Formation and Decomposition of Mn-N Dipoles during Quench-Ageing in Fe-Mn-N Alloys

Kohsuke Tagashira, Hisashi Hayakawa[†] and Masatoshi Ohnishi^{††}

Department of Mechanical Systems Engineering,
Muroran Institute of Technology, Muroran 050, Japan

The formation and decomposition of Mn-N dipoles in extra low carbon steels have been investigated during ageing at several temperatures between 523 and 623 K by means of measurements of the electrical resistivity and its deviation from Matthiessen's rule (DMR). The amount of nitrogen atoms which contributed to the precipitation of nitride during ageing by the decomposition of quenched-in Mn-N dipoles, x , and the amount of single nitrogen atoms in solid solution which contributed to the precipitation, y , were calculated from the changes in the electrical resistivity and DMR during ageing. The x increased with the increase of manganese content, whereas $x+y$ was almost constant irrespective of manganese content. It was found that the value of $x/(x+y)$ increased with the increase of manganese content but maintained constant for the same manganese content independent of ageing temperature or time. The binding energy of Mn-N dipoles is estimated to be approximately 4.8×10^{-20} J for the specimen containing 0.29 mass% manganese, but the value tends to decrease slightly with the increase of manganese content.

(Received October 23, 1991)

Keywords: iron-manganese-nitrogen alloy, extra low carbon steel, manganese nitrogen dipole, electrical resistivity, deviation from Matthiessen's rule, binding energy, quench-ageing, solute chemical interaction, precipitation

I. Introduction

It is well known that carbon or nitrogen in low carbon steels has a strong influence on the formation of recrystallization texture of cold rolled sheets. The roles of such alloying elements during heat treatments in steel have been discussed as interstitial atoms in a single solid solution, precipitates such as carbide or nitride, as interstitial atoms combined with substitutional atoms, or as segregating atoms in the grain boundaries or dislocations. Strong effects of single interstitial atoms on the formation of recrystallization texture, however, is unexpected, because the diffusion mobility of solute interstitial atoms in ferrite is large and the extent of segregation of interstitial atoms into dislocations is small at recovery or recrystallization temperatures.

Recently, Abe *et al.*⁽¹⁾ proposed that a "dipole" or "S-I pair", a pair of a substitutional atom of transition metal and an interstitial atom, is formed in low carbon steels by a chemical interaction during heat treatment. Since the diffusion rate of dipoles in a solid solution may be controlled by the diffusion rate of their substitutional atoms in low carbon steels, the recovery due to the decrease of dislocation density at the early annealing stage should be strongly restrained by dipoles even if the pinning force of dislocation by dipoles is lower than the one by single interstitial atoms.

Some studies on the recrystallization texture formation

in low carbon steel sheets by introducing the concept of "dipole" in relation to its restraint effect on dislocation movements have been reported. For example, Osawa *et al.*⁽²⁾⁽³⁾ reported that the development of (111) recrystallization texture was retarded by the presence of both Mn and C in steel rather than by the presence of either Mn or C alone. Hutchinson and Ushioda also obtained similar results⁽⁴⁾. These are not always consistent with the results obtained by Hughes and Page⁽⁵⁾ that the pole intensity ratio $I(111)/I(100)$, which may be regarded as a measure of deep drawability of steel sheets, and the r -value of steel sheets are maximum at a specific assortment of Mn and C contents. Tagashira *et al.*⁽⁶⁾ also reported that the development of the (111) recrystallization texture was affected by the coexistence of Mn and N. The interaction between a substitutional atom and an interstitial atom in austenitic irons as well as ferritic iron were discussed by Shohoji⁽⁷⁾⁽⁸⁾.

In this report, the formation and the decomposition of Mn-N dipoles during quench-ageing will be discussed based on the measurement of electrical resistivity and its deviation from Matthiessen's rule (DMR) in extra-low carbon Fe-Mn-N alloys in which chemical interaction between manganese atoms and nitrogen atoms has already been recognized by the internal friction measurement⁽⁹⁾.

II. Specimens and Experimental Procedure

1. Specimens

Hot rolled low carbon steel sheets of 3 mm thickness containing four different Mn contents were cold rolled to

[†] Present address: Nippon Yakin Kogyo Co., Ltd.

^{††} Present address: Nisshin Steel Co., Ltd.

Table 1 Chemical composition of specimens (mass%).

Steel	N	C	Mn	Si	P	S
1	0.045	<0.003	0.07	<0.001	0.0005	0.0012
2	0.042	<0.003	0.29	<0.001	0.0005	0.0006
3	0.044	<0.003	0.58	<0.001	0.0005	0.0006
4	0.044	<0.003	1.17	<0.001	0.0005	0.0007

1.2 mm thickness. Then these sheets were annealed at 973 K for at least 3.6×10^5 s in wet hydrogen gas for decarburizing and denitriding. The levels of carbon and nitrogen contents became less than 0.003 mass%. Denitrided sheets were then nitrided in a mixed gas atmosphere ($72\%N_2 + 20\%H_2 + 8\%NH_3$). Nitrided sheets were heated for homogenizing at 973 K for 2.16×10^5 s in purified argon gas. At this stage, the nitrogen content for each steel was 0.01 to 0.045 mass%. In this investigation, the specimens containing 0.043 to 0.045 mass% nitrogen shown in Table 1 were used unless noticed otherwise.

Square rods of 1.2 mm were cut from the sheets and then drawn into wires 0.65 mm in diameter. Lead wires of pure iron 0.50 mm in diameter, which were fully decarburized and denitrided, were spot-welded with drawn specimens before quench-ageing treatment in advance.

2. Experimental Procedure

Specimens were at first heated at 973 K for 1.2 ks in a vacuum of less than 10^{-3} Pa for the purpose of the solution treatment, quenched in ice water and then aged at various temperatures between 523 and 623 K in 25 K steps in a salt bath ($56\%KNO_3 + 44\%NaNO_2$).

Electrical resistivities, ρ_{273K} and ρ_{77K} , on the isothermal ageing were measured at the liquid nitrogen temperature (77 K) and ice water temperature (273 K) by the four-probe method under the direct current of 300.0 mA. The resistivity measurement was carried out by inverting the poles of both potential taps and current electrodes in order to avoid the effects of thermoelectromotive force as much as possible. The change in the deviation from Matthiessen's rule (DMR) in electrical resistivity during ageing was obtained from the $\Delta\rho$ ($=\rho_{273K} - \rho_{77K}$), the description of which will be given in details later. The electrical resistivity and the DMR for decarburized and denitrided specimens were also measured.

III. Experimental Results and Discussion

1. Change in the electrical resistivity and the DMR during ageing

The change in electrical resistivity measured at 77 K during ageing is shown in Fig. 1 for various ageing temperatures between 523 and 623 K. As nitrogen atoms in supersaturated solid solution precipitated into nitride during ageing, the electrical resistivity decreased with the advance of precipitation reaction. The reduction in electrical resistivity increased with an increase in ageing temperature on the whole.

Fig. 1 The change in electrical resistivity at 77 K during isothermal ageing at 523, 573 and 623 K for Fe-Mn-0.04 mass%N alloys with varying manganese contents from 0.07 to 1.17 mass%.

The electrical resistivity of dilute alloys at temperature T is generally expressed by the following equation;

$$\rho_T = \rho(c) + \rho(T) + \Delta(c, T), \quad (1)$$

where $\rho(c)$ is the temperature independent residual (i.e. impurity) resistivity, $\rho(T)$ is the resistivity of pure matrix alloy at that temperature and $\Delta(c, T)$ is the term of the (DMR). The difference between electrical resistivity measured at T_1 and T_2 , is described as,

$$\Delta\rho = \rho(T_2) - \rho(T_1) + \Delta(c, T_2) - \Delta(c, T_1). \quad (2)$$

In this study, T_1 and T_2 are chosen 77 and 273 K, respectively. If c_0 and c_t are the concentrations of solute atom at ageing time $t=0$ and t , respectively, the change in electrical resistivity at 77 K and $\Delta\rho$ during ageing will be,

$$\Delta\rho_{77K} = \{\rho(c_0) - \rho(c_t)\} + \{\Delta(c_0, 77 K) - \Delta(c_t, 77 K)\} \quad (3)$$

$$\Delta(\Delta\rho) = \{\Delta(c_0, 273 K) - \Delta(c_t, 273 K)\} - \{\Delta(c_0, 77 K) - \Delta(c_t, 77 K)\}. \quad (4)$$

This $\Delta(\Delta\rho)$ means the change in DMR during ageing. If the measuring temperature of electrical resistivity is always kept constant, the changes in ρ_{77K} and $\Delta\rho$ during ageing must depend on only the change in the concentration of solute atoms in ferrite.

Figure 2 shows the change in $\Delta\rho$ during ageing at various temperatures that could be replaced with the change in DMR. The change in DMR decreased in the 0.07 mass%Mn specimens during ageing, whereas the DMR increased in the specimens containing manganese more than 0.29 mass%. The increase in DMR during ageing was getting larger with increasing manganese content. This DMR change during ageing has also been observed for Fe-Mn-C alloys⁽¹⁾ and Fe-Mn-Si-C alloys⁽¹³⁾.

By introducing the concept of dipole⁽¹⁾, this phenomenon can be explained as follows. That is, (1) Mn-N dipoles may be formed in α -iron after the solution treatment due to the chemical interaction between manganese and nitrogen, (2) quenched-in dipoles may decompose to single solute manganese atoms and single solute nitrogen atoms during ageing process, and the latter will soon diffuse into nitride precipitation sites, (3) the increase of single solute manganese atoms due to the decomposition of dipoles may affect an increase in DMR, (4) the decrease of supersaturated solute nitrogen atoms due to the precipitation may not have a strong effect on DMR change, (5) the amount of decomposition of dipoles may increase with manganese content.

2. Relation between the increase of DMR and the decomposition of dipole during ageing

Single solute nitrogen atoms intrude preferentially into Fe-Mn interstitial sites as stable octahedral sites in α -iron, where a substitutional atom Mn is in place of a solvent atom Fe on the octahedral site. As a result, the solute nitrogen atom in the Fe-Mn site will interact with “d shell electron” of the manganese atom and the scattering power of electron of a pair of Mn and N atoms will be weakened. Thus the contribution of Mn-N dipole toward DMR is expected to be lower than the sum of these single solute manganese and nitrogen atoms. If these dipoles decompose and single nitrogen atoms diffuse into the precipitation sites, the scattering power by single solute manganese atoms returns strong by again, then the DMR must increase.

When both the decomposition of Mn-N dipole and the precipitation of nitride are occurring simultaneously during ageing, then

If the mole quantities for both reactions are a and b , respectively,

If $x=a$ and $y=b-a$, x expresses the amount of nitrogen atoms which contribute to the precipitation of nitride during ageing by the decomposition of dipoles, y the amount of single nitrogen atoms in solid solution in

Fig. 2 The change in the deviation from Matthiessen's rule (DMR), $\Delta\rho$, during isothermal ageing at 523, 573 and 623 K for Fe-Mn-0.04 mass%N alloys corresponding to Fig. 1.

α -Fe which contribute to the precipitation, and $x+y$ total amount of nitrogen atoms contributing to the precipitation. In connection with both reactions, the changes in the electrical resistivity and DMR during ageing can be expressed as follows:

$$\begin{aligned} \Delta\rho_{77K} &= (\alpha_{\text{Mn}} - \alpha_{\text{Mn-N}} + \alpha_{\text{Fe}_n\text{N}})x + (-\alpha_{\text{N}} + \alpha_{\text{Fe}_n\text{N}})y, \\ \Delta(\Delta\rho) &= (\beta_{\text{Mn}} - \beta_{\text{Mn-N}} + \beta_{\text{Fe}_n\text{N}})x + (-\beta_{\text{N}} + \beta_{\text{Fe}_n\text{N}})y, \end{aligned} \quad (7)$$

where, α_{N} , $\alpha_{\text{Fe}_n\text{N}}$, α_{Mn} and $\alpha_{\text{Mn-N}}$ stand for values of the contribution of nitrogen atoms in solid solution, nitride, manganese atoms in solid solution and Mn-N dipoles toward ρ_{77K} , respectively. Similarly, β_{N} , $\beta_{\text{Fe}_n\text{N}}$, β_{Mn} and $\beta_{\text{Mn-N}}$ stand for values of the respective contribution toward $\Delta\rho$. If the coefficients α_i and β_i in eq. (7) are decided and also experimental values by electrical resistivity measurements are put in the place of $\Delta\rho_{77K}$ and $\Delta(\Delta\rho)$, then x and y can be calculated.

3. Determination of coefficients α_i and β_i in simultaneous eq. (7)

The ρ_{77K} and $\Delta\rho$ for decarburized and denitrided specimens just after quenching from 973 K are shown as a function of manganese content in Fig. 3. Both ρ_{77K} and

$\Delta\rho$ are proportional to manganese content. From the slopes of straight lines in Fig. 3, values of the contribution of manganese atoms in solid solution toward ρ_{77K} and $\Delta\rho$, α_{Mn} and β_{Mn} , respectively, were determined to be $260 \times 10^{-8} \Omega m/mol$ and $270 \times 10^{-8} \Omega m/mol$. The value of α_{Mn} is similar to the one obtained by Song *et al.*⁽¹⁰⁾ but larger than the value $190 \times 10^{-8} \Omega m/mol$ obtained by Abe *et al.*⁽¹¹⁾ The value of β_{Mn} is larger than the values of approximately $230 \times 10^{-8} \Omega m/mol$ obtained by both groups.

At the present stage, there is no effective way of determining the values of α_{Mn-N} and β_{Mn-N} . Therefore, it was assumed that these values were similar to those of α_{Mn-C} and β_{Mn-C} in the Mn-C dipole. In order to decide the values of α_{Mn-C} and β_{Mn-C} , 0.58 mass% and 1.17 mass%Mn specimens containing less than 0.002 mass% nitrogen and 0.003 to 0.004 mass% carbon were quenched from 973 K and aged at 523 K for 10^7 s. From the comparison of the solubility of carbon and nitrogen, it is probable that only carbon atoms will contribute to the precipitation during ageing at 523 K. In the first place, α_{Mn-C} and β_{Mn-C} are regarded as $0 \Omega m/mol$. Then total amounts of carbon atoms contributing to the precipitation of carbide, $x+y$, which could be calculated from the same equations used by Abe *et al.*⁽¹¹⁾, were found to be 2×10^{-4} mol for 0.58 mass%Mn and 3×10^{-4} mol for 1.17 mass%Mn. These values exceed the carbon contents in the steels. This contradiction is probably caused mainly by taking no account of α_{Mn-C} and β_{Mn-C} in the analysis.

Now let's move on to the next analysis to get the relation between the total amount of carbon, $x+y$, and α_{Mn-C} by assuming of β_{Mn-C} values. Figure 4 shows the calculated results for the 1.17 mass%Mn specimen. In order to restrain the carbon content below 0.004 mass% ($=1.8 \times 10^{-4}$ mol), the value of α_{Mn-C} can be estimated, for example, to be at least $400 \times 10^{-8} \Omega m/mol$ for $\beta_{Mn-C}=0 \Omega m/mol$ or $550 \times 10^{-8} \Omega m/mol$ for $\beta_{Mn-C}=$

$100 \times 10^{-8} \Omega m/mol$. The values of α_{Mn-C} and β_{Mn-C} were assumed to be $0 \Omega m/mol$ and $400 \times 10^{-8} \Omega m/mol$, respectively. The results of calculation for 1.17 mass%Mn specimens shown in Fig. 4 were the same as for the decarburized and denitrided 0.58 mass%Mn specimens. Now the values of α_{Mn-C} and β_{Mn-C} are diverted to those of α_{Mn-N} and β_{Mn-N} , respectively.

The influence of nitrogen content on ρ_{77K} was not recognized for 0.07 mass%Mn specimens after complete precipitation treatment at 523 K for 10^7 s. So the contribution of stable precipitates (γ' phase) to the electrical resistivity, α_{Fe-N} , are to be $0 \Omega m/mol$. Figure 5 shows the relation between the nitrogen content and ρ_{77K} for 0.07 mass%Mn specimens just after quenching from 973 K and after full ageing at 373 K for 10^7 s. The value of ρ_{77K} is approximately proportional to nitrogen level, c_N (at%), for each heat treatment, that is, $\rho_{77K}=6.1c_N+0.7$ for the specimen just after quenching, and $\rho_{77K}=0.9c_N+0.7$ for the specimen after full ageing. Then the contribution of nitrogen atoms in solid solution and metastable precipitates (α'' phase) to the electrical resistivity, α_N and α_{Fe-N} , are estimated to be $610 \times 10^{-8} \Omega m/mol$ and $90 \times 10^{-8} \Omega m/mol$, respectively. The value of α_N has been estimated as $700 \times 10^{-8} \Omega m/mol$ by Wagenblast *et al.*⁽¹¹⁾, or $595 \times 10^{-8} \Omega m/mol$ by Abiko *et al.*⁽¹²⁾ But no reliable value about α_{Fe-N} has been reported as yet. The value of β_{Fe-N} , contribution of metastable α'' phase toward DMR, was assumed to be zero as in the previous report⁽¹³⁾.

The value of β_N was estimated under the following hypotheses. (1) The amount of precipitating nitrogen atoms, that can be calculated from the equations proposed by Fast and Verrijip⁽¹⁴⁾ for estimating the solubility of nitrogen in equilibrium with the α'' and γ' phase, must be consistent with the amount of $x+y$ calculated from eq. (7) for the full-aged 0.07 mass%Mn specimens. (2) The value of β_N is independent of manganese contents in steel.

Fig. 3 The electrical resistivity at 77 K, ρ_{77K} , and the $\Delta\rho (= \rho_{273K} - \rho_{77K})$, as a function of manganese content for extra low carbon and nitrogen Fe-Mn alloys.

Fig. 4 Effect of β_{Mn-C} on the calculated carbon concentration contributing to the precipitation of cementites as a function of α_{Mn-C} for 1.17 mass%Mn specimens. α_{Mn-C} : the value of the contribution of Mn-C dipoles to ρ_{77K} , β_{Mn-C} : the value of the contribution of Mn-C dipoles to $\Delta\rho$.

Fig. 5 Relation between the concentration of nitrogen and the electrical resistivity for 0.07 mass%Mn specimens just after quenching from 973 K, ●, and after isothermal ageing at 373 K for 10^7 s, ○.

Figure 6 shows the relation between β_N and the mole fraction of nitrogen calculated from eq. (7) for 0.07 mass%Mn specimens quenched from 773 K and then aged at 573 K for 10^7 s. β_N should be about $90 \times 10^{-8} \Omega\text{m/mol}$, as the value of $x+y$ must coincide with $1.45 \times 10^{-3} \text{ mol}$, which is the amount of nitrogen calculated based on the above hypothesis (1). Similar value of β_N was obtained for specimens aged at another temperature. In this instance, the value was 30% larger than the value of $\beta_c^{(11)}$.

All coefficients in the simultaneous eq. (7) were determined as mentioned above, that is, $\alpha_N=610$, $\alpha_{Mn}=260$,

Fig. 6 Relation between β_N , which is the value of contribution of nitrogen in solid solution to $\Delta\rho$, and the mole fraction of nitrogen. x : the amount of nitrogen contributing to precipitations by the decomposition of Mn-N dipoles, y : the amount of nitrogen contributing to precipitations from single solute nitrogen atoms in solid solution, $x+y$: the amount of total nitrogen contributing to precipitations.

$\alpha_{Mn-N}=400$, $\alpha_{Fe-N}=0$ for stable precipitation or 90 for metastable precipitation and $\beta_N=90$, $\beta_{Mn}=270$, $\beta_{Mn-N}=0$, $\beta_{Fe-N}=0$ (unit: $\times 10^{-8} \Omega\text{m/mol}$).

4. The effect of manganese on the amount of Mn-N dipole

Mole fractions of x and y as a function of manganese content for various ageing temperatures are shown in Figs. 7 and 8. The result for the decomposition of Mn-C dipoles reported by Abe *et al.*⁽¹⁾ is also included in Fig. 7 for reference. The amount of x is nearly zero on the 0.07 mass%Mn specimens but tends to increase with manganese content, whereas the amount of y decreases. Both x and y decrease with the increase in ageing temperature. The total amounts of $x+y$ seem to be independent of the manganese content at any ageing temperatures. Concerning to the decrease of x with increasing ageing temperature, the increase of equilibrium concentration of dipoles with increasing temperature might be the main factor. As a result, the degree of supersaturated concentration of dipoles must decrease at higher temperatures.

The presence of dipoles in steels has been suggested based on experiments measuring internal friction⁽⁹⁾⁽¹⁴⁾⁽¹⁵⁾. According to the result by Enrietto the amount of dipoles decreases with the increase in solution treatment temperature⁽¹⁵⁾. In the present investigation, however, the amount of dipoles increases with the increase in solution treatment temperature.

The amount of $x+y$ in the specimens aged at 523 K exceeds slightly the nitrogen content of $1.8 \times 10^{-3} \text{ mol}$ measured by chemical analysis. For this reason, the values of some coefficients in eq. (7), especially the values of α_{Mn-N} and β_{Mn-N} , should be reconsidered in detail. In fact, if carbon content is assumed as 0.003 mass% ($=1.38 \times 10^{-3} \text{ mol}$), the value of α_{Mn-C} may be estimated to be $560 \times 10^{-8} \Omega\text{m/mol}$ from Fig. 4. This value would reduce $x+y$ to less than $1.8 \times 10^{-3} \text{ mol}$.

At first glance from Fig. 7, there seems to be a

Fig. 7 Relation between manganese content and the mole fraction of x for various ageing temperatures. Broken line: decomposition of Mn-C dipoles obtained by Abe *et al.*⁽¹⁾

Fig. 8 Relation between manganese content and the mole fraction of y for various ageing temperatures.

resemblance between two kinds of dipoles, Mn-C and Mn-N. Though the atomic concentration of carbon in the specimens used by Abe *et al.*⁽¹⁾ was higher than the nitrogen concentration in the specimens used in this study, the amount of decomposed Mn-C dipoles during ageing was less than Mn-N dipoles. This may be caused by the difference in the amount of interstitial atoms in solid solution. And the amount of dipoles may relate to the amount of interstitial solubility.

Figure 9 shows the relation between $x+y$ and x after the completion of precipitation treatments at various ageing temperatures. The x seems to be proportional to the $x+y$ as long as the manganese content is the same. The slopes increase with the increase of manganese content and are independent of ageing temperatures. Figure 10 shows the relation between $x+y$ and x throughout ageing at 573 K for various manganese contents.

It is easy to find a common relationship in Figs. 9 and 10 on the slopes of straight lines. For constant manganese content, both nitride precipitation and dipole decomposition proceed while keeping the same value of $x/(x+y)$ during ageing from the early to the final stage, that is, over all conditions from supersaturated solid solution to equilibrium. This suggests that the ratio of the amount of single nitrogen atoms by the decomposition of dipoles to the total amount of nitrogen contributing toward the precipitation is always kept in constant for the same manganese content in steels and is regardless of its equilibrium or non-equilibrium conditions.

If the ratio of the amount of single solute nitrogen atoms to the amount of residual dipoles during ageing is equal to the ratio just after quenching, y_0/x_0 , it can be expressed that $y_0/x_0 = (y_0 - y)/(x_0 - x)$. Therefore, $y_0/x_0 = y/x$, and then $(x_0 - x)/\{(x_0 + y_0) - (x + y)\} = x/(x + y) = \text{constant}$. Thus the same relation as in Fig. 10 might be valid between the total amount of nitrogen atoms in solid solution and the amount of dipoles existing during ageing.

Fig. 9 Relation between $x+y$ and x after complete precipitation treatment at various ageing temperatures.

Fig. 10 Relation between $x+y$ and x during ageing at 573 K for various manganese contents.

Figure 11 shows the relation between the binding energy of Mn-N dipole and manganese content calculated from cell model⁽¹⁾. The binding energy decreases slightly with manganese content. The energy level of Fe-Mn site or Fe-Fe site against intrusion of nitrogen atom might be varied by the manganese content. Enrietto⁽¹⁵⁾ assumed that a single solute manganese atom has an effect of decreasing the potential energy of such interstitial sites and that the lattice field affected by a manganese atom might extend to a few atomic space distances. If this assumption is right, nitrogen atoms will penetrate preferentially into Fe-Mn sites or Fe-Fe sites with lower energy levels due to the effect of solute manganese atoms rather than ordinary Fe-Fe sites. The

Fig. 11 Relation between the binding energy of Mn-N dipole and manganese content calculated from "cell model"⁽¹⁾.

number of Fe-Fe sites affected by manganese atoms will also increase with the manganese content. Though the binding energy of dipole, the average energy difference between Fe-Mn site and ordinary Fe-Fe site, should be essentially constant, it might decrease on appearance due to the existence of Fe-Fe sites which are affected by the substitutional manganese atom.

IV. Conclusion

Electrical resistivity was measured at 77 K and 273 K for extra low carbon steels containing four different kinds of manganese content which were heated at 973 K, quenched into ice water and then aged at various temperatures between 523 and 623 K. From the change in the electrical resistivity and DMR during ageing, following results were obtained.

(1) With the increase of manganese content, the amount of decomposition of Mn-N dipoles formed at the solution treatment increases and the amount of nitrogen atoms diffusing from Fe-Fe sites to precipitation sites decreases during ageing.

(2) The ratio of the amount of Mn-N dipole decomposition to the total amount of nitrogen contributing to the nitride precipitation increases with the manganese content but is independent of both ageing temperature and ageing time.

(3) The binding energy of Mn-N dipole is 4.8×10^{-20} J for 0.29 mass%Mn specimen and it decreases slightly with the increase of manganese content.

Acknowledgements

The authors wish to thank Emeritus Prof. H. Abe of the University of Tokyo for valuable discussions. They also thank Dr. A. Okamoto of Sumitomo Metal Industries Ltd. for the preparation of specimens, and Messrs. K. Hatakeyama, A. Obata and S. Ikeda, graduate students of Muroran Institute of Technology, for their cooperation in these experiments.

REFERENCES

- (1) H. Abe, T. Suzuki and S. Okada: *Trans. JIM*, **25** (1984), 215.
- (2) K. Osawa and K. Kurihara: *The Report of Low Carbon Steel Sheet Research Committee*, The Iron and Steel Institute of Japan, Tokyo, (1987), p. 108.
- (3) K. Osawa, K. Matudo, K. Kurihara and T. Suzuki: *Tetsu-to-Hagané*, **72** (1986), 1728.
- (4) W. B. Hutchinson and K. Ushioda: *Proc. of ICOTOM7*, (1984), 409.
- (5) I. F. Hughes and E. W. Page: *Met. Trans.*, **2** (1971), 2067.
- (6) K. Tagashira, W. B. Hutchinson and I. L. Dillamore: *Trans. JIM*, **26** (1985), 79.
- (7) N. Shohoji: *Surface and Coatings Technology*, **28** (1986), 365.
- (8) N. Shohoji: *J. Materials Science*, **21** (1986), 2147.
- (9) I. G. Ritchie and R. Rawlings: *Acta Met.*, **15** (1967), 491.
- (10) Y. W. Song, J. Kihara and K. Ushioda: *Tetsu-to-Hagané*, **75** (1989), 2051.
- (11) H. Wagenblast and S. Aaraj: *J. Iron Steel Inst.*, **180** (1955), 337.
- (12) K. Abiko and Y. Imai: *Trans. JIM*, **18** (1977), 113.
- (13) K. Tagashira, N. Sumita and H. Hayakawa: *Mater. Trans.*, *JIM*, **30** (1989), 10.
- (14) J. D. Fast and M. B. Verrijip: *J. Iron Steel Inst.*, **180** (1955), 337.
- (15) J. F. Enrietto: *Trans. Met. Soc. AIME*, **224** (1962), 43 and 1119.