Formability of C–Si–Mn–Al–Nb–Mo Ultra High-strength TRIP-aided Sheet Steels

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Formable 980–1 470 MPa grade ultra high-strength TRIP-aided sheet steels with bainitic ferrite matrix (TBF steels) have been developed for cold forming of automotive applications. Complex additions of 1.0%Al–0.05%Nb–0.2%M0 to 0.2%C–1.5%Si–1.5%Mn base steel increased both the volume fraction and carbon concentration of retained austenite films of the TBF steel, with refining of microstructure. Extremely much retained austenite was realized in the TBF steel austempered at 450–500°C, corresponding to hot-dip galvanization just after annealing. Good combinations of strength and elongation and strength and stretch-flangeability were achieved when the TBF steel was austempered at 450–500°C and 425–475°C, respectively. These good combinations were caused by fine lath structure and a large amount of metastable retained austenite film. It is noteworthy that the TBF steel exhibited an excellent combination of total elongation and stretch-flangeability when austempered at 325–350°C lower than $M_S$.

KEY WORDS: ultra high-strength steel; TRIP-aided steel; retained austenite; formability; aluminum; niobium; galvanization.

1. Introduction

In order to attain a drastic weight reduction and crashworthiness performance, automotive members such as a center-pillar etc. with tensile strength of 980–1 470 MPa are fabricated by hot press process (hot-forming and die quenching)1,2) because of difficulty of cold press. However, the hot press process is characterized by poor cost performance for production, so that ultra high-strength steels with good formability are required for cold stamping members. The transformation-induced plasticity (TRIP)3) of retained austenite is very useful in improving the formability of ultra high-strength steel. On the basis of such an idea, 780–1 470 MPa grade C–Si–Mn TRIP-aided steel with bainitic ferrite matrix or TRIP-aided bainitic ferrite steel (TBF steel) was recently developed by our research group.4–7) If the TBF steel was austempered at much lower than $M_S$, the matrix structure resembles to that of the steel subjected to quenching and partitioning process (Q and P process).8)

In the ultra high-strength steels, hot-dip galvanizability and high hydrogen embrittlement resistance are also required. According to a previous research about 780 MPa grade TRIP-aided steels with annealed martensite matrix,9) Al addition with the same amount of Si removal is expected to realize the hot-dip galvanizability, accompanied with increasing optimum austempering temperature, although it lowers the tensile strength. So, in this study the effects of Al addition on the microstructure and formability of the TBF steels were investigated. Furthermore, the effects of complex additions of Nb and Mo on these properties were also examined to achieve further good combination of strength and formability.

2. Experimental Procedure

In this study, five steels with different Si, Al, Nb and Mo contents were prepared as vacuum-melted 100 kg ingots followed by hot forging to produce 30 mm thick slabs. The chemical composition of these slabs is shown in Table 1, in which martensite start temperature ($M_S$) was calculated using the following relation,10)

$$M_S (°C) = 550 - 361 \times (\%C) - 39 \times (\%Mn) - 17 \times (\%V) - 20 \times (\%Cr) - 17 \times (\%Ni) - 10 \times (\%Cu) - 5 \times (\%Mo + \%W) - 0 \times (\%Si) + 15 \times (\%Co) + 30 \times (\%Al)$$

Table 1. Chemical composition (mass%) and estimated $M_S$ temperature (°C) of steels.

| steel | C   | Si  | Mn  | P   | S   | Al  | Nb  | Mo  | N   | $M_S$ |
|-------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-------|
| A     | 0.19| 1.54| 1.51| 0.006| 0.0025| 0.04| -   | -   | 0.0017| 424   |
| B     | 0.20| 0.99| 1.51| 0.005| 0.0026| 0.49| -   | -   | 0.0022| 434   |
| C     | 0.20| 0.49| 1.50| 0.005| 0.0025| 0.99| -   | -   | 0.0022| 449   |
| D     | 0.20| 0.99| 1.48| <0.005| 0.0012| 0.48| 0.045| 0.20| 0.0008| 434   |
| E     | 0.20| 0.49| 1.50| <0.005| 0.0012| 0.95| 0.051| 0.20| 0.0008| 447   |

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where %C, %Mn, %V, %Cr, %Ni, %Cu, %Mo, %W, %Si, %Co and %Al are added contents (mass%) of individual alloying elements.

The slabs were reheated to 1200°C and were hot-rolled to a thickness of 3.2 mm, finishing at 850°C and then coiled at 600°C, as shown in Fig. 1. After cold rolling to a thickness of 1.2 mm, the sheets were first annealed at 950°C (steels A, B and D) or 1000°C (steels C and E) and then austempered at 300–525°C for 200 s in salt bath.

The volume fraction of retained austenite was quantified from integrated intensity of (200)ψ, (211)ψ, (200)γ, (220)γ and (311)γ peaks of Mo-Kα radiation. The carbon concentration (C, mass%) was estimated by substituting the lattice constant (aψ, 10−10 m) measured from (200)ψ, (220)γ (311)γ peaks of Cu-Kα radiation into the following equation.

\[
a_\gamma = 3.5780 + 0.0330 \times (\%C) + 0.00095 \times (\%Mn) + 0.0 \times (\%Si) + 0.0002 \times (\%Ni) + 0.0006 \times (\%Cr) + 0.0220 \times (\%N) - 0.0056 \times (\%Mo) - 0.0004 \times (\%Co) + 0.0015 \times (\%Cu) + 0.0031 \times (\%Nb) + 0.0079 \times (\%N) + 0.0032 \times (\%Ti) + 0.0017 \times (\%V) + 0.0057 \times (\%W) \hspace{1cm} (2)
\]

where %Mn, %Si, %Ni, %Cr, %N, %Mo, %Co, %Cu, %Nb, %Ti, %V, and %W represent solute contents (mass%) of the individual alloying elements in retained austenite. For convenience, these solute contents were assumed to be equivalent to added ones.

Tensile tests were carried out on Instron type of testing machine using specimens of gage length of 50 mm, gage width of 12.5 mm and thickness of 1.2 mm.

The hole-expanding ratio (λ) was determined by the following equation,

\[
\lambda = \left( \frac{d_f - d_0}{d_0} \right) \times 100 \% \hspace{1cm} (3)
\]

where \(d_0\) and \(d_f\) are initial hole diameter (4.76 mm) and hole diameter at the moment which the crack-propagation pierced through thickness of the specimen, respectively. Punching rate is 10 mm/min and cross head speed on hole-expanding is 1 mm/min. The clearance between die and punch was 10% of sheet thickness.

3. Results

3.1. Microstructure and Retained Austenite Characteristics

Figures 2 and 3 show typical scanning electron micrographs of TBF steels austempered at 325°C and 450°C, respectively. Similar to steel A, microstructure of steels B and C mainly consists of bainitic ferrite and interlath retained austenite films when these steels were austempered at temperatures above 500°C. In addition, Al addition of 1.0 mass% reduces the prior austenite grain size and retained austenite films, as shown in Fig. 3(c). It is noteworthy that band structure disappears in steels B and C (Figs. 3(b), 3(c)), differing from the TRIP-aided steel with polygonal ferrite matrix. On the other hand, when austempered at temperatures below 500°C, martensite structure coexists with bainitic ferrite in the matrix of the steels B and C (Figs. 2(b), 2(c)), although a small amount of pro-eutectoid ferrite nucleates (see arrows). It was observed by TEM that fresh martensite structure to which relatively unstable retained austenite transforms during cooling after austempering exists in the steels austempered at temperatures above 500°C, especially

![Fig. 1. Schematic diagram of hot and cold rolling process and then annealing and austempering process of TBF steels, in which ‘AC’ and ‘OQ’ represent air cooling and quenching in oil, respectively.](image1)

![Fig. 2. Scanning electron micrographs of TBF steels austempered at 325°C, in which arrows represent pro-eutectoid ferrite.](image2)
Further complex additions of Nb and Mo (such as steels D and E) promote the refinement of the prior austenite grain. When steel E was austempered at 450°C, the retained austenite morphology changes from filmy to blocky and bainitic ferrite changes to granular type (Fig. 3(e)). When steels D and E were austempered at 325°C, pro-eutectoid ferrite can be found in the same way as steels B and C (Figs. 2(d), 2(e)).

Figure 4 shows a transmission electron micrograph of steel E austempered at 425°C. Fine NbMoC precipitates of about 10 nm in diameter are observed in the matrix, coexisting with coarse NbC of about 50 nm. Any fine NbMoC precipitate was not detected in steel E austempered at 325°C.

Figure 5 shows the variations in retained austenite characteristics as a function of austempering temperature for TBF steels. Al addition increases the carbon concentration of retained austenite and decreases its volume fraction. Further complex additions of 0.05% Nb and 0.2% Mo decrease the carbon concentration of the retained austenite, but its volume fraction is increased, especially when austempered at 450–500°C. In addition, optimum austempering temperature for retained austenite content is raised up to 450–500°C, corresponding to hot-dip galvanizing temperature (460°C).

3.2. Strength, Ductility and Formability

Figure 6 shows the variations in yield stress or 0.2% offset proof stress (YS) and tensile strength (TS) with austempering temperature (T_a) in the TBF steels. Al addition with the same amount of Si removal considerably decreases yield stress and tensile strength, especially in steel C. On the other hand, further complex additions of Nb and Mo increase these stresses and tensile strength of steel E. Note that these additions do not raise the tensile strength of steel D.

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These yield ratios are increased by complex additions of Al, Nb and Mo.

Figure 7 shows variations in total elongation ($TE_l$) and combination of strength and elongation ($TS/TE_l$) of the TBF steels as a function of austempering temperature. The combination of strength and elongation as well as total elongation is increased by complex additions of Al, Nb and Mo, particularly when austempered at 450–500°C and 325–350°C. Al addition of 0.5% reveals a small improvement of total elongation and combination of strength and elongation.

Figure 8 shows hole-expanding ratio ($\lambda$) and combination of strength and stretch-flangeability ($TS/\lambda$) in the TBF steels. The stretch-flangeability of the TBF steels is hardly influenced by Al, Nb and Mo, except for when austempered at 325–350°C. This result is differing from the report that Nb addition$^{13}$ and complex additions of Nb and Mo$^{14}$ enhance the strength–stretch-flangeability balance.

Figure 9 shows relationships between hole-expanding ratio and total elongation of steels with tensile strength of about 780, 980 or 1 270 MPa. It is found that complex additions of Al, Nb and Mo primarily improve total elongation in a tensile strength range of 780 and 980 MPa. On the other hand, they improve both the total elongation and hole-expanding ratio in a tensile strength range of 1 270 MPa.

4. Discussion

4.1. Carbon Concentration of Retained Austenite

According to previous study for TRIP-aided steels with polygonal ferrite matrix$^{9,15,16}$ (TPF steel) and with annealed martensite matrix$^9$ (TAM steel), Al addition of 0.5–1.0 mass% increases the carbon concentration of retained austenite. The increased carbon concentration is caused by that Al addition raises $T_0$ temperature at which austenite and ferrite of the same chemical composition have identical free energies.$^{17}$ The $T_0$ lines of Fe–C–(0.5–1.5)Si–1.5Mn–(1.0–0.04)Al systems computed using Thermo-Calc$^{18}$ are shown in Fig. 10, in which measured carbon concentrations of TBF steels are also plotted. In this figure, the measured carbon concentration of retained austenite nearly agrees with the computed $T_0$ line. So, high carbon concentration of steels B and C may be caused by elevation of $T_0$ line by Al addition.

In Fig. 5, complex additions of Al, Nb and Mo decreased the carbon concentration to the same level as steel A, espe-
In this study, the same amount of NbC and NbMoC in steel E, although the Si content is higher than that of steel A, the tensile strength of steel D was not increased, differing from NbMoC precipitates of 0.5% or 1.0%, compared with steel A. However, complex additions of 0.05% Nb and 0.2% Mo, despite of Si removal of 0.5% or 1.0%, compared with steel A. However, tensile strength of steel D was not increased, differing from steel E, although the Si content is higher than that of steel E. In this study, the same amount of NbC and NbMoC precipitates appeared in both the steels D and E (Fig. 4).

4.2. Microstructural Change

According to Drewes and Walker and DeArdo et al., Nb plays the following roles in conventional TRIP-aided steels (TPF steel).

(1) Nb in solid solution lowers the martensite start temperature. And, it promotes ferrite transformation in the same way as Al. Furthermore, in dissolved form it suppresses cementite precipitation in the temperature range of bainite formation, with consequent increase in the residual austenite content and its carbon content.

(2) In precipitated form as carbides, nitrides or carbonitrides, Nb has a grain refining effect, increasing the tensile strength. Furthermore, Nb suppresses undesired pearlite formation in the TRIP-aided steels.

In this study, a large amount of pro-eutectoid ferrite appeared in steels B through E. From the above reports, this may be because ferrite nucleation was promoted by Al and Nb. In addition, refined microstructure of steels D and E may be caused by coarse NbC precipitates which appeared in Fig. 4. Heller and Nuss reported that Nb suppresses ferrite initiation, differing from the above theory. This difference may be owing to the increased area of prior austenite grain boundary corresponding to coarse NbC precipitates.

In steel E, matrix structure changed from bainitic ferrite lath to granular bainitic ferrite (Fig. 3(e)). As mentioned above, Nb addition refines the prior austenite grain. So, it is expected that the refinement effect of Nb results in morphology change of matrix structure by suppressing the bainite transformation.

4.3. Strength

Yield stresses of steels D and E were increased by complex additions of 0.05% Nb and 0.2% Mo, despite of Si removal of 0.5% or 1.0%, compared with steel A. However, tensile strength of steel D was not increased, differing from steel E, although the Si content is higher than that of steel E. In this study, the same amount of NbC and NbMoC precipitates appeared in both the steels D and E (Fig. 4).
higher carbon concentration of retained austenite than steel A. In addition, prior austenite grain of these steels was refined. So, it is expected that TRIP effect of carbon enriched retained austenite and suppression of void initiation due to uniformly refined microstructure brought on the large uniform and total elongations.

Stretch-flangeability of steels D and E could not be improved by complex addition of Al, Nb and Mo, when austempered at 400–475°C (Fig. 8). This is different from result of a previous study\textsuperscript{13,14} that additions of Nb and Nb+Mo achieved high stretch-flangeability.Generally, the stretch-flangeability of the TRIP-aided steels is principally controlled by hole-surface damage on hole-punching such as voids at the matrix/second phase. The retained austenite morphology had changed from filmy to blocky in the steel E, as shown in Fig. 3(e). So, it is estimated that blocky retained austenite morphology disturbs the improvement of the stretch-flangeability in the Al–Nb–Mo steels, although microstructure was considerably refined.

When steels D and E were austempered at 325–350°C, the combination of strength and stretch-flangeability exhibited high value (Fig. 8). This result may be caused by the refined prior austenite grain and stabilized retained austenite. However, the detailed reason is under consideration.

5. Conclusions

(1) Al addition with removal of the same amount of Si increased carbon concentration of retained austenite and decreased its volume fraction in 0.5 mass% to 0.20%C–1.5%Si–1.5%Mn TBF steels. On the other hand, further additions of 0.05% of Nb and 0.2% of Mo decreased the carbon concentration, although they brought on fine and granular bainitic ferrite matrix with the increased volume fraction of retained austenite.

(2) Al addition with the same amount of Si removal decreased flow stress and strain-hardening rate, although it increased yield ratio. On the other hand, complex addition of further Nb and Mo increased the flow stress, as well as yield ratio.

(3) Complex additions of Al, Nb and Mo improved the combinations of strength and elongation and strength and stretch-flangeability, especially when the TBF steels were austempered at 450–475°C, corresponding to galvanization temperature. This was caused by uniform fine lath structure and stabilized much retained austenite films.

(4) The TBF steel exhibited an excellent combination of total elongation and stretch-flangeability when austempered at 325–350°C lower than $M_s$.

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