Effect of nitriding time on secondary recrystallization behaviors and magnetic properties of grain-oriented electrical steel

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ABSTRACT

The effect on secondary recrystallization behaviors and magnetic properties of grain-oriented electrical steel of nitriding time from 0 to 240 s in the acquired-inhibitor method has been studied. It was found that the volume fraction of nitride precipitates increased with increasing nitriding time. However, the average diameter of the nitride precipitates decreased with increasing nitriding time. Two kinds of nitride precipitates were found to have formed after primary recrystallization annealing. A fine rod-shaped precipitate was found to be Si_3N_4 and and a coarse, lozenge-shaped precipitate was $MnSiN_2$. Moreover, primary grain size decreased with increasing nitriding time due to retarding of the grain growth by precipitates. After secondary recrystallization annealing, the specimen that was nitrided for 30 s obtained the largest volume fraction of abnormal growth grains and largest area percentage of Goss grains. Conversely, specimens that were nitrided more or less than 30 s demonstrated poor secondary recrystallization and obtained low area percentage of Goss grains. Furthermore, the optimum nitriding time to obtain the best magnetic properties was 30 s. In addition, the optimum nitrogen content was 150 ppm.

1. Introduction

Grain-oriented electrical steel is an important functional material used as lamination cores in various transformers. Its magnetic properties affect the energy efficiency of transformers and are closely related to the sharpness of $(110)\langle 001 \rangle$ texture [1]. If the $(110)\langle 001 \rangle$ texture is strongly developed after secondary recrystallization annealing, superior magnetic properties, such as high magnetic flux density and low core loss are obtained. It is well known that volume fraction and size distribution of inhibitors play an important role in controlling the development of $(110)\langle 001 \rangle$ texture during secondary recrystallization. In 1958, May and Turnbull [2] demonstrated that MnS particles restrained the normal grain growth of primary recrystallization matrix, and stored the driving force for secondary recrystallization. In 1964, Taguchi and Sakakura [3] used AlN inhibitors to produce grain-oriented electrical steel by one-stage cold rolling. However, these inhibitors were precipitated out before cold rolling and affected primary recrystallization grain structure. In order to save energy and cut down operation costs, Takahashi and Harase [4] announced new metallurgical principles by using low slab reheating temperature at 1150 °C and conducted

nitriding to form nitride as inhibitors before cold-rolled sheet decarburization annealing. This process was called the acquired-inhibitor method. On the other hand, many factors such as grain size, texture, volume fraction and size of precipitates in the primary annealing matrix have been shown to affect the texture development and magnetic properties of grain-oriented electrical steel during secondary recrystallization annealing [5–8].

In the acquired-inhibitor method, nitriding is an important process to control the injection quantities of nitrogen atoms into steel sheet, size and volume fraction of nitride precipitates and grain size of primary annealing matrix. In our recent works, we studied the effects of precipitates and texture on the magnetic properties of non-oriented electrical steels [9,10]. This work stimulated us to study the effect of various nitriding times on the amounts of nitrogen injected into steel sheets, quantitative size and volume fraction of precipitates, and grain size of the primary annealing matrix. Moreover, the effect of nitriding time on secondary recrystallization behaviors, texture development and magnetic properties of grain-oriented electrical steel was also investigated.

2. Experimental procedure

Grain-oriented electrical steel containing 0.046 wt% carbon, 3.18 wt% silicon, 0.09 wt% manganese, 0.012 wt% phosphorus,

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0.007 wt% sulfur, 0.02 wt% aluminum and 0.003 wt% nitrogen was prepared by a 250 kg vacuum induction furnace. The ingot was reheated to 1100 °C for 2 h, and hot rolled in two steps by a two high pilot hot rolling mill with intermediate annealing at 1200 °C for 1 h. The thickness of hot bands after rough rolling was 15.4 mm, and after finishing rolling was 2.5 mm. After air cooling to room temperature, hot-rolled bands were annealed at 900 °C for 5 min in a fluidized bed furnace. Then, hot bands were cold rolled to 0.35 mm in one stage with a total reduction of 86%. The cold-rolled sheets were cut into 30 mm width × 60 mm length coupons in a longitudinal direction parallel to the rolling direction. Then, primary recrystallization annealings of cold-rolled sheets, including nitriding and decarburization annealing, were conducted in a tube furnace. During the nitriding treatment, the cold-rolled sheets were variously nitrided in an NH_3 atmosphere at 700 °C for 0, 15, 30, 60, 120 and 240 s. Then, the specimens were heated up to 800 °C and soaked for 5 min in a wet H_2–N_2 atmosphere with dew point at 25 °C for decarburization. Secondary recrystallization annealing was carried out in a 25% N_2 and 75% H_2 mixed atmosphere with a heating rate of 12 °C/h up to 1200 °C and soaked for 12 h under a 100% H_2 atmosphere for purification. After secondary recrystallization, magnetic flux density was measured at a magnetizing force of 800 A/m (B8), and iron loss was measured at 15 kG induction and 50 Hz. Thereafter, the specimens were pickled with HCl solution to reveal their macrostructure. After nitriding treatment, total nitrogen content injected into the steel sheet was measured by standard chemical analysis. After primary recrystallization annealing, grain sizes were measured by the intercept method based on ASTM standard E-112. Size and volume fraction of nitride precipitates in the specimens were observed by a field emission Jeol JSM 7000F microscope operated at 15 KV and analyzed by a Leco IA-3001 image analysis system. Types of nitride precipitates were observed by the thin-foil method using a TEM coupled with EDS for elemental analysis. After secondary recrystallization annealing, HKL electron backscatter diffraction (EBSD) was conducted to observe grain orientations in each of the specimens. For poor secondary recrystallization specimens, a Siemens D-5000 X-ray diffractometer with a texture attachment was employed to measure their (1 1 0), (2 0 0) and (1 1 2) pole figures. The diffractometer, employing Mo radiation, was operated at 40 kV and 25 mA. Three pole figures were used to calculate the orientation distribution by orientation distribution function (ODF) software with L=20.

3. Results and discussion

3.1. Effect of nitriding time on total nitrogen injected into steel sheets

The effect of nitriding time on total nitrogen content injected into the steel sheets is shown in Fig. 1. Nitrogen content gradually increased with increasing nitriding time. The nitrogen content in steel sheet nitrided for 30 s was approximately 150 ppm. However, nitrogen content in the steel sheet that was nitrided for 240 s was approximately 1600 ppm.

The nitriding atmosphere was a mixture of hydrogen, nitrogen and ammonia gas. Ammonia gas was cracked and dissociated into nitrogen and hydrogen atoms on the surface of the steel sheets at a temperature of around 500–550 °C. Thus, the nitrogen produced was nascent, and it was subsequently absorbed into the steel sheets, diffusing into the steel through the surface. The amounts of nitrogen absorbed into iron increased with increasing nitriding time (Fig. 1).
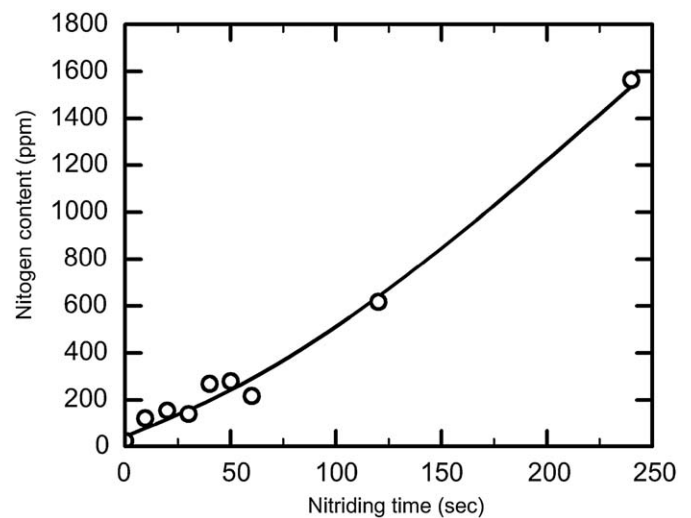

Fig. 1. Effect of nitriding time on total nitrogen content injected into the steel sheet.

3.2. Effect of nitriding time on volume fraction and size distribution of precipitates

After primary annealing, most of the nitrides were heterogeneously precipitated out at the surface layer. The thicknesses of the nitride layers were 25, 35 and 45 μm in the steels that were nitrided for 30, 60 and 120 s, respectively. The effect of nitriding time on dispersions of precipitates in the steel sheets is shown in Fig. 2. Only a few precipitates were seen in the specimen without nitriding treatment. However, there were many precipitates in the specimen that was nitrided for more than 30 s. Furthermore, amounts of precipitates in the steel sheets increased with increasing nitriding time. Precipitate size distributions in the steel sheets that were nitrided for 30, 60 and 120 s are shown quantitatively in Fig. 3. Peak precipitate densities of the three specimens were located in the size range 30–40 nm. Moreover, the peak precipitate intensity increased with increasing nitriding time. Volume fraction and average diameter of precipitates in the steel sheets that were nitrided for 30, 60 and 120 s are shown in Table 1. The range of precipitate volume fraction was from 1.33% to 2.00%. Volume fraction of precipitates increased with increasing nitriding time. The range of average precipitate diameter was from 47.5 to 52.5 nm. However, the average diameter of precipitate decreased with increasing nitriding time.

Nitrogen reacts with silicon to form silicon nitride or reacts with silicon and manganese to form manganese silicon nitride by a mechanism that will be discussed in Section 3.3 below. As can be seen in Fig. 1, nitrogen content in the steel sheet increased with increasing nitriding time. Therefore, the volume fraction of nitride precipitates increased with increasing nitriding time. As the nitriding time was extended, more new fine precipitates were formed. Thus, the average diameter of nitride precipitates decreased with increasing nitriding time.

3.3. Types of nitride precipitates

Fig. 2 shows that there were a few precipitates in the specimen without nitriding treatment. These precipitates were identified as MnS. However, there were many uniform dispersion precipitates in the steel sheets nitrided for more than 30 s. Two kinds of different size precipitates were seen in the matrix—one a fine precipitate and the other a coarse precipitate. Both precipitates were found not only in grain boundaries but also in the matrix.