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Precipitation and Recrystallization Behavior in Extra Low Carbon Steels

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Effects of precipitation on the recrystallization behavior of two Ti-added extra low carbon sheet steels were compared. The recrystallization temperature of the higher Ti-containing steel is higher than that of the lower Ti-containing steel. Small Angle Neutron Scattering (SANS) technique revealed no additional carbo-nitrides precipitation during the recrystallization annealing procedure in the low Ti-containing steel. However, in higher Ti-containing steel, new TiC precipitates, with a size range of several nm to several tens of nms, form during the recrystallization annealing process. This dynamic interaction of the precipitation of fine TiC particles with the recovery of dislocations seems the primary source of the retardation of the recrystallization in the higher Ti-containing extra low carbon steel.

KEY WORDS: Ti-containing extra low carbon steel; recrystallization temperature; TiC precipitates; SANS.

1. Introduction

Vacuum-degassed, interstitial-free (IF) sheet steels have excellent formability, and find wide applications in modern industries, especially for parts requiring good deep drawability. The high formability is achieved by the stabilization of interstitial elements by the addition of titanium and/or niobium, which combine with residual carbon, or nitrogen, to form very fine carbo-nitrides. Despite the advantage of good formability, IF steels with added Ti or Nb have the disadvantage of high recrystallization temperatures. It is generally agreed that addition of Ti or Nb can retard the recrystallization of cold rolled IF steels,[1,2] but the proposed mechanism of retardation varies among authors.[3–5] Yoda *et al.*[3] studied the effect of alloying elements, and concluded the differences in recrystallization behavior are related more to Ti in solution, perhaps due to a solute drag mechanism, than to the dispersion of fine TiC particles. On the other hand, Subramanian *et al.*[4] emphasized the effect of particle dispersion in Ti-containing IF steels. Hayakawa *et al.*[5] have reported that recrystallization temperatures sharply rises with increased titanium content, reaching a peak when the titanium solute is nil, and the acute recrystallization temperature is lowered with a decrease in the amount of fine TiC precipitates. There are good possibilities that these disagreements originate from the inaccuracy in the quantification of the particle size distribution and volume fraction. Extraction replica techniques are frequently used for TEM analyses, and equilibrium thermodynamic calculations for the evaluation of the volume fraction of precipitates. But, in most cases, precipitates are not in equilibrium during cooling, and quantitative analyses of fine precipitates, by the extraction method, are not very reliable.

In this study, the precipitation behavior during the recrystallization annealing treatment of Ti added extra low carbon steels was investigated using the Small Angle Neutron Scattering (SANS) method. Precipitation of fine TiC particles during recrystallization annealing treatment was observed and the differences in the recrystallization behaviors in these steels were interpreted in terms of the interaction of TiC precipitates with dislocations.

2. Experimental

Two extra low carbon steels, with the chemical compositions shown in **Table 1**, were vacuum-melted. The only difference in the chemical composition was the Ti content. Steel A has 0.026 wt% Ti, and steel B contains 0.082 wt% Ti. The effective titanium content, Ti*, is defined by the following equation.[3]

Table 1. Chemical Composition of the IF steels (wt%).

	C	Mn	P	S	Al	Ti	N	Fe	Ti*/C
A	0.0068	0.099	<0.001	0.013	0.038	0.026	0.0008	bal.	0.1
B	0.0070	0.10	<0.001	0.013	0.053	0.082	0.0010	bal.	2.1

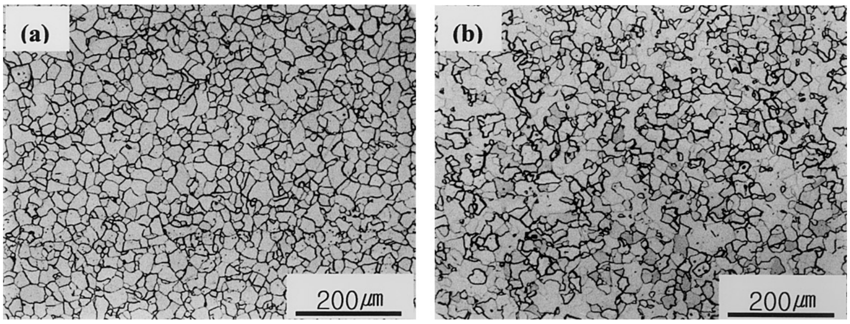

Fig. 1. Optical microstructures of the IF steels after the hot rolling procedure. (a) Steel A. (b) Steel B.

$$Ti^*(\%) = Ti(\%) - (48/32)S(\%) - (48/14)N(\%)$$

In calculation of effective Ti, it is assume that all sulfur and nitrogen combines with Ti and the rest of Ti can combine with carbon. This assumption may not be true in some steels, for example, steel B in this experiment.

The vacuum-melted ingots were reheated to 1 100°C then hot-rolled to a thickness of 30 mm. The 30 mm-thick slabs were reheated to 1 250°C, then hot-rolled to 3 mm. The finish rolling temperature was 930°C. To simulate the coiling process, the hot-rolled bands were kept for 1 h at 720°C, followed by furnace cooling to room temperature. The hot rolled bands were cold-rolled to a final thickness of 0.8mm. Recrystallization annealing was performed in the temperature range 500–800°C for 120 s in a salt-bath, followed by water quenching. The hardness of the annealed specimens was measured using the Vickers hardness method with a load of 5 kgf for 15 s.

The grain structures of the hot bands were investigated by optical microscopy. Precipitates were analyzed by transmission electron microscopy (TEM) using a carbon extraction replica technique. Energy dispersed spectroscopy (EDS) was mainly employed to identify the precipitates. TiS and $Ti_4C_2S_2$ were distinguished based on the relative ratio of the peak heights of Ti and S. The mole fraction of precipitates were calculated by the CALPHAD method.[6] The Thermo-Calc steels database 'tcfe2000'[7] was used for the calculation. The Small Angle Neutron Scattering (SANS) technique was used to resolve ultrafine precipitates (size <50 nm in diameter) in the hot rolled and annealed specimens. The SANS measurement were carried out on the HANARO SANS instrument at the Korea Atomic Energy Research Institute (KAERI) in Daejon, Korea. A neutron wavelength, $\lambda = 0.431$ nm, was used, and the beam wave length resolution ($\Delta\lambda/\lambda$) was 12%. The sample-to-detector distance was 4.61 m. The measured Q range was 0.01–0.1/Å, corresponding to the particle size of 6–60 nm. Absolute sample scattering intensities were calibrated using a standard porous silica sample, and background scattering was calibrated using the Cd mask and empty hole technique. Chemical extraction and isolation method was also employed to quantify the precipitates. Extraction of the whole precipitates from the steel matrices was employed by means of potentiostatic electrolysis in which methanol containing 10% maleic acid and 2% tetramethylammonium chloride was used as an electrolyte. The precipitates were collected by filtration using membrane filter of 45 mm diameter with pore size of 0.2 μm. ICP (Inductively Coupled Plasma) method was used to determine weight percent of Ti and X-ray fluorescence method was to determine S directly, using the precipitates collected on a filter.

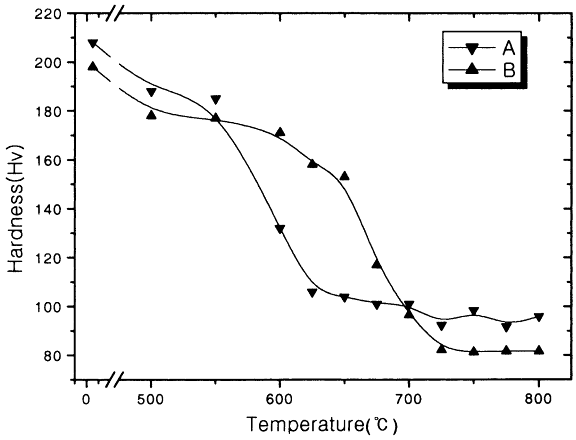

Fig. 2. The variation of alloy hardness with annealing temperature.

3. Results and Discussion

Figure 1 shows optical micrographs of the two extra low carbon steels. Steels A and B exhibited comparable grain size after hot rolling. The grain size of steel A was ~20 μm, and steel B was ~19 μm. The grain size distribution of steel A was more uniform than steel B. Precipitation of carbo-nitrides in hot bands was expected to be quite comparable in these steels.

Figure 2 shows the variation of the alloy hardness after annealing for 120 s at each annealing temperature. Steel A recrystallized at lower temperature than steel B. The half recrystallization temperature of steel A was about 590°C, 60°C lower than that of steel B. The grain size, precipitate size and distribution, and the residual solute content were reported as important hot band parameters, influencing the recrystallization behavior of IF steels.[8,9] Steels A and B have a similar hot band grain size. The rest of parameters such as the solute Ti content or the precipitate size and distribution are expected to be responsible for the differences in the recrystallization behavior of the two steels.

TEM observations of the precipitates extracted, by the carbon replica method, from steels A and B showed many common features. **Figure 3** shows the TEM image and X-ray spectra of a typical row of precipitates in steel B before annealing treatment. CuKα peaks in EDS spectra are from

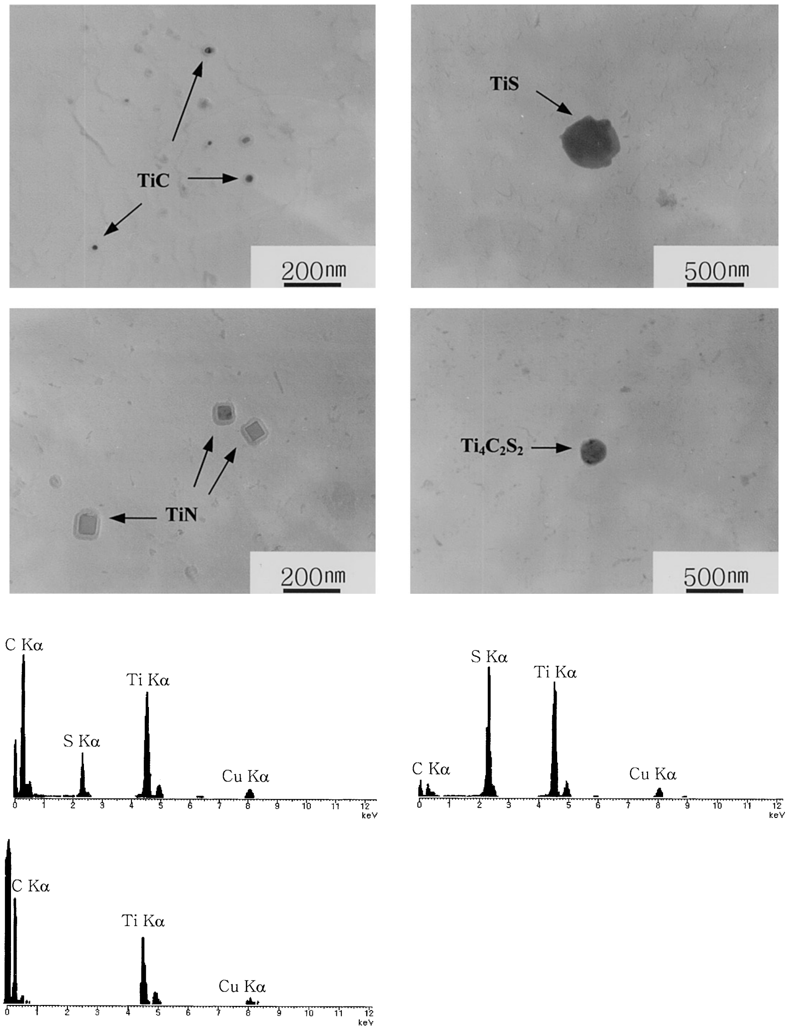

Fig. 3. TEM micrographs and ESD showing precipitates in hot rolled bands of steel A.

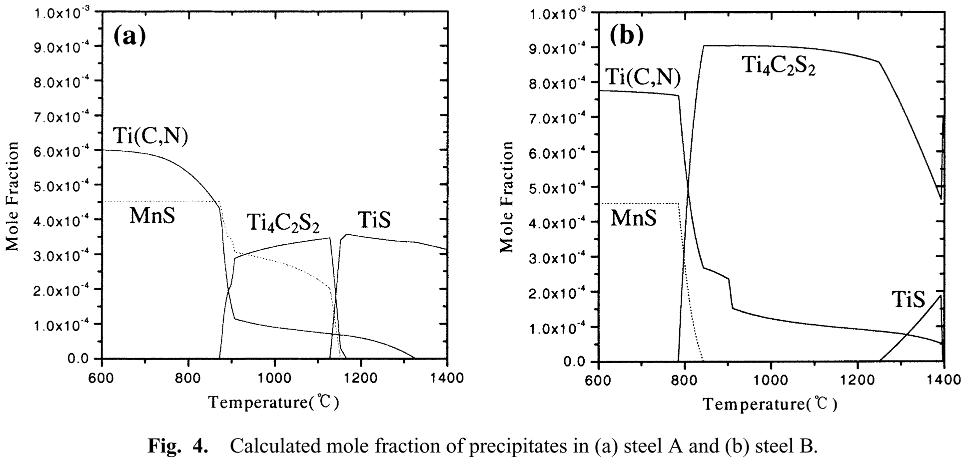

Fig. 4. Calculated mole fraction of precipitates in (a) steel A and (b) steel B.

the Cu grid to support the replica. The type of precipitates didn't change after annealing treatment. Some of the precipitates showed an intensity ratio of Ti/S of 2, corresponding to $Ti_4C_2S_2$, and others an intensity ratio of Ti/S of 1, corresponding to TiS. Some of the precipitates exhibited X-ray spectra for Ti only, which were assumed to be TiC or TiN. In general, TiC and TiN can be distinguished by their shape. Namely, the shape of TiC is more or less spherical, and TiN is a cubic. The average size of TiS, $Ti_4C_2S_2$, TiN and TiC were measured as 300 nm, 200 nm, 100 nm and 20 nm, respectively.

The mole fraction of each precipitates calculated by CALPHAD method is shown in **Fig. 4**. In steel B, large fractions of carbon and Ti are expected to precipitate as $Ti_4C_2S_2$. Thermodynamic calculation shows that $Ti_4C_2S_2$ decomposes into more stable MnS and TiC(N) at below 800°C but kinetically it is not feasible. Precipitation of MnS was not observed in TEM analysis for the extracted

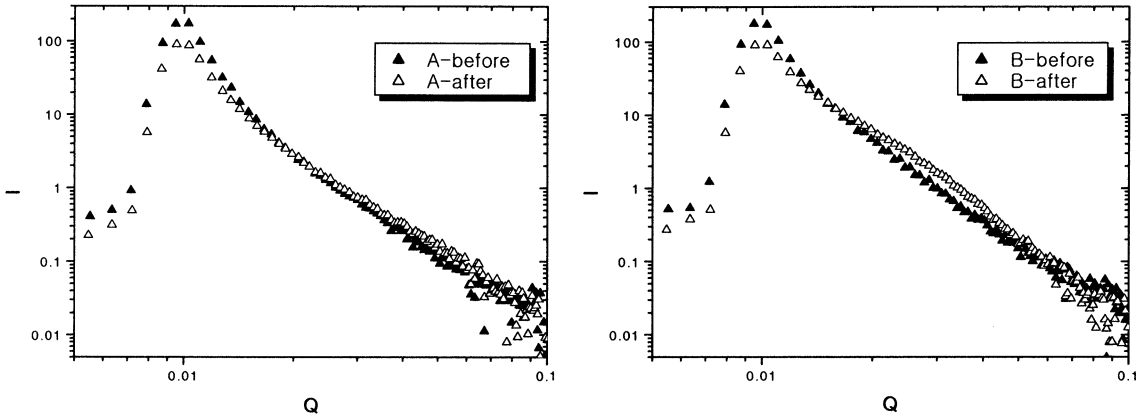

Fig. 5. SANS results before and after recrytallization treatment.

replica specimens of both steels. In steel A, stability of $Ti_4C_2S_2$ is lower than in steel B but calculation still shows that TiS is substituted to $Ti_4C_2S_2$ at below 1 150°C. But TEM analysis shows that the substitution is not complete as calculated. Decomposition of $Ti_4C_2S_2$ at below 900°C may not also significant as calculated. In this respect, we can say that thermodynamic calculation does not correctly represent the precipitation behavior in Ti added extra low carbon steels for normal heat treatment. But it still provides good information for the stability of alloy phases during heating and cooling processes.

Figure 5 shows the plots of, $\log I$ (Neutron scattering intensity) against Q (scattering vector), for steels A and B. We assumed the scattering of the plots to be from a distribution of spherical precipitates with a mean diameter, and the volume fraction is low, such that the interference between neighboring particles is negligible. As a whole, the intensity of steel B is higher than that of steel A. This means the volume fraction of fine TiC(N) carbides in steel B is higher than that of steel A in the Q range (6–60 nm). In particular, for steel A, the neutron scattering intensities, before and after recrystallization treatment, are similar. That is to say, no additional precipitation occurred during the recrystallization annealing procedure. However, in steel B, the scattering intensity increased in the Q range 0.02–0.05, after recrystallization. This result implies new precipitates, with a size range of 12 to 30 nm, form during the recrystallization annealing process.

Figure 6 shows the result of the chemical analysis on the residues of electrolytic extraction. In steel B, the amount of TiC precipitates increased significantly after recrystallization annealing heat treatment, while the weight fraction of other precipitates remained as before after recrystallization treatment. On the other hand, in steel A, only a small increase in TiC precipitation was noticed. These results of chemical extraction analysis are in good agreement with the results of SANS method. It is conforming that the precipitation of TiC particles in the size of 10–50 nm occurs during recrystallization heat treatment of steel B. It can be expected that cold rolling would introduce high density of dislocations, and that deformation induced precipitation (DIP) of TiC would occur during heating for recrystallization. The DIP would mostly occur at existing dislocations, and these precipitates will effectively retard the dislocation rearrangement, *i.e.* delay the recovery and also the recrystallization in steel B. **Figure 7** shows such particles precipitated at dislocations in steel B after annealing for 2 min at 600°C.

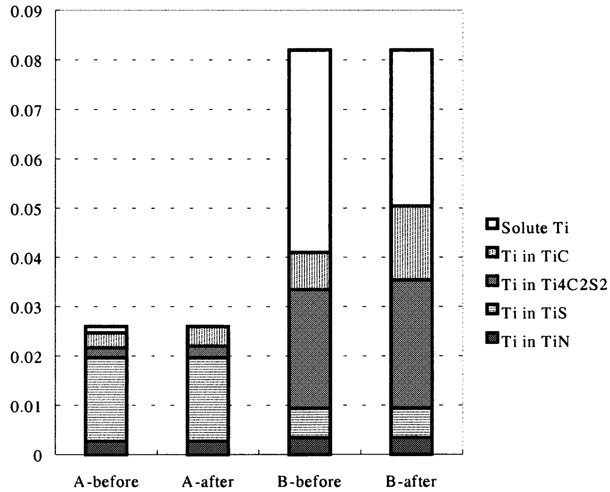

Fig. 6. The amounts of precipitated Ti in steels before and after recrytallization treatment.

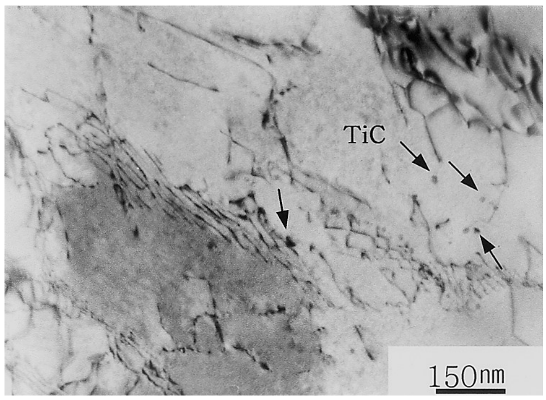

Fig. 7. Transmission electron micrographs of steel B after annealing for 2 min at 600°C.

It is much argued that precipitates or solute Ti are the most important factors influencing the recrystallization behavior of cold rolled extra low carbon steels. Antonione *et al.* reported that, in high purity iron (99.998%), recrystallization temperature raised about 350°C by the addition of 200 ppm Ti.[10] Yoda *et al.* also argued that recrystallization temperature of ultra low carbon steels containing Ti increases linearly with increasing solute Ti content.[3)] But, in their paper, the increase in recrystallization temperature was also reported in relation to the increase in TiC content. Systematic analysis to separate these two factors is not attempted. Solute-drag effect of solute Ti on the recrystallization of Ti-containing extra low carbon steels was much argued in line with the effect of impurity elements in high purity metals. But authors are not aware of literatures which theoretically or systematically evaluate the drag force of solute Ti during recrystallization of industrial steels. Further works are needed to estimate the actual roll of solute Ti on the recrystallization of Ti-containing steels.

The direct effect of TiC precipitates on the recrystallization kinetics is much in question. Assuming the dislocation density after 75% cold rolling is 10^{11} cm/cm^3, the stored energy per unit volume will be about 5×10^6 J/m^3. In steels A and B, the volume fraction of each precipitates is $2–9\times10^{-4}$ and the pinning force exerted by the precipitates is estimated to be in the range of $2–10\times10^4$ N/m^2. Because the pinning force exerted by the precipitates is only a few percent of the stored energy, Zener drag forces exerted by the precipitates would not effectively influence the early stage of recrystallization. It can be argued that parts of the stored energy will dissipate during recovery. But, in continuous annealing process, the heating rate exceeds five hundred degrees per minute and loss of stored energy during recovery would not be significant.

SANS results show significant differences in the steels A and B in the precipitation of TiC particles during recrystallization annealing treatment. Dynamic interaction of particle precipitation at existing dislocations *i.e.* dislocation pinning by precipitating particles could be one of the important factors affecting the recrystallization kinetics of the cold rolled sheets, if residual solutes are still abundant in the alloy after cooling from hot rolling temperature.

4. Conclusion

In this experiment the recrystallization behavior of two extra low carbon steels, with different Ti content, are compared. Precipitation of fine the TiC particles were not in equilibrium, particularly in the ferrite region, and residual solutes can precipitate during the recrystallization annealing treatment after cold rolling. This dynamic interaction of the precipitation of fine TiC particles with the recovery of dislocations seems primarily responsible for the retardation of the recrystallization of steel B compared to steel A.

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