganese steel 9 (0.16 mass% Mn), these are 40 and 19 mass ppm, respectively. Here, for precipitates of (Fe, Mn)S, the sum of atomic percentage of iron and manganese is equal to atomic percentage of sulfur. Therefore, the quantities of precipitated iron as (Fe, Mn)S in steels 3 and 9 are calculated to be 44 and 50 mass ppm, respectively. Figure 12 shows a comparison of the calculated equilibrium quantity of precipitated sulfur with the experimental result. The quantity of precipitated sulfur at equilibrium is about 80 mass ppm, irrespective of the manganese content. Thus, the ratio of the measured quantity of precipitated sulfur to the calculated one is about 40–50% in this case. That is, the actual quantity of precipitated sulfur does not depend on the manganese content.

Figure 13 shows the TEM images of the carbon extraction replicas taken from the vicinity of the fracture surfaces
of steel 3 (0.06Mn–0.009S) and steel 9 (0.16Mn–0.008S) when deformed at 1 223 K. Here, the precipitates were analyzed by EDS, and were seen to be (Fe,Mn)S. It is clear that the precipitates in steel 3 are more distributed and smaller than those in steel 9. Figure 14 shows the distribution of the precipitate size in steels 3 and 9. Here, the areas of the precipitates were measured from the TEM images. While most precipitates are under 4.5×10^3 nm^2 in steel 3, about half of the precipitates are over 4.5×10^3 nm^2 in steel 9.

That is, when PS is constant, an increase in manganese content does not change the quantity of precipitated (Fe,Mn)S, however, it changes the size of the precipitates, causing them to become larger, in the same manner as (Fe,Mn)S, however, it changes the size of the precipitates, content does not change the quantity of precipitated (Fe,Mn)S, however, it changes the size of the precipitates.

4. Discussion

The precipitation size of (Fe,Mn)S becomes large with increasing manganese content. Regarding the growth rate of (Fe,Mn)S, the diffusion velocity of manganese is so small that the growth rate of (Fe,Mn)S is thought to be controlled by the manganese diffusion. Here, we suppose that the precipitate size is in proportion to the sum total of diffusion distance with manganese atoms. At a constant temperature and a constant time, the total distance should be in proportion to the manganese content (\(C_{\text{Mn}}\)). Furthermore, we assume that RA decreases with increasing the number of precipitates. That is, RA is proposed to decrease with increasing PS/C_{Mn}. Figure 15 shows the relationship between PS/C_{Mn} and RA for the data in Fig. 11. Here, PS is a value calculated by Thermo-Calc. It is apparent that RA corresponds to the index PS/C_{Mn} when PS/C_{Mn} is below 0.1. On the other hand, RA is below 15% at PS/C_{Mn} above 0.1, irrespective of PS/C_{Mn}. Therefore, PS/C_{Mn} must be below 0.06 in order to restrain nonductile fracture, which occurs at RA below 40% at TT of 1 223 K.

Next, we consider the influence of temperature and time on the precipitate size. Average diffusion distance (\(z_m\)) is approximately expressed as follows,\(^{15}\)

\[
z_m = (2D_t\delta)^{0.5} \quad \text{..........................(1)}
\]

Here, \(D\) is diffusion coefficient and \(t\) is diffusion time. Furthermore, the diffusion coefficient of manganese (\(D_{\text{Mn}}\)) at austenite grain boundaries is expressed as follows,

\[
D_{\text{Mn}} = D_0 \exp(-Q_{gb}/kT) \quad \text{..........................(2)}
\]

Here, \(D_0\) is frequency factor, \(Q_{gb}\) is activation energy at grain boundaries, \(k\) is Boltzmann constant and \(T\) is temperature. Therefore, precipitate size index (\(I_p\)) will be defined by the following equation:

\[
I_p = A \cdot C_{\text{Mn}} \cdot z_m = A \cdot C_{\text{Mn}} \cdot (2D_0)^{0.5} \cdot \exp(-Q_{gb}/2kT) \\
= C_{\text{Mn}} \cdot (Ht/300)^{0.5} \cdot \exp(-Q_{gb}/2kT) \quad \text{..........................(3)}
\]

Here, \(A\) is a constant of 1/(2\(D_0\cdot300)^{0.5}\). That is, RA is proposed to decrease with increasing PS/I_p and expressed as follows,

\[
RA = 100 - B \cdot PS/I_p \quad \text{..........................(4)}
\]

Here, \(B\) is a constant.

Figure 16 shows the relationship between RA and PS/(C_{Mn} \cdot (Ht/300)^{0.5}) at TT of 1 223 K. For steel 10, the improvement of hot ductility by the increase in Ht is recog-
nized by an increase in the precipitate size.

Now, the calculated PS increases mainly by increasing the sulfur content and decreasing TT, and at high temperatures, is accelerated by increasing the manganese content. Figure 17 shows the relationship between RA and PS/C\(_{Mn}\) at RHT of 1 573 K for Ht of 300 s. Here, the RHT and the Ht are 1 573 K, 300 s, respectively. When RA is above 15%, RA decreases with increasing PS/C\(_{Mn}\) at a constant TT, and increases with increasing TT.

Figure 18 shows the data plotted as ln(100−RA) vs. 1/TT at PS/C\(_{Mn}\) from 0.03 to 0.05. From the Eq. (4), the gradient is \(Q_{gb}/2k\) and is estimated at about 10 000. Then, \(Q_{gb}\) is calculated to 1.7×10^5 J/mol. Here, the activation energy of manganese lattice diffusion in austenite is 2.6×10^5 J/mol.\(^{19}\) On the other hand, the activation energy of grain boundary diffusion is estimated to be about two thirds of the activation energy of lattice diffusion,\(^{20}\) so it seems that the determined \(Q_{gb}\) is sound. Figure 19 shows the relationship between RA and PSI\(_{l}\) for the data in Fig. 17. RA decreases with increasing PSI\(_{l}\), at PSI\(_{l}\) below 300, and the constant B of the Eq. (4) is decided to be 0.3. On the other hand, RA is below 15% at PSI\(_{l}\) above 300. Then, PSI\(_{l}\) must be below 200 in order to restrain nonductile fracture at RHT of 1 573 K, because nonductile fracture occurs at RA below 40%.

As for the influence of RHT, it is necessary to consider solved sulfur in the reheating process. Figure 20 shows the relationship between RA and solved sulfur at various PSI\(_{l}\). Here, the TT and the Ht are 1 223 K and 300 s, respectively. The solved sulfur at RHT is calculated by Thermo-Calc. It is understood that RA increases as a result of a decrease in the solved sulfur with decreasing RHT, because unsolved sulfur would exist as large sulfides.

5. Conclusions

The hot ductility of low manganese steels at a high strain rate was studied. The following conclusions were obtained.

(1) Hot ductility is deteriorated in the low temperature austenite region, and a decrease in manganese and an increase in sulfur accelerate this ductility loss.

(2) A decrease in the reheating temperature and an increase in the holding time before deformation improve hot ductility.

(3) The fracture surface is classified into 2 types. One is the transgranular ductile surface and the other is the intergranular nonductile one attributed to precipitates of (Fe,Mn)S. The surface is completely ductile at RA above 40%. A partial nonductile surface is observed at RA below 40%, and the fracture surface becomes completely nonductile at RA about 10%.

(4) The quantity of sulfides increases with increasing sulfur and manganese contents and decreasing temperature. The size of the sulfides becomes large with increasing manganese content, temperature and holding time.

(5) Hot ductility in the austenite region is improved by
a decrease in the quantity of sulfides and an increase in the size of sulfides at high reheating temperatures, and by a decrease in the solved sulfur at low high reheating temperatures.

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