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Effect of Nitrogen on Carbonitride in High Speed Steel

Ke Xiaotao and Chen Liang*

Department of Pangang Group Research Institute Panzhihua, China

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***Corresponding author:** Chen Liang, Department of Pangang Group Research Institute Panzhihua, China

Abstract

The vanadium-nitrogen alloying technology was used to investigate the effect of vanadium-nitrogen alloy on the carbides in high-speed steel after replacing vanadium-iron alloy. The morphology, composition and quantity of carbides in steel were analyzed in detail, and the replacement of some carbon with nitrogen was verified. The theoretical basis and experimental data for the application of vanadium-nitrogen alloys in high-speed steel is provided by this theory in this paper.

Keywords: Vanadium-nitrogen alloying; Carbides; High speed steel

Introduction

Considering the alloying elements in high-speed steel and reducing its cost, the development of low-alloy high-speed steel has been paid attention to by various countries and has been applied to a certain extent. For example, low-alloy high-speed steels such as W3Mo2Cr4VSi and W4Mo3Cr4VSi has been developed in China [1,2]. The effects of nitrogen content in vanadium-nitrogen alloying steel on the morphology, composition and quantity of carbides in low-alloy high-speed steel were studied in this paper. The theory of replacing some carbon with nitrogen was verified, which is the vanadium-nitrogen alloy in high-speed steel. The application provides theoretical basis and experimental data.

Experimental Methods

Materials

The steels were melted in inductive furnace with a capacity of 150kg. The molten steel was cast as 50kg ingot. The molten compositions of the steels are shown in Table 1. The ingots were forged to φ20mm bars. The specimens were machined from annealing bars.

Table 1: The molten composition of the steels %.

Steel	C	Si	Mn	P	S	Cr	Mo	W	V	N
1	0.7	0.18	0.29	0.028	0.023	4.37	3.34	2	2.35	0.104
2	0.65	0.19	0.28	0.027	0.023	4.45	3.28	1.95	3.78	0.166

Experimental Methods

Heat Treatment The specimens with a size of φ20×15mm were heated in a resistor furnace, quenched in salt bath. Quenching process: Heating temperature was changed from 1150 to 1280°C, holding time was 40 to 60 min, salt bath temperature was 580 to 610°C, holding time was 15min. Tempering process: Heating temperature was 560°C, and holding time was 1h. Repeated tempering 3 times.

SEM analysis

The shape and composition of carbides under different heat treatment conditions were observed and analyzed by SEM.

Chemical phase analysis

The chemical electrolysis was used to separate carbide from the specimen at different states. The type and amount of carbides in steels were measured by quantitative analysis of XRD.

Results and Discussion

Carbide Shape

The SEM photos of carbides of 1# and 2# specimen in different states are shown in Figure 1. The results of the energy spectrum analysis are shown in Table 2.1 and Table 2.2. The results show that the carbides in the annealed state have a small amount of MC primary carbides, mainly containing vanadium. A large number of small particle carbides contain more Cr, Mo and W, while containing a small amount of vanadium. The carbide composition of the two tested steel is not much different Figure 2.

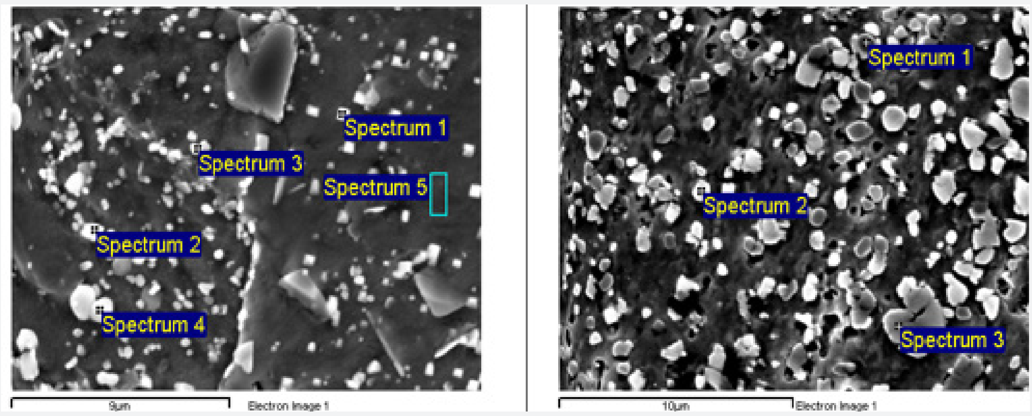

Figure 1: Shape of carbide in the annealed.

Table 2.1: Energy analysis results of carbides for 1#.

1#	S	V	Cr	Fe	Mo	W	Total
Spectrum1		9.74	4.61	59.96	13.52	12.17	100
Spectrum 2		5.47	3.74	84.7	2.91	3.18	100
Spectrum 3		8.29	4.16	68.46	10.01	9.07	100
Spectrum 4	0.72	5.14	3.81	88.51		1.82	100
Spectrum 5	0.55	2.74	3.94	91.4		1.37	100

Table 2.2: Energy analysis results of carbides for 2#.

2#	V	Cr	Fe	Mo	W	Total
Spectrum 1	45.21	3.49	44.89	3.18	3.23	100.00
Spectrum 2	6.24	4.27	63.86	12.38	13.25	100.00
Spectrum 3	4.56	3.95	72.10	9.19	10.20	100.00

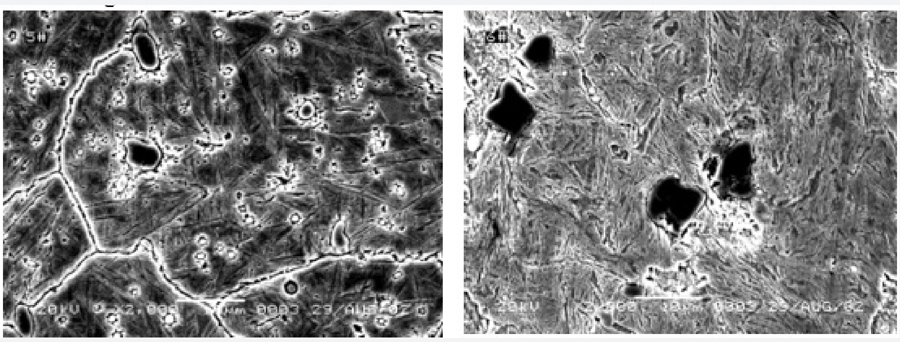

Figure 2: Shape of carbide after quenched
1# quenching at 1210 °C
2# quenching at 1210 °C

Carbide composition

The compositions of carbides in the investigated steels are given in Table 3.

Table 3: The compose of phase in steels

Steel No.	State	Phase	Lattice constant	Crystal system
1#	Annraling	M6C	a0=11.04～11.05	F
		VC	a0=4.14～4.15	F
		V（CN）	a0=4.15～4.16	F
		M23C6	a0=10.58～10.60	F

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		Cr N	a0=4.14	F
		(CrFeMoW)7C3	a0=13.982，c0=4.506	H
		α-MnS	a0=5.224	C
		Mo2N	a0=4.163	C
	Quenching	V（CN）	a0=4.11～4.12	F
		VC	a0=4.15～4.16	F
		V2（CN）	a0=2.910～2.980，c0=4.598～4.708	CH
		α-MnS	a0=5.224	C
		Cr N	a0=4.14	F
	Tempering	VC	a0=4.15～4.16	F
		V（CN）	a0=4.12～4.13	F
		V2（CN）	a0=2.910～2.980，c0=4.598～4.708	CH
		α-MnS	a0=5.224	C
		Cr N	a0=4.14	F
2#	Annraling	M6C	a0=11.04～11.05	F
		VC	a0=4.14～4.15	F
		V（CN）	a0=4.11～4.12	F
		Cr N	a0=4.14	F
		α-MnS	a0=5.224	C
	Quenching	V（CN）	a0=4.11～4.12	F
		VC	a0=4.15～4.16	F
		α-MnS	a0=5.224	C
		Cr N	a0=4.14	F
	Tempering	VC	a0=4.16～4.17	F
		V（CN）	a0=4.13～4.14	F
		α-MnS	a0=5.224	C
		Cr N	a0=4.14	F

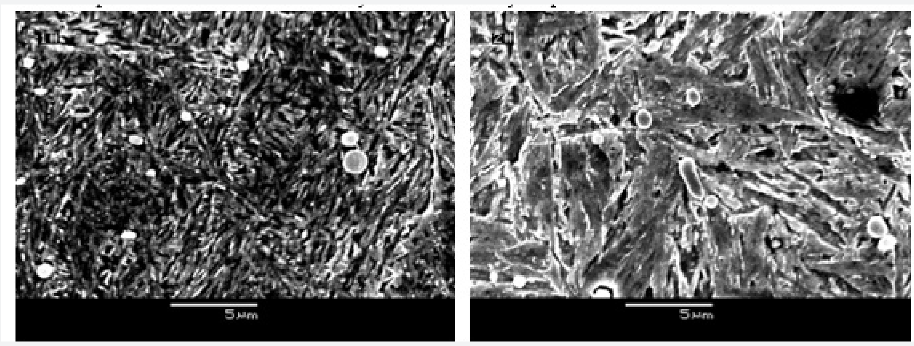

Figure 3: Shape of carbide after tempered
1# quenching at 1210^{O}C and temper at 560 ^{O}C
2# uenching at 1210^{O}C and temper at 560 ^{O}C

At as-annealed states, the type of carbides is very complex. The main carbides are M_6C, MC, M(CN), M_7C_3, $M_{23}C_6$ and nitride of Cr, Mo, only MC, M(VN) remain at as-quenched and as-tempered state. Nitrogen can combine with V and Cr to form the nitride, which can be found in as-annealed, as-quenched and as-tempered states. Furthermore, α-Mn S phase can be found in both steels. M_6C, M_7C_3 and $M_{23}C_6$ can easily dissolve into austenite during quenching and tempering process and disappear after quenching. On the other hand, the carbides or nitrides of vanadium and nitrides of chromium have higher stability and can remain in steels after quenching. These nitrogen-contained phases play an important role in the improvement of wear ability and high temperature hard ness. The lattice constant of V(CN) is slightly less than that of VC, indicates that the nitrogen

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dissolved in VC can reduce the lattice constant of VC. The carbide of vanadium in the nitrogen-added steel is practically V(CN). The parameters of Cr N and VC are almost identical. In addition, the types of carbide are different in steel 1# and steel 2#. There is a carbide of V2(CN) in steel 1#, which doesn't exist in steel 2#. V2(CN) has a lesser lattice constant and belongs to a close-packed hexagonal system which is different from V(CN) with face-centered cubic lattice system Figure 3.

Carbide amount

Table 4: The total amount of carbides and proportion of elements in carbides wt.%.

Steels	States	Sum	Fe	Cr	Mn	W	Mo	V	Total [N]	Solution [N]
1#	A	11.633	2.928	1.433	0.05	2.227	2.61	2.29	0.095	0.009
	Q	3.701	0.117	0.234	0.021	0.831	0.664	1.749	0.085	0.019
	T	5.265	0.145	0.585	0.021	1.124	1.392	1.909	0.089	0.015
2#	A	8.269	1.117	0.304	0.025	1.852	1.581	3.248	0.142	0.024
	Q	4.266	0.054	0.122	0.024	0.943	0.364	2.625	0.134	0.032
	T	4.551	0.064	0.147	0.025	0.955	0.371	2.851	0.138	0.028

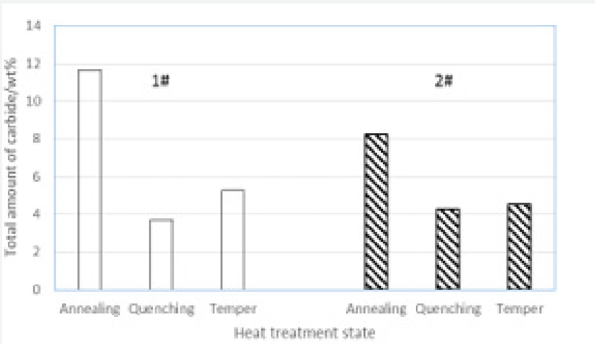

Figure 4: Changes in the total amount of carbides under different heat treatment states.

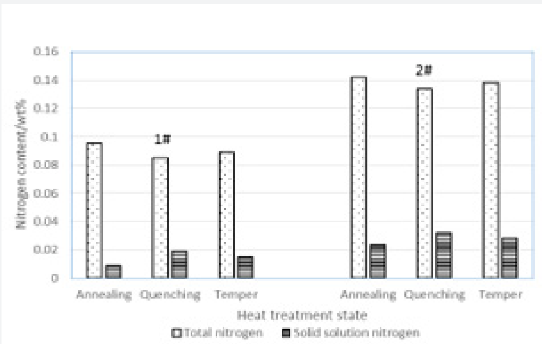

Figure 5: Changes in nitrogen content under different heat treatment conditions.

The total amount of carbides and the proportion of elements in carbides at different states are given in Table 4. The total carbide and nitrogen content distribution under different heat treatment conditions are shown in Figures 4 and Figures 5. The as-annealed steel has the most quantity of carbide among the three states. The amount of carbide decreases obviously after quenching, and increases again at the as-tempered state, but the amount of carbides is less at as-tempered state than that in as-annealed state. Both steels obeyed the above general law of carbide evolution in high-speed steel. Although the sum of carbides is relatively high in steel 1#.

The changes in the content of each element in carbide have the same trend as that of the sum of carbides. The content was of the highest at the as-annealed state and decreased after quenching and increased again in the as-tempered state. In contrast to other element, the contents of W, Mo, Cr changed more obviously, whereas the content of V changed little. The contents of W, Mo in carbides increased obviously and the contents of Cr, V changed little, when the steels were treated from quenching to tempering, indicating that Wand Mo have a stronger ability of secondary precipitation. The content of N in carbides was stable, and did not change after the heat treatment. The nitrogen was mainly present in carbides and the amount accounted for 80%-90% of the total nitrogen in steel, and the remained is dissolved in solution. As the content of nitrogen increases, both the content of nitrogen in carbides and in solution increases.

Discussion

Since the carbides can precipitate almost completely during annealing for high-speed steels, the amount of carbides is of the most in annealed steel. The carbides can dissolve into austenite at high heat temperature, so the amount of carbide is of the lowest after quenching process. The carbides can precipitate from martensite and austenite during tempering; and the amount will increase slightly. In the case of the investigated steels the type of carbides are different become of high nitrogen, two new phases V(CN) and Cr N, which don't exist in the ordinary HSS, were found. The results also show that the total amount of carbides is lower than that of conventional high-speed steels, which results from the low carbon content, because it was found that the total content of carbides increases with the carbon content. Furthermore, the low amount of retained austenite in the steel also accounts partly for the low total amount of carbides due to the fact that the amount of carbides resulting from the decomposition of the retained austenite decreases dramatically.

Conclusion

a. The steels containing high content of vanadium and nitrogen can be made by vanadium-nitrogen alloying, the nitrogen content of which is as high as 0.17%.

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b. There are significant differences in the morphology and quantity of carbides in high speed steel under different heat treatment conditions. In the retracted state, the number of carbides is of the highest, and there is a small amount of large vanadium-containing MC primary carbides; a large number of small-grain carbides contain more Cr, Mo, and W, and contain a small amount of vanadium. After quenching process, the carbide is dissolved in a large amount, and a small amount of insoluble large-sized MC carbide remains. After the tempering process, the primary carbide is spheroidized, and the secondary carbide is finely dispersed.

c. The composition of the annealed carbide phase is complicated, mainly including M6C, MC, M(CN), M7C3, and nitrides of Cr and Mo. After quenching and tempering process, MC and M (VN) remain. Nitrogen-containing high-speed steel mainly produces vanadium carbonitrides and chromium nitrides; nitrogen solid solution into VC reduces the lattice constant of the VC phase.

d. Under different heat treatment conditions, the amount of carbides in the steel is of the highest in the annealed state, the amount of carbides after quenching process is significantly reduced, and it is increased after tempering process; the nitrogen in the nitrogen-containing high-speed steel is mainly present in the carbides. It accounts for about 80%-90% of the total nitrogen, and the rest is in the form of solid solution nitrogen.

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