Influences of Manganese on Internal Friction and Carbon Solubility Determined by Combination of Infrared Absorption in Ferrite of Low-carbon Steels

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The influence of Mn on the solubility of C in ferrite in equilibrium with cementite was investigated in low-carbon steels containing Mn ranging from 0 to 1 mass% over the temperature range from 573 to 973 K. The internal friction method was employed together with chemical analysis of C by means of infrared absorption after combustion.

It has been clarified that Mn hardly changes the solubility of C in ferrite in equilibrium with cementite (about 0.018 mass% at 973 K), whereas Mn reduces the Snoek peak height despite the fact that the amount of C in solid solution is constant.

The proportionality constant K in the equation, Sol.C (mass ppm) = K \times O^{-1_{\text{max}}}(10^{-4}), was experimentally determined as a function of the Mn content. K increases with increase in Mn content; this is speculated to be caused by the lattice strain introduced by Mn atoms and/or the chemical interaction between Mn and C atoms.

KEY WORDS: low-carbon steel; Snoek peak; internal friction; solubility of carbon; manganese; cementite; infrared absorption.

1. Introduction

The production of steel sheets with properties such as non-ageing and paint-bake-hardenability demands strict control of the amount of C in solid solution within a range of single mass ppm. In this case, it is of great importance to understand the precipitation behaviour of C, and even the solubility of C in ferrite as basic data. Commercial steel sheets contain intentionally added alloying elements as well as impurities. However, no clear-cut information is available with regard to the effect of foreign atoms on the solubility of C in ferrite despite many previous studies. Furthermore, the influence of foreign atoms on Snoek peak has not been well understood, although the internal friction method is widely employed to determine the amount of C in solid solution.

In the present study, the influence of Mn on Snoek peak and the solubility of C in ferrite in equilibrium with cementite was investigated, since Mn is one of the most important elements in low-carbon steels.

2. Specimens and Experimental Procedures

2.1. Specimens

The chemical compositions of the steels used are listed in Table 1. Specimens of the ternary system, Fe–Mn–C, were prepared first by adding a slightly higher amount of C than the maximum solubility level in ferrite, simultaneously reducing impurity elements as low as possible. However, Al with 0.04 mass% was added in order to remove N in solid solution by fixing N as AlN, since N in solid solution contributes to Snoek peak. In fact, this amount of Al is usually added to the commercial low-carbon Al-killed steels.

Vacuum melted 10 kg ingots were hot-rolled, annealed and cold-rolled as shown in Fig. 1. All of the N was confirmed to be fixed by Al as AlN. Therefore, it is the carbon in solid solution which contributes to Snoek peak. Internal friction specimens, 115×5×0.8 mm², were carefully prepared from cold-rolled sheets with a thickness of 0.8 mm using a fine cutting machine.

2.2. Experimental Procedures

The above mentioned cold-rolled specimens were subjected to the two kinds of heat-treatment, A and B as shown in Fig. 1.

Heat-treatment A in Fig. 1 was carried out to determine the proportionality constant which converts the Snoek peak height into the amount of C in solid solution with a unit of mass ppm. Specimens with

| Table 1. Chemical composition of specimens used. (mass%) |
| C | Si | Mn | P | S | Al | N |
|---|---|---|---|---|---|---|
| 0.029 | 0.007 | 0.01 | 0.0001 | 0.0001 | 0.038 | 0.0006 |
| 0.028 | <0.005 | 0.16 | 0.0003 | 0.0001 | 0.045 | 0.0007 |
| 0.028 | <0.005 | 0.42 | 0.0007 | 0.0004 | 0.034 | 0.0005 |
| 0.027 | 0.006 | 0.96 | 0.0001 | 0.0005 | 0.034 | 0.0013 |

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varying amounts of C were prepared by decarburization annealing in air at 973 K for different times up to 18,000 s. These specimens were annealed in a salt bath at 973 K for 300 s followed by water-quenching, and subsequently subjected to internal friction measurements. It was confirmed that the annealing at 973 K for 300 s is sufficient in terms of time and temperature to make the distribution of C uniform through the thickness of the specimens. Furthermore, the same specimens employed for internal friction were also subjected to chemical analysis of C by means of the infrared absorption method after combustion.

In the case of heat-treatment B, cold-rolled specimens were subjected to annealing at 973 K for 300 s, which was confirmed to result in the dissolution of carbides until the solubility limit of C. Annealing for 300 s at 973 K was confirmed to be long enough to achieve saturation level of the Snoek peak height. Subsequently, internal friction was measured for the specimens annealed at varying temperatures over a range from 573 to 873 K followed by water-quenching. The solubility of C in equilibrium with cementite at these temperatures was determined by employing the proportionality constant $K$ which is pre-determined in heat-treatment A.

A special tool was devised both to prevent the bending of specimens and to cool the specimens evenly during water-quenching in heat-treatments A and B. It took less than 1 s to move specimens from the salt bath into the water bath for quenching. The annealed specimens were pickled as soon as possible and were kept in a liquid nitrogen vessel until they were subjected to internal friction measurement.

The internal friction apparatus was an inverted torsion pendulum type. Internal friction was measured during heating. The heating rate was 0.033 K/s and the frequency measured was 1.5 Hz. The maximum strain introduced to a specimen by torsion was about $10^{-4}$.

3. Experimental Results

The Snoek peak profiles for the specimens quenched from 973 K in heat-treatment B are shown in Fig. 2 with regard to the influence of Mn content. The Snoek peak height decreases with increase in Mn content. The half-width value tends to increase slightly with increase in Mn content. However, no separation of Snoek peak was observed. Fig. 3 shows the relationship between the total amount of C determined by infrared absorption and the Snoek peak height for the specimens quenched from 973 K after holding for 300 s in heat-treatment A. It is clear that $Q_{\text{max}}$ (the Snoek peak height above back ground value) increases with increase in total C content, reaching the saturated value at a certain amount of total C without further increase in $Q_{\text{max}}$. It is considered that the total amount of C in the inflection point corresponds to the solubility of C at 973 K in equilibrium with cementite. Although the data scatter a lot, the solubility of C is considered to be hardly dependent on Mn content and is about 180 mass ppm irrespective of Mn content.

The proportionality constant $K$ in Eq. (1)

$$\text{Sol. C (mass ppm)} = K \times Q_{\text{max}}^{-1} \times 10^{-4}$$

(1)

can be determined as a function of the Mn content based on Fig. 3. Fig. 4 shows the dependence of $K$ on Mn content. $K$ increases with increase in Mn content.

The solubility of C at other temperatures in ferrite
Fig. 3. Relationship between total C content determined by chemical analysis and Snoek peak height \(Q_{\text{max}}^2\) as water-quenched from 973 K after holding for 300 s.

![Graph showing solubility of C with total C content.]

Fig. 4. Changes in proportionality constant \(K\) in relation to Mn content.

was determined by simple multiplication of \(K\) in Fig. 4 by \(Q_{\text{max}}^2\) at each temperature, assuming that \(K\) does not depend on temperature. The solubility of C over a temperature range from 573 to 973 K is shown in Fig. 5; this scarcely changes with Mn content.

4. Discussion

4.1. Influence of Mn on Solubility of C in Ferrite

Some previous studies have been reported concerning the influence of Mn on the solubility of C in ferrite. The results obtained in the present study are plotted together with previous results in Fig. 6. The present study indicates that the solubility of C hardly changes with Mn content up to 1 mass\%, and has good agreement with that by Swartz who determined the solubility of C by internal friction for the specimen with 0 mass\% Mn.

Both Petrova et al. and Abe proposed that the solubility of C in ferrite increases with increase in Mn content. Petrova et al. reported that Mn increases the solubility of C in ferrite, e.g., with 1 mass\% Mn addition, the solubility increases from 190 to 360 mass ppm at 973 K. Since undissolved cementite is generally observed for specimens with C content as high as 300 mass ppm after water-quenching from 973 K, their results are inconsistent with the empirical data. The method employed by them for the determination of the solubility limit is not a direct one. It was based on a calculation after measuring the activity of C by the CO–CO₂ mixture gas method. As discussed later, it is generally accepted that not only the activity of C in matrix but also the partitioning of Mn between matrix and cementite is supposed to be taken into account in calculating the solubility of C based on thermodynamics. Therefore it is inferred that the discrepancy in their results compared with the actual phenomenon stems from the fact that they did not consider the influence of partitioning of Mn between matrix and cementite.

Abe reported that the solubility of C, defined as the summation of single solute C atoms and C atoms combined as Mn–C complex (dipole), increases with increase in Mn content. The method used was based on the analysis of electrical resistivity that the \(J_p\) (the amount of electrical resistivity at 273 K subtracted by that at 77 K) increases with increase in Mn content, the deviation from Matthiessen's rule. It was assumed in Abe's analysis that the contribution of Mn–C complex to the electrical resistivity at 77 K is half as that of single solute C and its contribution to \(J_p\) is zero. However, these assumptions have not been proved experimentally and are considered to be arbitrary.

On the contrary, Kleemola and Kuusisto, and Borchers and König reported that the solubility of C decreases with increase in Mn content. Kleemola and Kuusisto disregarded the influence of Mn on the proportionality constant \(K\) which converts the Snoek peak height into C in solid solution in ppm. Based on the experimental results that the Snoek peak height decreases with Mn content, they simply concluded that the solubility decreases with increase in Mn content.

Borchers and König took into consideration the fact that the proportionality constant \(K\) depends on the Mn content, using the internal friction method together with chemical analysis like the procedures...
taken in the present study. However, in their study only two data points were used in order to determine the constant $K$. Since the scatter of data in the relationship between $Q^{-\infty}_{\text{max}}$ and the total amount of C is so large, the question of the reliability of their results remains.

A recent study by Song et al.\(^{31}\) based on the measurements of electrical resistivity combined with internal friction and chemical analysis concluded that Mn hardly changes the solubility of C in ferrite, by determining the contribution of Mn-C complex to electrical resistivity.

According to Nishizawa,\(^{8}\) the solubility of C in ortho-equilibrium with cementite is thermodynamically expressed in Eq. (2)

$$\ln \left( \frac{C}{C_0} \right) = \frac{1}{T} \left[ 3(1-K^{\text{eq}}/e) - W^{\text{eq}}_{\gamma \delta} / kT \right] X \quad \ldots \ldots \ldots \ldots (2)$$

where, 
- $C$: the solubility of carbon when alloying element with X at% is present 
- $C_0$: the solubility of carbon in Fe-C binary system 
- $K^{\text{eq}}/e$: the partitioning coefficient of alloying element between matrix and cementite 
- $W^{\text{eq}}_{\gamma \delta}$: the interaction parameter between C and alloying element in ferrite.

Since the equilibrium condition of the present study is supposed to be para-equilibrium, Eq. (2) is not considered to be directly applicable to the present case. However, the following tendency is expected: Mn may not affect the solubility of C, since the two factors, that negative $W^{\text{eq}}_{\gamma \delta}$ increases the solubility, and $K^{\text{eq}}/e$ greater than the unit value decreases the solubility, may be balanced out in the case of Mn as an alloying element.

### 4.2. Influence of Mn on Snoek Peak

Since the Snoek peak height is known to be affected by texture and grain size, the discussion of these effects is presented first.

It is well known that the cold rolled and annealed texture is influenced by the presence of Mn and [111] annealing texture decreases with increase in Mn content. In order to negate the influence of texture on internal friction, cold-rolled sheets with various Mn contents are subjected to annealing at 1203 K for 120 s followed by air cooling to obtain random texture, irrespective of the Mn content. Internal friction was measured in these specimens after annealing at 973 K for 500 s followed by water-quenching. The Snoek peak height increased compared with the specimens processed in Fig. 1 with non random textures. However, the relative ratio of decrease in the Snoek peak height with Mn scarcely changed even after randomizing the annealing texture. Therefore, it is concluded that the difference in annealing texture of the specimens processed in Fig. 1 does not affect the relative height of Snoek peak.

As to the influence of grain size on Snoek peak, Stark et al.\(^{11}\) reported that after annealing at 923 K and water-quenching the specimens with 0.025 mass% C, $Q^{-\infty}_{\text{max}}$ is 0.009 for specimen with a grain size between 15 and 23 μm, whereas it is 0.012 for specimens with a larger grain size between 165 and 250 μm. The grain sizes of the specimens used in the present study are 31, 13, 15 and 10 μm for the steels with 0, 0.16, 0.42 and 0.96 mass% Mn, respectively. Since the differences in grain size in the steels used are very small compared with those of specimens used by Stark et al.,\(^{11}\) grain size does not affect Snoek peak significantly in the present study. Therefore the influence of Mn itself must be considered as the reason why $Q^{-\infty}_{\text{max}}$ decreases with increase in Mn content despite the fact that the amount of C in solid solution is constant.

With regard to the influence of alloying elements on the Snoek peak height, it is well known that a sub-peak appears in the N Snoek peak due to the
presence of Mn. Based on the above mentioned findings, the existence of an interaction between Mn and N was suggested, leading to the model described as follows. The jumping situation of N atoms in the vicinity of Mn atoms is different from that near Fe atoms, which is responsible for producing the subpeak. The theory by Koiwa on the influence of substitutional atoms on Snoek peak suggests that each sub-peak does not necessarily correspond to the jump of each interstitial atom which interacts differently with the substitutional atom. Therefore it seems to be very difficult to prove the above described model concerning the influence of alloying elements on Snoek peak.

Abe suggested that the decrease in the Snoek peak height stems from the interaction between Mn and C, i.e., the formation of Mn–C complex which does not contribute to the Snoek peak height. Moreover Yotsui et al. reported that the Mn addition produces the sub-peak for the spectrum of magnetic aftereffect. It is possible that the hypothesis mentioned above holds true. However, the present authors reported that the addition of P reduces the Snoek peak height even more drastically than Mn, despite the fact that P has no attractive interaction with C. Therefore, it is concluded that the chemical interaction between C and the alloying elements is only one of the reasons for the reduction in the Snoek peak height. Since Snoek peak is principally related to the stress-induced diffusion of interstitial atoms as shown in Fig. 7, some disturbances in Snoek peak are expected as a result of the presence of foreign atoms due to the change in binding constant when Fe atoms are replaced by foreign atoms with different atomic radius. Evaluating the elastic strain by means of the difference in atomic radius by \( r_X = r_{Fe}/2 \), where \( r_X \) stands for the atomic radius of X atom, the elastic strains calculated in the cases of P and Mn are 0.11 and 0.05, respectively. The greater influence of P than Mn on Snoek peak is expected based on the differences in elastic strain, which is in agreement with the experimental results. Therefore it may be concluded that the greater the difference in the atomic radius, the greater the reduction in the Snoek peak height.

Furthermore, it has been turned out that the relaxation intensities \((J)\) evaluated by Eq. (3),

\[ J = 2\cdot\Delta f/f_{\text{peak}} \]

are about 0.02 irrespective of Mn content despite a constant amount of C in solid solution (180 ppm) for the specimens water-quenched from 973 K in the heat-treatment B in Fig. 1. Here, \( f_{\text{peak}} \) is the frequency at Snoek peak and \( \Delta f \) is the frequency change before and after Snoek peak. This implies that, regarding the reason for the decrease in the Snoek peak height with increase in Mn content, the number of C contributing to the relaxation process decreases, while the relaxation intensity is unchanged.

In fact, the following two predominant factors, the chemical interaction and the lattice strain, are considered to coexist. In order to discuss the influence of Mn on Snoek peak more quantitatively, further detailed research is required on the interaction between C and the substitutional atoms in Fe.

5. Conclusions

The influence of Mn on the solubility of C in ferrite in equilibrium with cementite was investigated in lowcarbon steels containing Mn ranging from 0 to 1 mass% over a temperature range from 573 to 973 K. The internal friction method was employed together with chemical analysis of C by means of infrared absorption after combustion. The results obtained are summarized as follows:

1. Mn hardly changes the solubility of C in ferrite.
2. The Snoek peak height decreases with increase in Mn content, whilst the amount of C in solid solution is constant irrespective of Mn content.
3. The proportionality constant \( K \) in the equation, \( \delta \) (mass ppm) = \( K \times Q_{\text{sol}}^{\text{ppm}} \), was determined experimentally, and is shown to increase with increase in Mn content. This is inferred to be caused by lattice strain introduced by Mn atoms and/or the chemical interaction between Mn and C atoms.

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REFERENCES

1. For an example, Y. Imai, K. Masumoto and M. Sakamato: Bull. Jpn. Inst. Met., 7 (1968), 137.
2. E. F. Petrova, M. I. Lashpina and L. A. Shvartsman: Metalloved i Termichesk. Obrabotka Metal, (1960), No. 4, 22.
3. H. Abe: Memoirs of The Low-Carbon Sheet Steels Research Committee, ISIJ, Tokyo, (1987), 203.
4. H. J. Kleemola and E. A. Kuustisto: Scand. J. Metall., 5 (1976), 151.
5) H. Borchers and W. König: Arch. Eisenhüttenwes., 34 (1963), 453.
6) J. G. Swartz: Trans. Metall. Soc. AIME, 239 (1967), 68.
7) Y. W. Song, J. Kihara and K. Ushioda: Tetsu-to-Hagane, 75 (1989), 2051.
8) T. Nishizawa: Bull. Jpn. Inst. Met., 12 (1973), 491.
9) L. J. Dijkstra: Philips Res. Rep., 2 (1947), 357.
10) G. Lagerberg and E. G. Wolff: Acta metall., 6 (1958), 136.
11) P. Stark, B. L. Averbach and M. Cohen: Acta metall., 6 (1958), 149.
12) For an example, L. J. Dijkstra and R. J. Sladek: Trans. Metall. Am. Inst. Min. Met. Eng., 197 (1958), 69.
13) M. Koiwa: Phil. Mag., 24 (1971), 81.
14) H. Abe: The 14th Comm. (Internal Friction), Japan Soc. Promotion Sci. (JSPS), (May, 1986), 4.
15) M. Yotsui, H. Numakura, M. Koiwa and H. Matsui: Collected Abstracts of the 1988 Autumn Meeting of Jpn. Inst. Met., Japan Inst. Met., Sendai, (1988), 553.
16) H. Saitoh and K. Ushioda: Collected Abstracts of the 1987 Autumn Meeting of Jpn. Inst. Met., Japan Inst. Met., Sendai, (1987), 447.
17) A. Kawamoto, K. Abiko and H. Kimura: Collected Abstracts of the 1988 Autumn Meeting of Jpn. Inst. Met., Japan Inst. Met., Sendai, (1988), 266.