

# Atom Probe Analysis on Precipitation Kinetics of TiC in Isothermal Aging of Ferritic Steel

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## Abstract

*Titanium carbide (TiC) is used for particle strengthening in engineering steel. Understanding the precipitation kinetics is important to control the precipitation state and the consequent strengthening. Elaborated ferritic model steels showed under-aging, peak-aging and over-aging regions of particle strengthening due to isothermal aging. The evolution of particle size, number density and amount of dissolved Ti atoms were investigated in detail by atom probe tomography and the samples were considered to cover the stages from nucleation to coarse growth of TiC. The evolution of size distribution of the precipitates was compared with that simulated by a conventional model and the origin of the difference between the experimental and the calculated results was discussed.*

## 1. Introduction

Particle strengthening is a fundamental strengthening mechanism for metallic material, and has been used conventionally for steel material. When alloying elements such as Ti, Nb and V for particle-strengthening of steel are added, carbides such as TiC, NbC and VC and their compounds are formed in the steel. These carbides are hard, and effective for particle strengthening even when they are in the state of fine particles,<sup>1)</sup> and as their solubility is very small, great particle-strengthening is realized even with the addition in a small amount. In addition, as the solubility of these carbides is higher in austenite, precipitation with a high number density is possible by dissolving carbides in austenite, owing to high supersaturation in ferrite after phase transformation.

Accordingly, to utilize carbides for particle strengthening in actual steel material, the general practice is to precipitate them at the austenite/ferrite transformation interface or after transformation to ferrite.<sup>2,3)</sup> To increase particle strengthening, refining of precipitated particles and dispersing them with high number density are required, and therefore, it is important to understand the precipitation kinetics of the subject precipitate. However, in the case of precipitation during transformation or after completion of phase transformation, nucleation takes place at various sites such as the interface, dislocations and ferrite matrix, and precipitation kinetics is not a simple phenomenon. In addition, because phase transformation takes place

in a continuous manner and precipitation starts following the transformation, in the steel that accompanies phase transformation, it was difficult to study the precipitation kinetics of carbide from the early stage of precipitation to the advanced stage of growth.

To study precipitation kinetics, there is a method, as practiced in other alloying systems, to quench the state of a metal supersaturated with solid-soluted atoms and reheat it for aging heat treatment. However, when a carbon steel is quenched from the carbide-solubilizing temperature, the steel transforms to martensite and dislocations of high density are introduced. Therefore, in the subsequent process of aging, the influence of the dislocation and or the recovery on precipitation kinetics cannot be separated. Then, by using a ferritic steel that does not transform from a solution treatment temperature to room temperature, we succeeded in producing a model steel, in which TiC is uniformly precipitated in the ferrite matrix that has low dislocation density. With this, size dependence of resistance force to dislocation of each TiC particle could be estimated for the first time.<sup>4)</sup>

In the model steel, phase transformation, change in dislocation density due to phase transformation and recovery in the subsequent aging do not occur. Therefore, by using the steel with Ti and C dissolved in a supersaturated state as the starting initial material, study on nucleation and growth of the TiC is possible. In addition, atom probe tomography (hereinafter referred to as APT) was used aiming

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at observation of the whole process of formation of precipitates from atoms in the solid-solution state. This article describes the result of the detailed analysis of the precipitation kinetics of TiC in the isothermal aging of the above-mentioned ferritic model steel. Furthermore, the result is compared with the result of calculation based on a conventional nucleation theory, and points of similarity and difference are discussed.<sup>5)</sup>

## 2. Experimental<sup>4)</sup>

### 2.1 Sample

A steel having a chemical composition of Fe-0.03C-0.10Ti-0.2Mn-3.0Al (mass%) was melted in a vacuum furnace. The obtained steel ingot was hot-rolled to a thickness of 12 mm, and round bars of 11 mm in diameter  $\times$  95 mm in length were mechanically cut out. The round bars were annealed at 1300°C for 10 minutes and subsequently quenched into water for the solution treatment.

As for this model steel, examination by a dilatation test proved that, as designed, the austenite phase was not formed in the temperature range from a room temperature up to the 1300°C for the solution treatment, and only the ferritic phase was formed. According to the transmission electron microscopy observation of the steel after the solution treatment, dislocation was rarely observed.<sup>6)</sup> Furthermore, the concentration of the precipitated Ti in the electrolytic extraction method of the solution-treated steel was less than 0.01 mass %, and the steel after solution treatment was of the ferritic phase with low dislocation density, and supersaturated with solution-soluted Ti and C as desired.

Next, aiming at the formation of very fine TiC precipitates, the solution-treated steel was isothermally aged at 580°C for 15 min–512 h and water-quenched to a room temperature.

### 2.2 Mechanical test and observation of precipitation state

To study the evolution of the mechanical properties owing to precipitation, an A2 type tensile test specimen was taken from the center section of the isothermally aged round bar, and the tensile test was conducted under the condition of a gauge length of 24 mm and a test speed of 15 MPa/s. Amounts of particle strengthening due to TiC and solid-solution strengthening of C atoms were determined as the increment of the yield strength from that of low-temperature aged steel. The yield strength was estimated as 0.2% proof stress.

Specimens for APT measurement were taken out from the same round bar that provided the tensile test specimen. Specimens for the APT measurement were mechanically-polished and each was processed to a piece of about 0.3 mm  $\times$  0.3 mm  $\times$  1 mm, and finally processed to a needle-shaped specimen for APT by electropolishing<sup>7)</sup>. APT measurements were conducted under the condition of specimen temperature: 65 K, pulse fraction: 20–25%, pulse frequency: 20 kHz, and the detection efficiency was assumed as 0.35.<sup>8)</sup> The steels aged for each time period measured several times with 2–10 million atoms and a three-dimensional elemental mapping were obtained each time. Based on the obtained elemental maps, TiC precipitates in the steel were identified by the maximum separation method<sup>9)</sup> and their states were examined.

## 3. Results and Discussion

Figure 1 shows change in 0.2% proof stress vs. isothermal aging time at 580°C. The model steel that can evolve sequentially the precipitation state by isothermal aging, ranging from under-aging (0–4 h), via peak-aging (8–32 h), and to the over-aging region (64–512 h) was successfully created. Based on the results of this experiment and the estimation of solid-solution strengthening by C, the incre-

ment of particle strengthening in the peak-aging region of this steel was estimated as high as 320 MPa<sup>4)</sup>.

Figure 2 shows Ti atom maps of the steel isothermally aged at 580°C observed by APT.<sup>4)</sup> In the steel without isothermal aging (0 h), Ti atoms stay completely in the state of solid solution. However, in the steel with aging for 0.25–1 h, TiC clusters in indeterminate shapes are observed. In the material with aging time for longer than 2 h, plate-shaped Ti precipitates were formed. As these Ti clusters and precipitates (TiC particles) are distributed homogeneously with high number density, they are considered as precipitates nucleated on the matrix. TiC particle size grows larger as the aging time increases. Furthermore, decrease in the concentration of Ti solid-soluted in the matrix is seen in the under-aging region.

Figure 3 shows evolutions vs. aging time of (a) mean particle size, (b) number density and (c) solid-soluted Ti concentration, obtained from the result of observation by APT.<sup>4)</sup> The mean TiC particle diameter (size) (a) is expressed as the equivalent volume diameter based on the assumption that the particle is of spherical configuration, and derived from the number of constituent atoms of the TiC particle (Ti+C) observed by APT, and the TiC lattice constant. The TiC particle diameter grows larger as the aging time increases. However, near and in the peak-aging region, the mean particle size remains on a plateau. The TiC particle size in the peak-aging region in aging at 580°C was 2–3 nm in terms of equivalent volume diameter. The error-bar of the mean particle diameter denotes the stand-

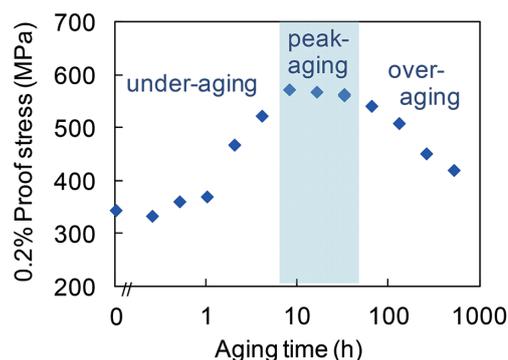


Fig. 1 0.2% proof stress as a function of aging time at 580°C<sup>4)</sup>

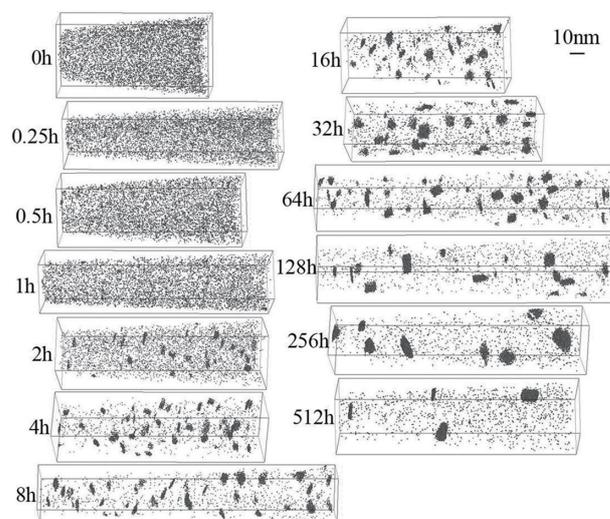


Fig. 2 Ti atom maps of non-aged and aged samples at 580°C<sup>4)</sup>

ard deviation of the distribution of the actually observed individual particle size.

The size distribution tended to widen as the aging time increased. The TiC number density ( $b$ ) was determined by dividing the number of particles by the analyzed volume. The number density tended to increase in the under-aging region, decrease slightly in the peak-aging region, and decrease in the over-aging region. In addition, the solid-soluted Ti concentration ( $c$ ) is calculated by subtracting Ti that contributed to the precipitates in the analyzed volume, and it is considered that the difference between the chemical composition of Ti and the solid-soluted Ti concentration corresponds to the volume fraction of the precipitates. The solid-soluted Ti concentration rapidly decreased in the latter half of the under-aging region. In this steel, the beginning of the peak-aging region corresponds to where the volume fraction of the precipitate becomes nearly saturated. However, as the peak-aging region appeared depending not solely on the volume fraction of the precipitate but also on the balance with respect to particle size, number density and the resistance force of each particle of the precipitate, the peak-aging region does not appear in all precipitate systems in the same manner.<sup>8)</sup>

**Figure 4** shows the Cu particle precipitation evolution state in Fe-1.4 mass% Cu alloy at 500°C aging, calculated on the basis of diffusion-controlled precipitate growth based on a conventional nucleation theory,<sup>5, 10-13)</sup> and is shown to explain the four characteristic precipitation stages that appear along with the homogeneous nucleation and growth. The region I is the nucleation stage wherein, although number density increases, the mean particle diameter scarcely changes, and region II is the growth stage wherein the mean particle diameter increases proportionally with respect to the square root of aging time; meanwhile, the number density of precipitate increases in the early stage and becomes constant thereafter, region III is the

plateau stage wherein the mean particle diameter and number density remain unchanged, and region IV is the coarsening stage wherein number density decreases and the mean particle diameter increases proportionally with respect to the cubic root of aging time.<sup>14)</sup>

The driving force in the nucleation and growth stages is the degree of supersaturation of solute atoms, and all precipitates above the size of critical nucleus grow. In the meantime, coarsening is promoted by the precipitate/matrix interface energy, and under the circumstance that the solid-soluted atoms are decreased mostly to the equilibrium concentration level, large precipitates grow and small precipitates disappear. In the plateau stage, the diffusion field of precipitates overlaps one another, but none of the precipitates has disappeared yet; therefore, the number density and the mean particle diameter remain almost unchanged in this stage.

When Fig. 3 is compared with Fig. 4, in Fig. 3 of this research, four regions in nucleation and growth are found to appear in the precipitation kinetics of TiC precipitates in isothermal aging. Firstly, when the evolution of mean particle size in isothermal aging in Fig. 3(a) is viewed, as a plateau stage is observed in the middle as mentioned above, this region can be identified as region III (plateau stage), and the region behind it and the region ahead of it can be identified as region II and as region IV, respectively. In region II, the rate of growth of mean particle size vs. aging time is slightly less than the rate expressed in terms of the square root of aging time. In region IV, after 128 h, the mean particle size increases proportionally to the cubic root of aging time.

When solid-soluted Ti concentration in Fig. 3(c) is viewed, the concentration drops sharply in the time period in region II based on the evolution of mean particle size of precipitates observed in Fig. 3(a). This corresponds to the rise in volume fraction of precipitate in this region, and is considered as a characteristic evolution where-

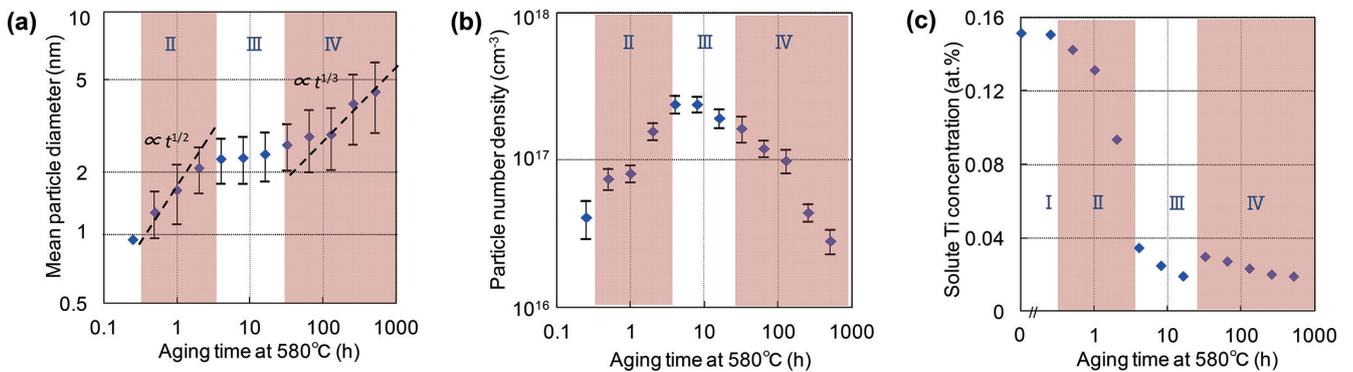


Fig. 3 Evolution with aging time at 580°C of (a) Mean diameter, (b) Number density of TiC particles and (c) Concentration of dissolved Ti in the matrix<sup>4)</sup>

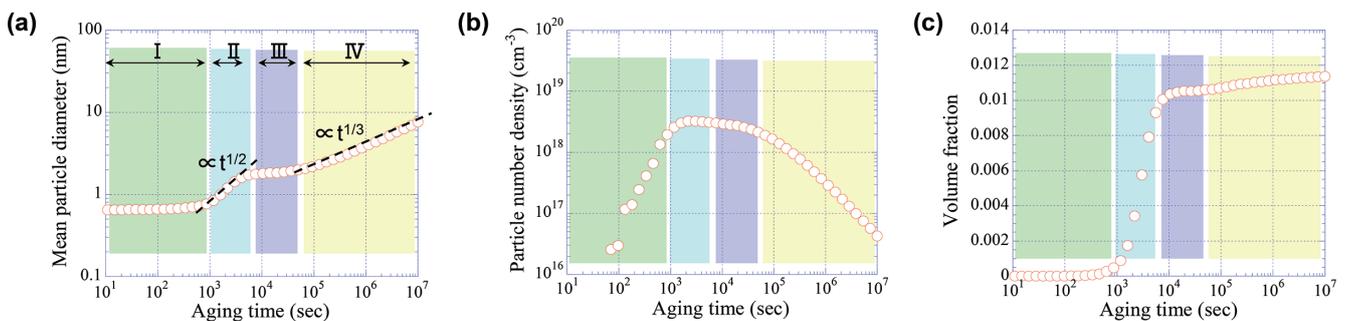


Fig. 4 Simulated Cu precipitation evolution in Fe-1.4 mass% Cu alloy<sup>5)</sup>

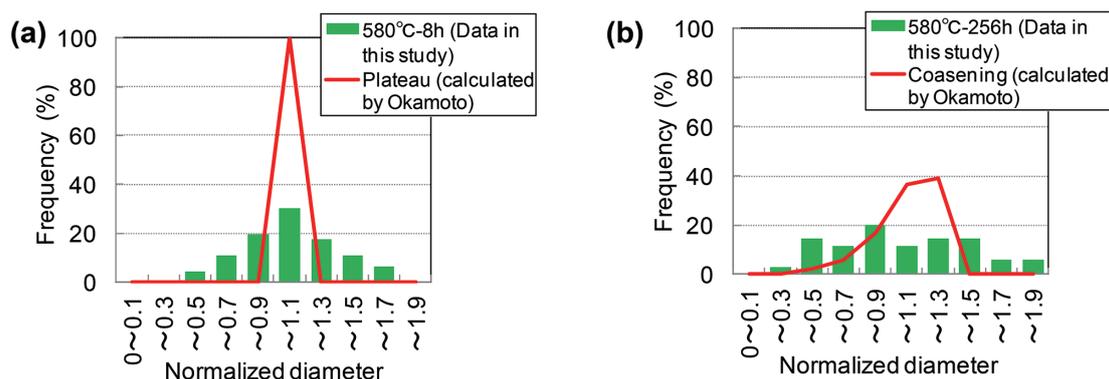


Fig. 5 Particle size distribution of TiC compared with the conventional model, in (a) Plateau and (b) Coarsening stages<sup>5)</sup>

by precipitates grow, incorporating surrounding solid-soluted Ti. On the other hand, during the same time period in Fig. 3(b), different from the evolution of number density in region II as explained in Fig. 4, number density of particles continues to increase. This means that, in this experiment, nucleation continues even in region II. Namely, this shows that, different from the calculation result as to Fe-Cu, nucleation and growth stages are ongoing concurrently. Practically, in region II of this experiment, the rate is less than the square root, verifying that nucleation and growth stages are ongoing concurrently. In the steel employed in this experiment, based on the result of observation conducted separately, growth of cementite immediately after the start of isothermal aging, and the resolution of cementite along with the precipitation of TiC were observed.<sup>6)</sup>

Fujita et al. performed a precipitation-simulating calculation in the precipitation of alloy carbide by tempering of martensite, assuming that cementite already exists at the time of the start of aging because precipitation of cementite precedes the precipitation of the alloy carbide. In the model, a stable alloy carbide is formed owing to C supplied by the cementite that is solid-soluted by tempering.<sup>15)</sup> In the present study, it is considered that nucleation of TiC was affected by the decrease in driving force for the precipitation due to the decrease in solid-soluted C concentration on account of the precipitation of cementite that took place prior to TiC precipitation.<sup>6)</sup> This means that, as suggested by Fujita et al., C required for the growth of TiC is supplied by the resolution of cementite.

Next, the region of plateau of mean particle size and number density of precipitated particles is not wide, and the region looks like it is gradually transferring to the coarsening stage from the plateau stage. This is considered to be attributed to early start of coarsening. Okamoto et al. reported in the calculation of precipitation kinetics of NbC in austenite that: the smaller the mean particle diameter is, and the wider the particle diameter distribution range is at the termination of the growth stage, the shorter the time of the plateau stage becomes, and the earlier the decrease in number density of precipitated particles takes place.<sup>14)</sup> As aforementioned, in this experiment, the co-occurrence of nucleation and growth stages is considered to be the reason for the widened particle size distribution.

Okamoto et al. evaluated the particle diameter distribution change in the respective regions, and showed that the size distribution becomes smallest and exhibits a sharp peak at the termination of region II (growth stage), or the start time of region III (plateau stage).<sup>14)</sup> In the meantime, in region IV (coarsening stage), the size distribution becomes wider, and in this region however, it is shown that the distribution with respect to the particle diameter normalized by mean particle diameter does not change. **Figure 5** shows TiC

particle size distributions actually obtained in this experiment in (a) 8 h-aged steel in the plateau stage and the one in (b) 265 h-aged steel in the coarsening stage. It was practically shown that the particle size distribution of 8 h-aged steel is narrow, and the particle size distribution of the 256 h-aged steel is wide. However, both of the precipitation particle size distributions obtained in the experiment are much wider than those predicted by the calculation as shown with solid lines. This is considered to be due to the nucleation stage prolonged on account of the aforementioned reason, and the influence rendered thereby.

Further, in this examination, the shape of TiC precipitate is assumed to be of spherical configuration, and the experiment result is compared with the calculation result without consideration of the effect of the shape of TiC precipitate. Practically, as TiC precipitate is a plate-shaped precipitate that has coherent interfaces and incoherent interfaces, the energy difference of such interfaces and the change in interface and energy during growth also need to be taken into consideration.<sup>14,16)</sup> Further study is required to realize more detailed quantitative understanding.

#### 4. Conclusion

In this article, as basic study using APT, an attempt to understand the precipitation kinetics in the TiC particle-strengthening steel was introduced. By using a Ti-added low carbon ferritic single phase model steel, evolutions of size, number density and volume fraction of TiC precipitates in isothermal aging were studied, and the characteristic stages in nucleation and growth were experimentally revealed. However, deviations from the result of precipitation model calculation were also observed, and further study is needed to realize more detailed quantitative understanding. APT is an effective technique in fine precipitate analysis in steel material, and is expected to greatly contribute to the development of steel material in future.

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