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A Novel Cyclic-Quenching-ART for Stabilizing Austenite in Nb–Mo Micro-Alloyed Medium-Mn Steel

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Abstract: In the context of obtaining an excellent elongation and tensile-strength combination in the third generation of advanced high strength steel, we emphasized the practical significance of adjusting the retained austenite fraction and stability in medium-Mn steel to obtain better mechanical properties. A novel cyclic quenching and austenite reverse transformation (CQ-ART) was used to obtain a large retained austenite content in Fe-0.25C-3.98Mn-1.22Al-0.20Si-0.19Mo-0.03Nb (wt.%) Nb–Mo micro-alloyed medium-Mn steel. The results show that after twice cyclic quenching and ART, the alloy exhibited optimum comprehensive properties, characterized by an ultimate tensile strength of 838 MPa, a total elongation of 90.8%, a product of strength and elongation of 76.1 GPa%, and the volume fraction of austenite of approximately 62 vol.%. The stability of retained austenite was significantly improved with the increasing of the number of cyclic quenching. Moreover, the effects of CQ-ART on the microstructure evolution, mechanical properties, C/Mn partitioning behavior, and austenite stability were investigated. Further, the strengthening effect of microalloying elements Nb–Mo was also discussed.

Keywords: medium Mn steel; cyclic quenching; austenite reversal transformation; austenite stability

1. Introduction

Nowadays, medium-Mn steels (~3–11 wt.% Mn) have become an appealing topic due to their high metastable retained austenite (RA) content and unique fine microstructures such as dual-phase structure (fine γ and α) or tri-phase structure (fine γ , α and/or martensite) [1–3]. These steels are very promising for automotive applications due to their excellent strength, elongation, crashworthiness and safety [4–6]. Since the excellent comprehensive performance of medium Mn steel strongly depends on the high RA content with appropriate stability, it is very important to control the RA [7–10]. Medium Mn steel is generally produced by austenite reverse transformation (ART) process to obtain a certain amount of metastable RA at ambient temperature. Generally, the mechanical stability of RA is affected by its chemical composition (C and Mn content) [8], grain size [9,10], and morphology [11]. RA with excessive stability cannot exhibit an extensive transformation induced plasticity (TRIP) effect, which hinders the transformation of RA to martensite under continuous strain conditions, resulting in poor mechanical properties. However, RA with poor stability is easy to rapidly transform into martensite under a low stress conditions and cannot produce extensive TRIP effect, resulting in unsustainable work hardening rate (WHR) in medium Mn steel [12]. In the past few years, scholars have proposed to refine austenite grain size in steel by rapidly heating and cyclic quenching (CQ) in order to improve austenite stability in medium carbon Ni–Cr–Mo steel [13]. This paper draws on

rapidly heating and cyclic quenching heat treatment technology, attempts to use cyclic quenching to destroy the orientation relationship between the new and original phase before intercritical annealing to refine the martensite structure, and then generates finer strip austenite in the subsequent reverse transformation process, thereby further increasing the content and stability of austenite in medium Mn steel to improve the comprehensive mechanical properties.

Herein, a cycle quenching and austenite reverse transformation (CQ-ART) with rapid heating is proposed to obtain high RA content in medium Mn steel. The microstructural characteristics and their effects on tensile properties, work hardening rate and austenite stability as well as the C and Mn partitioning behavior were studied. In addition, the role of microalloying elements was also discussed.

2. Experimental Procedure

The experimental material with the chemical composition of 0.25C-3.98Mn-1.22Al-0.20Si-0.19Mo-0.03Nb-Fe (wt.%) shown in Table 1 was melted in an intermediate frequency induction furnace and then cast into a 15 Kg bullet-shaped billet, subsequently forged to 100 mm (wide) × 30 mm (thick) slab. Afterwards, the slab was hot-rolled to 3.8 mm-thick plates, followed by machined to remove the oxide scale and the flat surface was obtained, and then cold rolled to a final thickness of 1.9 mm sheets via 3 passes. Using a Thermo-Calc (Thermo-Calc Software, Stockholm, Sweden) the intercritical region temperature (Ac1 of 632 °C, Ac3 of 862 °C) calculations were observed.

The CQ-ART processes used in the present work are shown schematically in Figure 1a. For once cyclic quenching (CQ1) and ART sample (put the sample into the muffle furnace after the temperature is constant), the sample was water quenched after austenitization at 900 °C for 30 min. For twice cyclic quenching (CQ2) and ART sample, the sample is added to the same cyclic quenching heat treatment for 10 min based on CQ1. For thrice cyclic quenching (CQ3) and ART sample, the sample is added to the same cyclic quenching heat treatment for 5 min based on CQ2. Finally, all samples were annealed at 690 °C for 1 h before air cooling to ambient temperature (abbreviated as CQ1-ART, CQ2-ART and CQ3-ART, respectively). All samples were heated in a way that the muffle furnace reaches the set temperatures and then put into the sample for isothermal holding, thus achieving the effect of rapidly heating.

The samples after heat treatment were processed into standard plate-shaped tensile specimens with a 12.5 mm width in the rolling direction (Figure 1b). Tensile tests using a microcomputer controlled electronic testing machine (UTM5504GD) (Jinan Wanchao Electric Equipment Co., Ltd., Shandong, China) with the strain rate of 3 mm/min. The microstructures of the CQ-ART specimens were observed by SEM (FEI, Hillsboro, OR, USA) and TEM (JEOL, Tokyo, Japan). Specimens for SEM observation were etched in a 4 vol.% Nital. Specimens for TEM observation were prepared by cutting the thin sheets into 0.6 mm thickness along with rolling direction by wire cutting, grinding them to 0.05 mm thickness by hand, and punching out the discs with a diameter of 3 mm, followed by electro-polished in a twin-jet machine with a mixed solution of 10% perchloric acid (HClO₄) and 90% alcohol (C₂H₄OH) at about −25 °C. The concentration of Mn was determined by TEM-EDS.

The phase composition analysis of the experimental steel was carried out on an X-ray diffractometer (XRD) (Bruker, Karlsruhe, Germany) with CuKα radiation ($\lambda = 1.5405$). The V_γ (RA) content was determined by the diffraction intensities of (200) α , (211) α , (311) γ , (200) γ and (220) γ peaks, and was calculated using Equation (1) [14]:

$$V_\gamma = 1.4I_\gamma / (I_\alpha + 1.4I_\gamma) \quad (1)$$

where, I_γ is the integrated intensity of austenite and I_α is the integrated intensity of ferrite.

Table 1. Chemical compositions of the investigated steel (wt.%).

C	Mn	Al	Si	Mo	Nb
0.25	3.98	1.22	0.20	0.19	0.03

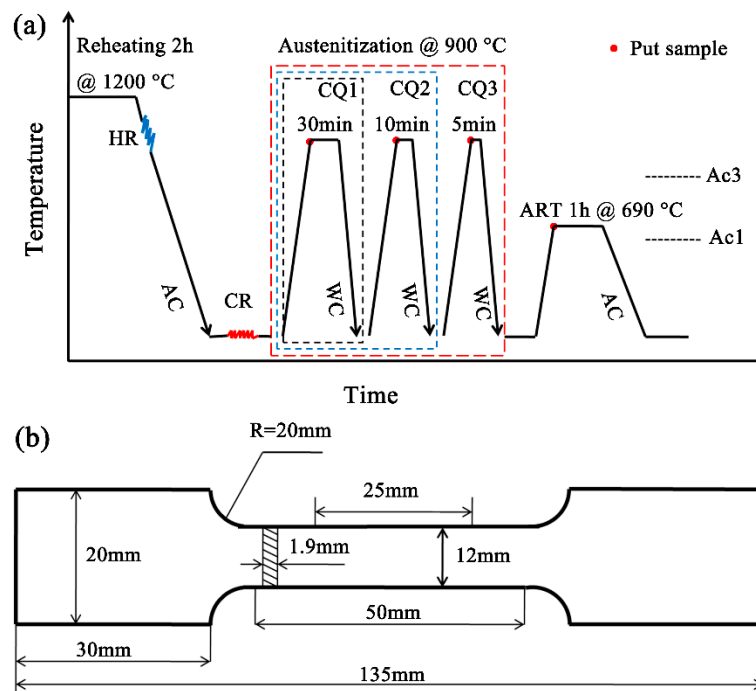


Figure 1. (a) Schematic diagram of the different heat treatment process; (b) specimen for tensile tests.

3. Results and Discussion

3.1. Microstructural Design Strategies

The austenite/ferrite (γ/α) phase fraction and the C/Mn concentrations in the γ phase of the experimental steel at different temperatures were calculated by thermodynamic simulation software Thermo-Calc and are shown in Figure 2a,b, respectively. Obviously, with the increasing of intercritical temperature, the experimental steel evolution progresses from a single α phase region to a γ/α dual phase region, and finally to a single γ phase region. As shown in Figure 2b, the C and Mn concentrations are strongly affected by temperature. Due to the relatively low solid solubility of Mn in ferrite phase, a large amount of Mn will be segregated into the γ phase, which improves the stability of austenite. However, with the increasing proportion of austenite phase, the average amount of Mn partitioning to each austenite grains decreased. Thus, there is an optimum temperature to maximize the amount of RA after annealing. Moor et al. [15] proposed a model for calculating austenite content at ambient temperature based on the resulted of Thermo-Calc. It is further deduced that there exists an optimal intercritical annealing temperature to maximize the content of RA. The martensite transformation (M_s) temperature of the experimental steel can be calculated by the Equation (2) from the variation of the content of each element in the austenite with temperature [16]:

$$M_s = 539 - 432x_C - 30.4x_{Mn} - 17.7x_{Ni} - 12.1x_{Cr} - 7.5x_{Mo} + 30x_{Al} \quad (2)$$

where x (C, Mn, Ni, Cr, Mo and Al) are their concentrations in austenite in wt.%, respectively. According to the Koistinen–Marburger (KM) [17] Equation (3), the amount of transformation of austenite into martensite during cooling can be calculated. Finally, the RA content at each temperature can be obtained by subtracting the content transformed austenite from the total austenite content at different temperatures (Equation (4)) in Figure 2a, and the results are shown in Figure 2c.

$$f_{\alpha'} = 1 - \exp[-\alpha(M_s - T)] \quad (3)$$

$$f_{\gamma} = f_{TC,\gamma} - f_{\alpha'} \quad (4)$$

where $f_{\alpha'}$, α , f_{γ} , T and $f_{TC,\gamma}$ are the amount of transformation of austenite into martensite during cooling, material constants with a value of 0.011, RA content, the ambient temperature (20 °C) and the equilibrium austenite content at different temperatures, respectively. Figure 2c summarized the measured RA at different temperatures. It is obvious that with increasing of the intercritical annealing temperature, the RA content reached the maximum value (23.4 vol.%) at 690 °C then decreased. When the intercritical annealing temperature exceeded 690 °C, the fresh martensite is formed during the annealing and cooling process resulting in a gradual decrease in RA content. Mn is the critical element for stabilizing austenite, which has been discussed in our previous studies [8,9]. Thus, the intercritical annealing temperature can be set to 690 °C in order to increase the Mn content in the experimental steel to obtain a larger RA content at ambient temperature.

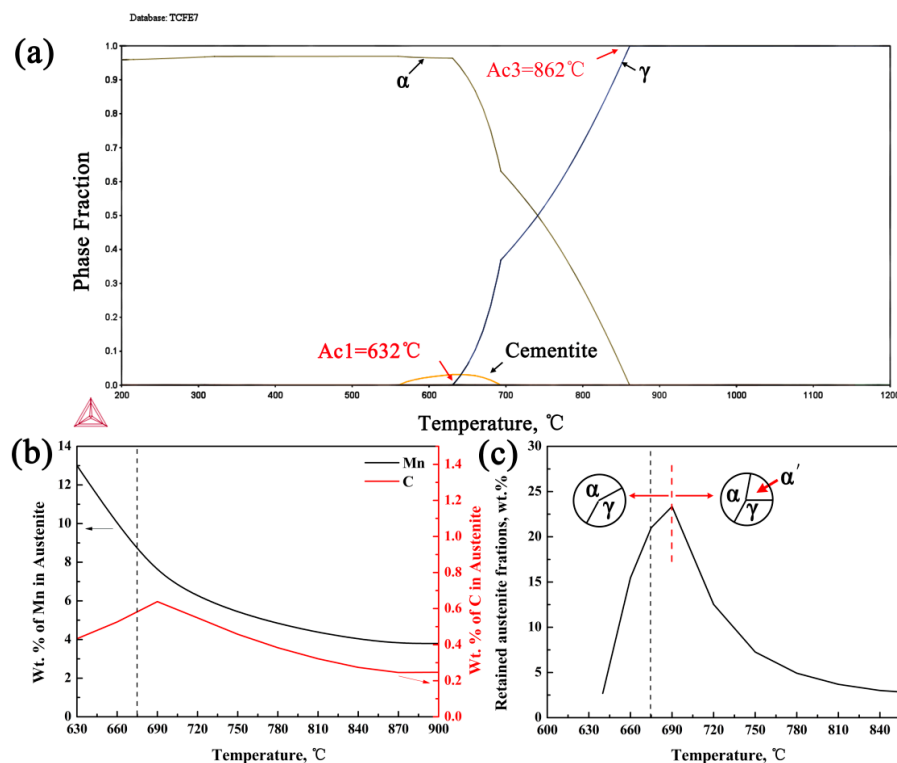


Figure 2. (a) Phase composition of experimental steel at different temperatures; (b) temperature dependence of C and Mn contents in austenite; (c) calculation of retained austenite (RA) fractions at different temperatures (γ : austenite, α : ferrite, α' : martensite).

3.2. Microstructure and Mechanical Properties

Figure 3a–c and d–f exhibits the SEM and TEM microstructure of CQ-ART samples, respectively. Obviously, the microstructure of CQ1-ART sample mainly consisted of strip-shaped RA and ferrite (see Figure 1a,d), while that of CQ2-ART sample consisted of relatively fine and short strip-shaped RA and ferrite (see Figure 1b,e). It was preliminarily inferred that austenite grain can be refined by increasing the number of cyclic quenching. For the CQ3-ART sample, the microstructure is obviously smaller than the CQ1-ART sample and comparable to the CQ2-ART sample, indicating that the change in grain size after thrice cyclic quenching has stabilized. Thirty TEM images were used to characterize austenite grain size by Digital Micrograph software. The measured width of RA in CQ1-ART sample is from 0.16–1.85 μm , while the RA width of the CQ2-ART and CQ3-ART samples are from 0.13–1.25 μm and 0.12–1.60 μm , respectively (see Table 2). Obviously, the average width of the strip-shaped RA decreased from 0.62 to 0.40 μm with the increase in numbers of cyclic quenching. This result reveals that the austenite grain size after treatment by CQ-ART is significantly reduced because the sheets were repeatedly heated rapidly to near the austenitizing temperature, isothermal holding for a short

time, and then rapidly cooled, causing the recrystallized austenite grains to be forcibly interrupted before they could grow up and then producing finer lath martensite during the subsequent quenching process [13]. At the same time, in the subsequent ART process, the reverted RA readily nucleated along the lath martensite boundary, and finally, a strip-shaped RA having a relatively small size can be obtained at ambient temperature. As reported by Morsdorf et al. [18] the reverse transformed strip-shaped RA readily nucleated along the lath martensite or original austenite grain boundary; thus, the finer strip-shaped RA at ambient temperature can be obtained by refining the size of the martensite lath.

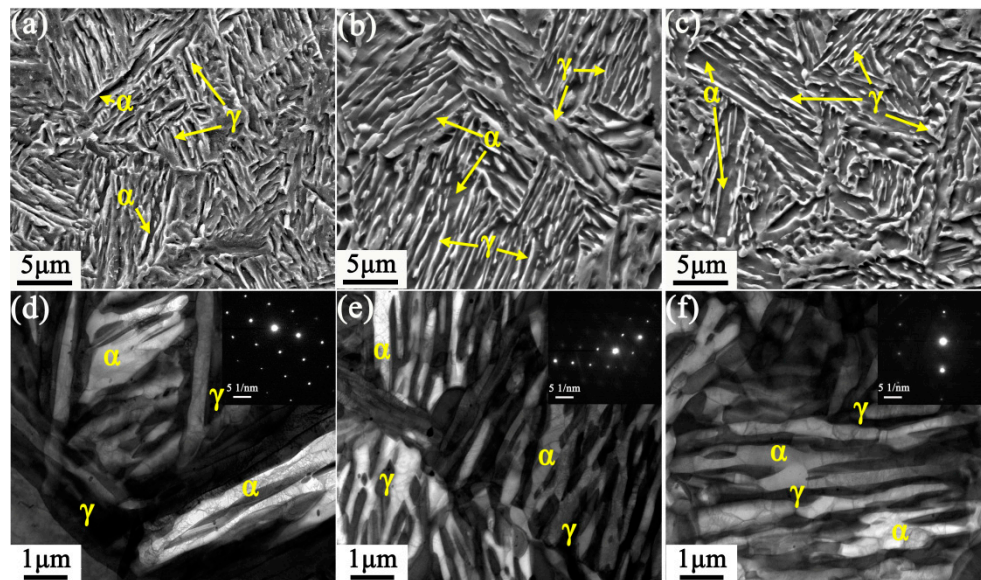


Figure 3. SEM and TEM micrographs of (a–c) and (d–f) for cycle quenching and austenite reverse transformation (CQ-ART) samples, respectively, (a,d) CQ1-ART sample, (b,e) CQ2-ART sample and (c,f) CQ3-ART sample.

Table 2. Statistical data of austenite width by Digital-Micrograph.

Retained Austenite Width	CQ1-ART	CQ2-ART	CQ3-ART
RA _{ave} (μm)	0.62	0.40	0.42
RA _{min} (μm)	0.16	0.13	0.12
RA _{max} (μm)	1.85	1.25	1.60

The XRD patterns and measured austenite fraction of the samples are presented in Figure 4a–c. As shown in Figure 4a, the diffraction intensities of $\gamma(200)$ austenite peak of the CQ2-ART and CQ3-ART samples has a markedly enhanced tendency compared to the CQ1-ART sample. RA content and transformation ratio of austenite was calculated by Equation (1). The estimated austenite fraction of CQ1-ART, CQ2-ART and CQ3-ART samples before tensile tests were ~49.2 vol.%, ~62.0 vol.% and ~64.8 vol.% respectively, of which ~88%, 90% and 58% austenite transformation to martensite after tensile tests, respectively. Given the increasing content of retained austenite, it can be inferred that the austenite content increases with the number of cyclic quenching and becomes slow after three cyclic quenching.

The tensile properties of the CQ-ART process samples are summarized in Figure 4d. For CQ1-ART sample, characterized by tensile strength (UTS) of 784 MPa, total elongation (TE) of 83.7%, and UTS $\times$ TE (product of strength and elongation, PSE) of 65.6 GPa%. By contrast, the conventional ART steels exhibited a PSE from 11.5 to 26.5 GPa%, and austenite content from 25.2 vol.% to 34.2 vol.% [19]. In the CQ2-ART sample, characterized by UTS of 838 MPa, TE of 90.8%, and PSE of 76.1 GPa%; and in the CQ3-ART sample, the UTS of 806 MPa, while TE is reduced to 55.1% compared to CQ1-ART.

The changes in the UTS of the three different process samples are slight, while the TE increased initially and then sharply decreased with increasing the number of cyclic quenching. Given that the significant difference in TE between the CQ1-ART and CQ3-ART sample, it is proposed that austenite has appropriate stability combining with Figure 4c. The CQ1-ART sample contained ~49.2 vol.% of austenite, of which ~88% of the austenite was transformed into martensite after tensile strain to fracture. In comparison, the CQ3-ART sample contained ~64.8 vol% austenite, of which ~58% of the austenite transformed into martensite after tensile strain to fracture. Interestingly, the corresponding TE values of the two samples differed by more than 30%. Thus, the TE values of experimental steel are indirectly determined by the amount of transformation from austenite to martensite. This indicates that the high stability of RA in CQ3-ART sample leads to difficulty in transforming austenite to martensite. As a result, the ductility of CQ3-ART sample was low (TEL = 55.1%), which is consistent with the conclusions in [18]. Those results indicated the CQ-ART process can significantly improve the stability of RA, thus obtaining a high fraction RA after quenching to ambient temperature. A caveat is in order here. Any inclusions may be included in the microstructure of the sample, which during the tensile test can be considered as crack nucleation sites and reduce mechanical properties. For this question, further research is needed. The influence of inclusions on mechanical properties in microstructure requires further study.

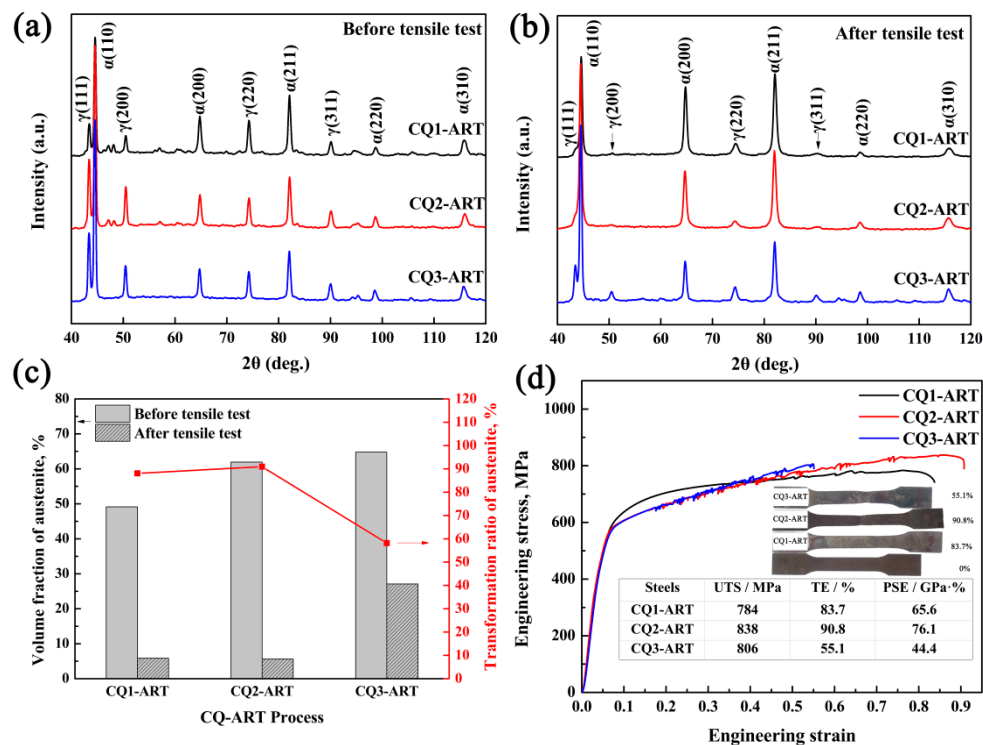


Figure 4. (a) XRD pattern of the before tensile test samples, (b) XRD pattern of the after tensile test samples, (c) austenite fraction calculated using Equation (1) and transformation ratio of austenite, and (d) engineering stress-strain curves.

3.3. Mn and C Partitioning Behavior

Partitioning of Mn and C leads to difference of retained austenite content at ambient temperature after austenite reverse transformation [20–22]. The Mn concentration in RA of experimental steel at ambient temperature was quantitatively characterized by TEM-EDS. As shown in Table 3, the average Mn concentration in RA was 6.16 wt.% for CQ1-ART sample, and 7.31 wt.% and 7.19 wt.% for CQ2-ART and CQ3-ART samples, respectively. Interestingly, for CQ3-ART sample, the maximum Mn concentration in RA (8.32 wt.%) is higher than that in CQ1-ART (7.69 wt.%) and CQ3-ATR (7.93 wt.%)

samples; it is proposed that was associated with a large amount of granular austenite in CQ3-ART sample (Figures 3c and 5d). Since Mn is partitioning from adjacent ferrite grains, the RA grains are stabilized by the enrichment of Mn (Figure 5a–d) [15]. The measured Mn concentration of RA in the CQ1-ART, CQ2-ART, and CQ3-ART samples are shown in Figure 5d. It is obvious that there is significant Mn partitioning between the RA grains and ferrite grains. The Mn concentration in the granular RA (γ_G) is higher than that of the filmy RA (γ_F). Additionally, Mn concentrations in the RA after twice or thrice cyclic quenching are significantly higher than that in the once cyclic quenching, indicating that the significant increase in the average Mn concentration in the austenite is treated by the CQ-ART process. In addition, C is also an important element affecting the stability of austenite, and the C concentration of austenite was calculated as [23]:

$$\alpha_\gamma = 3.556 + 0.0453x_C + 0.00095x_{Mn} + 0.0056x_{Al} \quad (5)$$

where x_C , x_{Mn} , and x_{Al} are C, Mn and Al concentration in austenite, in wt.%. α_γ is the austenite lattice parameter in Å, and calculated from Equation (6) [24].

$$\alpha_\gamma = \frac{\lambda}{2 \sin \theta} \times \sqrt{h^2 + k^2 + l^2} \quad (6)$$

where λ , θ , and (h, k, l) are the x-ray wavelength, the diffraction angle, and the lattice parameters, respectively. The C concentration in RA was 0.5171 wt.% for CQ1-ART sample, and 0.5139 wt.% and 0.5124 wt.% for CQ2-ART and CQ3-ART samples, respectively. After CQ-ART process, the C concentration in austenite decreases slightly, which is related to the increase of total amount of RA. Since the total amount of RA increased, the average C concentration distributed to a single austenite grain decreased. These results indicate that the C concentration changes slightly after CQ-ART treatment, but the Mn concentration in RA increased significantly. It is well known that C atom belongs to interstitial solutes, which can rapidly diffuse between α and γ , and achieve dynamic equilibrium. In contrast, the Mn atom belongs to the substitutional solutes with a much smaller diffusion coefficient than interstitial diffusion atom, which requires a long intercritical annealing time to diffuse into and enrich the austenite [25].

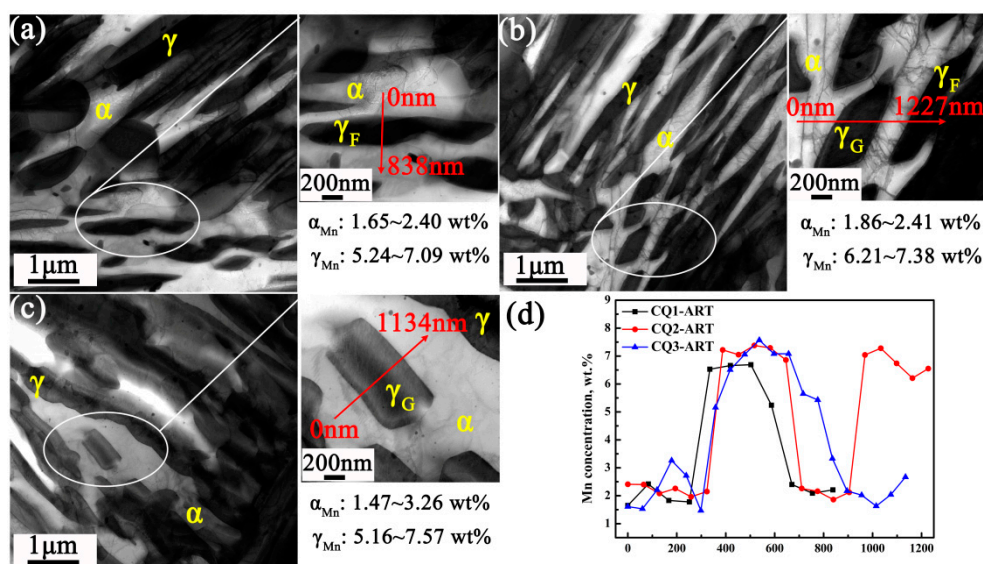


Figure 5. (a) TEM image of the CQ1-ART sample; (b) TEM image of the CQ2-ART sample; (c) TEM image of the CQ3-ART sample; (d) corresponding Mn concentrations measured by the TEM-EDS in (a)–(c), where γ , γ_F , γ_G and α refer to austenite, filmy austenite, granular austenite and ferrite, respectively.

Table 3. Data of Mn concentration in retained austenite by TEM-EDS.

Mn Concentration	CQ1-ART	CQ2-ART	CQ3-ART
RA _{ave} (wt.%)	6.16	7.31	7.19
RA _{min} (wt.%)	5.24	6.07	5.01
RA _{max} (wt.%)	7.69	7.93	8.32

Hu et al. simulated the nucleation and growth of austenite grains in intercritical region, and proposed the following diffusion flux equation used to describe the speed of interfacial motion between α and γ phases [25]:

$$\begin{aligned} (C_{Mn}^{\gamma*} - C_{Mn}^{\alpha*}) \frac{dx_{Mn}}{dt} &= (J_{Mn}^{\gamma} - J_{Mn}^{\alpha}) \\ J_{Mn}^{\gamma} &= -D_{Mn}^{\gamma} \left(\frac{\partial c_{Mn}^{\gamma}}{\partial x} \right) \end{aligned} \quad (7)$$

where $C_{Mn}^{\gamma*}$ and $C_{Mn}^{\alpha*}$ are concentration of solute Mn at the γ and α interface, respectively. J_{Mn}^{γ} and J_{Mn}^{α} are the diffusion flux of the Mn for γ and α phase, respectively. D_{Mn}^{γ} , c_{Mn}^{γ} and x are the diffusion coefficient of Mn for γ phase, the Mn solute atom concentration for γ phase and the displacement of the interface moved, respectively. Equation (6) shows that the lath of martensite and its initial Mn content control the diffusion flux. As we mentioned above, multiple cyclic quenching will produce finer lath martensite during subsequent quenching process. Combining with the results in Table 3, it can be seen that the CQ2-ART sample exhibits martensite matrix with high manganese concentration (7.31 wt.%) while the CQ1-ART sample exhibits martensite matrix with relatively low manganese concentration (6.87 wt.%). This result indicated that the cyclic quenching is equivalent to providing a longer holding time to promoting the enrichment of Mn in prior austenite, which results in more Mn content in the austenite after multiple cyclic quenching, thereby improving the stability of austenite and obtaining more RA at ambient temperature.

3.4. Deformation Behavior and Austenite Stability

Tensile tests are performed on the CQ2-ART samples at engineering strain of 10% and 20%, and the corresponding specimens were characterized by XRD (Figure 6a). After 10% and 20% tensile strains, ~29% and ~34% austenite transformed to martensite, respectively. Figure 6b–c shows the WHR and true stress–strain curves of the cyclic quenching samples. For the CQ2-ART sample (Figure 4c), the WHR curve can be divided into four stages by their slope changes, namely S1, S2, S3 and S4. S1, characterized by a large negative slope value, is determined by the deformation of the soft-phase ferrite [26,27]. S2, which exhibited a small negative slope value, is determined by the coordinated deformation of ferrite-dominated and partially relatively low-stability austenite [28,29], because there is a reduction by ~29–34% in the amount of austenite at this stage (Figure 4a). S3 is characterized by strong WHR due to the coordinated deformation of austenite-dominated, ferrite and the martensite produced by the TRIP effect [30–32], because there is a reduction by ~34–100% in the austenite content at this stage (see Figures 3d and 4a). Estimating the tensile flow stress of experimental steels using Equation (7) [33]:

$$\sigma = f_{\alpha}\sigma_{\alpha} + f_{\gamma}\sigma_{\gamma} + f_m\sigma_m \quad (8)$$

where σ_{α} , σ_{γ} , σ_m are flow stresses of ferrite, austenite and martensite, respectively. f_{α} , f_{γ} , f_m are ferrite, austenite and martensite content, respectively. Then, Equation (7) and ε are differentiated to obtain Equation (8). Finally, considering that the austenite with different stability will have a discontinuous TRIP effect with increasing stress [12], Equation (8) is written as Equation (9) [25]:

$$\frac{d\sigma}{d\varepsilon} = f_{\alpha} \frac{d\sigma_{\alpha}}{d\varepsilon} + f_{\gamma} \frac{d\sigma_{\gamma}}{d\varepsilon} + f_m \frac{d\sigma_m}{d\varepsilon} \quad (9)$$

$$\frac{d\sigma}{d\varepsilon} = f_{\alpha} \frac{d\sigma_{\alpha}}{d\varepsilon} + (f_{\gamma} - f_{atm}) \frac{d\sigma_{\gamma}}{d\varepsilon} + f_{mta} \frac{d\sigma_{atm}}{d\varepsilon} \quad (10)$$

where f_{atm} is the phase transformation induced martensite content, σ_{atm} is the flow stress of the phase transformation induced martensite. As we mentioned above, in the S1 st, the deformation mainly occurs in ferrite. As shown in Figure 6b–d, the soft-phase ferrite has a low σ_{α} , which is not enough to offset the increasing true stress, resulting in a rapid decrease in WHR. In the S2, the WHR decreased slowly, and austenite content in the CQ2-ART sample decreased, indicating that the small portion of austenite produces a TRIP effect (Figure 6a). Since σ_{atm} is higher than σ_{γ} [34], the WHR decline in the S2 phase of all samples becomes slowly mainly due to the small part of the low-stability austenite producing a TRIP effect, and the strain-induced martensite transformation (SIMT) has a certain strengthening effect to offset part of the true stress (in combination with Equation (9)) [7,10]; In the S3, the WHR fluctuated and increased slowly stage, which is mainly produced by ferrite and austenite-dominated deformation. Similarly, due to a large number of austenite with different stability continuously produces TRIP effect, the strong SIMT strengthening effect causes a sudden increase in WHR. With the continuous increasing of strain, the SIMT strengthening effect counteracts the stress concentration, resulting in a decrease in WHR, which eventually leads to the fluctuation of WHR in the S3. Until S4, the WHR decreased with serrated behavior.

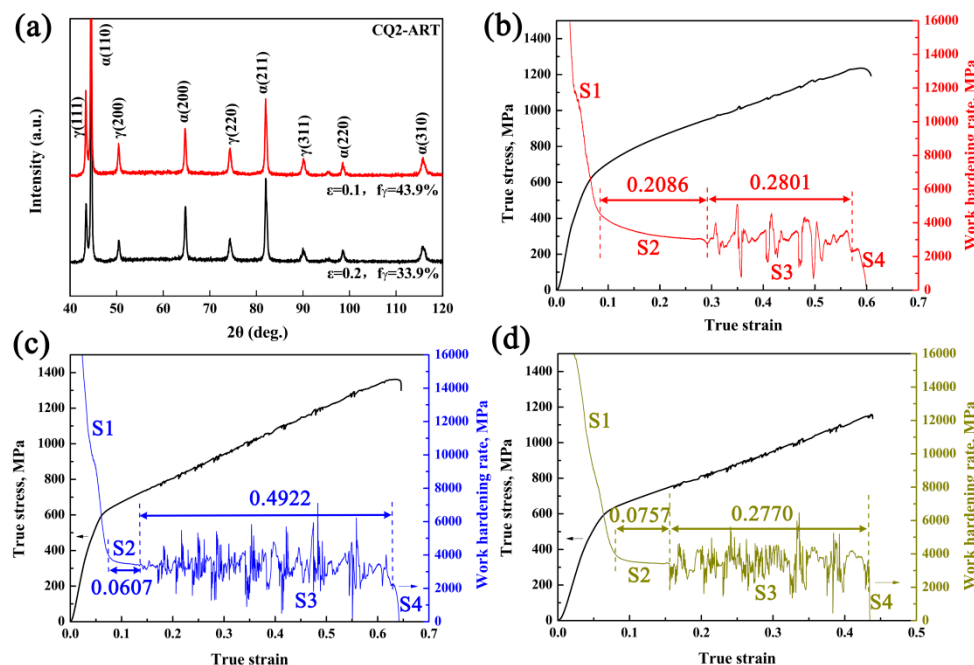


Figure 6. (a) XRD pattern of CQ2-ART sample at different engineering strains, work hardening rate and true stress–strain curves of the cyclic quenching samples: (b) CQ1-ART, (c) CQ2-ART, (d) CQ1-ART.

The length of austenite deformation strain (S2 and S3) of CQ1-ART, CQ2-ART and CQ3-ART samples were ~47.4%, ~55.3% and ~35.3%, respectively. Combining the result presented in Figure 4c and Equation (9), only a small part of austenite content undergoes SIMT to produce a TRIP effect, which means that $f_{atm} \times \sigma_{atm}$ is too small at the corresponding true stress ε . It is worth noting that the CQ3-ART sample has a higher austenite volume fraction (~64.8 vol.%), of which only 58% produces an SIMT, indicating that some of the austenite is too stable to produce a TRIP effect. Generally, the stability of austenite can be calculated by the following formula [35]:

$$k\varepsilon = -\ln\left(\frac{f_{\gamma}}{f_{\gamma 0}}\right) \quad (11)$$

where f_{γ} , $f_{\gamma 0}$, and k are retained austenite content at strain ε , initial austenite content, and austenite stability, respectively. The higher k value corresponds to the lower the driving force required for the

occurrence of SIMT, and thus the lower austenite stability. As shown Figure 7, it is obvious that the austenite in CQ3-ART sample with higher stability ($k = 0.87$) produced SIMT transition under large strain, and a large amount of austenite will be retained after the tensile test. In contrast, the austenite in CQ1-ART ($k = 2.13$) and CQ2-ART ($k = 2.40$) samples have relatively low stability and are prone to produce SIMT at lower strains (consistent with Figure 4c). These results reveal that the austenite strain is mainly dependent on the appropriate stability of austenite rather than its volume fraction. In addition, the phase proportion of CQ1-ART, CQ2-ART and CQ3-ART samples (austenite to ferrite) were about in proportion of 5 to 5, 6 to 4 and 6.5 to 3.5, respectively (Figure 4a,b). With the increase of the numbers of cyclic quenching, the austenite grain size is significantly reduced while promoting the Mn partition, which improved the stability of the RA significantly. Thus, the CQ2-ART sample has the optimum grain size, phase proportion and RA stability. RA with high fraction and appropriate stability provided a strong guarantee for the TRIP effect in the deformation process.

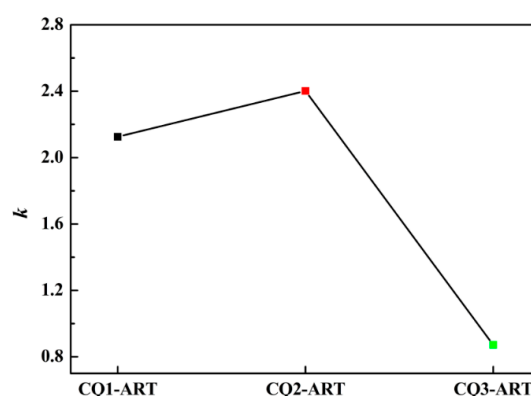


Figure 7. k -parameters for different samples.

3.5. Strengthening Effect of Microalloying Elements Nb and Mo

It has been reported [36,37] that the addition of Nb has significant effects on grain refinement, phase transformation behavior, carbon enrichment in austenite and ferrite nucleation. Figure 8 shows TEM micrographs of Nb/Mo precipitates. Figure 8a–c, d–f and g–i correspond to CQ1-ART, CQ2-ART and CQ3-ART samples, respectively, it can be clearly seen that most Nb precipitates in the form of NbC compounds, while a small portion of Nb exists in the form of solid solution [36]. Interestingly, the grain size of Nb precipitates at ferrite, dislocation line and γ/α grain boundary increase sequentially. In addition, there are a large number of Nb precipitates with a size of about 10–20 nm in the ferrite grains of the three samples (see Figure 8a,d,g). These Nb precipitates hinder the dislocation movement and play a role of precipitation strengthening [36]. At the same time, Nb precipitates with a size of 30–45 nm at the γ/α grain boundary, and solute Nb is liable to segregate seriously at the γ/α grain boundaries (see Figure 8b,e,h). Thus, the dragging effect of Nb precipitates obstruction the growth and recrystallization of austenite and reduces the growth rate of ferrite [37]. The Nb precipitates with a size of 15–35 nm on the dislocation line are shown in Figure 8c,f,i). Dislocations are pinned by precipitates, and their movement is hindered during deformation. Therefore, more external stresses need to be added to overcome the strengthening effect of precipitates on dislocation pinning and ultimately make dislocations by pass or cut through precipitates, thereby increasing the strength of the matrix. The critical driving force (ΔG_v) of ferrite nucleation can be expressed by chemical driving force (ΔG_{ch}) and strain-induced driving force (ΔG_{st}) [36]:

$$\Delta G_v = \Delta G_{ch} + \Delta G_{st} \quad (12)$$

As we mentioned above, ΔG_{st} can be consumed by the precipitation of NbC during deformation; thus, ΔG_v is reduced, resulting in a delay in the transformation of austenite to ferrite. The precipitates

of Nb and (Nb, Mo) are given in Figure 8j. It was found that Mo in Nb–Mo microalloyed medium Mn steel mainly exists in the form of solid solution, and a small amount of Mo exists in the form of composite with NbC. Cao et al. [38] considered that the addition of Mo affected the activity of C element, thus inhibiting the precipitation of NbC in austenite, resulting in the precipitation of large amounts of NbC in ferrite. Zhang et al. [39] suggested that when microalloyed carbides precipitated of ferrite in Nb–Mo alloy steel, Mo would enter into NbC lattice to replace part of Nb atoms to form (Nb, Mo) C, resulting in the decrease of interfacial energy between (Nb, Mo) C and ferrite matrix, thereby reducing the energy barrier of (Nb, Mo) C nucleation. Therefore, the addition of Mo would promote the precipitation of Nb. In addition, Mo could significantly inhibit the coarsening of NbC [40]. In summary, the Nb/Mo elements not only precipitate (Nb, Mo) C in the grain particles hinder the movement of dislocations, thereby increasing the strength, but also segregating at the austenite/ferrite grain boundaries, delaying the transformation of austenite to ferrite.

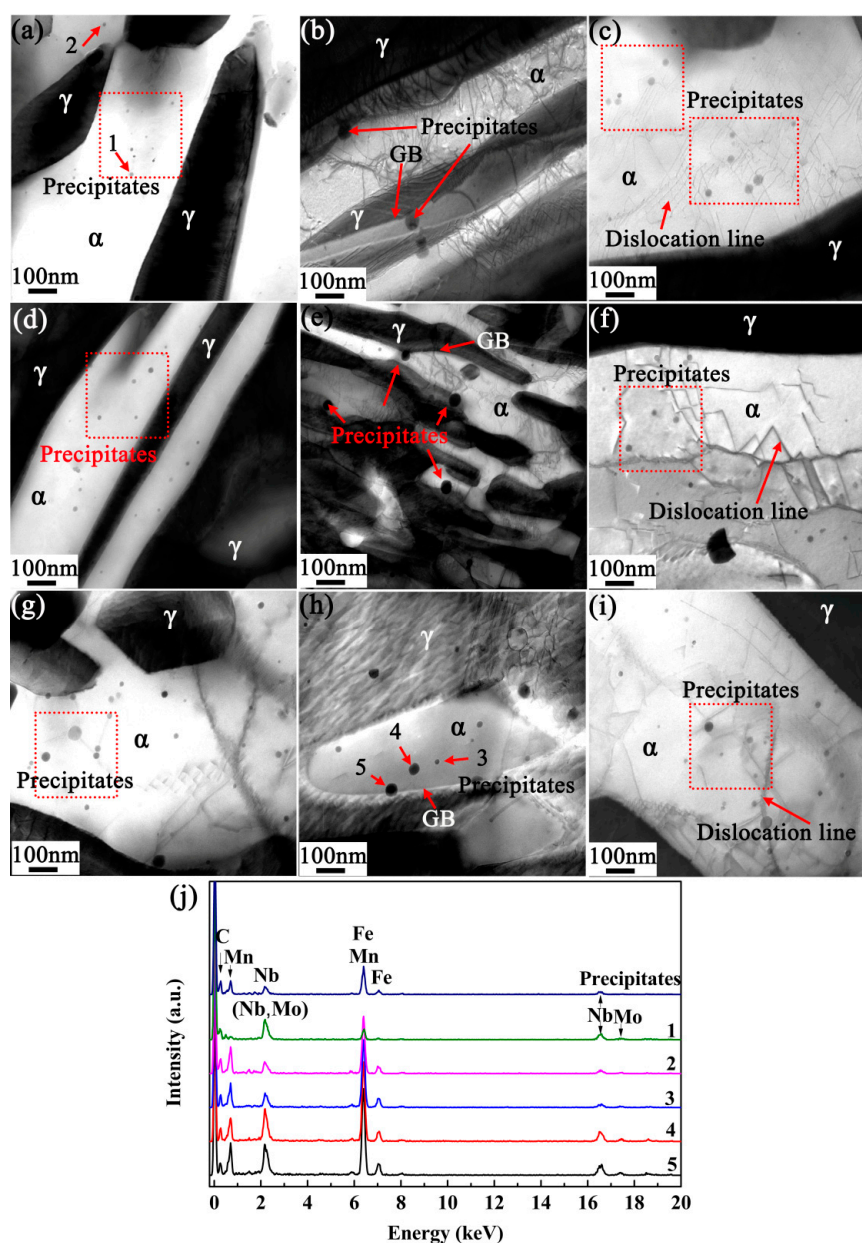


Figure 8. TEM image of precipitates in experimental steels: (a–c) CQ1-ART sample, (d–f) CQ2-ART CQ1-ART sample, (g–i) CQ3-ART CQ1-ART sample and (j) precipitate TEM-EDS results (GB: grain boundary).

4. Conclusions

A novel heat treatment process called CQ-ART was studied in Fe-0.25C-3.98Mn-1.22Al-0.20Si-0.19Mo-0.03Nb medium manganese TRIP steel. The main findings are as follows: (a) the CQ2-ART sample exhibited optimum combination of properties, i.e., the tensile strength of 838 MPa, the total elongation of 90.8%, and the product of strength and elongation of 76.1 GPa%; (b) cyclic quenching is equivalent to providing a longer holding time to promote the enrichment of Mn in the original austenite, while lowering the M_s temperature to form a finer martensite matrix. In the subsequent intercritical annealing process, the distribution of Mn between austenite and ferrite occurs on fine martensite matrix with high initial Mn concentration, resulting in finer and manganese-rich reversed austenite; (c) the CQ2-ART sample has the optimum grain size, the ratio of the γ/α phase and the appropriate RA stability. RA with high fraction and appropriate stability provides a strong guarantee for the TRIP effect during deformation; (d) (Nb, Mo) precipitates pin dislocations, which hinder the movement of dislocations and play a role of precipitation strengthening. At the same time, precipitation at the γ/α grain boundary delays the transformation of austenite to ferrite and plays a role of fine grain strengthening.

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