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Precipitates in Compact Strip Production (CSP) Process Non-Oriented Electrical Steel

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Abstract: Nitrogen and Sulfur in non-oriented electrical steel would form precipitates, which would severely affect its magnetic properties. Precipitates in compact strip production (CSP) process non-oriented electrical steel were investigated using a transmission electron microscope (TEM) and scanning electron microscopy (SEM). The precipitation mechanism and influence on grain growth were analyzed experimentally and theoretically. The results showed that the main particles in steel were AlN, TiN, MnS, Cu₂S, and fine oxide inclusions. The spherical or quasi-spherical of MnS and Cu₂S were more liable to precipitate along grain boundaries. During the soaking process, the amount of MnS precipitated on the grain boundary was much larger than that of Cu₂S. AlN and TiN in cubic shape precipitated inside grains or grain boundaries. Precipitates preferentially nucleated at grain boundaries, and TiN, MnS mainly precipitated during soaking. In the subsequent processes after soaking, AlN and Cu₂S would precipitate unceasingly with the decrease in the average size. The distribution density, the volume fraction, and the average size of the precipitates in the annealed sheets were $9.08 \times 10^{13}/\text{cm}^3$, 0.06%, and 54.3 nm, respectively. Precipitates with the grain size of 30–500 nm hindered the grain growth, the grains with 100–300 nm played a major role in inhibiting the grain growth, and the grains with the grain size of 70–100 nm took the second place.

Keywords: non-oriented electrical steel; CSP process; magnetic properties; precipitates; particle growth; driving force and pinning force

1. Introduction

Non-oriented electrical steel is a kind of soft magnetic alloys, which desire high magnetic induction and low core loss [1]. On account of the small columnar crystals, which belong to the cubic texture ($\{100\}<001>$) of continuous cast slab that would inherit to the finished product, the magnetic induction intensity of compact strip production (CSP) process non-oriented electrical steels would be higher than the traditional products. However, the magnetic properties would be deteriorated by inclusions, which are difficult to float during the casting process, and the small size of precipitates through inhibiting grain growth [2–7].

As a result of the solubility fall of certain elements, the major residual elements or impurities of Cu, Ti, S, N, etc. would form nitride and sulfide precipitates [8]. AlN, TiN, MnS, Cu₂S, etc. would obviously hinder the growth of crystal grains and strengthen γ -fiber texture components, leading to the decrease of magnetic properties of non-oriented electrical steel [1,5,9,10].

Many research works have been reported on the study of nitride and sulfide precipitates' precipitation mechanism in non-oriented electrical steel [5–7,9–14]. The particle nucleation rate and

growth depend on the nucleation driving force, the diffusivity of controlling element M in the matrix, and the interfacial energy associated with the matrix [8,15]. In the CSP process' non-oriented electrical steel, the size of precipitates would grow more in the soaking process, but the precipitation contents are less [5].

Meanwhile, models on the grain growth inhibition by precipitates are presented with the hypotheses that the grain growth will stop by the pinning force of particles [12–14,16,17]. Studies show that the relationship between grain sizes would be strongly inhibited by increasing the interfacial area between grains and particles [18–20]. The effect of different size of precipitates on the ferrite grain growth is also different in non-oriented electrical steel [7,10,14,21–26].

Given the above, the precipitation mechanism of precipitates in the CSP process' non-oriented electrical steel has not been studied comprehensively, and most of these studies only simulate the qualitative relationship between precipitation and grain growth theoretically. In the present study, by means of the thermodynamics analysis, kinetics calculation, TEM, and SEM, the precipitation behavior of AlN, TiN, MnS, and Cu₂S was studied. The pinning force of precipitates and driving force of grain growth were analyzed as well, with the aim to reduce the inhibition effects of precipitates on grain growth, thus enhancing the magnetic properties of CSP process' non-oriented electrical steel.

2. Materials and Methods

The main chemical composition of compact strip production (CSP) process non-oriented electrical steel used in the present study is given in Table 1. The continuous casting billet with 70 mm in thickness, which was soaked at about 1373 K, was hot-rolled to 2.3 mm in thickness by a six-high rolling mill. The hot bands were cold rolled in 79% deformation to 0.5 mm in thickness by a six-high rolling mill. Then, the cold-rolled sheets were annealed at 1093 K for 2 min in N₂:H₂ = 1:1 atmosphere for recrystallization and grain growth. The heating rate and cooling rate of the annealing process were 50 K/s and 25 K/s, respectively. The schematic of the thermos-mechanical cycle used in the present study is shown in Figure 1.

Table 1. The main chemical composition of non-oriented electrical steel.

Elements	C	Si	Mn	P	S	Als	N	Cu	Ti
Content, wt%	0.0030	0.65	0.25	0.075	0.0040	0.30	0.0035	0.030	0.0030

Figure 1. Schematic of the thermos-mechanical cycle used in the present study.

The microstructure and morphology of precipitates in steel were scientifically studied using a transmission electron microscope (TEM; JEM-2100F, JEOL, Tokyo, Japan) and scanning electron microscopy (SEM; Quanta 650FEG, FEI, Morristown, NJ, USA). Combining with energy dispersive

spectrometer (EDS) and selected area electron diffraction (SEAD), the compositions and morphology of precipitates could be characterized.

The carbon extraction replica test sample for TEM was prepared into a sample with a size of 8 mm (TD) $\times$ 10 mm (RD) by wire cutting and then roughly and finely ground. The samples were prepared by electro-polishing at 90 mA in 10% AA electrolyte for 120 s. The electrolyzed samples were coated with a layer of carbon film with a thickness of about 30 nm using a vacuum carbon spray instrument. After dividing the carbon film into a size of about 2 mm $\times$ 2 mm, it was placed in a 10% perchloric acid alcohol solution for electrolytic release, and then the molybdenum net with 3 mm in diameter was used to extract the carbon film. The samples were also prepared into SEM samples, and then electropolishing and observation with 100 fields in each sample were done at 3000–10000 magnification under SEM. The size and number of precipitates were analyzed using IPP (Image-Pro Plus, MEDIA CYBERNETICS, Rockville, MD, USA) software.

Magnetic properties of the core losses ($P_{15/50}$) were determined at the induction of 1.5 T and 50 Hz. Magnetic measurements were carried out for final-annealed sheets with 30 mm in width and 300 mm in length, both in rolling and transverse directions. The measured values were averaged to parallelize with the Epstein method.

3. Results and Discussions

3.1. Magnetic Properties

Residual elements (Nb, V, Ti, Cu, etc.), carbon, nitrogen, and sulfur in non-oriented electrical steel would form fine precipitates in the production process [1]. Precipitates would hinder grain growth, which ultimately increases the iron loss and mechanical properties. Meanwhile, precipitates would promote the formation of the γ -fiber texture and reduce magnetic induction [27]. An important purpose of non-oriented electrical steel slab soaking is to coarsen precipitates, thereby reducing the hazards of the precipitates [5].

The variation tendency between $P_{15/50}$ and $\sum (C + N + S + Ti)$ is shown in Figure 2. As the contents of elements (Si, Al, Mn, Nb, V, Cu, etc.) and technology for heating processing were nearly equivalent, the statistical results showed that $P_{15/50}$ increased obviously (increase 0.22 W/kg) with an increase of $\sum (C + N + S + Ti)$ in 95–105 ppm. It could be speculated that the increase in $P_{15/50}$ was caused by the precipitates formed by C, N, S, Ti, etc. Therefore, during the production of non-oriented electrical steel, it is necessary to strictly control the content of magnetic harmful elements. Meanwhile, it is necessary to study the precipitation mechanism of the precipitates and the influence law of the precipitates on the magnetic properties of non-oriented electrical steel.

Figure 2. The variation tendency between the core losses $P_{15/50}$ (W/kg) and $\sum (C + N + S + Ti)$ (wt%).

3.2. Morphology and Composition of the Precipitates

During the smelting and continuous casting process of the CSP process' non-oriented electrical steel, studies have shown that part of fine oxide inclusions could not grow and be absorbed by the ladle slag [28,29]. The fine oxide inclusions would remain in the slab, thereby worsening the magnetic properties. In addition, the precipitates would precipitate during production. Because of the rapid cooling process, the CSP process would have a more uniform structure and a smaller degree of segregation of continuous cast slab [1]. Therefore, the segregation in the slab center was ignored in this article. In order to study various inclusions and precipitates in the CSP process' non-oriented electrical steel, the species and size distribution of micro-inclusions and precipitates in samples were analyzed by SEM and TEM. The morphology of typical inclusions and precipitates is shown in Figure 3.

Figure 3. Typical precipitates and inclusions in the annealing sheets.

Figure 3 shows the typical precipitates and inclusions morphology in the annealing sheets. The main precipitates were AlN, TiN, MnS, Cu₂S, and the composite precipitates. Some fine oxide inclusions were also discovered on the grain boundary.

Because sulfur is one of the surface-active elements, it tends to segregate to the grain boundary [14,30]. During the long time soaking, a number of sulfur atoms segregate along the grain boundary. The diffusion of manganese and copper occurs simultaneously. When the solubility product of manganese, copper, and sulfur supersaturates, MnS and Cu₂S would nucleate at the grain boundaries [31]. Hence, the spherical or quasi-spherical of MnS and Cu₂S are more liable to precipitate along grain boundaries. As AlN and TiN nucleation mode is mainly heterogeneous nucleation [1,5,8], the cubic shape of AlN and TiN precipitates inside grains or grain boundaries.

It is obvious to see that the precipitates are mainly distributed in the grain boundary or in the crystal in Figure 4. Many tiny spherical and blocky precipitates less than 65 nm were observed throughout the grains and grain boundaries of hot-rolled band and annealed sheets. After counting and measuring the size of precipitates observed in the fields, the size of precipitates in the hot-rolled band and annealed sheets was mainly in the range of 30–500 nm. The precipitate size and density (number of precipitates in the unit area) within 30–500 nm in all the samples are shown in Figure 5.

Figure 4. Distribution of precipitates in the hot-rolled band (a) and annealed sheets (b) (SEM).

Figure 5. Statistics of precipitates in Continuous Casting billet, hot-rolled band, cold-rolled sheet, and annealed sheet.

As shown in Figure 5, the precipitates in the CSP process' non-oriented electrical steel tended to grow in the whole process. The distribution density and volume fraction of the precipitates before annealing also increased. After annealing, the precipitates further increased in size and volume fraction, but the corresponding distribution density decreased.

Because the cooling rate of the CSP process is fast and the time is short [32], a large number of precipitates had precipitated in continuous casting slab. As precipitates are difficult to precipitate and grow adequately, the average size of precipitates in the continuous casting slab was small [1,5]. Precipitates would further precipitate and grow during the soaking and hot rolling process, so hot-rolled

bands had fewer fine precipitates than the continuous casting billet. The final annealing process (820 °C, 2 min) provided thermodynamic and kinetic conditions for the precipitation and growth of precipitates. The average size, distribution density, and volume fraction further increased after annealing. The main sizes of the precipitates in the annealed sheet mainly distributed in 30–500 nm. The statistical results of the precipitates in the annealed sheets showed that the distribution density, the volume fraction, and the average size of the precipitates were $9.08 \times 10^{13}/\text{cm}^3$, 0.06%, and 54.3 nm, respectively.

3.3. Thermodynamic Analysis of Precipitates

Figure 6 shows the austenite and ferrite phases in non-oriented electrical steel, which were calculated using FactSage 7.2 software (Thermfact/CRCT, Montreal, QC, Canada and GTT-Technologies, Aachen, Germany). The currently investigated non-oriented electrical steel was within the single austenite phase during the soaking at about 1373 K. During the hot rolling process, the initial rolling, finishing rolling, and coiling were within the austenite, ferrite, and ferrite, respectively. The precipitates' precipitation temperature and amount were calculated by FactSage7.2; the results are shown in Figure 6b. It can be observed that the main precipitates were AlN, MnS, and TiN. The equilibrium precipitation temperature of them was 1479 K, 1578 K, and 1588 K, respectively. During soaking at about 1373 K, the precipitation amounts of AlN, MnS, and TiN under equilibrium conditions were 0.0067%, 0.0099%, and 0.0031%, respectively. The equilibrium precipitation amount of MnS and TiN at the soaking temperature of 1373 K basically reached the upper limit, but that of AlN would increase greatly as the temperature decreased. Therefore, the average size of AlN particles would decrease in the subsequent operation stage. On the contrary, the average size of MnS and TiN would not decrease after soaking.

Figure 6. Fe-Si-0.3 wt%Al-0.25 wt%Mn phase diagram (a) and precipitation curve of precipitates (b).

The database of FactSage 7.2 does not figure out the relevant data of Cu_2S , but it would react to precipitate with MnS [1]. In this experiment, because of the single γ phase during the soaking at about 1373 K, the solution and precipitation behavior of the Cu_2S and MnS in austenite were mainly discussed. The equilibrium solid solubility product formulas of Cu_2S [33] and MnS [34] are Equations (1) and (2).

$$\lg\{[\text{Mn}] \cdot [\text{S}]\}_{\gamma} = -9020/T + 2.929 - (-215/T + 0.097)[\%\text{Mn}] \quad (1)$$

$$\lg\{[\text{Cu}]^2 \cdot [\text{S}]\}_{\gamma} = 26.31 - 44971/T \quad (2)$$

The equilibrium precipitation temperature of MnS and Cu_2S was 1518.5 K and 1416.2 K, according to Table 1, as shown in Figure 7, and the precipitation temperature of MnS was very close to the result calculated by FactSage7.2 software. So, it could be speculated that Cu_2S would precipitate after MnS.

Figure 7. Equilibrium solubility product of MnS and Cu_2S and the precipitation curve of Cu_2S .

As shown in Figure 7, the decrease of equilibrium solubility product of Cu_2S with a decrease in temperature was much greater than MnS. Hence, the equilibrium precipitation temperature of MnS would gradually approach and be lower than that of Cu_2S as the S content decreased. Calculation by Equations (1) and (2) showed that the solid solubility products of MnS and Cu_2S were equal at 1394.07 K. That is, Cu_2S would precipitate below 1394.07 K, and the remaining sulfur was 0.00125%.

As the soaking of the slab is the main stage of precipitation and growth of the precipitates, the equilibrium precipitation amount of each precipitate under soaking is shown in Table 2. As shown in Table 2, the equilibrium precipitation ratios of MnS, Cu_2S , AlN, and TiN at the soaking temperature were 76.4%, 37.2%, 65.2%, and 99.3%, respectively. Since the S element is a grain boundary segregation element [1,8,14], the amount of MnS precipitated on the grain boundary during the soaking process was much larger than that of Cu_2S . Meanwhile, AlN and Cu_2S precipitated less in the soaking phase. The rest of AlN and Cu_2S would be finely dispersed in the grain boundaries and crystals in the subsequent heat treatment process, which seriously affected the grain growth during the annealing process.

Table 2. Equilibrium precipitation amount at the soaking temperature.

MnS, wt%		Cu_2S , wt%		AlN, wt%		TiN, wt%	
Max	Equilibrium	Max	Equilibrium	Max	Equilibrium	Max	Equilibrium
0.00106	0.0081 (76.4%)	0.00623	0.00232 (37.2%)	0.00725	0.00473 (65.2%)	0.00288	0.00286 (99.3%)

3.4. Kinetics Analysis of Precipitates

During the production process of the CSP process' non-oriented electrical steel, the soaking of the slab is the main stage of precipitation and growth of the precipitates. The currently investigated 0.65 wt% Si non-oriented electrical steel was within the single austenite phase during the soaking at about 1373 K, as shown in Figure 6. Therefore, the model is based on the following assumptions [8,14]:

1. Assuming the nucleation mode is homogeneous nucleation and grain boundary nucleation;
2. Assuming the nucleus is spherical, and neglecting the misfit or the elastic strain energy between the new phase and the matrix;
3. Assuming the interface of austenite and the new phase attain the partial equilibrium during the precipitation and growth process;
4. Assuming the diffusion of chemical element M, forming the precipitates in the austenite, is the restrictive factor of precipitate's growth.

3.4.1. Driving Force for the Nucleation

The critical nucleus size, r^* , and the activation energy for nucleation (or the free energy change of formation of the critical nucleus), ΔG^* , can be obtained from the following Equations (3)–(5) [8,35–37]

$$d_{\text{Homogeneous+Grain boundary nucleation}}^* = -\frac{4\sigma}{\Delta G_V} \quad (3)$$

$$\Delta G_{\text{Homogeneous nucleation}}^* = \frac{16\pi\sigma^3}{3(\Delta G_V)^2} \quad (4)$$

$$\Delta G_{\text{Grain boundary nucleation}}^* = A_1 \times \Delta G^* \quad (5)$$

where $A_1 = \frac{1}{2} \left(2 - \frac{3\sigma_B}{2\sigma} + \left(\frac{\sigma_B}{2\sigma} \right)^3 \right)$, σ_B is grain boundary energy (0.73 J/m²) [8], σ is the interfacial energy between the new phase and the matrix, V_m is the molar volume of the new phase, ΔG_V is the volume free energy reduction in creating a new phase from the matrix.

The chemical driving power of nucleation and the precipitation process can be represented as Equation (6) [38–40]. $[M]_0$, $[X]_0$ are the initial concentrations of elements M and X, $[M]$, $[X]$ are the equilibrium concentrations of elements M and X. R is the gas constant, and T is the temperature.

$$\Delta G_V = -\frac{RT}{V_m} \left[\ln \frac{[M]_0}{[M]} + \ln \frac{[X]_0}{[X]} \right] \quad (6)$$

Based on the above equations, the activation energies and the critical nucleus size for Cu₂S, TiN, AlN, and MnS nucleation can be calculated in austenite during the soaking at about 1373 K. The parameter values for calculation are summarized in Table 3.

Table 3. Parameter values for calculation [8,33].

Phases	Solubility Product	Diffusion of M, D , cm ² /s	Interfacial Energy, σ , J/m ²	Lattice Constant, nm
AlN	2.72–10062/T	$5.9 \exp(-241000/RT)$	$1.03504 - 0.3437 \times 10^{-3}T$	$a = 0.3111$, $c = 0.4978$
TiN	5.56–17205/T	$0.15 \exp(-251000/RT)$	$1.1803 - 0.5318 \times 10^{-3}T$	0.4239
MnS	2.9–8966.3/T	$1.7 \exp(-222000/RT)$	$0.9225 - 0.4157 \times 10^{-3}T$	0.52226
Cu ₂ S	26.31–4971/T	$0.19 \exp(-272000/RT)$	0.8	0.56286

The calculated activation energy and the critical nucleation radius for Cu₂S, TiN, AlN, and MnS are shown in Figure 8. The critical nucleus size decreased continuously with a decrease in temperature. The critical nucleus size of Cu₂S, TiN, AlN, and MnS was on the same order of magnitude. The activation energy of each precipitate decreased monotonously with a decrease in temperature. TiN, AlN, and MnS were nucleated more easily than Cu₂S in austenite. Cu₂S, TiN, AlN, and MnS were preferentially nucleated at grain boundaries.

Figure 8. Critical nucleation radius (a) and activation energy (b) for new phases nucleation vs. temperature.

3.4.2. Nucleation Rate and Precipitation-Time-Temperature

The homogeneous nucleation rate in the matrix and the heterogeneous nucleation rate on the grain boundary were taken into consideration in the present study. The formula for the relative nucleation rate (NrT) for the homogeneous nucleation and the heterogeneous nucleation on grain boundary could be calculated by Equations (7) and (8), respectively [8].

$$\lg\left(\frac{I}{K}\right)_{\text{Homogeneous nucleation}} = 2\lg d^* + \frac{1}{\ln 10} \left(-\frac{\Delta G^* + Q}{kT} \right) \quad (7)$$

$$\lg\left(\frac{I}{K}\right)_{\text{Grain boundary nucleation}} = 2\lg d^* + \lg \frac{\delta}{L} + \frac{1}{\ln 10} \left(-\frac{\Delta G_g^* + Q_g}{kT} \right) \quad (8)$$

where k is the Boltzmann constant ($1.3806505 \times 10^{-23}$ J/K), Q is the diffusion activation energy of the control element M in austenite (that is, the diffusion activation energy of a single atom), δ is the thickness of crystal interface (0.5 nm), L is the average grain diameter.

The formula for the precipitation-time-temperature (PTT) diagram for the homogeneous nucleation and the heterogeneous nucleation on grain boundary is calculated by Equation (9) and Equation (10), respectively [8,41,42].

$$\lg\left(\frac{t_{0.05a}}{t_{0a}}\right)_{\text{Homogeneous nucleation}} = \frac{2}{3} \left(-1.28994 - 2\lg d^* + \frac{1}{\ln 10} \times \frac{\Delta G^* + 2.5Q}{kT} \right) \quad (9)$$

$$\lg\left(\frac{t_{0.05g}}{t_{0g}}\right)_{\text{Grain boundary nucleation}} = 2 \left(-1.28994 - 2\lg d^* + \frac{1}{\ln 10} \times \frac{A_1 \Delta G^* + Q}{kT} \right) \quad (10)$$

The calculated relative nucleation rate and the precipitation-time-temperature (PTT) diagram for precipitates in austenite are shown in Figure 9. For the heterogeneous nucleation on the grain boundary, Cu_2S , TiN, AlN, and MnS had low relative nucleation rates compared with homogeneous nucleation. This calculation also implied that the heterogeneous nucleation on the grain boundary of Cu_2S , TiN, AlN, and MnS might preferentially happen.

The precipitation-time-temperature (PTT) diagram of Cu_2S , TiN, AlN, and MnS precipitation in the austenite region showed a C-shaped curve. The corresponding precipitation (5%) nose temperature of Cu_2S , TiN, AlN, and MnS was about 1108 K, 1453 K, 1374 K, and 1243 K for homogeneous nucleation, 1065 K, 1593 K, 1584 K, and 1414 K for grain boundary nucleation, respectively. Hence, TiN, AlN, and MnS were mainly precipitated during the period of soaking at 1373 K, but Cu_2S would precipitate slightly. Furthermore, combined with thermodynamic calculation (in Figures 6 and 7), the critical nucleation radius (in Figure 8a), and the activation energy (in Figure 8b) calculation results, it could be confirmed that TiN, MnS mainly precipitate during soaking and AlN, Cu_2S would precipitate

unceasingly with the decrease in the average sizes in the subsequent processes after soaking. The tiny Cu_2S in the CSP process' non-oriented electrical steel could also be better understood.

Figure 9. NrT (a) and PTT (b) curves of new phases precipitated in austenite.

3.4.3. Growth of Precipitates

Cu_2S , AlN, and TiN control elements of Ostwald ripening are Cu, Al, and Ti, respectively [8]. However, the precipitation behavior of MnS in non-oriented electrical steel is more complicated and must be determined first. It can be calculated by Equation (11) [8]. $\omega = A_{\text{Mn}}/A_{\text{S}}$ is the ideal chemical ratio of MnS, and A_{Mn} and A_{S} are the relative atomic mass of Mn and S, respectively.

$$Mn - \omega S = E = \sqrt{\frac{D_{\text{Mn}-\gamma}\omega}{D_{\text{S}-\gamma}}} \cdot 10^{2.9-8966.3/T} \cdot \left(\frac{D_{\text{S}-\gamma}}{D_{\text{Mn}-\gamma}} - 1\right) \quad (11)$$

The calculation of MnS controlling elements in the precipitation process of non-oriented electrical steel is shown in Table 4. It can be seen that $Mn-\omega S$ in non-oriented electrical steels was greater than E ; hence sulfur would be the controlling element in the Ostwald ripening process of MnS.

Table 4. Controlling element calculation of MnS in non-oriented electrical steel.

Computational Item	Values
$Mn-\omega S$	0.243146
E	0.026146
Controlling element	S

According to the Fe–Si phase diagram in (Figure 6a), it can be seen that the CSP process' non-oriented electrical steel was in the austenite zone during the soaking process (about 1373 K). The change of the average diffusivity of the kinetic control elements for the formation of each precipitated phase with temperature is shown in Figure 10. It can be seen from Figure 10 that the diffusion coefficients of Al and S in the γ -phase were much larger than those of Ti and Cu. As the temperature decreased, the diffusion capacity of Al and S in the γ -phase decreased, and the rate of decline was linear. As the temperature was less than 1200 K, the diffusion of Al, S, Ti, and Cu in the γ -phase was almost negligible, and the precipitation kinetic conditions of each precipitate were poor. Therefore, Cu_2S , TiN, AlN, and MnS would mainly precipitate during soaking at 1373 K.

Figure 10. Variation of the diffusion coefficients of control elements with temperature.

After nucleation, particles would mainly grow immediately. Lots of mathematical models have been developed to describe the particle growth in different situations. The theory of size change of the precipitated phase in the dilute solution was first proposed by Ostwald. In the present paper, the Ostwald ripening model of particles during the soaking process (about 1373 K) can be described by the following Equation (12) [8]:

$$\bar{r}_t \approx \left(\frac{8\sigma V_P^2 D C_0}{9V_B C_P R T} \right)^{\frac{1}{3}} \cdot t^{\frac{1}{3}} \quad (12)$$

where C_0 is the equilibrium concentration of an element in the matrix (mol/mol); C_P is the equilibrium molar concentration of an element in the precipitate (mol/mol); V_P is the molar number of precipitate (m^3/mol); V_B is the molar number of austenite (m^3/mol); D is the average volume diffusion rate of alloy atoms.

The calculated evolution of the particle size with time at 1373 K in austenite is shown in Figure 11. The average particle size of Cu_2S , TiN, AlN, and MnS increased with time. The increasing velocity of particles was great at the early stage, and the curve of the increasing velocity tended to even flat along with the reaction proceeding continuously. Due to the higher diffusion coefficient of S and Al in austenite during the soaking process, both MnS and AlN grew faster than Cu_2S and TiN. The growth rate and size of AlN and MnS were much larger than those of TiN and Cu_2S , as shown in Figure 11. After soaking for 40 min, the sizes of AlN, MnS, TiN, and Cu_2S were 105.02 nm, 42.72 nm, 5.42 nm, and 9.74 nm, respectively.

Figure 11. The growth potential of Cu_2S , TiN, AlN, and MnS in $\gamma\text{-Fe}$ at 1373 K.

3.5. Grain Growth Behavior

Grain size is controlled by the competition between the driving and pinning forces for grain growth, and grain growth would tend to occur as the driving force exceeds the pinning force [43]. Precipitates in the CSP process' non-oriented electrical steel tended to be stable above the recrystallization temperature, as shown in Figure 5. It can be judged that precipitates would play pinning or dragging action on the grain boundaries at the recrystallization temperature.

The pinning force of precipitates and the driving force of grain growth were discussed in this study. The driving force for grain growth is provided by the reduction of grain boundary energy. The driving force provided by dislocation density on the grain growth could be negligible in non-oriented electrical steel. A theoretical equation modified by Gladman [44] could be used for calculating the driving force, F_d , for grain growth, as shown in Equation (13). The pinning effect of precipitates on grain growth is caused by the reduction in grain boundary areas. The pinning force, which was analyzed by Zener formula, rigid boundary model (RBM), and flexible boundary model (FBM), is shown by Equations (14) and (16) [14,45,46], with the hypotheses that the grain growth will stop by the pinning force of particles.

$$F_d = \left(\frac{3}{2} - \frac{2}{Z} \right) \left(\frac{\gamma}{R} \right) \quad (13)$$

$$F_{Zener} = \frac{3\sigma \cdot f}{2D} \quad (14)$$

$$F_{RBM} = \frac{6\sigma \cdot f}{\pi \cdot r} \quad (15)$$

$$F_{FBM} = \frac{3\sigma \cdot f^{2/3}}{\pi \cdot D} \quad (16)$$

where F_d is the driving force, f is the volume fraction of particles, D is the average radius of the grains, Z is the size advantage (the ratio of the maximum grain size to the average grain size), and γ and σ are the grain boundary energy per unit area (taken as 0.8 J/m²) [47].

The values of the pinning force of precipitates and the driving force of grain growth were calculated and listed in Table 5, and the trend of F_d with grain size (R -critical) is shown in Figure 12. The pinning forces were calculated by Zener formula, rigid boundary model (RBM), and flexible boundary model (FBM) and showed that the precipitates in the annealed sheet of 30–500 nm would pin grain growth at different grain sizes. The pinning force caused by 100–300 nm particles was the largest and by 70–100 nm was the second. Hence, the 100–300 nm particles played the main role in hindering grain growth, as shown in Figure 12. It can be concluded that a few finer grains, which have a much larger driving force, can grow up, and a large amount of grains is impeded by the precipitates.

Table 5. The calculated pinning forces (F_p) of precipitates-annealed sheet samples.

Size, nm	D /nm	Number/cm ³	f /%	F_p (Zener)/Pa	F_p (RBM)/Pa	F_p (FBM)/Pa
30–70	34	6.53×10^{13}	1.88×10^{-3}	6.64×10^4	8.45×10^4	3.42×10^5
70–100	75	1.89×10^{13}	5.85×10^{-3}	9.36×10^4	1.19×10^5	3.31×10^5
100–300	188	6.31×10^{12}	3.07×10^{-2}	1.96×10^5	2.50×10^5	3.99×10^5
300–500	345	2.39×10^{11}	7.19×10^{-3}	2.50×10^4	3.19×10^4	8.26×10^4
500–1000	702	3.42×10^{10}	8.67×10^{-3}	1.48×10^4	1.89×10^4	4.59×10^4
1000–3000	1823	1.37×10^9	6.09×10^{-3}	4.01×10^3	5.10×10^3	1.40×10^4

Figure 12. Relationship between F_d and R_{critical} .

4. Conclusions

The precipitation behavior and effect on grain growth of precipitates in the CSP process' non-oriented electrical steel were characterized experimentally and theoretically. The conclusions would guide scholars, reducing the effects of precipitates and enhancing the magnetic properties of the CSP process' non-oriented electrical steel. The following results were obtained:

1. As the contents of elements and technology for heating processing are nearly equivalent, $P_{15/50}$ increases obviously with an increase in $\sum (C + N + S + Ti)$ in 95–105 ppm.
2. TEM and SEM results show that the main particles are AlN, TiN, MnS, Cu₂S, and fine oxide inclusions. The distribution density, the volume fraction, and the average size of the precipitates in the annealed sheets are $9.08 \times 10^{13}/\text{cm}^3$, 0.06%, and 54.3 nm, respectively.
3. Theoretical calculations show that precipitates are preferentially nucleated at grain boundaries. During the soaking process, TiN and MnS are the main precipitates, and AlN and Cu₂S would precipitate continuously, and the average particle size of AlN and Cu₂S particles decreases in the subsequent process after soaking.
4. Combined with SEM and theoretical calculation results, the average size of AlN and Cu₂S particles would decrease after soaking, but that of MnS and TiN is the opposite.
5. The precipitates in 30–500 nm would hinder the grain growth during annealing, and the 100–300 nm particles played the main role in hindering the grain growth.

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