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Effect of antimony surface treatment on nitrogen absorption during batch annealing of an electrical steel sheet

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Nitrogen absorption is usually observed during batch-type hot-band annealing of electrical steel sheets containing aluminium. This nitrogenizing causes the deterioration of magnetic properties, such as core loss and induction. In order to prevent nitrogenizing, we investigate an antimony treatment on the hot strip surface of electrical steel sheets containing aluminium. Potassium antimonyl tartrate and colloidal antimony oxides (Sb_2O_5) are effective against nitrogenizing. It seems that active sites on the surface of the hot strip after pickling are covered with antimony oxides to block the adsorption of nitrogen. Magnetic properties, after cold-rolling and continuous annealing of the nitrogenizing hot band, deteriorate due to small grains near the surface whose boundaries are pinned by aluminium nitrides.

1. Introduction

Hot-band annealing is widely used to improve the magnetic properties of electrical steel sheets. Yashiki and co-workers [1, 2] studied the effect of hot-band grain size on magnetic properties of non-orientated electrical steels and concluded that core loss and induction were improved with an increase in the hot-band grain size. Electrical steel sheets contain silicon, aluminium and manganese to decrease the core loss by increasing the electrical resistance. Hou *et al.* [3] studied the effect of aluminium, in the range 0.022–0.32 wt %, on the magnetic properties of electrical steel sheets and pointed out that those properties improved with increasing aluminium content. In the case of silicon steel containing aluminium, however, nitrogenizing occurs and aluminium nitrides form in the steel during batch-type hot-band annealing in a non-oxidized atmosphere, such as hydrogen and nitrogen mixed gas. These nitrides strongly inhibit grain growth during the final continuous annealing and deteriorate the magnetic properties [4]. Perrin *et al.* [5] studied the effects of antimony, tin and arsenic additions to prevent this nitrogenizing. However, these elements in steel inhibit grain growth during the final continuous annealing [6]. To solve these nitrogenizing and inhibiting problems, we intend to cover only the sheet surface of the steel with antimony. In this study, we investigate antimony treatment on the hot-band surface to prevent nitriding of aluminium in steel during batch-type annealing.

2. Experimental procedure

Four silicon steels containing aluminium hot bands and one silicon steel without an aluminium hot band (2.3 mm thick) were prepared by commercial basic oxygen steelmaking, vacuum degassing, continuous casting and conventional hot-rolling processes. These hot bands were pickled with hydrochloric acid (0.5 N) to remove scale. The chemical compositions of these hot bands are shown in Table I.

The pickled hot bands were dipped into the anti-nitrogenizing solutions (concentration, 1×10^{-5} to 1×10^{-2} mol l^{-1}; coated ratios, 1×10^{-4} to 1×10^{-7} mol m^{-2}), dried and annealed in a nitrogen atmosphere furnace between 973 and 1173 K for 17 h, then cooled to room temperature in nitrogen. The annealed steels were examined by quantitative analysis of nitrogen absorption and microstructures. Precipitates were identified by transmission electron microscopy (TEM, Hitachi HU-700H, at 100 kV) coupled with an energy dispersive X-ray analyser EDAX).

The annealed hot bands were cold-rolled to 0.5 mm thick by a four-high-pilot cold-rolling mill with total reduction of 78%. The continuous annealing was performed with a Shinku-Riko ULVAC CCT-QB simulator along the heat diagram in Fig. 1. Continuous annealed sheets were cut to 30×100 mm dimension, either longitudinal or transverse to the rolling direction for miniature Epstein frame specimens. Magnetic properties were measured using the miniature Epstein frame of Yokogawa Electric Works Measuring System.

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TABLE I Chemical compositions of hot bands (wt %)

Steels	C	Si	Mn	P	S	Soluble Al	N
1	0.005	0.52	0.59	0.099	0.005	0.246	0.0050
2	0.003	0.97	0.21	0.022	0.004	0.195	0.0055
3	0.003	1.58	0.57	0.048	0.003	0.302	0.0026
4	0.004	2.00	0.43	0.032	0.005	0.254	0.0032
5	0.003	0.50	0.30	0.070	0.008	Trace	0.0039

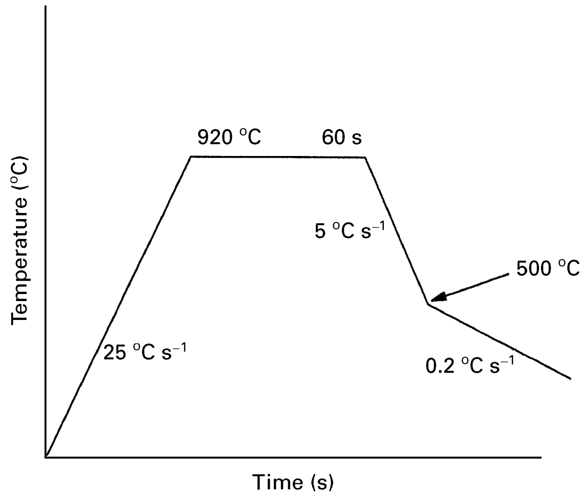


Figure 1 Heat treatment diagram of continuous annealing.

3. Results and discussion

To make the reaction of nitrogen absorption clear, steel 4 was annealed in nitrogen at 1123 K for 17 h without any treatment. Small grains were observed near the surface. Microstructural analysis conducted by TEM revealed that aluminium nitrides formed near the surface where the grain growth was inhibited (Fig. 2). Therefore, nitrogen absorption leads to a nitriding of aluminium in steel in this case. To minimize this nitriding, blocking or poisoning surface-active sites is effective. It is well known that group 4B, 5B and 6B elements of the periodic table poison surface-active sites; therefore, group 4B, 5B and 6B cations or oxo-complexes (MO_n^{m-}, where M is a metal) were investigated as anti-nitrogenizing agents (Table II). The antimonyl anion was the most effective agent in preventing the nitrogenizing.

Colloidal antimony oxides play the small role as the anti-nitrogenizing effect of antimonyl anion (Fig. 3). Therefore, antimony oxides on the surface also prevent nitrogenizing by blocking active sites. Because antimonyl oxide is present in a very small amount on the surface, it is impossible to detect antimony by surface-science techniques after annealing.

Fig. 4a, b shows the effect of antimonyl concentration in solution. Steel 1 (Fig. 4a) and steel 3 (Fig. 4b) reveal the same behaviour on nitrogenizing. At temperatures below 1073 K, the most concentrated solution (1×10^{-4} mol m^{-2}) treatment was effective, while the diluted solution (1×10^{-7} mol m^{-2}) treatment was ineffective or the same as no treatment. At temperatures over 1100 K, only the most concentrated solution (1×10^{-4} mol m^{-2}) treatment had the same effect on decreasing nitrogen absorption. Fig. 5 shows the anti-nitrogenizing effects of steels of different chemical compositions. Although steels 1, 2, 3 and 4 all contain aluminium, they have different silicon contents, but the behaviour of nitrogen absorption is almost the same. On the other hand, steel 5, which contains silicon and a trace amount of aluminium, does not exhibit nitrogenizing without treatment.

The magnetic properties, after cold-rolling and continuous annealing, of steel 4 after various nitrogenizing treatments are shown in Fig. 6. Iron loss deterioration of steel 4 increases as a function of nitrogen absorption. This is because a surface lap of small grains is produced due to an increase in nitrides at the surface.

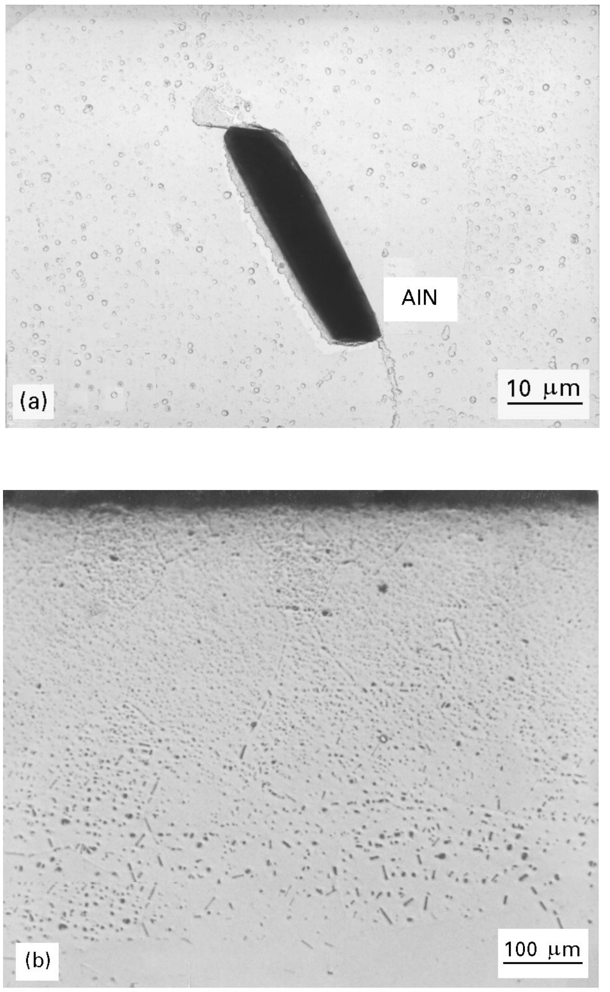
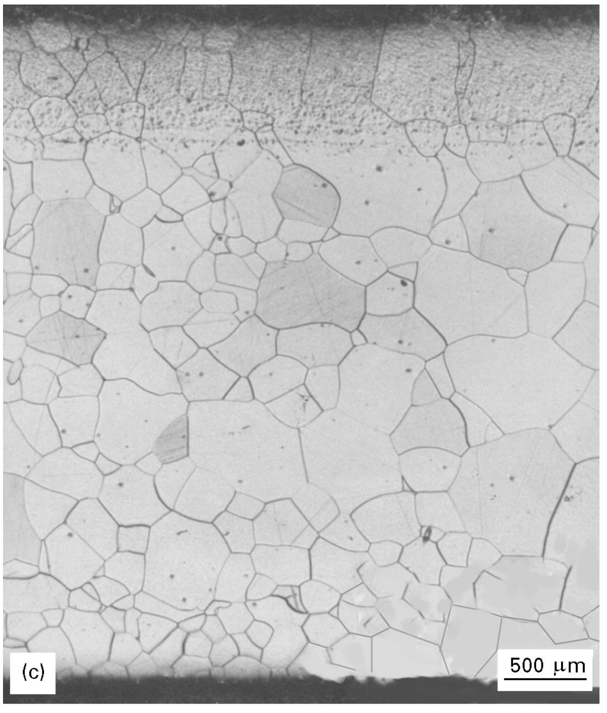


Figure 2 (a–d) Microstructure of steel 4 after annealing in nitrogen.



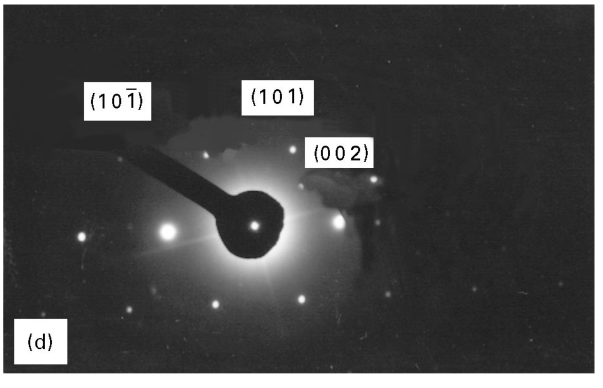


Figure 2 (*continued*).

TABLE II Effect of anti-nitrogenizing solution treatment[a]

Ions	Nitrogen absorption (wt p.p.m.)[b]
SbO^-	352
Te^{4+}	549
Bi^{3+}	632
SeO_3^{2-}	636
AsO^{3-}	648
Sn^{2+}	712
Pb^{2+}	753
Blank	752

[a] Pickled hot bands of steel 4 dipped into 0.1 mol l^{-1} solution (1×10^{-5} mol m^{-2} coated) and annealed in nitrogen at 1148 K for 17 h.
[b] Nitrogen absorption was calculated by subtracting the nitrogen content before hot-band annealing from the nitrogen content after hot-band annealing.

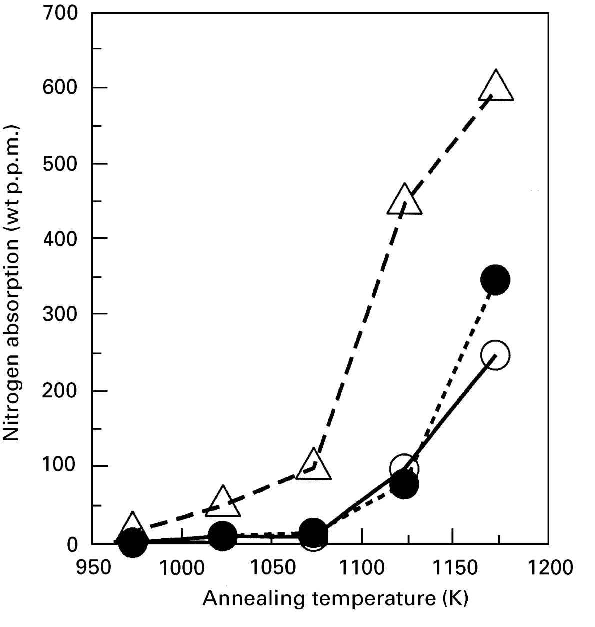


Figure 3 Nitrogen absorption with antimonyl treatment (steel 4): (△) no treatment, (●) SbO, (○) Sb_2O_5.

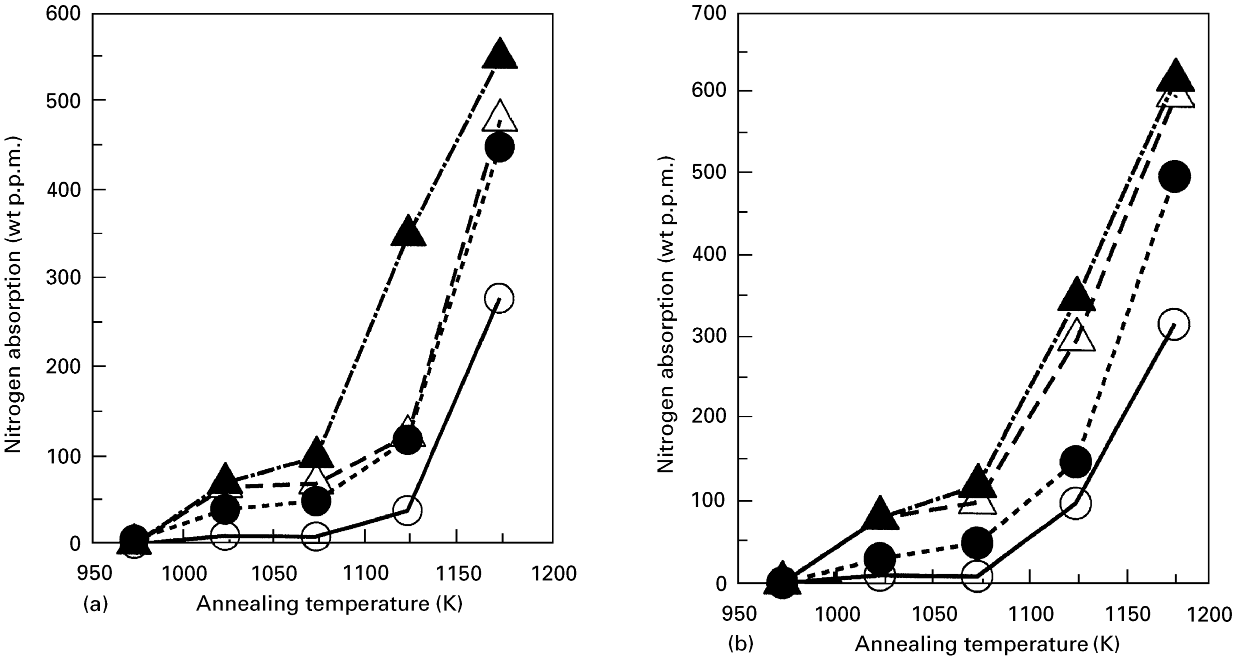


Figure 4 Effect of concentration of antimonyl ion on nitrogen absorption for (a) steel 1, and (b) steel 3: (▲) 1×10^{-4} mol m^{-2}, (△) 1×10^{-5} mol m^{-2}, (●) 1×10^{-6} mol m^{-2}, (○) 1×10^{-7} mol m^{-2}.

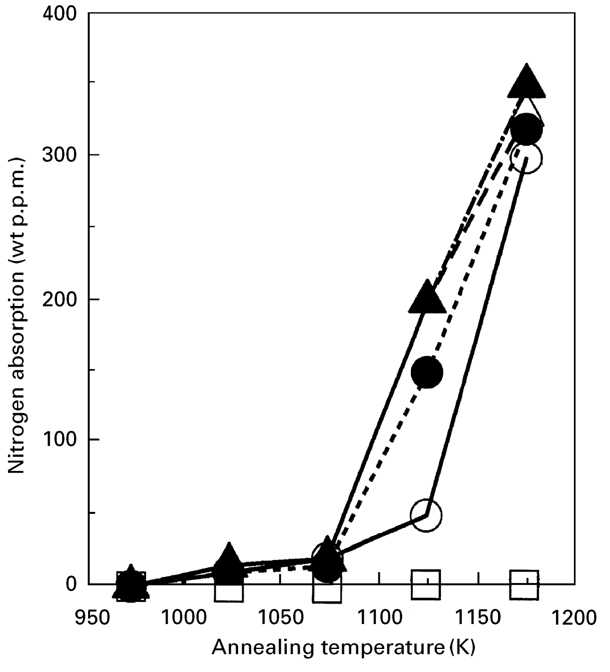


Figure 5 Effect of silicon content in steel on nitrogen absorption: (○) steel 1, (●) steel 2, (△) steel 3, (▲) steel 4, (□) steel 5.

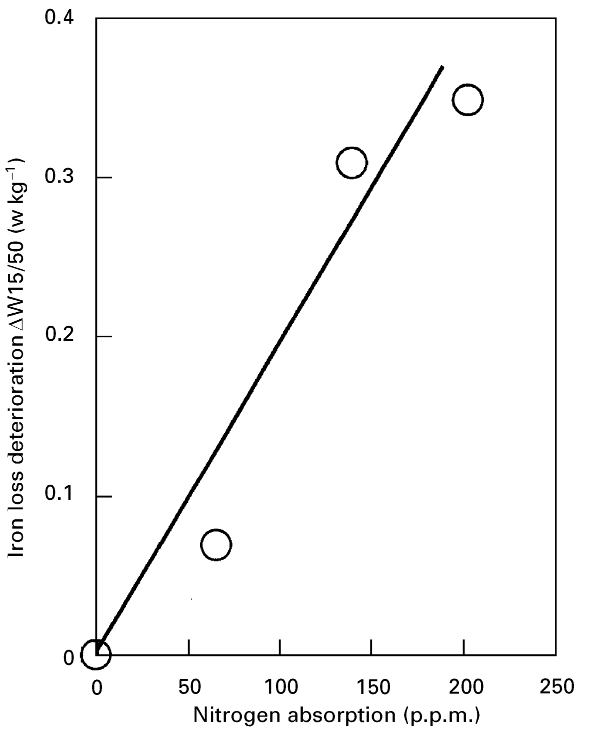


Figure 6 Deterioration of iron loss with nitrogen absorption in steel 4.

4. Conclusions

The following conclusions have been found with respect to nitrogenizing of aluminium in silicon steels:

1. Surface treatments with antimonyl solution and colloidal antimony oxides (1×10^{-7} mol m^{-2}) are effective in preventing the nitrogenizing of silicon steels containing aluminium at temperatures lower than 1073 K.
2. The silicon content of the steel has a negligible effect on nitrogenizing.
3. Nitrogenizing deteriorates the iron loss of the steel sheet.

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