Effect of Prior Structure to Intercritical Annealing on Rapid Formation of Ultrafine Ferrite + Austenite Structure and Mechanical Properties in 0.1%C-2%Si-5%Mn Steels

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Ultrafine ferrite + austenite steels with the chemical composition of 0.1%C-2%Si-5wt%Mn show excellent strength (TS = 1 200 MPa) and high ductility (TEL = 25%) balance, compared to conventional TRIP steels. This steel is expected as the third generation advanced high-tensile strength steels (AHSS). This steel can be produced by a simple intercritical annealing, however, longer annealing time is necessary to obtain appropriate ferrite + austenite structure. It is difficult to produce this steel by continuous annealing process. If the annealing time can be drastically reduced, this new TRIP steels can be commercialized. We focused on the effect of the prior microstructures before annealing on the formation of ferrite + austenite structure. The effect of the prior structure is not clear. Therefore, in this study, two kind of prior structures, ultrafine grained ferrite + cementite and martensite were used in 0.1%C-2%Si-5wt%Mn steels. It was found that the prior structure of ferrite + cementite can form large amount (20%) of austenite in a very short time (600 s). This is because cementite finely dispersed in the structure effectively acts as a preferential nucleation site of reverse transformed austenite and C and Mn are concentrated in cementite to enable a short time formation of austenite. Excellent strength-ductility balance (32 000 MPa%) which is superior to conventional TRIP steels is also obtained.

KEY WORDS: TRIP; ferrite; austenite; Mn; short time formation; prior structure; ferrite+cementite; martensite; strength; ductility; intercritical annealing; synchrotron radiation; in-situ XRD; tensile test.

1. Introduction

Two automotive engineering principles that have become more important than ever are lightweight design and collision protection, which respectively improve the fuel efficiency of cars and passenger safety, resulting in reducing their global environmental footprint. While a vehicle’s frame can be strengthened by using thicker steel plates or by adding reinforcing parts, these strategies also make the vehicle much heavier. High tensile strength steel (HTSS) is one technology that can meet these two mutually contradictory demands. However, the formability of steel sheets suffers as its strength increases, necessitating the development of high-strength and highly formable materials that can be shaped as needed for the vehicle parts desired. HTSS with a retained austenite microstructure has been the primary focus of research seeking to achieve the twin goals of high strength and high ductility.1–10)

When such a material is deformed, it hardens due to the strain-induced transformation to martensite of the metastable austenite in the matrix. This means that the deformation is not localized, but instead proceeds preferentially in the untransformed austenite, allowing such HTSS to deform considerably. This phenomenon is called transformation induced plasticity (TRIP) because the strain-induced martensitic transformation encourages plastic deformation; retained austenite steel is often called TRIP steel for the same reason.12) Today, researchers are working on developing materials with a strength–ductility balance (tensile strength [TS] × total elongation (TEL) equal to or greater than 30 000 MPa%, an accepted benchmark for next-generation automotive HTSS.13,14) Alternatives to this class of steels—third-generation, advanced high-strength steels (AHSS)—have also been proposed, including quenching and partitioning (Q&P) steels.15,16)

One promising AHSS is ultrafine-grained (UFG) ferrite–austenite steel, a kind of low-carbon steel with a middle manganese content (0.1%C-2%Si-5%Mn).12) Compared with conventional TRIP steels, it can be manufactured very simply, by means of intercritical annealing, and exhibits high strength (TS = 1 200 MPa) and ductility (TEL = 25%).13,14) Studies have also reported the effects of increasing the carbon content in such steels.15,16) However, today’s 0.1C-2Si-5Mn steel must be annealed for a relatively long time (3 600 s) to attain the optimal austenite volume fraction (approx. 20–30%).12) Modern cold-rolled TRIP steel is produced not by batch annealing in
a box furnace, but by continuous annealing. This process is a combination of heating in the intercritical region and austempering: while complex, it can be completed within 600 s.

In this study, our objective was to drastically reduce the time required to produce a UFG ferrite–austenite steel (to 600 s) to improve the commercial feasibility of 0.1C-2Si-5Mn steel with this microstructure. Our approach focused on how the austenite volume fraction of the final product was influenced by the prior microstructure before the intercritical annealing process, under several annealing temperature and time conditions: the two “prior structures” investigated were UFG ferrite–cementite and martensite. Similarly, we examined how the prior structure affected the strength and ductility of UFG ferrite–austenite steels after annealing.

Additionally, to investigate the mechanism of strength and ductility development in UFG ferrite–austenite steel, we observed specimens using in-situ X-ray diffraction (XRD) during tensile tests with synchrotron radiation in the SPring-8. We investigated dynamic changes in the austenite content of the steels during tensile deformation with high time resolution, and determined how this related to their strength and ductility. Of particular interest were the effects of the microstructure prior to intercritical annealing, namely on post-annealing mechanical properties and stress-induced transformation behavior, for potential insight into good engineering principles for achieving high strength and high ductility.

2. Experimental

2.1. Specimen Preparation, Tensile Tests and Structural Observations

Vacuum melting was conducted to prepare 20 kg steel ingots of the composition in Table 1, and these ingots were then hot forged at 1 200°C into square bars (38 × 38 mm). The square bars were rolled by warm multi-pass caliber rolling, specifically, each bar was soaked at 550°C for 1 h and then repeatedly rolled, reheating every three passes, until its cross section was reduced to 14 × 14 mm. The resulting steel was composed of ultrafine ferrite grains and cementite particles (Fig. 7(a)); it is termed UFG ferrite–cementite steel below. In addition, some of this rolled steels were austenitized at 1 200°C for 3 600 s and then air cooled to produce martensite steels (Fig. 7(b)). Below, materials may be denoted by the letters α (ferrite), γ (austenite), θ (cementite), and M (martensite).

Figure 1 shows that UFG α-θ and M steels were annealed for 600, 1 800, or 3 600 s at 625 or 675°C, within the intercritical region for ferrite and austenite. Conventional TRIP steels were also prepared for comparative purposes. Cold-rolled steel sheets (0.13C-2Si-1.6Mn; full composition in Table 2) were austempered as in Fig. 2: specifically, they were soaked at 830°C for 60 s, cooled gradually at 10 K/s to 700°C, then rapidly at 60 K/s to 400°C, and held at that temperature for 10, 60, or 480 s.

Table 1. Chemical composition of the steel used (wt%).

| C  | Si | Mn | P  | S  | Al | N  |
|----|----|----|----|----|----|----|
| 0.1| 2.0| 5.0| <0.01| <0.01| 0.002|

Table 2. Chemical compositions of conventional TRIP steels used (wt%).

| C  | Si | Mn | P  | S  | Al | N  |
|----|----|----|----|----|----|----|
| 0.13| 2.0| 1.6| 0.06| 0.0017| 0.03| 0.0032|

Structural observations of the square bars were made by field emission scanning electron microscopy (FE-SEM) and electron backscatter diffraction (EBSD) in the TD plane as shown in Fig. 3. First, the TD face was mechanically polished with #2000, and then electropolished to remove the top 100 μm to remove any stress-induced deformation zone generated by mirror polishing. Perchlorate-ethanol (1:9) was used for electropolishing.
used as the electrolytic solution. EBSD images were taken at an acceleration voltage of 15 kV and with a step size of 0.05 μm.

The interstitial carbon content of austenite grains was determined using a Rigaku SmartLab X-ray diffractometer. Lattice constants can be derived from Eq. (1) based on Bragg’s law and lattice spacing d:29)

\[ a = \frac{\lambda (h^2 + k^2 + l^2)^{1/2}}{2 \sin \theta} \] .................................. (1)

where \( \lambda = 1.542 \text{ Å} \) due to the Cu-K\( \alpha \) source, \( \theta \) is the measured scattering angle, and \( h, k, l \) denote the dimensions of the lattice plane \( (hkl) \). This equation was used to derive the austenite lattice constants for the \((111), (200), \) and \((220)\) planes. The retained austenite lattice parameter \( a_\gamma \) (Å) was defined by extrapolating \( \theta \) to 90° via \((\cos2\theta/\sin\theta) + (\cos2\theta/\theta)\).29,30) and was calculated using the Dyson and Holmes Eq. (2).31) The Mn contents in austenite grains that were measured with the FE-EPMA were used for the value of \( %\text{Mn}_\gamma \); the component weight percent was used in the case of conventional TRIP steel.

\[ a_\gamma = 3.5780 + 0.0330 \times (\%\text{C}_\gamma) + 0.00095 \times (\%\text{Mn}_\gamma). \] .................................. (2)

Tensile tests were performed using an Instron tensile test machine. Round-bar tensile specimens with the dimensions of \( \Phi 3.5 \text{ mm} \) and parallel length 24.5 mm as shown in Fig. 4 were sampled from heat-treated square bars. Tensile tests were conducted at a crosshead speed of 0.5 mm/min (strain rate: \( 4.9 \times 10^{-3} \text{ s}^{-1} \)). Displacement was measured using an extensometer (gauge length: 17.0 mm).

TEM observation and TEM-EDS measurement were carried out to observe cementite particles and to measure the content of Mn in cementite particles. Specimens were prepared by C extraction replica.

2.2. In-situ Transmission XRD during Tensile Tests

The changes in austenitic volume fraction during tensile tests were explored to directly investigate the effects of austenite on the strength and ductility of ferrite-austenite steel after intercritical annealing. Tensile test specimens were taken from heat-treated square bars; elongation proceeded along the RD axis. Plate specimens were prepared to the dimensions with the width of 2.5 mm and the parallel length of 12 mm as shown in Fig. 5. Plates were cut thin (0.5 mm) to permit the transmission of synchrotron radiation. Diffraction profiles had to be measured over a wide range of angles in a short length of time to precisely capture the changes in austenite volume fraction associated with tensile deformation. To achieve this, experiments utilized the beam lines BL19B2 and BL15XU in the SPring-8, which can emit X-ray radiation of sufficiently high intensity. Figure 6 shows a schematic diagram of the measurement system.22) X-ray energy was set to 30 keV and the beam size to 2.5 mm width × 200 μm height. The goniometer was outfitted with the small size tensile test machine developed for these measurements.22) Plates were irradiated normal to the axis of elongation. Behind the specimen was placed a 1D X-ray detector (MYTHEN), an 2D imaging plate (IP), or a 2D detector (PILATUS). In-situ transmission XRD measurements were taken simultaneously with the tensile tests.23–26) Tensile tests were carried out at a crosshead speed of 0.245 mm/min and with a time resolution of 2 s.

Initial austenite volume fractions were derived using Eq. (3) based on R, the theoretical diffraction intensity for \((hkl)\) and the area intensity ratios of the peaks, \((110)\alpha, (200)\alpha,\) and \((211)\alpha\) to \((111)\gamma, (200)\gamma,\) and \((220)\gamma\) at the observed scattering angles. The subscript \( j \) denotes the \( j \)th diffraction peak, and \( n \) the number of diffraction peaks (here, three for both \( \gamma \) and \( \alpha \)), included in the calculation.

\[ V_{\gamma} = \frac{1}{n} \sum_{j=1}^{n} \frac{I_j}{R_j} \] .................................. (3)

Subsequent austenite volume fractions (during tensile testing) were calculated by multiplying the initial \( \gamma \) volume fraction by the reduction ratio of sum of the area intensities...
of the (200)\(\gamma\) (211)\(\gamma\) and (311)\(\gamma\) peaks at the corresponding time.

3. Results and Discussion

3.1. Microstructures after Intercritical Annealing

Figure 7 shows SEM micrographs of the UFG ferrite–cementite and martensite microstructures prior to intercritical annealing. The former microstructure consists of elongated ferrite grains, and many cementite (white) particles scattered within ferrite grains and along their boundaries. In contrast, the martensite is composed of blocks and packets; cementite is not precipitated on the packet and block boundaries. Intercritical annealing was conducted to these microstructures.

Figure 8 shows the EBSD-IPF maps, the grain boundary maps, and phase maps of these two structures after intercritical annealing in 0.1%C-2%Si-5%Mn steels.
Grain boundaries are almost entirely high-angle boundaries. The high angle grain boundaries are mainly the interface between \(\alpha\) and \(\gamma\). Red and green in the phase maps respectively indicate the ferrite (\(\alpha\)) and austenite (\(\gamma\)) phases.

Intercritical annealing of UFG \(\alpha-\theta\) steel at 675°C resulted in an ultrafine equiaxed microstructure, consisting of \(\alpha\) and \(\gamma\) grains less than \(< 2 \mu m\) in diameter. This is attributable to \(\theta\) dispersed in the prior structure acting as a nucleation site for \(\gamma\) grains, which are globular around triple points but platey at single grain boundaries. In contrast, M steel annealed under the same conditions has a similar microstructure to that before annealing, in which both \(\alpha\) and \(\gamma\) appear as platey or acicular grains. Martensite consists of packet/block/lath structures: blocks consist of groups of laths having nearly the same crystallographic orientation, meaning that blocks inside the packet share the same (111) plane in the prior austenite grain. Acicular \(\gamma\) grains are visible at block boundaries in the phase maps and EBSD-IPF maps: they also appear within the blocks themselves, suggesting they also form at martensitic lath boundaries. Thus, martensitic lath and block boundaries appear to function as nucleation sites for austenite.

When heated for 3 600 s compared with 600 s, the \(\gamma\) grains resulting from the intercritical annealing of UFG \(\alpha-\theta\) steel are somewhat coarser, larger in size, and the volume fraction of \(\gamma\) grains is greater. For the M steel, longer annealing time yielded coarser \(\alpha\) and \(\gamma\) grains.

Figure 9 shows how the austenitic volume fraction in \(\alpha-\gamma\) steel varies with the intercritical annealing temperature and time. At all temperatures, the volume fraction rises with longer annealing time; for the same soaking time, it is higher when annealed at 675°C. This can be attributed to temperature increasing the austenite fraction in the \(\alpha-\gamma\) equilibrium and accelerating its diffusion. The UFG \(\alpha-\theta\) prior structure yielded a large \(\gamma\) volume fraction when annealed at 675°C for 3 600 s (36.4% vs. 24.3% for M). Even at the shortest annealing time, 600 s, the \(\gamma\) fraction is double that seen in the prior M structure post-treatment (20% vs. 10%).

Austenite is formed by reverse transformation: this process is illustrated in the schematics in Fig. 10. In the case of prior structure M, carbon supersaturated in the lattice precipitates at the block and lath boundaries as \(\theta\) particles: these combine and grow to form thin, acicular \(\theta\) grains, which in turn give rise to acicular \(\gamma\) grains (Fig. 10(b)). For the prior structure \(\alpha-\theta\), \(\gamma\) instead nucleates at the abundant \(\theta\) particles present within \(\alpha\) grains and at their boundaries, resulting in the equiaxed \(\gamma\) grains observed (Fig. 10(a)). Thus, the finely dispersed \(\theta\) seems to effectively act as a preferential nucleation site for the reverse transformation of \(\gamma\), resulting in large quantities of \(\gamma\) formed in a very short
amount of time (i.e., 21% volume after annealing for 600 s). Furthermore, while the carbon content of these finely dispersed \( \theta \) particles are obviously high, so is their manganese content: these characteristics obviate the need for dedicated \( \theta \) precipitation process or the Mn enrichment process.

The Mn content in the cementite particles is estimated to become high during the rolling process at 550°C to produce the steels having UFG \( \alpha+\theta \) microstructure. Thermo-Calc calculation shows that \( \theta \) has the chemical composition, \((\text{Fe}_{0.49}\text{Mn}_{0.51})_3\text{C}\). In contrast, because the M steels were quenched from 1200°C, the Mn and C can be assumed to be uniformly distributed throughout the martensite.

Figures 11 and 12 contain SEM and TEM images, respectively, of steels with prior structure \( \alpha+\theta \) and M after being heated to 675°C and then immediately water-quenched without soaking. The TEM samples were prepared by prepared by C extraction replica method. Figure 11(a) shows the elongated \( \alpha \) grains in the \( \alpha+\theta \) steel have recrystallized and are now equiaxed and \( \theta \) particles are also visible. Figure 11(b) shows in the M steel, small \( \theta \) particles precipitated in large numbers, and the beginnings of acicular grain formation are apparent.

Prior to annealing, \( \theta \) particles are abundantly present in the \( \alpha+\theta \) steel as shown in Fig. 12(a). Once heated to 675°C, they are fewer in number and smaller in size as shown in Fig. 12(b), because reverse \( \gamma \) transformation has already begun. In addition, Fig. 12(c) suggests that the acicular structures observed in the M steel in Fig. 11(b) seem to be \( \theta \), but also that some of them seems to be austenite. The TEM-EDS data in Fig. 13 indicate that Mn accounts for 50.8 wt% in cementite particles in the \( \alpha+\theta \) prior structure, effectively reflecting the steel’s theoretical stoichiometry. However, the Mn concentration in \( \theta \) is reduced immediately after heating to the intercritical region, having already begun to migrate into the austenite being generated by reverse transformation. The acicular \( \theta \) grains in the M steel were generated during the heating process. They contain less Mn than in similarly treated \( \alpha+\theta \) steel (36.6 wt%), presumably because there

![Fig. 11. SEM micrographs of the prior structures (a) \( \alpha+\theta \) and (b) M heated at 675°C without soaking followed by water quenching (675°C for 0 s).](image)

![Fig. 12. TEM micrographs of the specimens prepared by C extraction replica. (a) shows cementite particles in initial \( \alpha+\theta \) structure, (b) and (c) show cementite particles in \( \alpha+\theta \) structure and M structure heated at 675°C without soaking followed by water quenching (675°C for 0 s).](image)
was not enough time for Mn to diffuse and reach the ideal stoichiometry.

It is concluded that the abundance of Mn in the finely dispersed \(\theta\) particles in the \(\alpha+\theta\) structure allows highly stable \(\gamma\) grains to form in a relatively short amount of time. Figure 14 shows elemental maps of Mn in the \(\alpha+\gamma\) steel after annealing, as obtained by FE-EPMA. The \(\gamma\) grains present after the intercritical annealing of UFG \(\alpha+\theta\) steel at 675°C for 600 s are extremely high in Mn content (Fig. 14(a)), averaging 9.6 wt\% over five points with visibly high levels according to quantitative analysis. This is attributable to the abundance of Mn in \(\theta\) particles prior to annealing, which served as nucleation sites for \(\gamma\).

In contrast, Mn levels are relatively uniform over the elemental maps of the \(\alpha+\gamma\) steel produced from the M prior structure under the same annealing conditions (Fig. 14(b)). This may be an artifact of the thin acicular shape of the \(\gamma\) grains here, because it is difficult to measure Mn content in the only acicular \(\gamma\) grains excluding the data from surrounding \(\alpha\) grains. Considering the low diffusion rate of Mn in \(\alpha\) however, the mapping data appears valid, because it cannot rapidly diffuse from \(\alpha\) to \(\gamma\) under these annealing conditions.

3.2. Mechanical Properties of Ferrite-austenite Microstructures

Figure 15 shows nominal stress–strain curves obtained for round-bar tensile specimens with the four \(\alpha+\gamma\) structures
shown in Fig. 8. Whereas the specimens obtained from the prior structure \(\alpha-\theta\) exhibit discontinuous yielding, the specimens obtained from the prior structure M display continuous yielding. Presumably, the already-low dislocation density of the steel was further reduced by annealing, resulting in the discontinuous yielding observed, whereas M steel’s mobile plate mobile dislocation remained after the heat treatment. However, in both cases, longer annealing time was associated with lower yield stress and higher tensile strength. The yield stress of steel is determined by the ferrite grain size, as reported by Kumakura.\(^{23,24}\) When \(\alpha-\theta\) steel was annealed, these grains became coarser with increasing annealing time as shown in Fig. 8. In the case of M steel, annealing clearly coarsens the martensitic blocks, decreasing the yield stress in proportion to the annealing time. Furthermore, Fig. 9 clearly shows that the time-related increases in tensile strength are attributable to higher \(\gamma\) fraction, which also increases with annealing time.

When \(\alpha-\theta\) steel was annealed for a very short time (600 s), the product showed good yield strength (870 MPa), tensile strength (960 MPa), and total elongation (33.5%). This equates to a strength and ductility balance of 32 200 MPa\(\%\), well exceeding the benchmark of 30 000 MPa\(\%\). While annealing for a longer time (3 600 s) slightly decreased the yield stress (770 MPa), it actually increased the tensile strength and total elongation (1 090 MPa, 32.4%), achieving an even better strength and ductility balance (35 300 MPa\(\%\)). In comparison, the short (600 s) and long (3 600 s) annealing times of M steel resulted in respective strength and ductility balances of 22,780 MPa\(\%\) (YS: 600 MPa, TS: 897 MPa, TE: 25.4\%) and 31 330 MPa\(\%\) (YS: 550 MPa, TS: 970 MPa, TE: 32.3\%).

Thus, the UFG ferrite–austenite steels exhibited a superior balance of strength and ductility when originating from a UFG ferrite–cementite microstructure compared with a martensitic one. The primary reason is likely the former’s higher austenitic volume fraction, as demonstrated in Fig. 9.\(^{37,38}\)

### 3.3. Changes in Austenite Volume Fraction during Tensile Deformation

Why does 0.1C–2Si–5Mn UFG ferrite–austenite steel exhibit high strength and ductility, and why is the balance of these two properties superior for materials derived from ferrite–cementite steel than from martensite steel? To determine the mechanisms responsible, specimens were measured using in-situ synchrotron XRD as they underwent tensile tests.\(^{22–24}\) We successfully measured the dynamic changes in \(\gamma\) volume fraction within these steels as they underwent tensile deformation. Figure 16 shows the observed changes in the austenite volume fractions of \(\alpha-\gamma\) steel specimens, obtained by annealing \(\alpha-\theta\) or M steel at 675°C for 3 600 s, alongside their nominal stress–strain curves.\(^{25,26}\) For comparison, data are also shown for a conventional TRIP steel, austempered for 480 s. These plate tensile test specimens used in-situ measurements exhibited slightly greater uniform elongation than the round-bar specimens illustrated in Fig. 15, likely a consequence of the near-half strain rate (crosshead speed: \(3.0 \times 10^{-4}\) s\(^{-1}\) vs. \(4.9 \times 10^{-4}\) s\(^{-1}\)). Similar to the round-bar tests, specimens derived from \(\alpha-\theta\) steel achieved superior strength and ductility to those obtained from M steel. One plausible mechanism is that \(\gamma\) was better retained in the former until higher strain extent, despite the rapid progression of strain-induced transformation after the onset of plastic deformation. Conventional TRIP steel exhibited typical TRIP behavior, with \(\gamma\) remaining even in the high-strain extent, despite the low initial \(\gamma\) fraction (10%).

### 3.4. Change in Austenite Stability with Intercritical Annealing Conditions

Table 3 shows that the concentration of carbon in austenite (\(C_\gamma\)) decreases with increasing in annealing time, presumably because this behavior is paralleled by an increase in the \(\gamma\) volume fraction (\(\gamma_\%\)). The product of these two values (\(\gamma_\% \times C_\gamma\)) serves as an index of the degree to which the carbon dissolved in the steel is localized within the austenite: its maximum value (0.1) derives from its compositional weight (0.1\%).\(^{40}\) The \(\gamma_\% \times C_\gamma\) of UFG ferrite–austenite steels ranges from 0.033–0.057 when obtained from M, suggesting a large proportion of the carbon dissolved in martensite matrix. When the prior structure was \(\alpha-\theta\) steel, in contrast, it ranges from 0.073–0.091, signifying that annealing for 3 600 s caused nearly all of the cementite in the steel to change into austenite: in general, the transformation occurred quite efficiently even when only annealed for 600 s. The fact that the carbon added when the \(\alpha-\theta\) steel was prepared initially precipitated as cementite is critically responsible for its efficient and extensive dissolution in the subsequent \(\gamma\) phase formation. Conventional TRIP steel contains 0.13\% C, achieving \(\gamma_\% \times C_\gamma = 0.097\). The corresponding concentration ratio—74\% (= 0.097 + 0.13)—is essentially equivalent to the 73% achieved by the \(\alpha-\theta\) steel after annealing for 600 s. These data signify that the efficacy of the intercritical annealing of a ferrite–cementite steel rivals that of austempering for conventional TRIP steels.

Austenite stability can be evaluated using the \(M_{d0}\) parameter as in Eq. (4).\(^{40}\) \(M_{d0}\) is the temperature at which, when a single-phase austenite structure undergoes a true tensile strain of 0.30, 50% of the entire structure transforms...
into the martensite phase. Higher temperatures signify greater austenite instability.

\[
\text{Md30} = 413 - 462(C + N) - 9.2\text{Si} - 8.1\text{Mn} - 13.7\text{Cr} - 9.5\text{Ni} - 18.5\text{Mo} \quad \ldots \quad (4)
\]

Steels obtained from the \(\alpha-\theta\) and M prior structure had respective \(\text{Md30}\) values of 200°C and 227°C after annealing at 675°C for 3 600 s. The former was better able to retain austenite in its microstructure due to its high stability, which lasted until the high strain extent despite the high initial \(\gamma\) fraction. This mechanism was likely responsible for its superior ductility as well. The high ductility of conventional TRIP steel derives from the austempering process, which potently concentrates large amounts of carbon into a small amount of austenite; however, it is afforded only low strength due to the low \(\gamma\) volume fraction. The \(\gamma\) volume fraction is much higher, in comparison, in the 0.1C-2Si-5Mn ferrite–austenite steel obtained by the intercritical annealing of ferrite–cementite steel. While the austenite grains do not have as high a carbon concentration as in the conventional TRIP steel, the large amount of dissolved manganese acts to stabilize them, enhancing the steel with high ductility. Plates specimens results were used in Fig. 17, because total elongation is dependent on specimen shape. The 0.1C-2Si-5Mn ferrite–austenite steel exhibited excellent mechanical properties overall, even for the shortest annealing time examined (600 s).

4. Conclusion

In this study, the effect of prior structure namely, UFG ferrite–cementite and martensite on the microstructure and mechanical properties in 0.1C-2Si-5Mn UFG ferrite–austenite steels produced by intercritical annealing were investigated using synchrotron XRD, with the objective of realizing the manufacture of such steels in a short annealing time. Following conclusions were obtained.

(1) Equiaxed ferrite and austenite grains structure with the grain size less than 2 \(\mu\)m was obtained after annealing at 675°C from the prior structure, ultrafine grained ferrite-cementite structure. On the other hands, a mixture of platy ferrite and acicular austenite structure was obtained from the prior structure, matensite structure.

(2) Ultrafine grained ferrite–austenite steel obtained by annealing \(\alpha+\theta\)-675°C×600 s had a \(\gamma\) volume fraction of 36.4%, compared with 24.3% for steel derived from martensitic structure as prior structure. Even when annealed for less time (600 s), steel obtained from ultrafine grained ferrite-cementite structure had nearly twice the \(\gamma\) volume fraction as that obtained from martensitic structure (20% vs. 10%). Thus, an ultrafine grained ferrite–austenite microstructure can be produced by

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Table 3. Volume fractions of austenite \(\gamma\), carbon contents in austenite \(C_{\gamma}\) and \(\gamma\times C_{\gamma}\), in ferrite + austenite structures in 0.1%C-2%Si-5%Mn steels and a conventional TRIP steel.

| Steel           | \(\gamma\) (vol.%) | \(C_{\gamma}\) (mass%) | \(\gamma\times C_{\gamma}\) |
|-----------------|---------------------|-------------------------|-----------------------------|
| \(\alpha+\theta\)-675°C×600 s | 20.9 | 0.35 | 0.073 |
| \(\alpha+\theta\)-675°C×3 600 s | 36.4 | 0.26 | 0.096 |
| M-675°C×600 s | 9.7 | 0.34 | 0.033 |
| M-675°C×3 600 s | 24.3 | 0.23 | 0.057 |
| Conventional TRIP | 9.8 | 0.99 | 0.097 |

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Fig. 16. Nominal stress - nominal strain curves and change in austenite volume fraction with tensile strain in 0.1%C-2%Si-5Mn steels and a conventional TRIP steel by In-situ XRD using synchrotron radiation in SPring-8. Dotted lines represent volume fraction of austenite and solid lines represent nominal stress. (Online version in color.)

Fig. 17. Effect of volume fraction of austenite grains on strength-ductility balance of TSxTEL. (Online version in color.)

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Fig. 17 gives an overarching picture of how prior structure, annealing conditions, and elemental composition affect the strength and ductility balance of ferrite–austenite versus TRIP steel, based on the plate tensile test data shown in Fig. 16. The 0.1C-2Si-5Mn ferrite–austenite steels explored in the present work have a balance of strength and ductility superior to that of the conventional TRIP steel. The high ductility of conventional TRIP steel...
means of intercritical annealing of ultrafine grained α-θ steel in a very short time (600 s).

3) In an ultrafine grained ferrite-cementite structure steel, manganese content was very high in cementite particles (FeS, MnS)/C, finely dispersed in the microstructure; these effectively acted as preferential nucleation sites for the reverse transformation of austenite, permitting ferrite and cementite grains to form austenite in a short amount of time.

4) When an ultrafine grained ferrite-cementite structure steel was annealed for a very short time (600 s), the ultrafine grained ferrite-austenite steel obtained showed good yield strength (870 MPa), tensile strength (960 MPa), and total elongation (33.5%), corresponding to an excellent strength and ductility balance of 32 200 MPa%.

5) In-situ synchrotron XRD during tensile tests in SPring-8 revealed that specimens obtained from an ultrafine grained ferrite-cementite structure had a superior strength and ductility balance to those obtained from martensitic grains and cementite-austenite steel obtained showed good yield strength (870 MPa), tensile strength (960 MPa), and total elongation (33.5%), corresponding to an excellent strength and ductility balance of 32 200 MPa%.

6) The high ductility of conventional TRIP steel is a consequence of significant carbon enrichment in a small volume of austenite; however, conventional TRIP steel is not ideal, with significant carbon and manganese in austenite grains, stabilizing them well.

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REFERENCES

1) V. F. Zackay, E. R. Parker, D. Fahr and R. Bush: Trans. Am. Soc. Metals, 60 (1967), 252.
2) M. Takahashi: Tetsu-to-Hagané, 100 (2014), 82 (in Japanese).
3) K. Ushioda and M. Takahashi: Bull. Iron Steel Inst. Jpn., 11 (2006), 779.
4) H. Hayashi: J. Jpn. Soc. Technol. Plast., 46 (2005), No. 534, 546 (in Japanese).
5) K. Ushioda: Scand. J. Metall., 28 (1999), 33.
6) Y. Hosoya and Y. Funakawa: High Tensile Strength Steel for Auto Mobile, JFE 21st Century Foundation, Tokyo, (2008), 119 (in Japanese).
7) T. Maki: Tetsu-to-Hagané, 81 (1995), NS547 (in Japanese).
8) K. Sugimoto, B. Yu, Y. Mukai and S. Ikeda: ISIJ Int., 45 (2005), 1194.
9) Y. Sakuma, O. Matsumura and H. Takechi: Metall. Trans. A, 22 (1991), 489.
10) H. Takechi: JOM, 60 (2008), No. 12, 22.
11) J. Kobayashi, S-M. Song and K. Sugimoto: ISIJ Int., 52 (2012), 1124.
12) T. Furukawa and O. Matsumura: Netsu Syori (J. Jpn. Soc. Heat Treat.), 37 (1997), 204 (in Japanese).
13) S. Torizuka and T. Hanamura: Bull. Iron Steel Inst. Jpn., 17 (2012), 852 (in Japanese).
14) T. Hanamura, S. Torizuka, A. Sunahara, M. Imagumbai and H. Takechi: ISIJ Int., 51 (2011), 685.
15) T. Hanamura and S. Torizuka: PTM 2015 – Proc. Int. Conf. on Solid-Solid Phase Transformations in Inorganic Materials, PTM2015, Elsevier, Amsterdam, (2015), 1043.
16) H. Natsumeda, A. Kishitaka and S. Hashimoto: Tetsu-to-Hagané, 102 (2016), 525 (in Japanese).
17) A. Ohmori, S. Torizuka, K. Nagai, N. Koseki and Y. Kogo: Tetsu-to-Hagané, 89 (2003), 781 (in Japanese).
18) A. Ohmori, S. Torizuka and K. Nagai: ISIJ Int., 44 (2004), 1063.
19) S. V. S. Narayana Murty and S. Torizuka: ISIJ Int., 48 (2008), 1088.
20) S. Torizuka, E. Muramatsu, S. V. S. Narayana Murty and K. Nagai: Scr. Mater., 55 (2006), 751.
21) S. Torizuka, A. Ohmori, S. V. S. Narayana Murty and K. Nagai: Scr. Mater., 54 (2006), 563.
22) H. Adachi, Y. Miyajima, M. Sato and N. Tsuji: J. Jpn. Inst. Light Met., 64 (2014), 463 (in Japanese).
23) M. Kumakura, S. Torizuka, H. Adachi and T. Hanamura: CAMP-ISIJ, 28 (2015), PS-32, CD-ROM (in Japanese).
24) M. Kumakura, S. Torizuka and H. Adachi: CAMP-ISIJ, 29 (2016), 345, CD-ROM (in Japanese).
25) T. Adachi, S. Torizuka and H. Adachi: CAMP-ISIJ, 31 (2018), No. 1, 353, CD-ROM (in Japanese).
26) T. Adachi, S. Torizuka and H. Adachi: CAMP-ISIJ, 30 (2017), No. 2, PS-38, CD-ROM (in Japanese).
27) A. Itami, M. Takahashi and K. Ushioda: Tetsu-to-Hagané, 81 (1995), 573 (in Japanese).
28) B. D. Cullity Trans. by G. Masumura: Elements of X-ray Diffraction, 2nd ed., AGNE, Tokyo, (1992), 298 (in Japanese).
29) A. Taylor and H. Sinclair: Proc. Phys. Soc., 57 (1945), 160.
30) J. B. Nelson and D. P. Riley: Proc. Phys. Soc., 57 (1945), 160.
31) D. J. Dyson and B. Holmes: J. Iron Steel Inst., 208 (1970), 469 (in Japanese).
32) ASTM E975-13: 2003, Standard Practice for X-ray Determination of Retained Austenite in Steel with Near Random Crystallographic Orientation.
33) M. Enomoto: Materials Jpn., 54 (2015), 168 (in Japanese).
34) M. Azuma, M. Takahashi and N. Fujita: Shinritetsu Giho, 392 (2012), 45 (in Japanese).
35) M. Umemoto and K. Tsuchiya: Tetsu-to-Hagané, 88 (2002), 117 (in Japanese).
36) The Japan Institute of Metals and Materials: Metal Data Book, Rev. 3, Maruzen, Tokyo, (2000), 21 (in Japanese).
37) K. Shinoda and T. Yamada: Netsu Syori (J. Jpn. Soc. Heat Treat.), 20 (1980), 326 (in Japanese).
38) O. Matsumura, Y. Sakuma and H. Takechi: Trans. Iron Steel Inst. Jpn., 27 (1987), 570.
39) J. Han, W. Cao, C. Huang, C. Wang, H. Dong and J. Li: ISIJ Int., 55 (2015), 2229.
40) K. Nohara, Y. Ono and N. Ohashi: Tetsu-to-Hagané, 63 (1977), 772 (in Japanese).