Effect of Vanadium on the Microstructure and Properties of Fire-resistant Weathering Steels

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Abstract: Methods such as dilatometer, optical microscope, electrolytically extraction and TEM were used to investigate the effects of vanadium addition on the CCT diagrams, the microstructural evolution and tensile properties at both room temperature and 600°C in three series of hot-rolled high-strength, low-alloy weathering steels containing both V and Mo (the first with 0.60%Mo, the second with 0.3%Mo+0.0020%B and the last with 0.30% Mo content). The results of this study have brought the following conclusions: ① The addition of 0.10%V has a limited effect on the CCT curves of 0.60%Mo weathering steels and 0.30%Mo-B weathering steels whereas the addition of 0.20%V promoted the formation of polygonal ferrite in the 0.60%Mo weathering steel. ② The control of the bainite fraction in the microstructure is essential for weathering fire resistant steels in order to obtain good high-temperature yield strength and high YS ratio even for steels containing 0.60%Mo. ③ Precipitates of vanadium were found in all vanadium-containing experimental steels and they seemed to become finer and denser as the vanadium content increased or accelerated cooling after hot-rolling was used. ④ If a suitable fraction of bainite was introduced in the microstructure, the Mo content could be reduced to about 0.30%Mo while the high-temperature yield strength and YS ratio were still kept at high level. ⑤ The addition of vanadium, especially combined addition of vanadium and nitrogen, would result in additional strengthening at both room temperature and 600°C, at least for the plates that were subject to accelerated cooling after hot-rolling. The effect of vanadium might be attributed to the precipitation of vanadium.

1 Introduction

Traditionally, the fire-resistance of steel-frame building structures such as columns and beams is achieved by applying fire protection coatings that prevent the steel temperature from exceeding 350°C in the fire-resistance test because the yield strength of conventional steels drops to two-thirds or less of the specified room-temperature yield strength and falls below the structurally necessary yield strength at elevated temperature of 350°C or above. However, if a new steel with better strength performance at elevated temperatures are used, the fire-resistant coating work will be sharply reduced to lower the construction cost, to shorten the construction period and to effectively utilize the interior space.

In respond to above needs, a significant amount of research has been carried out in Japan, Korea and other countries, and several fire-resistant steels with different strength levels have been developed[1~3]. These steels represent a notable improvement over conventional steels in terms of elevated temperature yield strength. The yield strength of the fire resistant steels at 600°C was set at the minimum of two thirds of the specified room-temperature yield strength while maintaining low yield ratio, good weldability and other properties.

It has been indicated that the combined addition of niobium and molybdenum, while coupled with appropriate controlled rolling and controlled cooling conditions, is extremely effective in the development of fire-resistant steels with a tensile strength of 400N/mm^2 or 490N/mm^2[4]. The good high temperature strength of these steels are considered to be the result of the precipitation strengthening with niobium, solid-solution strengthening with molybdenum, and inhibition of the growth of Nb(C,N) with the segregation of molybdenum at high temperature[4]. It has also been reported that the high-temperature yield strength of the HSLA steels containing Nb and Mo depended mainly on the percentage of the Mo addition, Mo was essential to obtain a mixed microstructure of polygonal ferrite and bainite, and the MC carbides became finer and denser as the amount of Mo increased. Therefore, the enhanced high-temperature yield strength of these steels was contributed to both bainitic transformation hardening and the precipitation hardening caused by a uniform distribution of fine MC particles[5]. Vanadium is very different from niobium in the behavior of precipitation. It is unclear whether or not the combined addition of vanadium and molybdenum, while combined with proper processing conditions, has similar effect of the HSLA steels containing Nb and Mo.

The purpose of the present work is to investigate the effect of vanadium on the microstructural evolution and properties of several hot-rolled Mo-containing weathering steels with emphasis on its effect on high-temperature strength of these experimental steels.

2 Experimental Procedures

2.1 Experimental steels

In this study, on the basis of Nippon Steel Company's fire-resistant weathering steel, three series of experimental weathering steels (the first with 0.60%Mo, the second with 0.3%Mo+0.0020%B and the last with 0.30% Mo content) were designed to investigate the effect of vanadium on the microstructure, tensile properties both at room temperature and at high temperature up to 600°C. In addition, steel 33 was microalloyed with the VN alloy to enhance nitrogen content for comparison.

The experimental steels were melted in a vacuum melting furnace in the laboratory and cast into 40 kg ingots. After being reheated at 1200°C, the ingots were fogged into a slab of 40mm×170mm×160mm for hot rolling. Table 1 shows the steel compositions of the laboratory heats prepared by vacuum-induction melting.

Hot rolling

The hot-rolling experiment was done using a 400 pilot mill with a prepared slab of 40mm in thickness. The slabs was soaked at 1250°C, 1200°C or 1100°C for 1 h and then rolled into a 12mm thick plate through four passes, and air cooled. Some specimens were cooled in a coolant for 20 s to about 600°C, and then put into a furnace holding at 600°C for 1 h and furnace cooled to ambient temperature for comparison. The rolling parameters are given in Table 2.

2.3 Test methods

The tensile properties of the plates were tested using round specimens with a diameter of 5mm (gauge length: 30mm) machined from each plate in the transverse direction. The elevated-temperature test was conducted in accordance with ISO 783.

The microstructures of the plates under different conditions were examined by optical microscope.

Continuous-cooling-transformation (CCT) diagrams were determined by using a dilatometer to examine the effect of chemical compositions on the microstructural evolution. Dilatometer specimens in the shape of rods of 10mm in length and 3mm in diameter were prepared from the as-rolled plate. Dilation-temperature curves were obtained by austenitizing each specimen for 5 min at 1000°C and then cooling at rates between 200°C/h and 150000°C/h. The dilatometer specimens were examined by optical microscopy, and their hardness was determined with a Vickers hardness tester using a 10 kg load. In order to quantitatively analyze the amount of vanadium content as precipitates in plate, all precipitates were electrolytically extracted by using 7.5% potassium chloride+1% citric acid solution. The electrical current density and temperature were

20mA/cm2 and 0～5°C respectively. After extraction, filtrated residue containing precipitates was dissolved chemically and analyzed by I.C.P.

A H800 transmission electron microscopy was used to examine the precipitates with carbon extraction replica specimens, and a Philips Tecnai 20 HR-TEM (high resolution transmission electron microscopy) equipped with EDX (Energy Dispersive X-ray analyzer) operating at 200 kV was used to examine the microstructure with the thin-foil specimens and carbon extraction replica.

Table1 Chemical compositions of the steels used (wt.%)

Nominal steel	Steel No.	C	Si	Mn	P	S	Cu	Cr	Mo	Ni	V	Ti	B	Als	O	N
0.60Mo weathering steel	11	0.09	0.25	0.70	0.014	0.008	0.31	0.51	0.60	0.17	-	0.015	-	0.09	0.0036	0.0035
	12	0.07	0.22	0.62	0.015	0.007	0.30	0.51	0.59	0.17	0.05	0.015	-	0.06	0.0011	0.0022
	13	0.07	0.22	0.65	0.014	0.007	0.31	0.53	0.60	0.17	0.10	0.015	-	0.05	0.0015	0.0027
	14	0.06	0.21	0.58	0.013	0.007	0.31	0.52	0.60	0.16	0.20	0.015	-	0.07	0.0019	0.0028
0.30Mo-B weathering steel	21	0.07	0.22	0.60	0.013	0.008	0.31	0.52	0.32	0.18	-	0.036	0.0020	0.09	0.0025	0.0030
	22	0.07	0.22	0.58	0.014	0.007	0.31	0.54	0.31	0.18	0.05	0.028	0.0024	0.05	0.0029	0.0033
	23	0.07	0.21	0.64	0.014	0.007	0.31	0.53	0.30	0.18	0.10	0.030	0.0026	0.05	0.0022	0.0026
0.30Mo weathering steel	31	0.07	0.18	0.63	0.008	0.006	0.32	0.50	0.29	0.13	-	-	-	-	0.0073	0.0063
	32	0.07	0.18	0.59	0.008	0.006	0.31	0.50	0.29	0.14	0.10	-	-	-	0.0085	0.0025
	33	0.07	0.21	0.61	0.008	0.015	0.29	0.50	0.30	0.14	0.10	-	-	-	0.0062	0.0120

Table 2 Processing variables for experimental steels

	Steel No.	Slab reheating temperature	The arrangement of thickness reduction	Finishing rolling temperature	Cooling after rolling
Process 1	11,12,13,14,21,22,23	1200℃	40mm→30mm→22mm→16mm→12mm	900℃	Air cooled to room temperature
Process 2	11,13,14,31,32,33	1100℃		850℃	Air cooled to room temperature
Process 3	31,32,33	1250℃		940℃	Air cooled to room temperature
Process 4	31,32,33	1250℃		940℃	cooled in a coolant for 20 s to 600℃, held for 1 h ,and then furnace cooled to room temperature.

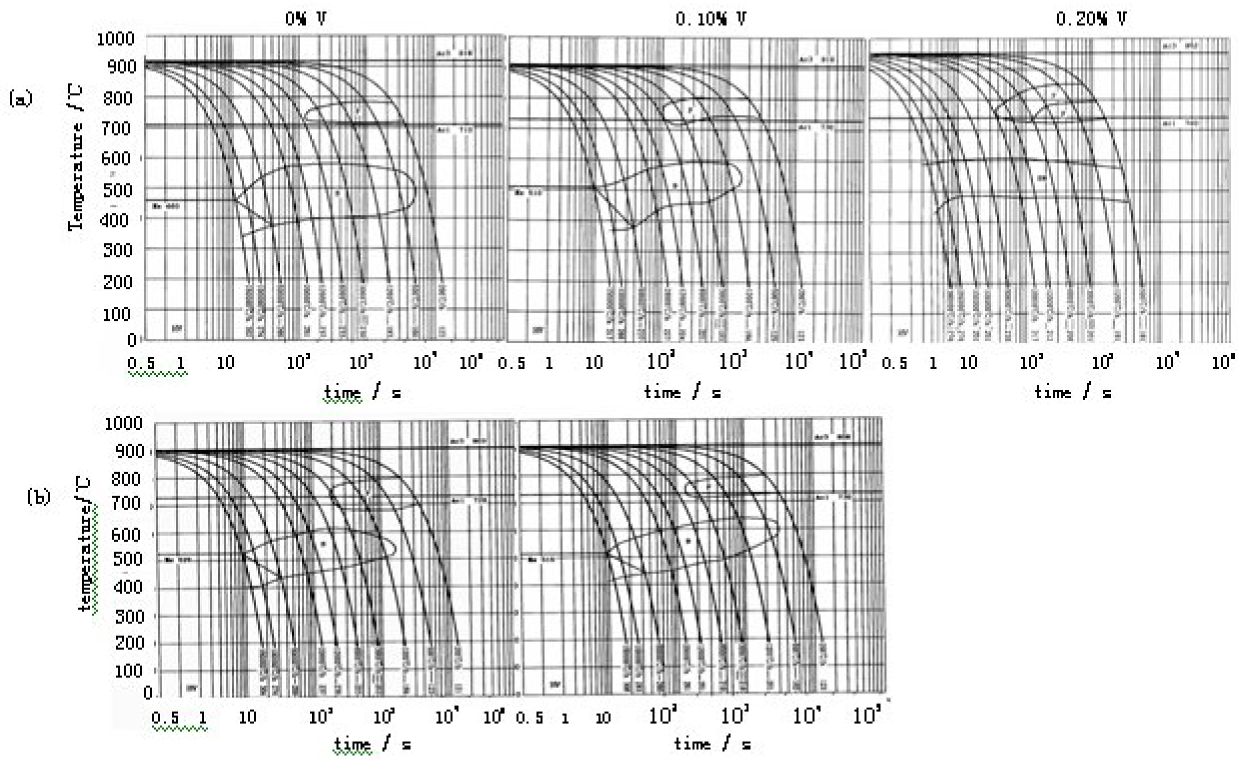
3 Experimental Results

3.1 The CCT diagram

Fig.1 shows the CCT diagrams for the 0.60Mo weathering steel and 0.30Mo-B steel with or without vanadium addition. These diagrams were constructed from the dilatometric and metallographic data.

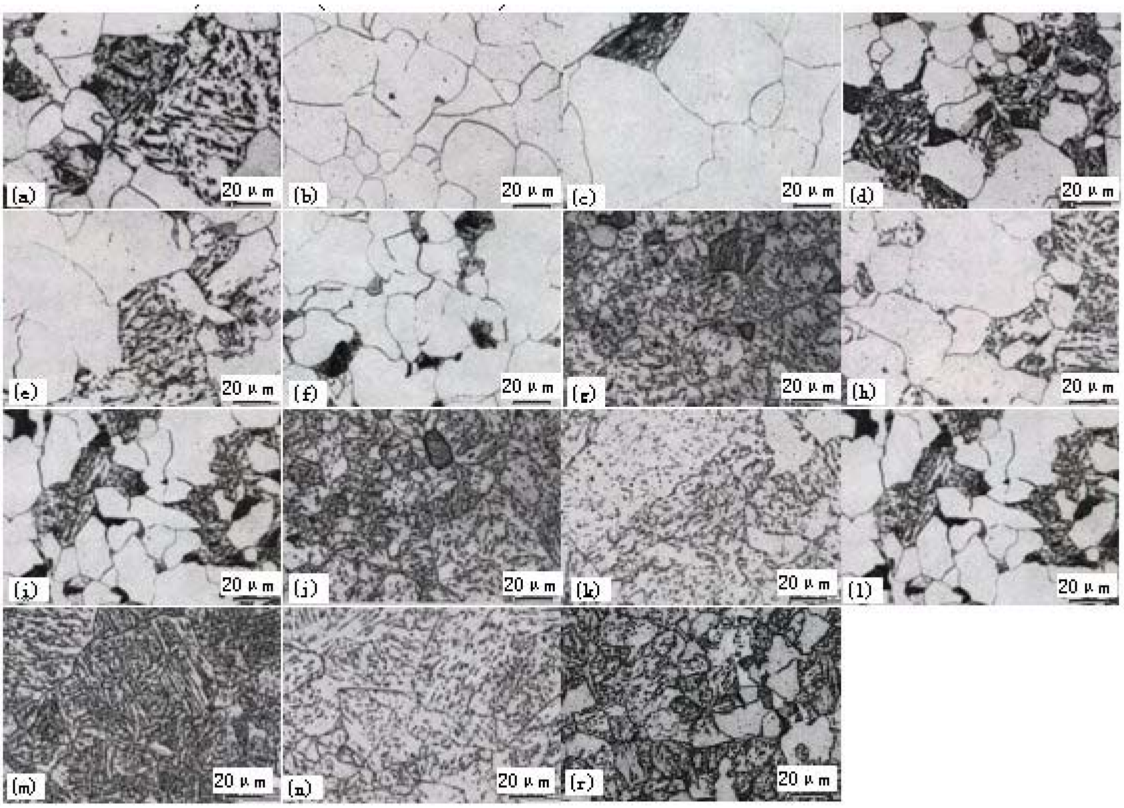
The CCT diagraphs showed that the ferrite phase transformation and bainite phase transformation were separated. For steel 11, steel 13, steel 21 and steel 23, the ferrite can be obtained only at very lower cooling rate(less than 6000°C/h). Bainite can be obtained when the cooling rate is between about 6000°C/h and about 20000°C/h. However, the ferrite can be obtained at a wider range of cooling rate up to about 20000°C/h in steel 14(with 0.20%V). It is also found that the transformation temperatures of steel 14 (with 0.20%V) were higher than those of steel 11 (without vanadium) and steel 13 (with 0.10%V), and the transformation field of ferrite was shifted toward the higher-cooling-rate regime. As a result, the range of cooling rates for the formation of a mixture of polygonal ferrite (PF) and bainite (B) was widened. The microstructure at various cooling rate was compared in Fig.2 for steel 11, steel 13 and steel 14. In steel 11, a mixture of PF and B was obtained even at a low cooling rate of 500°C/h. As the cooling rate increased, the transformation microstructures became dominated by B, and no significant differences in the transformation microstructure was detected when the cooling rate changed from 3000°C/h to 12000°C/h. The microstructure change in steel 13 was similar to steel 11, but the bainite transformation range was shifted to higher cooling rates(about 6000°C/h to 20000°C/h).In steel 14, in addition to ferrite and bainite, pearlite was present in the microstructure at lower cooling rate, and ferrite can be obtained at a wide range of cooling rate. In contrast, in the case of the 0.30Mo-B steels, steel 23 (with 0.10%V) had a wider range of cooling rates for bainite transformation. No significant differences in the bainite microstructure between the 0.60Mo weathering steel and the 0.30-B weathering steel were detected when the vanadium content didn't exceed 0.10%, as shown in Fig.3.

Therefore, the difference between CCT diagraphs was subtle when the vanadium content didn't exceed 0.10%, the slight differences in the CCT diagraphs between these steels may result from the differences in the content of other elements such as carbon and boron, and the effect of vanadium addition (0.10%V) could be neglected. However, the addition of 0.20%V promoted the formation of ferrite.



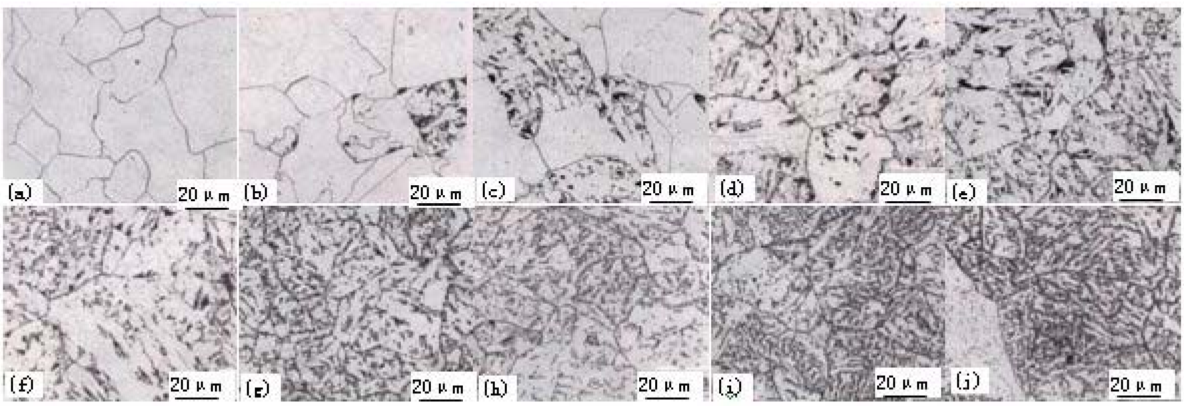
(a) 0.60Mo weathering steel; (b) 0.30Mo-B weathering steel

Fig. 1 Effect of vanadium on CCT diagrams



(a) steel 11,500℃/h,PF+B； (b) steel 13,500℃/h, PF； (c) steel 14,500℃/h,PF+B+P；(d) steel 11,1200℃/h, PF+B； (e) steel 13, 1200℃/h, PF+B；(f) steel 14, 1200 ℃/h ,PF+B+P； (g) steel 11, 3000℃/h, B； (h) steel 13, 3000℃/h, B+PF； (i) steel 14, 3000℃/h, PF+B+P; (j) steel 11, 6000℃/h, B； (k) steel 13,6000℃/h, B； (l) steel 14, 6000℃/h, PF+ B+P； (m) steel 11, 20000℃/h, B+M； (n) steel 13, 20000℃/h, B；(r) steel 14,20 000℃/h, B+PF

Fig. 2 Light micrographs of the microstructures for various cooling rate in the 0.60Mo weathering steels.



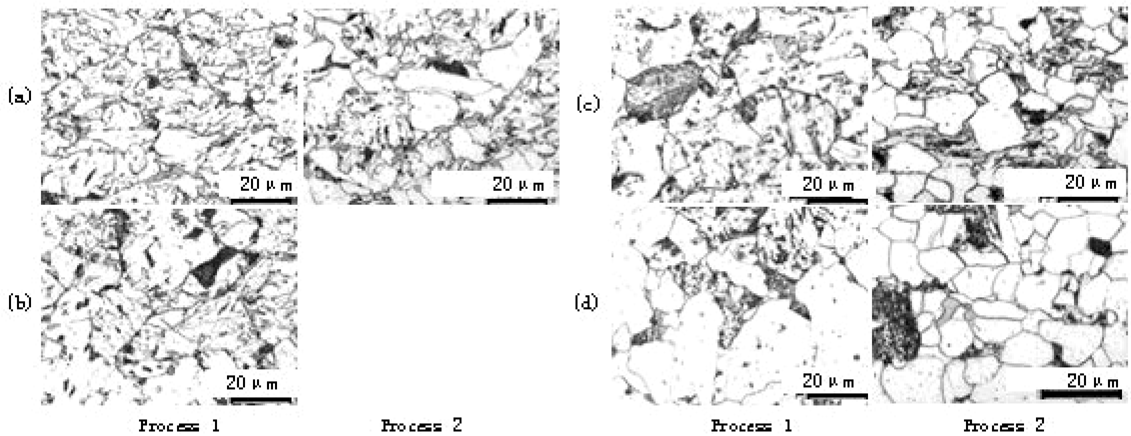
(a) steel 21,500℃/h, PF; (b)steel 23, 500℃/h, PF+B; (c) steel 21, 1200℃/h, PF+B; (d)steel 23, 1200℃/h, B; (e) steel 21. 3000℃/h, B; (f) steel 23, 3000℃/h, B; (g) steel 21, 6000℃/h, B; (h) steel 23, 6000℃/h, B; (i) steel 2, 20000℃/h, B; (j) steel 23, 20000℃/h, B.

Fig. 3 Light micrographs of the microstructures for various cooling rate in the 0.30Mo-B weathering steels.

It was also evident that the combined addition of 0.30%Mo and 0.0020%B was as effective as the addition of 0.60%Mo in affecting phase transformation behavior of the weathering steel.

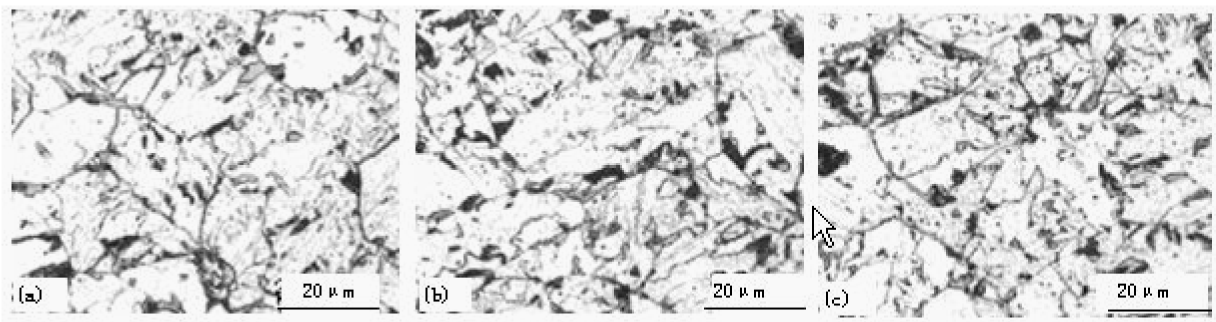
3.2 Microstructural observation by optical microscope

Optical micrographs of the 0.60 Mo weathering steels at various hot-rolled conditions are shown in Fig. 4. The as-rolled microstructures of steel 11(without vanadium addition), steel 12 (with0.05%V) and steel 13(with 0.10%V) for process 1(the slab reheating temperature being 1200°C) were predominately composed of bainite. However, the microstructure of steel 14 (with 0.20%V) exhibited a large fraction of polygonal ferrite in addition to bainite. As the slab reheating temperature was lowered to 1100°C (process 2), the bainite in the as-rolled microstructu decreased,and the amount of PF seemed to increase with vanadium content. Fig.5 shows the optical micrographs of the as-rolled 0.30Mo-B weathering steels for process 1. The as-rolled microstructures were also composed mainly of bainite.



(a) steel 11 (base steel); (b) steel 12 (0.05%V); (c) steel 13 (0.10%V); (d) steel 14 (0.20%V)

Fig .4 Optical micrographs showing the effect of V addition on the microstructure of 0.60Mo weathering steels.

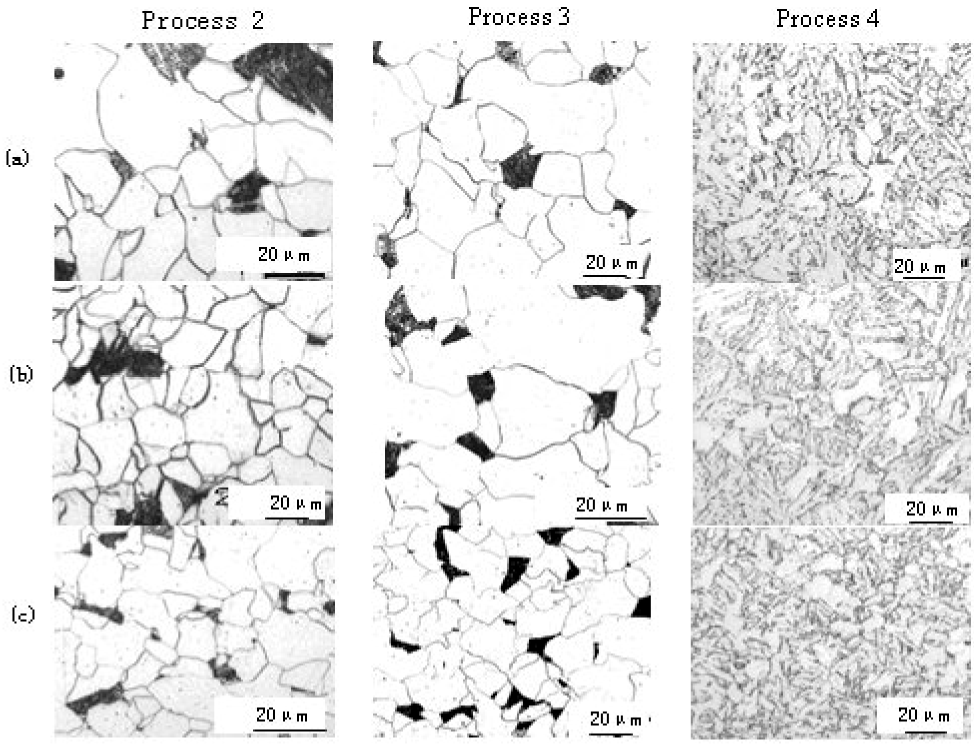


(a) steel 21 (base steel); (b) steel 22 (0.05%V),; (c) steel 23 (0.10%V)

Fig. 5 Optical micrographs showing the effect of V addition on the microstructure of 0.30Mo-B weathering steels.

Optical micrographs of the 0.30 Mo weathering steels at various hot-rolled conditions are given in Fig. 6. As illustrated by Fig.6, the as-rolled microstructure of 0.30Mo weathering steels for process 2 was composed of PF and P (pearlite). As the reheating temperature was increased to 1200°C (process 3), the microstructure exhibited bainite and martensite in addition to ferrite and pearlite. When accelerated cooled after hot-rolling (process 4), the microstructure became dominated by bainite and at the same time, pearlite disappeared.

Table 3 summarizes the microstructure and area fraction of bainite+martensite in various steels examined.



(a) steel 31(base steel); (b)steel 32 (0.10%V); (c) steel 33 (0.10%V with enhancement of nitrogen)

Fig. 6 Optical micrographs showing the effect of V addition on the microstructure of 0.30Mo weathering steels.

Table 3 Ferrite grain size and volume fraction of bainite in various experimental steels.

Nominal steel	Steel No.	Process	Microstructure	Bainite+martensite area fraction (Pct)
0.60Mo weathering steel	11	Process 1	bainite	100
		Process 2	Ferrite+bainite+Martensite	70
	12	Process 1	Bainite	100
	13	Process 1	bainite	100
		Process 2	Ferrite+bainite+Martensite	40
	14	Process1	Ferrite+bainite	45
		Process 2	Ferrite+bainite+Martensite	11
0.30Mo-B weathering steel	21	Process 1	bainite	100
	22	Process 1	bainite	100
		Process 5	bainite	100
	23	Process 1	bainite	100
		Process 5	bainite	100
0.30Mo weathering steel	31	Process 2	Ferrite+pearlite+martensite	2
		Process 3	Ferrite+pearlite+bainite+martensite	11
		Process 4	Ferrite+bainite	80
	32	Process 2	Ferrite+pearlite	0
		Process 3	Ferrite+pearlite+bainite+martensite	10
		Process 4	Ferrite+bainite	82
	33	Process 2	Ferrite+pearlite	0
		Process 3	Ferrite+pearlite+bainite+martensite	20
		Process 4	Ferrite+bainite	75

3.3 Tensile properties

The tensile properties of the as-rolled plates both at room temperature and 600°C at different hot rolling conditions are plotted as a function of vanadium content in figure 7 ～ figure 9 for various experimental steels, respectively.

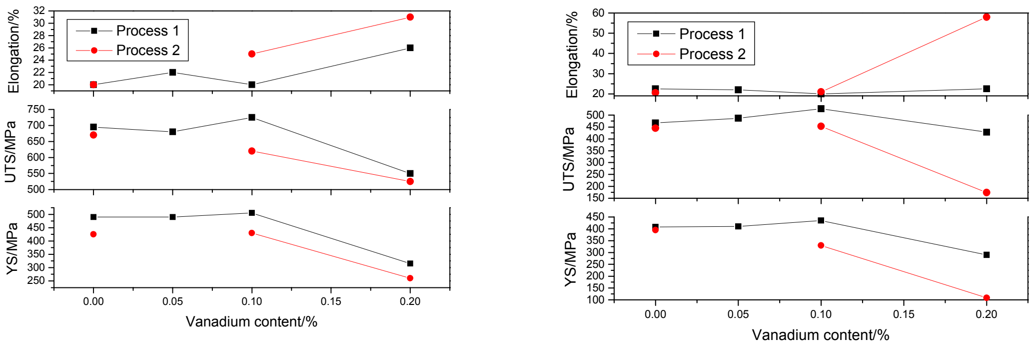


Fig. 7 (a)Room-temperature tensile properties and (b) high-temperature(600 ℃) tensile properties of 0.60Mo weathering steels.

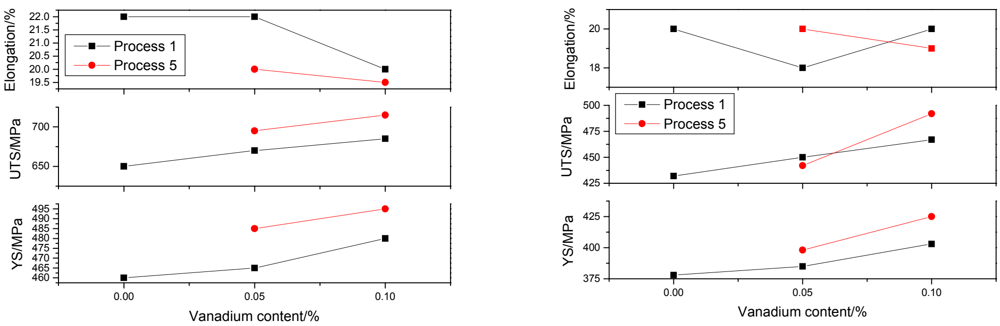


Fig. 8 (a) Room-temperature tensile properties and (b) high-temperature(600℃) tensile properties of 0.30Mo-B weathering steels

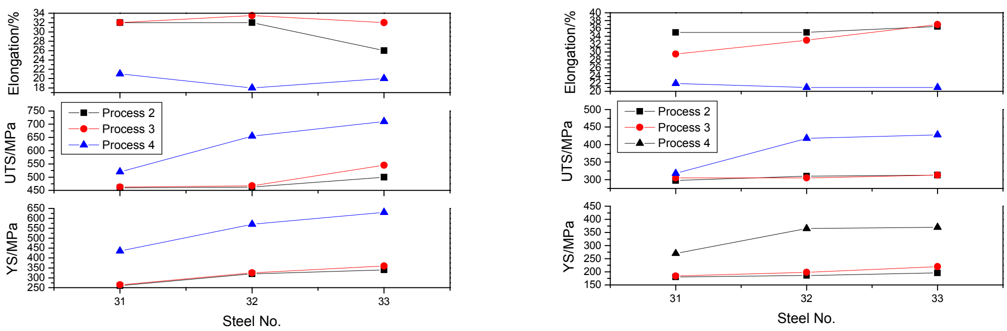


Fig. 9 (a) Room-temperature tensile properties and (b) high-temperature(600 ℃) tensile properties of 0.30Mo weathering steels

As shown in Figure 7(a), the room temperature strengths of the 0.60Mo weathering steel soaking at 1200°C were limitedly affected by the vanadium content in the range of 0 to 0.10%, then decreased obviously when the vanadium content was increased to 0.20% as the result of an increase of the amount of ferrite in the microstructure (Fig.4(d)). However, figure 7(b) shows that its high-temperature (600°C) strengths increased slightly with increased vanadium content in the range of 0 to 0.10%, then decreased obviously when the vanadium content was increased to 0.20%. Fig.7 also indicates that the strengths both at room temperature and 600°C decreased as the soaking temperature for hot-rolling was reduced from 1200°C to 1100°C due to the change of microstructure from bainite to bainite+ferrite (Fig.4), especially for the steel with 0.20% vanadium. In the case of process 2, the base steel had the highest bainite area fraction, and its high-temperature strength was also the highest.

It was revealed from figure 8 that both room temperature yield strength and high temperature yield strength for the 0.30Mo-B weathering steel slightly increased with V content (less than 0.10%).

In the case of 0.30Mo weathering steels (Fig.9), the addition of 0.10%V (steel 32) enhanced both room-temperature yield strength and high-temperature (600°C) for all three hot-rolling processes, especially for process 4. Combined additions of both vanadium and nitrogen through VN alloying further increased the room-temperature strengths, but did not cause a significant change in the high-temperature strengths (compare steel 32 and steel 33 in Fig. 9(a) and 9(b)). The change of the slab reheating temperature from 1100°C to 1250°C had little effect on both the room-temperature and high-temperature strengths for steel 31 and 32, but caused slightly increase in both the room-temperature and high-temperature strengths for steel 33.However, Accelerated cooling after hot-rolling markedly increased the room-temperature strengths and high-temperature strengths for all three steels.

3.4 State of vanadium in as-rolled plates

Table 4 showed the results of vanadium content as precipitates in the as-rolled plates for various experimental steels. It is obvious that the vanadium content as precipitates increased with the vanadium content in the steels, and an increase in the nitrogen content promoted the precipitation of vanadium in the as-rolled plates, especially when the microstructure was dominated by bainite.

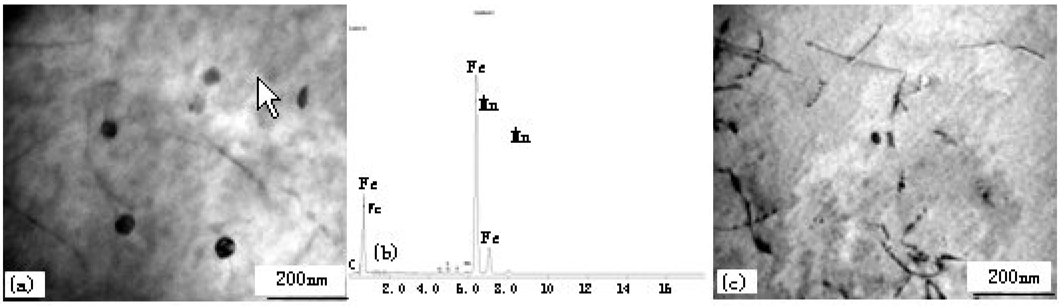
Table 4 Vanadium content as precipitates in the as-rolled plates for various experimental steels.

Nominal steel	Steel No.	Process	$V_{as\ ppt.}$,%
0.60Mo weathering steel	Steel 12	Process 1	0.007
	Steel 13	Process 1	0.014
		Process 2	0.003
	Steel 14	Process1	0.042
0.30Mo-B weathering steel	Steel 22	Process 1	0.007
	Steel 23	Process 1	0.020
0.30Mo weathering steel	Steel 32	Process 2	0.009
		Process 3	0.016
		Process 4	0.059
	Steel 33	Process 2	0.030
		Process 3	0.039

3.5 Microstructural analysis by electron microscope

A lot of examinations were carried out in the carbon-extraction replica specimens of as-rolled steels. Figure 10 shows the morphology, distribution of precipitates obtained in as-rolled 0.60%Mo weathering steels. In addition to large cubic TiN particles, smaller round carbides were found in all steels. As the vanadium content in the steels increased, the carbides tended to be denser, especially for steel 14 containing 0.20%V. Fig.11 shows the TEM images of thin-foil specimens of steel 14. It was found that the large carbides (Fig.11 (a)) contained vanadium and titanium (Fig.11(b)), so they was thought to be carbides precipitating at higher temperature. Small carbides along dislocation lines were also observed (Fig.11(c)).

Fig. 10 Precipitates morphology observed in carbon extraction replica of 0.60Mo weathering steels showing the effect of vanadium content



(a)large carbides; (b) characteristic EDAX spectra of the large carbide; (c)small carbides along the dislocation lines

Fig. 11 Precipitates morphology observed in thin-foil of steel 14

4 Discussion

As well known to all of us, the properties of steels are markedly affected by their microstructure including the constitution of phases and precipitates. Fig.12 to Fig.13 shows the change of tensile properties with vanadium content as precipitates and microstructure of steel plates for all experimental steels. It was revealed that the control of B+M area fraction played a very important role in controlling the tensile properties both at room temperature and 600°C of all the experimental steels. At a given microstructure, both the room-temperature yield strength and high-temperature yield strength increased as the vanadium content as precipitates increased.

As shown in figure 12(a) and 12(b), the 0.60Mo Weathering steels and 0.30Mo-B weathering steels exhibited microstructure dominated by bainite (except for the steel with 0.20%V), and hence showed high yield strength at 600°C, low yield strength (YR) (about 70%) and high YS ratio(greater than 80%). Furthermore the precipitation of small amount of vanadium (less than 0.02%) caused a slight increase in yield strength at both room temperature and 600°C. As for steel 14(with 0.20%V),even though the present of ferrite in the microstructure resulted in the decrease of yield strength at both room temperature and 600°C, the YS ratio was higher than the steels with lower vanadium content. In the case of 0.30Mo weathering steels (Fig.13), the microstructure was mainly composed of ferrite and pearlite for process 2 and process 3, although the precipitation of vanadium did increase the yield strength at both room temperature and 600°C and the addition of nitrogen seemed to further enhance the effect of vanadium, the high-temperature yield strength did not exceed 220 MPa and the YS ratio was lower than 66.7% except the base steel (steel 31) that had low room-temperature yield strength. In contrast, the existence of proximately 80% bainite for process 4 dramatically increased the yield strength both at room temperature and 600°C. However, the precipitation of vanadium not only increased the room-temperature yield strength and high-temperature yield strength, but also resulted in high YR.

The present experimental results demonstrated that the Mo content might be reduced to about 0.30Mo if a suitable fraction of bainite was introduced in the microstructure while the high-temperature yield strength and YS ratio were still kept at high level. The addition of vanadium, especially combined addition of vanadium and nitrogen, would exhibit additional strengthening, at least for the plates that were exerted accelerated cooling after hot-rolling (process 4).

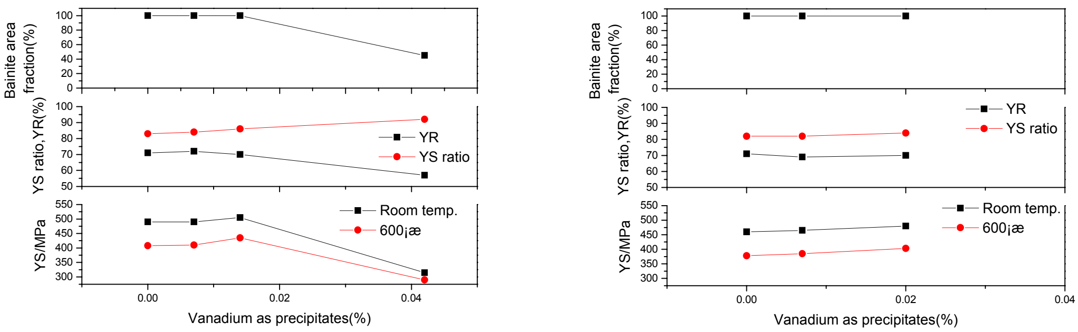


Fig. 12 The change of tensile properties with vanadium content as precipitates and microstructure of steel plates for the experimental steels.

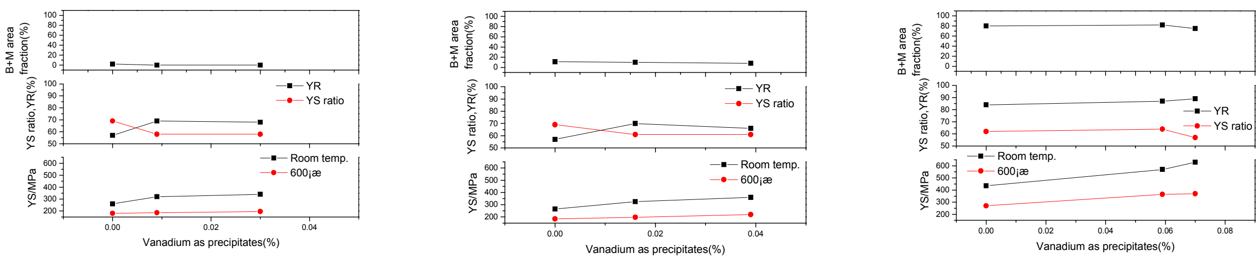


Fig. 13 The change of tensile properties with vanadium content as precipitates and microstructure of steel plates for the 0.30 Mo weathering steels.

5 Conclusions

The results of this study led to the following conclusions.

(1) The addition of 0.10%V has a limited effect on the CCT curves of 0.60%Mo weathering steels and 0.30%Mo-B weathering steels whereas the addition of 0.20%V promoted the formation of polygonal ferrite in the 0.60%Mo weathering steel.

(2) The control of the bainite fraction in the microstructure is essential for weathering fire resistant steels in order to obtain good high-temperature yield strength and high YS ratio even for steels containing 0.60Mo.

(3) Precipitates of vanadium were found in all vanadium-containing experimental steels and they seemed to become finer and denser as the vanadium content increased or accelerated cooling after hot-rolling was used.

(4) If a suitable fraction of bainite was introduced in the microstructure, the Mo content could be reduced to about 0.30%Mo while the high-temperature yield strength and YS ratio were still kept at high level.

(5) The addition of vanadium, especially combined addition of vanadium and nitrogen, would result in additional strengthening at both

room temperature and 600°C, at least for the plates that were subject to accelerated cooling after hot-rolling. The effect of vanadium might be attributed to the precipitation of vanadium.

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