Microstructure and Mechanical Properties of a Hot-rolled High Manganese TWIP Steel Containing 0.3%V

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In this paper, the microstructure, precipitates and mechanical properties of a 0.3%V-alloying high Mn austenitic TWIP steel after hot rolling and aging treatment were investigated, aimed to improve the yield strength of high Mn austenitic steel. Experimental results showed that an elongated and unrecrystallized grain structure could be obtained at a finish rolling temperature of 850°C or below in 0.3V steel. The amount of VC precipitates was very small and most vanadium remained in solution after hot rolling. Therefore, the solute drag effect of dissolved vanadium rather than the Zener pinning effect of VC precipitates was mainly responsible for the inhibition of recrystallization. The yield strength increase of 0.3V steel with decreasing finish rolling temperature was much more remarkable than that of V-free steel. Quantifying possible strengthening mechanisms revealed that most of the YS increase was due to the dislocation strengthening in 0.3V steel. The aging treatment for 30 min promoted the precipitation of VC, but the precipitation amount was still much less than the equilibrium precipitation amount. The comparative analysis on precipitation kinetics of VC in high Mn and low Mn steels indicated that the former had a more sluggish precipitation rate than the latter. This result was further analyzed in terms of the effect of Mn on the solubility product of VC in austenite.

KEY WORDS: TWIP steel; vanadium microalloying; precipitation; recrystallization; aging treatment.

1. Introduction

Urbanization has led to a rapid increase in the demand for liquefied natural gas (LNG), which is termed green energy. Traditionally, Ni-based invar alloys, 9% Ni alloys, aluminum alloys and austenitic stainless steels are used in the storage and transportation of LNG. However, these materials have disadvantages, such as costly plates or welding consumables. Therefore, much attention has focused on replacing expensive Ni-based alloys with inexpensive high-manganese (Mn) TWIP steels.^{1–4)} Hot rolled high-Mn TWIP steels are generally used in storage and transportation of LNG for their sufficient ductility and toughness.^{5,6)} But the development of hot rolled high-Mn TWIP steels is limited by their relatively low yield strength, even with a high Mn or chromium (Cr) content.^{7–9)}

It is well known that the addition of microalloying elements such as Nb, V and Ti can improve the strength of steels by means of both grain refinement and precipitation hardening. In particular, vanadium microalloying is believed to be more suitable for high Mn TWIP steels with medium or high carbon contents, as compared to niobium and titanium microalloying.¹⁰⁾ This is because VC has a relatively larger solubility in austenite and this makes it possible for VC precipitates to be readily controlled by adjusting

the reheating and annealing temperatures.¹⁰⁾ To date, the research works on V-microalloying of high Mn TWIP steel have mainly focused on cold rolled and recrystallization annealed sheets,^{10–14)} and there are only a few studies on hot-rolled V-microalloying TWIP steels,¹⁵⁾ presumably due to the fact that TWIP steels were initially developed for lightweight and safety enhancement of automobiles. Gwon *et al.*¹⁵⁾ investigated the effect of V contents on the microstructures and tensile properties of hot rolled TWIP steels, with a finish rolling temperature of 900°C and an additional annealing treatment at 1 000°C. They found that the yield strength could be increased by about 170 MPa by adding 0.3%V due to both grain refinement and precipitation hardening of VC. However, it is not clear how hot rolling and aging process affect the microstructures and properties of the V-microalloying TWIP steel.

Moreover, it was reported that the solubility of microalloying carbonitrides in austenite was influenced by the Mn contents, and therefore the precipitation kinetics could be altered by the addition of Mn.^{16–21)} However, the Mn contents in these studies were relatively low, which were no more than 5 mass%.^{16–21)} Therefore, the studies on precipitation kinetics of VC in high Mn TWIP steel needs to be carried out.

In this paper, a high Mn TWIP steels containing 0.3%V was firstly hot rolled with various finish rolling temperatures and subsequently aged at different temperatures, then the microstructures and mechanical properties were investi-

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gated; in the meanwhile, the strengthening mechanisms of studied steels were analyzed. Finally, theoretical analysis on precipitation kinetics of VC was conducted to explain the difference of precipitation kinetics of VC observed in high Mn and low Mn steels.

2. Experimental Procedure

The chemical compositions of the studied steels are presented in **Table 1**. The V-free steel is used as a reference steel to study the role of V. Both steels are Twinning Induced Plasticity (TWIP) steels.²²⁾ The two experimental steels were melted in a 100 kg induction melting furnace within Ar atmosphere, and the steel ingots were hot forged into 120×110×60 mm³ blocks. After soaking at 1 200°C for 1 h to fully dissolve the vanadium carbides, the billets were hot rolled to a plate with thickness of 12 mm by six passes in a pilot two high hot rolling mill with a total reduction ratio of 80%, followed by water cooling to room temperature to suppress the precipitation of carbide. The finish-rolling temperatures were 800, 850 and 900°C, respectively. In order to further promote VC precipitation, aging treatments were performed on the finish-rolled plate at 850°C in temperature range from 650 to 800°C for 30 min.

The metallographic observation was performed by using FEI Quanta 650FEG field emission scanning electron microscope (SEM) and H-800 transmission electron microscope (TEM). The EBSD data were processed by EDAX OIM software. The annealing twin boundaries of austenite, Σ3 grain boundaries were determined according to the Brandon criterion,²³⁾

$$\Delta\theta \leq 15^\circ \Sigma^{-\frac{1}{2}} \dots\dots\dots (1)$$

where $\Delta\theta$ is the critical deviation angle from an exact Σ3 boundary.

Thin foils for TEM observation were prepared using a twin-jet polisher in a mixed solution of 90% glacial acetic acid and 6% perchloric acid at −20°C. Carbon extraction replicas were prepared for precipitate analysis including precipitate types and size. The specimens were polished, and then etched in 4% nital for 2 min. A carbon coating about 20 nm in thickness was deposited on surface using an evaporator operated at a high vacuum. The carbon film coated surfaces of specimens were scribed using a blade to produce squares about 2×2 mm² in size. The replicas were released in 4% nital etched solution, and then analyzed in a transmission electron microscopy (TEM-Tecnaï G²F20). The particle size was measured by a quantitative image analyzer. In addition, the composition analysis for precipitates was conducted using nano-beam EDS analysis.

The amount of VC precipitates after hot rolling and subsequent aging treatment was also measured by the physical-chemical phase analysis, and the detailed procedures are as

follows. 80×25×10 mm³ samples cut from the rolled plates were firstly electrolyzed at −10°C with current density of 0.04–0.06 A/cm² in a water solution of 10 g/L tetramethyl ammonium chloride and 10 vol% acetylacetone methanol. After the electrolysis, most of the precipitate powder closely adhered to the surface of samples and a small amount of precipitates could fall off into the electrolyte solution. The former was collected by brushing the surface of samples, and the latter was collected by microporous membrane filter with pore size of 0.2 μm from the electrolyte. Both of them were then dissolved in a mixed solution of concentrated sulfuric acid and nitric acid. Subsequently, the concentration of V in the solution was measured by the spectrophotometry in an inductively coupled plasma atomic emission spectrometer (ICP–AES). The elemental mass fraction of the VC precipitates can be calculated:

$$w_V = \frac{C_V \times V}{m \times 10^6} \dots\dots\dots (2)$$

where w_V is the V mass fraction of the VC precipitates in the specimen electrolyzed, C_V (μg/mL) is the concentration of V in the solution where the VC precipitates are dissolved, V (mL) is the volume of the solution, and m (g) is the mass of the specimen electrolyzed. The mass fraction of C was calculated according to the measured V mass fraction assuming that the atomic ratio of V/C is 1.

The tensile tests were performed by using a WE-300 tensile test machine. The tensile specimens with Φ8 mm and 40 mm gauge length were machined from rolled plates after rolling. The testing speed was 2 mm/min and the testing temperature was 25°C. The impact tests were performed by using a JBN-300N on standard Charpy V-notch specimens (size: 10×10×55 mm³) under −196°C. In addition, Vickers hardness measurements were performed on both hot rolled and aged samples under a load of 5 kg.

3. Results and Discussion

3.1. Microstructure and Precipitates of the Hot-rolled Steel

Figure 1 shows the EBSD images of the austenite grains and the annealing twins of the experimental steels with various rolling temperature from 800 to 900°C. The austenite grains of the experimental steel after finish rolling at 900°C are equiaxed, and the austenite grains are flattened as the finishing temperature is lowered to 850 and 800°C. The extent of austenite grain flattening seems to be greater as the finish rolling temperature decreases.

Σ3 grain boundaries are the annealing twin boundaries in the austenitic steel. It can be seen from Fig. 1 that there are Σ3 grain boundaries in the experimental steels with various rolling temperatures. **Figure 2** shows the ratio of Σ3 grain boundaries of the 0.3V steel with different finish rolling temperatures. As the finish rolling temperature decreases, the Σ3 grain boundary ratio decreases. It is generally believed that annealing twins are formed by austenite grain boundary migration during recrystallization, rather than the result of intragranular slip activity.²⁴⁾ As the finishing temperature decreases, the recrystallization of the experimental steel is retarded, and the grain boundary migration of the austenite structure is hindered, so the proportion of the

Table 1. Chemical compositions of studied steels (mass%).

Steel grade	C	Si	Mn	S	P	V	Al
V-free	0.46	0.15	22.3	0.0019	0.0051	–	0.028
0.3V	0.44	0.17	24.4	0.0054	0.0057	0.3	0.0016

Fig. 1. EBSD images of the austenite grains of the 0.3V steels with various finish rolling temperatures. (a) 800°C; (b) 850°C; (c) 900°C. Black lines represent grain boundaries with a misorientation more than 15°, and red lines represent annealing twin boundaries.

Fig. 2. Ratio of Σ3 grain boundaries of the 0.3V steel at different finish rolling temperatures. (Online version in color.)

Fig. 3. EBSD image of the V-free steel with finish rolling temperature of 740°C. Black lines represent grain boundaries with a misorientation more than 15°, red lines represent annealing twin boundaries.

Σ3 grain boundary is continuously reduced. Pu's research showed that the decrease of the ratio of Σ3 grain boundary was also related to the deformation of austenite grains.²⁵⁾ He believed that the orientation of the annealed twins under the rolling deformation in the low-temperature non-recrystallization zone deviated from its specific orientation, causing twin boundaries to transform into random grain boundaries. In addition, a hot rolling experiment was performed on the V-free steel at a relatively low finish rolling temperature of 740°C and its microstructure after rolling was examined, as shown in **Fig. 3**. It is apparent that the austenite grains are equiaxed, indicating that the recrystallization process was completed during rolling. The ratio of Σ3 grain boundaries is measured to be 60%, which is much higher than that of the 0.3V steel. These results reveal that the addition of V inhibits recrystallization indeed and significantly increases the upper limit temperature of the non-recrystallization of the high Mn TWIP steel.

The results of physical-chemical phase analysis on VC phase are given in **Table 2**. The equilibrium fractions of VC at different temperatures were calculated by ThermoCalc software with the TCFE 9 database and also given in this table for comparison. It can be seen that the amount of VC precipitates increases as the finish rolling temperature decreases, but it is much less than the equilibrium amount. This means that the precipitation process is so sluggish that

most V remains in solution in austenite after rolling.

Figure 4 shows the TEM images of VC precipitates after finish rolling at 800°C, 850°C and 900°C for the 0.3V steel, respectively. The mean VC diameter was measured to be around 8.5 nm at different temperatures. **Figure 5** shows the high resolution TEM image of a VC particle in the 0.3V steel after finish rolling at 800°C. The crystal structure of the VC precipitates is of NaCl type, and the interplanar spacing on the (111) plane was measured to be 0.24 nm.

In hot-rolled steel, austenite recrystallization may be suppressed both by the solute drag effect and by the Zener pinning effect of precipitation.^{20,26)} Humphreys and Hatherly discussed the effect of particles on recrystallization nucleation in terms of particle limited subgrain size and concluded that the nucleation at deformation heterogeneities such as deformation bands or shear bands would be suppressed if $F_v/r > 0.15 \mu\text{m}^{-1}$ for alloys containing low volume fractions of particles;²⁶⁾ otherwise, the nucleation event would take place. Here, F_v is the volume fraction of particles and r is the mean radius of particles. The values of F_v/r for the studied 24Mn-0.3V steel are calculated, as given in Table 2. All these values are much smaller than the critical value ($0.15 \mu\text{m}^{-1}$) for suppression of nucleation, and therefore, the Zener pinning effect of particles is not great

Table 2. Precipitated amount and calculated values of F_V/r , P_D , P_Z and the precipitation strengthening of the hot-rolled 0.3V steel.

Samples		V precipitated (mass%)	C precipitated (mass%)	Volume fraction of VC	F_V/r (μm^{-1})	P_Z (MPa)	P_D (MPa)	Precipitation strengthening (MPa)
V900	Measured	0.0015	0.0010	3.42×10^{-5}	0.004	0.005	0.12	17
	Equilibrium at 900°C	0.094	0.020	1.56×10^{-3}				
V850	Measured	0.0075	0.0015	1.23×10^{-4}	0.014	0.017	0.15	32
	Equilibrium at 850°C	0.175	0.038	2.91×10^{-3}				
V800	Measured	0.012	0.0028	2.05×10^{-4}	0.024	0.029	0.22	41
	Equilibrium at 800°C	0.229	0.050	3.81×10^{-3}				

Note: V900, V850 and V800 denote the as-hot-rolled samples of the 0.3%V steel obtained by finish rolling at 900, 850 and 800°C, respectively.

Fig. 4. TEM images of VC precipitates with various finish rolling temperatures in the 0.3V steel. (a) 800°C, (b) 850°C, (c) 900°C, (d) EDS analysis. (Online version in color.)

Fig. 5. High resolution TEM images of VC precipitates after 800°C finish rolling in the 0.3V steel. (a) TEM image, (b) Inverse Fourier transformation analysis.

enough to inhibit the nucleation of recrystallization for the studied steel.

During primary recrystallization, a growing grain in an alloy containing a dispersion of particles is acted on by two opposing pressures, the driving pressure for growth (P_D) and the Zener pinning pressure arising from the particles (P_Z). Therefore, the net driving force for recrystallization, P , can be expressed by:^{20,26)}

$$P = P_D - P_Z = \frac{1}{2} \rho G b^2 - \frac{3\gamma F_v}{2r} \dots\dots\dots (3)$$

where ρ is the dislocation density, G is the shear modulus, b is the Burgers vector and γ is the grain boundary energy of austenite. According to this equation, recrystallizing grains will not grow unless P is positive. The values of Zener pinning pressure, $P_Z = \frac{3\gamma F_v}{2r}$ at different temperatures were calculated according to the measured F_v and r values, taking γ as 0.8 J/m^2 ,²⁶⁾ and the calculated P_Z values were found to be in the range of 0.005–0.029 MPa, as given in Table 2. The values of driving pressure, $P_D = \frac{1}{2} \rho G b^2$ can be determined through the dislocation density that can be estimated from the Taylor relation:^{27,28)}

$$\sigma = \sigma_0 + \alpha M G b \sqrt{\rho} \dots\dots\dots (4)$$

Therefore, the driving pressure P_D is obtained as

$$P_D = \frac{1}{2} \rho G b^2 = \frac{1}{2} \cdot \frac{(\sigma - \sigma_0)^2}{\alpha^2 M^2 G} \dots\dots\dots (5)$$

where σ is the flow stress at high temperatures, σ_0 is the yield stress at high temperatures, M is the Taylor factor (3.06 for FCC metals²⁹⁾), α is a constant (0.35³⁰⁾) and b is the Burgers vector (0.255 nm). The shear modulus G was determined using the calculation procedure proposed by Kang *et al.*³¹⁾ to be 55 980, 53 960 and 51 940 MPa at 800, 850 and 900°C, respectively. The values of flow stress and yield stress of the studied 0.3V steel used in the P_D calculation were taken from the reference,³²⁾ in which the deformation behaviors of high Mn austenitic steels containing V at different temperatures were investigated. The calculated values of driving pressure are approximately in the range of 0.12–0.22 MPa, as shown in Table 2. Such values are about one order of magnitude higher than the Zener pinning pressure P_Z (see Table 2), indicating that the precipitation of VC cannot suppress the recrystallizing austenite grain growth effectively.

In summary, the Zener pinning effect of VC precipitation

is too small to inhibit both nucleation and grain growth of austenitic recrystallization effectively for the studied steel since the amount of VC precipitation is very small. As a result, the inhibition of austenite recrystallization can be mainly attributed to solute drag effect of solute vanadium. The retardation effect of solute vanadium on austenite recrystallization has been validated in low alloy steels even though its effect is much weaker than of solute Nb and Mo.³³⁾ Vanadium can segregate at recrystallizing grain boundaries and decreases the boundary mobility, thereby reducing the growth rate of recrystallizing grains. However, more studies are required to reveal the solute drag effect of V in high Mn austenitic steel, especially the possible synergistic effect of V and high Mn content.

3.2. Mechanical Properties of the Hot-rolled Steel

Table 3 shows the mechanical properties of the two experimental steels with different finish rolling temperatures. It is seen that the yield strength of the 0.3V steel is significantly improved compared to the V-free steel at 850°C or below without sacrificing much ductility, whereas there is little difference in tensile strength between the two steels. The impact absorbed energy at -196°C is lowered by adding 0.3%V, but the lowest impact energy of 89 J obtained by finish rolling at 800°C still far exceeds the requirement of relevant international standard (a minimum value of 47 J is required in ISO 21635³⁴⁾). It is noted that the addition of 0.3%V deteriorates the impact toughness at cryogenic temperature significantly but has little influence on the tensile ductility at room temperature. As mentioned below, compared to the V-free steel, the 0.3V steel has a higher density of dislocations due to deformation in the non-recrystallization region. It is speculated that the initial high density dislocation could inhibit the deformation twinning to some content, and this inhibitory effect is more significant at lower temperature or rapider deformation rate, thus leading to a large decrease of impact toughness at cryogenic temperature while only a small decrease of tensile ductility at room temperature. However, further works are needed to reveal the effect of initial high dislocation on deformation behaviors of TWIP steels and its mechanisms.

Moreover, with the decrease of finish rolling temperature, both yield strength (YS), tensile strength (TS) of the two studied steel increase, while the total elongation and the impact absorbed energy decrease. The YS increase of 0.3V steel with decreasing temperature is much more remarkable than that of V-free steel. For example, the YS

Table 3. Mechanical properties of the two studied steels after hot rolling.

Steel grades	Finish rolling temperature (°C)	Samples	Tensile strength (MPa)	Yield strength (MPa)	Total elongation (%)	Impact absorbed energy at -196°C (J)
V-free	900	M900	871	286	71	177
	850	M850	969	335	63	165
	800	M800	1 001	385	55	151
0.3V	900	V900	850	300	72	158
	850	V850	990	511	60.5	103
	800	V800	1 007	570	54	89

of the samples M850 and M800 increases only by 49 and 99 MPa respectively compared to the sample M900. In contrast, the YS of the samples V850 and V800 increases significantly by 211 and 270 MPa respectively compared to the sample V900. Such YS increase may be resulted from grain refinement, precipitation strengthening and dislocation strengthening. For the V-free steel, the YS increase should be mainly attributed to grain refinement of austenite caused by recrystallization. For the 0.3V steel, however, the samples V850 and V800 seem to have a larger grain size than the sample V900 due to the lacking of repeated recrystallization refinement, as shown in Fig. 1. Therefore, the YS increase of the samples V850 and V800 cannot be attributed to grain refinement. As for the precipitation strengthening, it can be quantified using the Ashby-Orowan equation³⁵⁾ as follows:

$$\sigma_p = \frac{0.538Gb f_V^{\frac{1}{2}}}{x} \ln\left(\frac{x}{2b}\right) \dots\dots\dots (6)$$

where σ_p is the increment of yield strength (MPa); G is the shear modulus at room temperature which was calculated as 64 230 MPa; b the Burgers vector (0.255 nm); f_V the volume fraction of particles; x the mean diameter of VC precipitate (nm). The calculated values of precipitation strengthening are in the range of 17–41 MPa and listed in Table 2. Compared to the sample V900, the YS increase of the samples V850 and V800 caused by precipitation strengthening are only 15 and 24 MPa, which are much lower than the measured YS increase (211 and 270 MPa for the samples V850 and V800, respectively). As a result, it is inferred that the dislocation strengthening could provide most of the YS increase for the samples V850 and V800.

Figure 6 shows the TEM images of the samples V800 and V850. It is seen that a large amount of dislocation cells or micro-bands with thickness of approximately 1 μm were introduced by rolling deformation in non-recrystallization temperature regime, and the dislocation substructures seem finer at lower finish rolling temperature. The average dislocation density introduced by hot deformation can be roughly estimated by Eq. (4), with the values of flow stress at high temperature also taken from the literature.³²⁾ The calculation results show that the values of dislocation density introduced by finish rolling at 850 and 800°C are $1.20 \times 10^{14} \text{ m}^{-2}$ and $2.0 \times 10^{14} \text{ m}^{-2}$, respectively.

According to the Taylor relation (Eq. (4)), the YS increase due to dislocation strengthening can be expressed by

$$\Delta\sigma_{dis} = \alpha M G b (\sqrt{\rho_L} - \sqrt{\rho_H}) \dots\dots\dots (7)$$

where ρ_L is the dislocation density obtained by finish rolling at 850 or 800°C, and ρ_H is the dislocation density obtained by finish rolling at 900°C. ρ_H is assumed to be $\sim 10^{11} \text{ m}^{-2}$, a typical value for annealed or completely recrystallized metals.²⁶⁾ α , G , M and b have the same meanings and values as in Eqs. (4) and (5). The values of dislocation strengthening increment were thus calculated to be about 192 and 248 MPa for the samples V850 and V800, respectively. The sum of increments due to both dislocation and precipitation strengthening are 207 MPa for V850 and 272 MPa for V800, which are close to the measured YS increases of 211 MPa for V850 and 270 MPa for V800, respectively. It is obvious that the contribution of dislocation strengthening is a dominant factor.

3.3. VC Precipitation during Aging Treatment after Hot Rolling

As mentioned previously, the amount of VC precipitates was much less than the equilibrium amount and most vanadium remained in solution in the austenite after finish rolling at different temperatures. In order to further promote the precipitation of VC and improve the strength of the studied steel, aging treatments at different temperatures were performed on the V850 sample. **Figure 7** shows the Vickers hardness of the as-rolled sample and the samples subsequently subjected to aging treatment at different temperatures for 30 min. It is seen that the hardness increases with the increase of aging temperature until it reaches the

Fig. 7. Vickers hardness and estimated yield strength of the 0.3V steel after aging heat treatment. (Online version in color.)

Fig. 6. TEM images of the samples V800 (a) and V850 (b).

maximum value at 750°C, above which the hardness begins to decrease. The corresponding yield strength of the samples was estimated according to the yield strength-hardness relationship, $YS \text{ (MPa)} = 2.318HV - 107.4$, which was obtained by linear regression on the measured yield strength and hardness of the as-rolled samples with different rolling temperatures. As shown in Fig. 7, the maximum YS increment of about 90 MPa can be achieved by the aging treatment at 750°C for 30 min.

Figure 8 shows the TEM images of VC precipitates of V850 sample subjected to aging at 650–800°C for 30 min. Numerous dispersed nano-sized VC particles with near-spherical shape were observed in the matrix of steel, thereby leading to the increase of hardness after aging treatment. The mean diameters of VC particles were measured to be 6.26 ± 1.60 nm, 6.28 ± 1.62 nm, 6.13 ± 1.58 nm and 6.26 ± 1.61 nm for the samples aging-treated at 650, 700, 750 and 800°C, respectively, which were almost the same. According to the Ashby-Orowan equation (Eq. (4)), the precipitation hardening is proportional to the volume fraction of particles, given the fact that the particle sizes remain unchanged. It is therefore inferred that the change trend of hardness in Fig. 7 can also reflect the change trend of amount of VC precipitates particles with aging temperature. Since the maximum precipitation hardening was obtained by

aging at 750°C, the precipitation amount is also the largest at this temperature.

The results of physical-chemical phase analysis on the V850 sample and the sample subsequently subjected to aging treatment at 750°C for 30 min are given in **Table 4**, and the equilibrium precipitation amount at 750°C calculated by Thermo-Calc software with the TCFE 9 database is also listed in this table for comparison. The fraction of VC precipitation increases significantly from 1.23×10^{-4} for the as-rolled sample (V850) to 1.86×10^{-3} for the aging-treated sample (V850A). The precipitation hardening of VC was calculated according to Eq. (4) and the results are also listed

Table 4. Precipitation amount and precipitation hardening of the hot rolled sample (V850) and the sample subsequently subjected to aging at 750°C.

Samples	V precipitated (mass%)	C precipitated (mass%)	Volume fraction of VC	Precipitation hardening (MPa)
V850	0.0075	0.0015	1.23×10^{-4}	32
V850A	0.110	0.026	1.86×10^{-3}	125
Equilibrium amount at 750°C	0.262	0.085	4.74×10^{-3}	/

Fig. 8. TEM images of VC precipitates of the 0.3V steel aged at different temperatures after finish rolling at 850°C. (a) 650°C, (b) 700°C, (c) 750°C, (d) 800°C, (e) EDS analysis.

in Table 4. The YS increase due to aging at 750°C is thus obtained as 125–32=93 MPa, which is basically the same as the estimated YS increase shown in Fig. 7.

As shown in Table 4, although the aging treatment can promote the precipitation, the fraction of VC precipitation after aging treatment at 750°C for 30 min is still much less than the equilibrium fraction, and only less than half of the equilibrium amount of VC was precipitated. It seems that the precipitation of VC in high Mn austenitic steel is slower than that in low alloy steels with the typical Mn contents of 0.5–1.5 mass%. For instance, Medina *et al.*^{36,37)} reported the precipitation kinetics of VC in a wide range of chemical compositions with (0.11–0.37)C–(1.1–1.42)Mn–(0.043–0.12)V–(0.01–0.019)N (in mass%), and found that the precipitation of VC from deformed austenite could be finished in 200 s or below at the fastest precipitation temperatures. For the studied high Mn austenitic steel, however, the precipitation of VC is far from finished even after isothermal holding for 30 min (1 800 s) at the fastest precipitation temperature of 750°C.

In fact, the retardation of precipitation kinetics by more Mn addition can be attributed to the effect of Mn on the activities of the precipitating species, as a result of which VC solubility is affected. We derived the solubility products of VC in austenite for both 24Mn steel and 1Mn steel by regression on the solubility data calculated by Thermo-Calc, as shown in Fig. 9. It is clear that 24Mn steel has a larger solubility product of VC than 1Mn steel since Mn decreases the activity of both V and C elements.²²⁾ A larger solubility product of VC in high Mn steel can result in a lower supersaturation degree of VC precipitation, which further leads to a smaller thermodynamic driving force for VC precipitation and a slower precipitation rate in comparison to low Mn steel. According to Yong's theory,^{38,39)} the relative precipitation-temperature-time (PTT) diagram for VC precipitation can be calculated by the following equation:

$$\log \frac{t_{0.05da}}{t_{0da}} = -1.28994 - 2 \lg d_d^* + \frac{1}{\ln 10} \times \frac{(1+\beta)^{3/2} \Delta G^* + \frac{5}{3} Q}{kT} \quad (8)$$

where $t_{0.05da}$ that corresponds to the fraction precipitated 5% is defined as the start time of precipitation, t_{0da} is an almost temperature independent parameter, d_d^* is the critical diameter of nucleus, ΔG^* is the critical nucleation energy, Q is the activation energy for V atom in bulk, β is a parameter introduced in the model, k is the Boltzmann constant and T is the absolute temperature. The detailed description for this model and the parameters used for calculation can be referred to the literature.²²⁾ By Eq. (8) and the solubility product equation shown in Fig. 9, the relative PTT diagram of both 24Mn-0.3V and 1Mn-0.3V steels for VC precipitation was obtained, as shown in Fig. 10. It can be seen that both PTT curves have a “C” shape; the PTT curve is shifted to longer times and lower temperatures as Mn content is increased from 1% to 24%, indicating that the addition of a high Mn content retards the precipitation of VC. This result is in a qualitative agreement with the above mentioned comparative analysis with respect to high Mn and low Mn steels. The fastest precipitation temperature, *i.e.* nose temperature of PTT curve of the 0.3V steel is 748°C, which is in very

Fig. 9. Solid solubility products of VC in the steels with Mn contents of 24% and 1%, respectively. [V] and [C] represent mass percent (mass%) of dissolved V and C in austenite, respectively. (Online version in color.)

Fig. 10. Calculated PTT curves of 24Mn-0.3V and 1Mn-0.3V steels. (Online version in color.)

good agreement with the experimental result (750°C).

4. Conclusion

(1) The addition of 0.3%V could inhibit the austenite recrystallization effectively at a finish rolling temperature of 850°C or below, leading to the flattened grains along the rolling direction. There was a very small amount of VC precipitated and most vanadium remained in solution in austenite after hot rolling. Therefore, the solute drag effect of dissolved vanadium rather than the Zener pinning effect of VC precipitates was mainly responsible for the inhibition of recrystallization.

(2) The yield strength of 0.3V steel was significantly improved compared to the V-free steel at the finish rolling temperature of 850°C or below without sacrificing much ductility. The yield strength increase of 0.3V steel with decreasing finish rolling temperature was much more remarkable than that of V-free steel. Strengthening mechanisms analysis revealed that most of the YS increase was resulted from the dislocation strengthening.

(3) The aging treatment after hot rolling could promote

the precipitation of VC to some extent, thereby leading to an increase in hardness of samples. But the precipitation amount was much less than the equilibrium precipitation amount even after aging treatment for 30 min. The comparative analysis on precipitation kinetics of VC in high Mn and low Mn steels indicated that the former had a more sluggish precipitation rate than the latter. Further theoretical analysis showed that, compared to low Mn steel, the addition of high Mn raised the solubility of VC in austenite and then lowered the thermodynamic driving force for VC precipitation, which retarded the precipitation of VC significantly.

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