Influence of Manganese and Sulfur on Hot Ductility of Carbon Steels at High Strain Rate*

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Synopsis

For the sake of understanding the mechanism of the cracking in continuous casting and hot direct rolling, the mechanical behavior at elevated temperatures and in a wide range of strain rates must be investigated. Many previous reports described the hot ductility in low speed tensile tests, but only a few researchers have been concerned with high speed tensile tests.

Hot ductility of austenite in low and plain carbon steels has been examined at strain rates up to 200/s by using a hot working simulator. When Mn: S ratio is less than 20 in carbon steels, or sulfur content is greater than 30 ppm in the carbon steel without addition of manganese, the embrittlement with intergranular fracture is observed. The embrittlement is restrained if the sulfur content is less than the order of 10 ppm or Mn: S ratio is greater than 50. Thin-layered precipitates of MnS are observed on the fracture surfaces in a 0.19 % carbon steel with Mn: S ratio of 35. The effect of carbon content on the embrittlement is poorly understood. For a low carbon steel containing 0.26Mn and 0.015S, the ductility decreases with decrease of the cooling rate from the solution-treating temperature or decrease of the strain rate when the solution-treating temperature is 1 573 K. If the temperature is up to 1 673 K, however, the recovery of ductility is not achieved despite of slow cooling and low strain rate. On the other hand, the ductility in ferrite and austenite-ferrite two phase region is good at the strain rate of 10^{-4}/s.

Key words: hot ductility; high strain rate; carbon steels; intergranular fracture; manganese and sulfur contents.

I. Introduction

Ductility for carbon steels in austenite region, especially in the lower temperature range, must be clarified because ductility loss causes many defects or cracks in continuous casting process and leads to poor workability in hot direct rolling process. Many previous reports described the investigations of hot ductility with special respect to segregation behavior of impurities, such as sulfur and phosphorus; most of these tensile tests have been performed at slow speed with the strain rate range less than 10/s which is easy to practice. It is reported that, in the low temperature range of austenite, intergranular fracture occurs due to segregation of impurities to the austenite grain boundaries to lead to ductility loss. The strain rate at which the failure occurs due to concentration of slips at the tip of cracks may be higher than the nominal strain rate. In the case of hot direct rolling, the strain rate may be higher than 10/s, and in the case of continuous casting, it may be much higher than 10^{-4}/s. The research of hot ductility for steels at the strain rates higher than 10/s has hardly been performed thoroughly. Influence of manganese and sulfur contents and its relation with carbon content, and thermal cycle dependence are not systematically understood at high strain rates.

The present study is concerned with the high ductility after over-heating treatment for continuously cast carbon steels in the tensile test, mainly at a high strain rate of 200/s, by using a high speed tensile testing machine with the highest speed 2 000 mm/s. Influence of chemical compositions like manganese and sulfur on ductility loss is investigated at the high strain rate of 200/s in the low temperature range of austenite or just above the Ar3 point. Furthermore influence of initiation of austenite-ferrite transformation on ductility loss is also studied.

II. Experimental Procedures

1. Apparatus

To simulate hot working processes, the employed testing machine was specially designed; the block diagram of this simulator is schematically shown in Fig. 1. The machine is equipped with an electrical hydraulic servo system. The speed of crosshead ranges from 10^{-3} to 2 000 mm/s. Specimens are heated in a high frequency induction coil, and can be subjected to a wide range of thermal histories. The highest heating rate is 500 K/s, and cooling rate can be increased up to 80 K/s if nitrogen gas is used as coolant. Control of straining and temperature can be programmed.

2. Materials

The chemical compositions and processing conditions of continuously cast carbon steels are listed in Table 1. The carbon contents ranged from 0.05 to 0.19 %. From the columnar structure zone of cast slabs, tensile specimens were machined with their principal axis parallel to the width direction of cast slabs; the central zone of tensile specimens is 10 mm in length and 8 mm in diameter, as shown in Fig. 2. Uniform deformation can be observed at this central zone, and then the strain and strain rate are calculated from uniaxial relations.

Moreover, other samples are used to examine the influence of chemical compositions. Chemical compositions of the 0.06 and 0.19 % carbon steels are
listed in Table 2. The 15 kg ingots, melted in a vacuum furnace, were hot-forged and rolled to 20 mm thick plates at the finishing temperature of 1273 K, and the tensile specimens were cut with their principal axis parallel to the rolling direction to be of the same size as the above experiment.

3. Testing Procedures

A PR-13 thermocouple is spot-welded at the surface of specimens for temperature control and measurement. The chamber is evacuated to 5 × 10⁻⁴ torr by a diffusion pump, and tensile load is applied. As shown in Fig. 3(a), the specimens are usually heated to 1673 K at a rate of 20 K/s, solution treated at this temperature for 60 s, and then cooled at 10 K/s down to a testing temperature ranging from 1073 to 1473 K. After soaking for 120 s at the testing temperature, the specimens are tested at specific speeds. The above thermal cycle is used as the basic type of procedure. In addition to this basic thermal cycle, solution-treating temperature is changed to 1523 or 1573 K, and cooling rate is also changed to 1 K/s. For the purpose of comparison, two types of thermal cycles are employed: (1) Heat directly to testing temperature, and soak at this temperature (see Fig. 3(b)), (2) Cool down from the solution-treating temperature to 873 K at an average rate of 3 K/s, maintain at 873 K for 60 s, and reheat (see Fig. 3(c)). The tension speed is usually 2000 mm/s, and occasionally ranges from 10⁻¹ to 2000 mm/s. The fracture surfaces are observed with a scanning electron microscope (SEM), while precipitates on them are analyzed by energy-dispersive X-ray (EDX) method. Auger electron spectroscopy (AES) is also used to detect sulfur content segregated in the austenite grain boundary.

III. Experimental Results

1. Variation of Hot Ductility through Thickness in Cast Slabs

The variations of hot ductility through thickness direction in slabs for the continuously cast steels 05C, 16C and 19C are shown in Figs. 4, 5 and 6, respectively. Both steels 05C and 16C exhibit the same...
good ductility all over the columnar structure zone except for the center segregation zone where lower ductility appears. On the other hand, the ductility for the steel 19C decreases gradually from the surface zone to the central zone. The chemical analysis data of the steel 19C are nearly identical through the thickness of slabs and the same as those listed in Table 1. The data of the columnar structure zone for the steel 05G or 16C are treated together because the dependence of ductility on geometric configuration does not appear through the thickness in the columnar structure zone. While the only data from the surface zone are adopted for the steel 19C.

2. Hot Ductility of Low and Plain Carbon Steels and Its Thermal Cycle Dependence

The variations of ductility tested at 200/s with thermal histories, solution-treating temperatures and cooling rates are shown for the steels 16C, 19C and 05C in Figs. 7, 8 and 9, respectively. The steel 16C exhibits high ductility with reduction in area more than 60 % all over the testing conditions. Hot ductility is not changed even for slow cooling from 10 to 1 K/s. Embrittlement appears in the steel 19C in the case that solution treatment is performed at 1 673 K. Decrease of solution-treating temperature from 1 673 to 1 573 K brings about disappearance of such embrittlement. Ductility for the steel 05C is lower than that for the steel 16C or 19C. The ductility loss is observed in the specimen tested after solution treatment, particularly at 1 673 K. This embrittlement is reduced as the decrease of the solution-treating temperature: decrease of the cooling rate from 10 to 1 K/s leads to good ductility in the case that specimen is solution treated at 1 573 K. It is to be noted that the decrease of the cooling rate can not recover ductility loss after solution treatment at 1 673 K. When the specimen is once cooled down from solution treatment at 1 673 K to ferrite region like 873 K and reheated, the obtained ductility becomes as good as that of specimen heated directly to the testing temperature.

3. Strain-rate Dependence of Ductility

The strain-rate dependence of hot ductility for the steel 05C is shown in Fig. 10. The specimens are tested at the different strain rates at 1 173, 1 273 and 1 423 K after solution treatment at 1 573 K. It is generally said that ductility improves with decrease of strain rate; in the present tests, in the specimen tested at 1 273 K after solution treatment at 1 573 K, the poor ductility disappears at strain rates less than 10^-1/s. As the testing temperature increases to 1 423 K, the ductile–brittle transition strain rate increases to 10/s. Here to be noted, in the specimen tested at 1 173 K, no improvement of ductility is observed even at slow strain rate of 10^-2/s. In the solution treatment at 1 673 K, the same results as those at 1 573 K are obtained.

4. Influence of Chemical Compositions on Hot Ductility

For the steels 06CA and 06CB tested at 10^-2/s in the temperature range including the austenite–ferrite two phase region, the temperature dependence of ductility and maximum stress is shown in Fig. 11. Judging from the maximum stress of the steel 06CA, the austenite–ferrite two phase region of these steels is located between 1 073 and 1 123 K. For 0.06 % carbon steel containing 51 ppm sulfur (06CB), hot ductility becomes very low in the austenite region, while it becomes high in the austenite–ferrite and ferrite regions. Reducing sulfur content from 51 ppm to
less than 5 ppm (06CA), the embrittlement in the austenite region is eliminated perfectly. Sulfur certainly deteriorates the ductility in austenite region, but no bad influence is observed in ferrite region.

A series of 0.06 and 0.19 % carbon steels with various sulfur and manganese contents is tested at 200/s. The variation of ductility at 1173 K after solution treatment at 1673 K is depicted in Fig. 12. In this testing condition severe deterioration of ductility is detected in the austenite region. For the steels without addition of manganese, embrittlement with reduction in area less than 50 % is observed for the sulfur content more than 30 ppm, while the value of reduction in area increases to more than 80 % for the sulfur content less than the order of 10 ppm. No severe loss of ductility is observed despite of sulfur content of 100 ppm for the steels containing 0.5 % manganese. Influence of carbon content on ductility is not distinct in Fig. 12.

5. Observations of Microstructures

The fracture surfaces of the specimens for the con-
tenuously cast steels 05C, 19C and 16C are presented in Figs. 13, 14 and 15, respectively. For the specimen of the steel 05C tested at 1273 K and 200/s after solution treatment at 1573 K, typical intergranular fractures occurred (Fig. 13(a)). By closer examinations, some intergranular fracture surfaces are observed with dimples with the diameter of several micrometers. While smooth fracture surfaces without plastic deformation are also detected in Fig. 13(b). No precipitates can be found in the present examination. For the steel 19C, tested at 1173 K and 200/s after solution treatment at 1673 K, the lowest ductility is attained. Figures 14(a) and 14(b) show the thin-layered structures consisting of stick-shaped and slender precipitates in the fracture surfaces of the steel 19C; these precipitates are found to contain Mn, Fe and S by the EDX analysis as shown in Fig. 14(c).

Since some of the Fe signals are possibly detected from the matrix, the precipitates can be identified as (Fe, Mn)S or MnS. On the fracture surfaces of the specimen close to the center in slab of the steel 19C tested at 200/s and 1173 K after directly heating to the temperature, the precipitates of MnS are also detected. In the ductile fracture surface of the steel 16C, tested at 1173 K and 200/s after solution treatment at 1673 K, not so many plate-shaped precipitates are observed (Fig. 15(b)). Through EDX, Mn, S, Fe and Cu are detected from the precipitates, which are identified as (Mn, Cu)S or (Fe, Mn, Cu)S (Fig. 15(c)).

For the steel 05C cooled to 1173 K after solution treatment at 1673 K, the austenite grain boundaries of the specimen is examined with AES by sputtering the fracture surface with Ar⁺ ion at a rate of the order
of $10^{-3}$ A/s. The sulfur content decreased with the ion etching time as shown in Fig. 16. The sulfur content in the austenite grain boundary is about 9% with excluding carbon and oxygen, and 4% with including these elements. Thus the true sulfur content may be from 4 to 9%, and sulfur is found to segregate in the austenite grain boundary without any precipitation.

For the steels 06CB, 19CB and 19CC containing sulfur without addition of manganese, intergranular fracture surfaces without precipitation are observed as well as for the steel 05C. The examples of fracture surfaces at 1 173 K for the steel 06CB are depicted in Figs. 17(a) and 17(b). With decrease of sulfur content or increase of manganese content, ductility is improved and the fracture surfaces are changed from intergranular to transgranular, as illustrated in Figs. 17(c) and 17(d).

IV. Discussion

1. Intergranular Embrittlement

Taking into account the facts that austenite intergranular fracture takes place (Figs. 13 and 17) and that the segregation of sulfur in the grain boundary is observed (Fig. 16), it is clear that segregation of sulfur to grain boundaries without precipitation causes fragile grain boundaries, which leads to embrittlement. That is to say that the origin of embrittlement is the segregation of sulfur to austenite grain boundaries during solution treatment. This embrittlement occurs at higher temperatures and at lower strain rates in the case of higher solution-treating temperature. When solution-treating temperature is low, the embrittlement is reduced with decrease of cooling rate.

The mechanism of embrittlement has been proposed in previous works as follows. The embrittlement observed in the austenite region is due to depositions of sulfur or oxygen as sulfides or oxides along the austenite grain boundary in cooling stage after complete dissolution during solution treatment. Fine precipitates of sulfide along the grain boundary can enhance embrittlement, while the embrittlement is restrained when these precipitates are coarse.

The above explanation for embrittlement, however, ignores the facts that more intensive embrittlement is observed at higher solution-treating temperature and that precipitates are not observed. The embrittlement is enhanced with an increase of solution-treating temperature; it is partly because of the increase of segregation. Due to decrease of strain rate, external force acting at the fragile grain boundary also decreases and ductility improves. Furthermore, since the sulfur segregation disappears by lowering the cooling rate, ductility can be recovered.

For the steel 19C, the precipitation of MnS is observed in the following two cases: (1) a specimen close to the center in the slab tested after directly heated to the testing temperature, and (2) a specimen close to the slab surface tested after solution-treatment. In the continuously cast slabs, center part is held at the elevated temperature just below the melting point for longer time than the surface of slab. Segregation of sulfur progresses during the long holding time at higher temperatures, and sulfur combines with manganese, forming MnS precipitates during cooling.

2. Fracture Maps by Manganese and Sulfur

The diagram of fracture mode in manganese and sulfur contents for carbon steels is shown in Fig. 18, representing the influence of both manganese and sulfur. Open triangle mark denotes the brittle intergranular fracture, and open circles are for ductile transgranular fracture, tested at 1 173 K and 200/s. Square mark represents the case where precipitates of MnS are observed in the fracture surfaces. The results in previous works are shown by solid marks. In Fig. 18, at the right and low part where sulfur is richer and manganese is less, the embrittlement is more intensive. When sulfur content is decreased to less than 10 ppm, the embrittlement does not occur at all. Since Mn:S ratio has much influence on hot ductility rather than sulfur content, ductile-brittle transition can be decided by Mn:S ratio. Then plotting content pairs with Mn:S=40 for sulfur content more than 10 ppm, as shown in the broken line...
of Fig. 18. The steel 19C depicted with the square mark comes into under this border line. The previous works have been dealt with commercial carbon steels containing manganese over than 1 000 ppm. Further studies are necessary in the range of manganese content from 100 to 1 000 ppm. Restraint of embrittlement with addition of manganese is due to decrease of segregated sulfur content: manganese connects sulfur within the grains and suppresses movement of sulfur to grain boundaries.

3. Hot Ductility in Austenite–Ferrite Two Phase Region

It has been shown in the previous work that deformation resistance in ferrite phase at low strain rate is by several times smaller than that of austenite phase at the same temperature. Because of this, proeutectoid ferrite formed along grain boundaries causes localized deformation and this leads to lower ductility for steels in austenite–ferrite two phase region. As shown in Fig. 11, however, the present testing results reveal that embrittlement observed in the austenite region originating from sulfur segregation is suppressed by precipitation of ferrite. Furthermore, for the steel which has good ductility in austenite region, embrittlement does not appear in austenite–ferrite two phase region.

V. Conclusion

The ductility in austenite region for continuously cast carbon steels and the influence of manganese and sulfur on hot ductility for carbon steels are investigated systematically with various thermal cycles and a wider range of strain rates up to 200/s. Through precise discussions, the authors have found.

1) Influence of manganese and sulfur on ductility loss at a high strain rate of 200/s is similar to that at low strain rates from $10^{-4}$ to 10/s. The embrittlement with intergranular fracture occurs in low temperature range of austenite for carbon steels containing sulfur more than 30 ppm or with Mn:S ratio less than 20. The embrittlement is due to segregation of sulfur in the austenite grain boundary, where about 200 times concentration of sulfur content is observed through AES. When sulfur content is decreased to less than the order of 10 ppm, the embrittlement does not appear even if manganese content is less than 100 ppm.

2) For the 0.05 % carbon steel containing 0.26 % Mn and 0.019 % S, at solution-treating temperature 1 573 K, the ductility is improved with decrease of cooling rate or strain rate. In the case of solution-treating temperature of 1 673 K, ductility is deteriorated severely, and the recovery of ductility is not achieved even if cooling rate is decreased or strain rate is lowered.

3) For the 0.19 % carbon steel containing 0.67%Mn and 0.019S, when Mn:S ratio is 35, the loss of reduction in area is confirmed and the thin-layered precipitation of MnS is observed on the fracture surfaces.

4) The embrittlement at the lower temperature range of austenite is relieved with progress of ferrite formation at a strain rate down to $10^{-2}$/s.

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