Non-Metallic Inclusions and Acicular Ferrite in Low Carbon Steel

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The formation of non-metallic inclusions with variations in various oxygen, nitrogen and titanium contents in low carbon steels has been studied. The relationship between the nature of non-metallic inclusions and the formation of acicular ferrite has been also investigated. It is found that the non-metallic inclusions observed in this study are mainly consist of Ti_2O_3 and TiN together with a small amount of other complex oxides containing Mn and Si. It has been confirmed that Ti_2O_3 and TiN play an important role in formation of acicular ferrite as a nucleation site and an austenite grain refiner, respectively. But it is not clear yet whether TiN acts as a nucleation site or not. It is also found that the volume fraction of inclusions is more effective than the type or size distribution of the non-metallic inclusions on the formation of acicular ferrite.

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1. Introduction

The mechanical properties of steels critically depend on their microstructures. It is believed that the interlocking acicular ferrite in wrought steels as well as weld metals give rise to superior mechanical properties, especially toughness, because propagating cleavage cracks are deflected as they cross an acicular ferrite microstructure with its many different orientations.¹⁾ Acicular ferrite nucleate intragranularly at point sites, mainly non-metallic inclusions and secondary acicular ferrite form by sympathetic nucleation from the ferrite laths formed earlier by inclusions.^{2,3)} Therefore, acicular ferrite has to compete with allotriomorphic ferrite or Widmanstätten side plates, usually nucleated at austenite grain boundaries, during austenite-ferrite transformation.

From the published literatures on acicular ferrite in weld metals,⁴⁻⁶⁾ it is well established that non-metallic inclusions are effective nucleation sites for acicular ferrite and a variety of mechanisms for the acicular ferrite formation were proposed. There are many kinds of non-metallic inclusions which are reported to be effective in stimulating intragranular nucleation. Some titanium compounds are found to be potent⁷⁻⁹⁾ and it is suggested that the size distribution, density and chemistry of the inclusions are important in controlling acicular ferrite nucleation.^{10,11)} Most studies on improvement in mechanical properties with fine non-metallic inclusions have been aimed at increasing the toughness of the weld metals or the heat affected zone in HSLA steels,^{12,13)} and attempts to apply this method to structural wrought steels have been reported quite recently.^{14,15)}

In the present work, the effect of the nature of non-metallic inclusions on the formation of acicular ferrite in low carbon steels has been investigated. The formation of non-metallic inclusions with variations in oxygen, nitrogen and titanium contents and in austenite grain size has also been studied.

2. Experimental

Thirteen 1 kg ingots of low carbon steels were made in a vacuum induction melting and casting furnace. The chemical compositions of the steels and the average solidification rates from 1873 to 1673 K are given in Table 1. In order to simplify the chemistry of non-metallic inclusions, high-purity materials were used to exclude such elements as aluminum, calcium, magnesium, and sulfur that are commonly included in commercial steels. The manganese content was kept relatively high to maintain a high enough hardenability to suppress the formation of coarse allotriomorphic ferrite grains along the prior austenite grain boundaries and the titanium content was altered to see its effect on the formation of non-metallic inclusions. The oxygen and nitrogen contents in the melts could be varied by changing the atmosphere (Ar or N_2) in the melting chamber and/or by adding Fe_2O_3 into the melts.

For homogenization, the specimens were heated at 1273 K for 2 h. Then small portions of the ingots were cut, polished and etched with 2% Nital solution for optical microscopy in order to investigate the effect of the melting and casting conditions on the formation of non-metallic inclusions. The non-metallic inclusions were observed in the area of 1 mm² but it was difficult to identify the inclusions less than 0.5 μ m in diameter. The chemistry of the inclusions were also investigated by TEM equipped with energy dispersive spectroscopic apparatus.

The remains of the ingots were heated again at 1273 K for 1 h and subsequently hot rolled between 1123 and 1223 K to destroy the cast structures. They were then air cooled and machined into cylindrical samples (Φ 8 mm $\times$ L10 mm). These cylindrical samples were austenized at 1523 K for 20 min and cooled down to room temperature at 3 K/s using a thermomechanical simulator. The microstructures of the heat-treated specimens were observed under an optical microscope.

Table 1 Chemical composition of steels and solidification rate.

Steel number	O mass%	N mass%	C mass%	Si mass%	Mn mass%	Ti mass%	Solidification rate, K/s
1	0.004	0.002	0.11	0.19	1.61	0.0060	7
2	0.010	0.002	0.14	0.19	1.60	0.0051	7
3	0.010	0.001	0.14	0.15	1.66	0.0230	7
4	0.007	0.001	0.14	0.20	1.69	0.0045	5
5	0.009	0.008	0.16	0.16	1.52	0.0009	5
6	0.004	0.012	0.14	0.21	1.72	0.0110	7
7	0.003	0.026	0.14	0.19	1.76	0.0100	7
8	0.004	0.010	0.12	0.19	1.78	0.0078	5
9	0.008	0.002	0.12	0.18	1.62	0.0260	5
10	0.019	0.012	0.15	0.05	1.17	0.0015	7
11	0.005	0.001	0.13	0.19	1.80	0.0130	2
12	0.004	0.001	0.15	0.20	1.74	0.0200	0.01
13	0.012	0.001	0.14	0.17	1.72	0.0091	15

3. Results and Discussion

3.1 Size distribution of non-metallic inclusion in steels

The theoretical calculation²⁾ and the experimental work¹⁶⁾ reported that the effective non-metallic inclusion size for intragranular nucleation is between 0.5 and 6 μm and most inclusions in Ti-killed steel were found to be larger than 0.4 μm .¹⁶⁾

Figure 1 shows the size distribution of inclusion in steels of different compositions. Steel 4, 7 and 12 have higher oxygen, nitrogen and titanium contents than steel 1. While the increase in oxygen content (steel 4) led to large portion of inclusions above 1.5 μm , increasing nitrogen content (steel 7) produced larger portion of inclusions between 0.5 and 1.0 μm . Namely, the average diameter of inclusions changed from 1.4 to 1.6 μm as the oxygen content increased from 40 to 70 ppm, but it decreased to 1.0 μm when nitrogen changed from 20 to 260 ppm. Goto *et al.*¹⁷⁾ reported that the average size of inclusions increased with increasing oxygen content and their result agrees with the present results. This indicates that the inclusions formed in the two cases are mainly comprised of oxides. On increasing titanium content to 200 ppm (steel 12), the percentage of inclusions between 0.5 and 1.0 μm increased up to 88% and the average diameter was 0.8 μm .

3.2 Volume fraction of non-metallic inclusions

The volume fraction of non-metallic inclusions is calculated by eq. (1) after the harmonic mean and the number of inclusions per unit volume are obtained by the deHoff's eqs. (2) and (3)¹⁸⁾

$$V = \frac{\pi}{6} d_i^3 N_V \quad (1)$$

$$N_V = \frac{2}{\pi} \frac{N_A}{d} \quad (2)$$

$$\frac{1}{d} = \frac{1}{n} \sum_i \frac{1}{d_i} \quad (3)$$

where

N_V : number of inclusions per unit volume

Fig. 1 Relationship between compositions of steel and size distribution of inclusion.

N_A : number of inclusions per unit area

d_i : apparent diameter of i th inclusion among n inclusions

d : harmonic mean of inclusion size

V : volume fraction of inclusions.

The volume fractions of inclusions in the steels with different oxygen contents are shown in Fig. 2. It increases with increasing oxygen content up to 200 ppm. A similar result in the weld metals has been also published by Liu and Olson.¹⁹⁾ They reported that the nucleation of acicular ferrite within prior austenite grains is enhanced with increasing oxygen content by 200 ppm because of insufficient number of nuclei below this level of oxygen. Figure 2 shows that higher nitrogen contents lead to higher volume fractions at similar oxygen contents. In fact, yellow angular particles of TiN were frequently observed in the steel specimens with higher nitrogen contents. It seems that the variation of titanium content in this study did not affect the volume fraction of the inclusions significantly.

Fig. 2 Effect of oxygen content on the volume fraction of inclusion.

Fig. 3 Calculated phases relation of the Fe-Ti-O-N system in Fe-rich corner at 1523 K.

3.3 Formation of non-metallic inclusion

The thermodynamic calculation using the CALPHAD method²⁰⁾ has been carried out to evaluate the stability of various non-metallic inclusions, especially the possibility of TiN and Ti_2O_3 formation at 1523 K. From the calculation, it is revealed that Ti_2O_3 is the most stable phase and the other titanium oxides such as TiO and Ti_3O_5 are not thermodynamically stable phases at 1523 K which is the soaking temperature of the steels in the present study. The computer software Thermo-Calc²¹⁾ has been employed for the present calculation and the used data set of the thermodynamic parameters has been constructed based on Scientific Group Thermodata Europe (SGTE) solution and substance databases incorporated into Thermo-Calc. The phases included in the calculation were liquid, austenite, ferrite, TiO, Ti_2O_3 , Ti_3O_5 , TiN, MnO, SiO_2 , and the contents of carbon, manganese and silicon in steel are set constant as 0.14, 1.8 and 0.2 mass%, respectively.

Calculated phase relations of the Fe-Ti-O-N system in Fe-rich corner at 1523 K is presented in Fig. 3. The slope of the

Fig. 4 Calculated mole fractions of inclusions. (a) steel 7, (b) steel 11 (c) steel 2.

boundary line between the stable and unstable regions of TiN is about 0.5 and the boundary lines with 20 and 120 ppm N were very close each other. This indicates that the titanium to oxygen ratio should be higher than two for TiN to be stable non-metallic inclusions while the nitrogen content itself does not affect the stability of TiN in low oxygen contents significantly.

Although nitrogen content itself is a minor factor to determine the stability of TiN in steels as shown in Fig. 4, it seems to affect the size of TiN. Namely, the increase in nitrogen content in steels seemed to form not only fine TiN (few tens of nanometer order in diameter) below solidus temperature, but also coarse TiN inclusions (micrometer order) in the liq-

uid state or during solidification. From the literature²²⁾ on the function of TiN as an austenite grain refiner, it is known that coarse TiN can not pin austenite grain boundary effectively, which forms when the titanium content exceeds certain critical points which depended on nitrogen contents, although increasing nitrogen and titanium contents generally increase the volume fraction of TiN phase. This critical titanium content decreases with increasing nitrogen content.

The effect of nitrogen contents on the formation of non-metallic inclusions calculated by CALPHAD method is shown in Fig. 4. The TiN seems to be formed above solidus temperature with high nitrogen contents (Fig. 4(a)-steel 7) but the TiN only precipitate below solidus temperature in case of low nitrogen contents (Fig. 4(b)-steel 11). And TiN does not form when the oxygen content is relatively high (Fig. 4(c)-steel 2), because of insufficient titanium in steel to form TiN. This result could explain why the point A in Fig. 2 deviated from the extrapolated line which contains more than 80 ppm nitrogen. No TiN phase was confirmed by TEM analysis in the steel.

As shown in Figs. 5(a) and (b), tiny TiN precipitates were

found by SEM and TEM analysis although these could not be counted due to the resolution limit of optical microscopy and it is also confirmed that the inclusions above 1 μm in diameter contained lots of TiN particles with a small amount of other complex oxides containing manganese and sulfur in the steel 7. But it is thought that the amount of fine TiN precipitates in steel 7 is not sufficient to suppress austenite grain growth because the austenite grain size is bigger than those in steel 1. In the case of steel 11, it seems that increasing titanium at low nitrogen content also gives more chance for fine TiN phase to form. The number of fine TiN inclusions below 1 μm increases because lower nitrogen content of steel 11 than steel 7 leads to increase in the critical titanium content. And most oxides observed in this study proved mainly Ti_2O_3 by TEM analysis as expected from the calculation.

From these results, it may be said that the non-metallic inclusions observed in the present study (larger than about 0.5 μm) is mainly comprised of oxides but that nitride is also found when the nitrogen contents in the steels are high. Namely, TiN would be formed at a lower temperature as long as the amounts of remaining free nitrogen and titanium were

Fig. 5 (a), (b) TEM micrographs (c) EDS spectrum (d) electron diffraction spot pattern ($B = [110]$) of TiN Phases in steel 7.

large enough to produce titanium nitride after forming more stable titanium oxide.

3.4 Effect of inclusion volume fraction on microstructure

The variation in the fraction of acicular ferrite with volume fraction of non-metallic inclusions in the steels is presented in Fig. 6. The acicular ferrite fraction increases with increasing volume fraction of non-metallic inclusions. The acicular ferrite fraction varied not linearly proportional to the volume fraction of non-metallic inclusions. Lee and Pan²³⁾ suggested that the number of inclusions, mainly containing titanium oxide, may be responsible for increasing the tendency of acicular ferrite nucleation but that MnS and TiN dominant inclusions appear not to control the nucleation of acicular ferrite. Although it was not possible to show whether TiN acted as an effective nucleation site for acicular ferrite or not in the present study, it seems at least that there exists a minimum volume fraction of inclusions for the formation of stable acicular ferrite, which is above 1×10^{-4} as shown in Fig. 6. In the present study, the formation of stable acicular ferrite means more than 0.5 in volume fraction of acicular ferrite. It seems that the small volume fraction of oxide in slow cooled steels shown in Fig. 6 results from the fact that there is sufficient time for inclusions to grow and float up during solidification.

The microstructures of the steels, which have similar prior austenite grain sizes about 100 μm but different volume fractions of inclusions, are shown in Fig. 7. When the volume fraction of inclusion is 1.45×10^{-4} , the microstructure is a mix of polygonal ferrite and Widmanstätten side plates nucleated at and grown from prior austenite grain boundaries as well as intragranularly nucleated acicular ferrite. In this case, the fraction of acicular ferrite is about 0.5. When the volume fractions of inclusions increased to 3×10^{-4} , the acicular ferrite fraction increased significantly up to 0.82, while some polygonal ferrite and Widmanstätten side plates are still observed at prior austenite grain boundaries. However, bainitic structure is formed when the volume fraction of inclusion is 0.6×10^{-4} .

Fig. 6 Variation of acicular ferrite fraction with volume fraction of inclusion.

3.5 Effect of austenite grain size on microstructure

The relationship between the prior austenite grain size and acicular ferrite fraction is given in Fig. 8. Lee and Pan²⁴⁾ and Barbaro *et al.*³⁾ reported that the critical grain sizes for the formation of acicular ferrite are about 50 and 110 μm , respectively. In the present study, the acicular ferrite fraction increased with increasing prior austenite grain size as long as it is larger than about 150 μm except steels 12 of Table 1. It has low volume fractions of acicular ferrite due to slow cooling

Fig. 7 Effect of volume fraction of inclusion on microstructure of steel. (a) volume fraction of inclusion 1.45×10^{-4} (b) volume fraction of inclusion 3×10^{-4} (c) volume fraction of inclusion 0.6×10^{-4} .

Fig. 8 Effect of average austenite grain size on acicular ferrite fraction.

Fig. 9 Relationship between acicular ferrite fraction and austenite grain size in steel 13.

during solidification as mentioned before. It is concluded that both the prior austenite grain size and the volume fraction of inclusions are important factors to warrant the formation of acicular ferrite.

In order to examine the effect of the prior austenite grain size only and exclude other factors such as the volume fraction of inclusions or the austenitizing temperature, steel 13 has been heat treated as follows. After holding 5 minutes at 1623 K, different degrees of compression were applied to each samples at 1373 K followed by cooling to room temperature in order to produce different prior austenite grain sizes with the same inclusion character. Figure 9 shows the influence of the prior austenite grain size on the fraction of acicular ferrite. While the formation of acicular ferrite begins at about 70 μm , a prior austenite grain of larger than about 100 μm seems to be required for the stable formation of acicular ferrite. Namely, acicular ferrite did not form when the prior austenite grain sizes were relatively small even though the volume fractions of non-metallic inclusions seemed large enough to produce acicular ferrite. Instead, bainitic structure

Fig. 10 Effect of austenite grain size on microstructure of steel. (a) 70 μm (b) 150 μm (c) 480 μm .

was formed. Figure 10 also shows the microstructures of the steels with different prior austenite grain sizes. It is also confirmed that the fraction of acicular ferrite decreases with decreasing prior austenite grain size as the area to form acicular ferrite decreased. From the above results, it is concluded that the formation of acicular ferrite becomes more stable when austenite grain is larger than 100 μm at least under the conditions used in the present study.

4. Conclusions

- (1) It is found that the non-metallic inclusion obtained in

this study mainly composed of Ti_2O_3 and TiN phase and both phases play an important role in the formation of acicular ferrite microstructure.

(2) The minimum volume fraction of inclusions for the formation of stable acicular ferrite is about 1×10^{-4} .

(3) The prior austenite grain size suitable for the stable formation of acicular ferrite should be larger than $100 \mu\text{m}$.

(4) The volume fraction of inclusions and austenite grain size are important parameters to control acicular ferrite formation.

REFERENCES

- 1) R. Honeycombe and H. K. D. H. Bhadeshia: *Steels: Microstructure and properties*, John Wiley & Sons, Inc., New York, (1996), pp. 140–150.
- 2) R. A. Ricks, P. R. Howell and G. S. Barrihle: *J. Mater. Sci.*, **17** (1982), 732–740.
- 3) F. J. Barbaro, P. Krauklis and K. E. Easterling: *Mater. Sci. Technol.*, **5** (1989), 1057–1068.
- 4) D. J. Abson, R. E. Dolby and P. H. M. Hart: *Proceedings of the Conference on Trend in steels and consumables for welding*, Abington, The Weld Institute, (1979), pp. 75–101.
- 5) R. C. Cochrane and P. R. Kirkwood: *Proceedings of the Conference on Trend in steels and consumables for welding*, Abington, The Weld Institute, (1979), pp. 103–121.
- 6) M. Ferrante and R. A. Farrar: *J. Mater. Sci.*, **17** (1982), 3293–3298.
- 7) J. M. Gregg and H. K. D. H. Bhadeshia: *Metall. Mater. Trans.*, **25A** (1994), 1603–1611.
- 8) J. H. Shim, Y. W. Cho, S. H. Chung, J. D. Shim and D. N. Lee: *Acta Mater.*, **47** (1999), 2751–2760.
- 9) S. Matsuda and Kageyama: *Tetsu-tò-Hagane*, **62** (1976), 1356–1362.
- 10) Z. Zhang and R. A. Farrar: *Mater. Sci. Tech.*, **12** (1996), 237–260.
- 11) Y. T. Pan and J. L. Lee: *Materials and Design*, **15** (1994), 331–338.
- 12) J. M. Dowling, J. M. Corbett and H. W. Kerr: *Metall. Trans. A*, **17A** (1986), 1611–1623.
- 13) O. Grong and D. K. Matlock: *International Metals Reviews*, **31** (1986), 27–48.
- 14) I. Madriaga, J. L. Romero and I. Gutierrez: *Metall. Mat. Trans. A*: **29A** (1998), 1003–1015.
- 15) J. H. Shim, Y. W. Cho, S. H. Chung, J. D. Shim and D. N. Lee: *J. Kor. Inst. Met. & Mater.*, **36** (1998), 1993–2002.
- 16) J. L. Lee and Y. T. Pan: *Metall. Trans.*, **24A** (1993), 1399–1408.
- 17) H. Goto, K. Miyazawa and K. Tanaka: *ISIJ Int.*, **35** (1995), 286–291.
- 18) R. T. DeHoff: *Quantitative Microscopy*, McGraw-Hill Book Company, New York, (1968), p. 128.
- 19) S. Liu and D. L. Olson: *Weld. J.*, **65** (1986), 139s–149s.
- 20) L. Kaufman and H. Bernstein: *Computer Calculation of Phase Diagram*, Academic Press, New York, (1970).
- 21) B. Sundman, B. Jansson and J. O. Andersson: *CALPHAD*, **9** (1985), 153–190.
- 22) F. B. Pickering: *35th MWSP CONF. PROC.*, ISS-AIME, **XXXI** (1994), 477–491.
- 23) J. L. Lee and Y. T. Pan: *Metall. Trans.*, **22A** (1991), 2818–2822.
- 24) J. L. Lee and Y. T. Pan: *Mater. Sci. Eng.*, **A136** (1991), 109–119.