Review of Applications of Vanadium in Steels

Gan Yong，Dong Han

（China Iron & Steel Research Institute Group）

1 Introduction

The majority of vanadium is present in titanomagnetite. Compared to the presence of iron in the crust (at the mass ratio of 7.07%), the presence of vanadium appears very scarce (at the mass ratio of 0.023%). Is this a special providence of God? Trace amount of vanadium present in the steel can play a significant role in performance improvement.

Now, the overwhelming majority of vanadium produced is used in steel products to improve their performance. It is an important micro-alloying element and alloying element in the steel. The addition of vanadium into steel can enhance the strength, toughness and plasticity of steel, improve fabrication and service performance. It is relatively easy to control the precipitation strengthening effect of vanadium carbide in the interphase and ferrite. Vanadium carbonitride (V(C, N)) is used during reheating process of thermal treatment to refine the grain of austenite. The steel doped with vanadium is imparted with the effective anti-tempering softening behaviors during the tempering process. At present vanadium is widely used in the high strength hot rolled ribbed rebars, high-strength low-alloyed steel, alloyed structural steel, micro-alloyed forging steels, spring steel, steel bolts, super-high strength steel, die steel, high speed steel, martensite heat-resistant steel and other types.

There is no doubt that vanadium discovered in the first half of the nineteenth century played a catalytic role in the development of alloyed steel in the twentieth century. In the latter half of the nineteenth century scientists began their research and development of alloyed steels and developed some technologies of alloyed steels: In 1868 the first alloyed steel the self-hardened steel was made by Robert Mushet; In 1883, Robert Hadfield invented the famous high-manganese steel. During the early twentieth century, vanadium steel aroused attention from all people, as the vanadium steel was first implanted into the artificial bone joints. Another well-known application of vanadium steel is Ford Model T (front axle) in 1908. At that year Ford learnt advantages of vanadium steel from J. Kent Smith, a British metallurgist that its strength tripled that of raw steel with good toughness and cutting machining performance. Therefore Ford decided to build better and lighter Model T autos at lower costs with vanadium steels. The vanadium steels used in cars today differ from those used in Model T.

Over 100 years of development, people have developed complete know-how on production and application of vanadium [1-3] and deepened understanding of its role in the steel while technologies of its applications in the steel have been evolved continuously. The applications of vanadium depend on understanding of the known roles of vanadium in the steel and more effective applications in the future depend on further understanding of the unknown roles of vanadium in the steel. The overwhelming majority of vanadium produced in the world is used as an alloying element in steels (80%～90%). In Order to save resources we must focus on the effective utilization of vanadium in the steel. The output of hot rolled ribbed steels accounts for 1/4 of steel production in China. Therefore high performance development (high strength, high ductility, low yield ratio, fire resistance, corrosion resistance, etc.) is an inevitable trend and rational use of vanadium in this type of widely applied and heavily consumed steels is a topic of great interest and concern.

2 The behavior of vanadium in the steel

The position of vanadium in the chemical periodic table determines its chemical properties. Vanadium falls into the fourth cycle and VB family in the table. It has three electrons on the third layer and it is an element for forming strong carbide and nitride. With a cubic structured body and center, it can be dissolved in the steel at any temperature. There is a certain amount of carbon and nitrogen in the steel which react with vanadium and precipitate from the steel in the form of carbide, nitride, or carbonitride. As a focus of attention, the process and condition of solution and precipitation of vanadium have been extensively researched in the recent years. For the comprehensive knowledge in this respect, refer to "The Second Phase of Iron and Steel Materials" by Yong Qi-long [4]. Meanwhile, the solution and precipitation of vanadium will also affect the microstructure evolution and the features of the microstructure will accordingly affect various properties of steel.

The solubility product of V(C, N) in austenite is much higher than that of niobium carbide under general situation of low content of nitrogen. Below 900 ℃, V(C, N) can be completely dissolved in austenite. In addition its solubility in the austenite is greater than in the ferrite. Thus its major role lies in the interphase precipitation during γ/α phase transition and precipitation strengthening in the ferrite.

The role of vanadium in the steel can be perceived from the perspective of solubility product. In Figure 1, the major roles of vanadium in steel are:

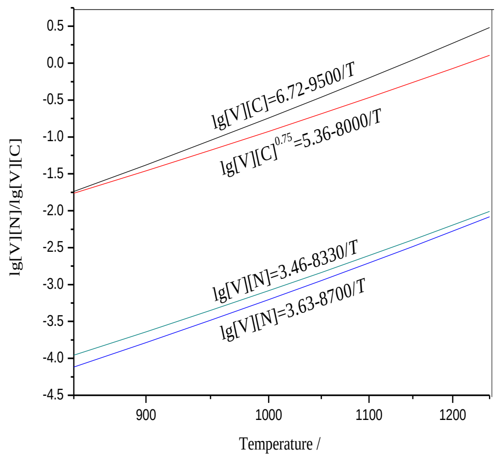

Figure 1 Solubility of Vanadium Carbide and Vanadium Nitride in Austenite [5]

(1)Vanadium carbide and vanadium nitride have a high solubility product in the austenite. Relatively speaking, it is unlike to generate cracks caused by precipitation at high temperature. During solidification the appearance of cracks in the billet tends to be small.

(2)Vanadium carbonitride features low precipitation temperature, solid solution in austenite and small drag force of grain boundary migration. This is conducive to recrystallization of austenite, which facilitates recrystallization control rolling and homogeneous structure along the steel section. Within a wide temperature range the uniform recrystallized grains can be obtained and the finish rolling temperature has little effect on the mechanical properties. Compared with other micro-alloyed steels and alloyed steels, vanadium steel has small rolling resistance, similar to that of carbon-manganese steel.

(3)Precipitation in the ferrite or martensite results in strengthening effect. Generally the precipitation strengthening increment in the ferrite ranges from 50 to 100MPa. Through increase of nitrogen content in the steel the precipitation of vanadium can be promoted and greater precipitation strengthening effect can be achieved. It is a good technology for producing high-strength hot-rolled ribbed steel because it economizes amounts of vanadium and improves the amount of precipitation strengthening. In general the vanadium dissolved in the steel accounts for 50% of vanadium content. Through increasing the nitrogen content in the steel the content of dissolved vanadium can be lowered to 20% and the precipitation strengthening effect of vanadium can be explored to the maximum extent. As vanadium in steel exists by way of replacement solution, the solid solution strengthening effect is much less than precipitation strengthening effect.

(4)The strong combination of vanadium with nitrogen can form vanadium nitride which helps to reduce the strain aging of steels. This feature is important for the service property of rebars after undergoing cold deformation.

(5)Addition of vanadium into martensitic steel can enhance the anti-tempering and softening properties of steel, enabling the steel to maintain the martensitic lath shape or precipitate vanadium carbide, produce secondary hardening effect during the course of tempering as shown in Figure 2.

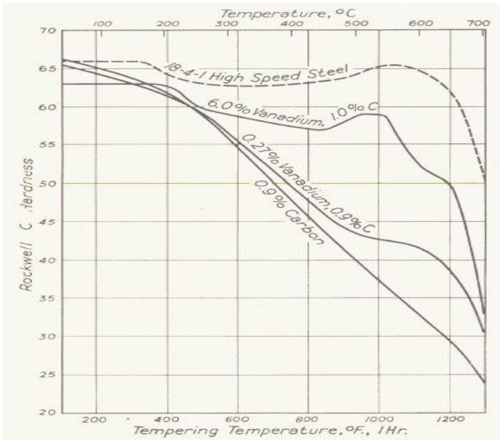

Figure 2 Addition of Vanadium Can Improve the Tempering Resistance and Softening Property of Steel [6]

In recent years, scientists have been studying the role of vanadium in steels, trying to maximize the alloying roles of vanadium:

(1)Increase of the precipitation strengthening effect

In general the vanadium precipitation strengthening increment ranges from 50 to 100MPa. Is there any possibility for further enhancement of the precipitation strengthening increment? It can only be achieved by further refined precipitation of vanadium carbonitride particles and increase of the volume percentage of precipitating phase. Yong Qilong believes that if the diameter of precipitated V(C,N) is refined to 5～7nm (the equivalent to the diameter of turning particle bypassing the mechanism after cutting the dislocation) and the volume percentage of the precipitation phase is 0.8%～0.9%, the precipitation strengthening increments may reach 200MPa. Typically, only around 50% of vanadium can be precipitated. First, more amount of precipitation should be obtained (the easiest way is to facilitate precipitation of vanadium by using the nitrogen in the steel). Then, through process control finely precipitated phase particles should be obtained as much as possible.

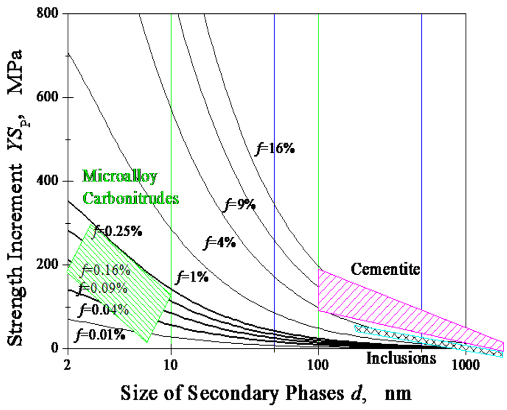

Figure 3 Relationship between Precipitation Strengthening Increment, Precipitation Phase Size and Volume Fraction [7]

(2)Intragranular ferrite nucleation

V(C, N) can be precipitated from manganese sulfide or titanium oxide particles in the steel. Intragranular ferrite (IGF) can be generated and the ferrite grain can be significantly refined by taking particles of vanadium carbonitride as the ferrite nucleation sites. For low carbon steel, manganese sulfide or titanium oxide in the steel can promote formation of intragranular ferrite in the matrix. Moreover, refined microstructure of welding heat affected areas can be formed through intragranular ferrite (ferrite lath). For medium-carbon ferrite-pearlite steel, the formation of intragranular ferrite can clearly separate the original austenite grain, increase volume fraction of ferrite in the steel and improve the toughness of steel.

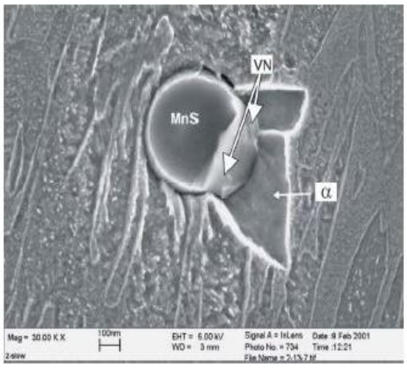

Figure 4 Vanadium Nitride Promotes the Formation of Intragranular Ferrite [S. Zajac]

(3)Improvement of the delayed fracture resistance of steel can be achieved through precipitation hydrogen traps[8] of vanadium carbide, improvement of tempering resistance and softening performance or grain boundary strengthening and austenite grain refinement when heating[9]. With strength increasing until 1 200MPa, the phenomenon of delayed fracture will appear due to the increased sensitivity of hydrogen in steel, thus further enhancement of strength of this type of steel is restricted. Therefore the problem of delayed fracture must be solved to obtain higher strength. The idea of the solution should is focused on reduction of the steel sensitivity to the presence of hydrogen, that is, a certain amount of hydrogen in steel does not affect performance. Segregation of hydrogen on the micro interface (grain boundary, etc.) should be prevented so that the hydrogen is fixed to the defects in the crystal, such as precipitation phase. Theoretically, any precipitation phase can absorb hydrogen. For example cementite precipitated on the grain boundary can trap hydrogen, but it can easily lead to intergranular fracture. If it is dispersed and finely precipitated, it can capture more hydrogen. However, it is tough to control the cementite in the grain. Vanadium carbide is a good choice. Hydrogen trapping activation energy of vanadium carbide is small（26～36kJ/mol） and its intragranular fine distribution and dispersion can be easily controlled. In addition its great anti-tempering softening ability (to avoid the formation of coarse cementite on grain boundary), and grain refinement (larger grain boundary volume fraction) are favorable to improve resistance to delayed fracture. Integrated control of grain boundary control (grain boundary), structure control (structure) and hydrogen trap ([H] trapping) constitute the major factors to GST technology.

The research in this area has been a hot issue in recent years. Based on the research, Japan, China, South Korea and so on have developed technologies of 1200～1600MPa delayed fracture resistant martensitic steel, which is applied in the high strength bolts, providing basis for research and development of other high strength steels. With increasing strength of high-strength and low-alloyed steel, X120 steel for oil and gas transmission pipes has been produced, which is developed towards a higher level. The strength of steel plate for engineering machinery is moving towards 1 180MPa. The strength of steel for construction has come to 980MPa, potentially toward higher strength; there is an urgent demand for oil well pipes of 150ksi and 170ksi used for deep and ultra-deep mining where the hardness of the wear-resistant steel ranges from HB360～HB550 and the strength of alloy structural steel exceeds 1200MPa. Moreover the delayed fracture resistance technology (GST technology) focused on controlling precipitation of vanadium carbide will lay a foundation for upgrading steels.

3 The application of vanadium in steels

As is all known, due to the solution and precipitation characteristics of vanadium in the steel, among the alloying elements of steel, vanadium is the one used widely and in large quantities. It is a major precipitation strengthening element in the high-strength low-alloy structural steel (15MnVN), micro-alloy non-quenched and tempered steel (49MnVS3) and the secondary hardening element in hot die steel (H13) and cold work die steel (D2) as well as the major precipitation strengthening element in the heat treatment of martensitic steel capable of improving the properties against spring-reduction…. It is one of the most effective elements in the low-alloyed steel and alloyed steel.

Vanadium, as a micro-alloying element can be added into the following types of steel like high-strength hot rolled ribbed rebars for construction, high-strength low-alloyed steel plate of medium thickness, pipeline steel, sheet steel, microalloyed forging steels, spring steel, bolts steel; Vanadium, as an alloying element can be added into the die steel, high speed steel, ultra-high strength steel, bearing steel and martensitic heat-resistant steel.

It can be seen from Figure 1, the solubility product of vanadium nitride in the austenite is lower than that of vanadium carbide by two orders of magnitude. During hot rolling of steel, the phase induced by strain is almost pure vanadium nitride. Nitrogen in vanadium steel plays an important role, especially in increase of precipitation kinetics. A higher content of nitrogen is required to make VN more effective. Under normal circumstances, it can work when the nitrogen content in austenite is greater than 0.015%. When the density of vanadium carbonitride is low and the mass fraction is same, then a bigger volume fraction is required to refine the grain.

In table 1 the types and grades of commonly used vanadium micro-alloyed and alloyed steels are listed. In general, only the tool and die steel, bearing steel, heat-resistant steel contain high content of vanadium, and other types of steel contain only trace amounts of vanadium. See paper [10] for more details of the applications of vanadium in steel. Hot rolled ribbed steel and low alloyed steel are used widely and in huge amount, in which vanadium is added as a micro-alloying element. It plays a role in precipitation strengthening and change in properties accordingly. Particular focus should be given to effective applications of vanadium in these steels. Besides the mechanical properties such as strength, attention should be paid to improvement of machining property and service performance. Moreover, efforts should be made to use vanadium together with other alloying elements so as to achieve both performance improvement and cost effectiveness.

3.1 Application of vanadium in high strength seismic resistant rebars

At present, micro-alloying technologies (and temp coring treatment and grain refinement technology) are widely used in the production of HRB400, HRB500 hot-rolled ribbed rebars in which vanadium micro-alloying process is prevailing. Precipitation of vanadium plays a role in grain refinement and precipitation strengthening in steel and is a proven micro-alloying technology. In recent years, in addition to high strength, better seismic performance of rebars has received wide attention.

From the perspective of steel conservation and improvement of seismic resistant behavior, experts suggest that micro-alloyed rebars of 400MPa grade and above be widely used [12]. The seismic resistant behavior of rebars focused on the high-strain low-cycle fatigue resistance, includes high-strain and low-cycle fatigue properties and cyclic toughness, strain aging sensitivity, cold brittleness, welding performance and strength-plasticity balance. The micro-alloying elements in the steel can react with carbon, nitrogen atoms to prevent them from gathering near the dislocation line, thus the strain aging is inhibited. Addition of vanadium can improve the performance of high strain and low cycle fatigue and cyclic toughness. In this way the seismic performance of rebars is improved. There are still some discussions about the seismic performance of rebars. The basic idea of Cai Qigong is that high strength for rebars is not required in the traditional seismic design in which "strong shear weak bending" and "plastic hinge" are used to absorb seismic energy. Instead a higher uniform plasticity is required to prevent rebars on the critical position from prematurely forming necking deformation, resulting in concentrated deformation and fracturing, ending up with loss of seismic capacity of the "plastic hinge"[13].

Table 1 Typical applications of vanadium in steels (commonly used vanadium steel and vanadium content) [11]

No	Types of Steel	Typical grades	Standard	Ranges of Vanadium Content/%
1	hot rolled ribbed rebar	20MnSiV（irregular steel code）	GB 1499.2-2007	0.02～0.10
2	high-strength low-alloyed structural steel	Q345/Q390/Q420/Q460/Q500/Q550/Q620/Q690	GB/T 1591-2008	≤0.20
3	alloyed structural steel	35CrMoV	GB/T 3077-1999	0.10～0.20
4	non-quenched mechanical structural steel	F49MnVS	GB/T 15712-2009	0.08～0.15
5	spring steel	50CrV4	DIN 17221-1988	0.10～0.25
6	bearing steel	M50（8Cr4Mo4V）	AMS 6491	0.90～1.10
7	hot work die steel	H13（4Cr5MoSiV1）	ASTM A681-1999	0.80～1.20
8	cold work die steel	D2（Cr12MoV）	ASTM A681-1999	0.50～1.10
9	high-speed steel	M2（W6Mo5Cr4V2）	ASTM A600-1999	1.75～2.20
10	ferritic heat resistant steel	15Cr11MoV	GB/T 1221-2008	0.25～0.40
11	martensitic stainless steel	90Cr18MoV	GB/T 1220-2008	0.07～0.12
12	ultra-high strength steel	300M（42Si2CrNi2MoV）	AMS 6257	0.05(min)

Studies show that vanadium nitride is more advantageous than FeV to achieve strengthening increments because increase in nitrogen during V-N micro-alloying promotes the disperse precipitation of vanadium carbonitride in the steel so that the strength is increased significantly. Data shows that with the same content of vanadium, the vanadium nitride microalloying scheme can achieve strength higher than FeV by 100MPa . The study by Yang Caifu shows that[14] in the low nitrogen vanadium steel (FeV micro-allying) most of vanadium is resolved in the ferrite matrix at the ratio of 56%, with only 36% of vanadium forming vanadium carbonitride; in the high nitrogen vanadium steel (vanadium nitride micro-allying) 70% of the vanadium is precipitated to form vanadium carbonitride with only about 20% of the vanadium resolved in the matrix. The increase of nitrogen in the steel reduces the grain size of vanadium carbonitride and significantly increases the volume fraction of precipitates.

Vanadium micro-alloying is an effective way for production of low-carbon and high strength rebars with good weldability. V-N microalloying used in the steel can significantly reduce the carbon content in steel so that the yield strength of rebars can reach up to 500MPa with good weldability. Panzhihua Steel and Chengde Steel in China has developed the V-N alloy production technology for production of high-strength vanadium micro-alloyed steel, which is consistent with the technological development world wide.

China Steel Industry Association and the construction industry have been committed for years to production and promotion of high-strength rebars and have played a critical role in upgrading rebars which are widely and densely used[15]. The high-strength rebars produced with vanadium micro-alloying technology has good overall performance and obvious advantages[16,17]: high strength, yield strength not less than 400 MPa, tensile strength not less than 570 MPa; carbon equivalent not more than 0.50%, good welding performance with adaptability to various welding methods; yield ratio (the ratio of tensile strength to yield strength) not less than 1.25; sound balance between strength and plasticity, bending performance; excellent high-strain low-cycle fatigue properties, lower strain aging sensitivity and brittle transition temperature and good seismic performance.

Vanadium micro-alloyed high strength rebars have been widely used in construction, dams, tunnels, bridges and other engineering projects. Application of vanadium micro-alloyed high-strength hot rolled ribbed rebars of grade 3 can enhance the engineering quality and save steel by 10%～20%. As rebars are widely used in great quantities, the high-strength rebars have significant energy saving and emission cutting effects.

3.2 Micro-alloyed non-quenched and tempered steel

The idea of the first micro-alloyed non-quenched and tempered steel in the world in 1972 was derived from micro-alloying principle of low-carbon steel, mainly the principle of strengthening precipitates. The strength of hot rolled or hot forged steel is significantly lower than that of steel under the quenched and tempered condition. The differences in strength can be compensated by the strengthened precipitation of micro-alloying element. At the same time energy conservation, parts deformation reduction, uniformity increase and acceptability of parts are achieved. According to statistics, China's annual output of microalloyed non-quenched and tempered steel amounts to 800 thousand tons or so most of which are vanadium micro-alloyed quenched and tempered steel. The steel is mainly used in hot rolled bars or hot forged parts with less room for deformation control and the expected microstructure performance can be obtained only by controlled cooling. As the precipitation temperature of vanadium carbonitride is at the lower range, the volume fraction and size of precipitates are easy to control by the cooling rate. Therefore, vanadium is mostly used in the microalloyed non-quenched and tempered steel at present. Niobium and titanium are also good options for non-quenched and tempered steel. In the future, the application of vanadium depends on the cost of added elements. People have begun to reduce the content of vanadium or choose the non-quenched and tempered steel technology without addition of vanadium.

3.3 High strength automotive sheet steel

In the hot-rolled finished steel plate, vanadium with the outstanding precipitation strengthening effect is widely used. The precipitation phase of vanadium during the annealing process may grow and reduce the precipitation strengthening effect, therefore vanadium is seldom used in the cold-rolled steel sheet annealing. With the increased strength of the steel sheet, a good plasticity is required. Through precipitation strengthening (the need to control the nitrogen content in steel and reduce the coarsening trend of precipitates), the target of improving the uniform plastic strain and strength can be achieved at the same time, such as: TRIP steel[18], high-strength steel and other high plasticity steel. When the strength of the steel sheet is more than 1000MPa, the cold stamping and forming will be susceptible to the problems like the springback of parts and greater mold loss. Then hot forming appears as an option. Now 22MnB5 steel is almost the only hot formed steel with the tensile strength of 1500MPa. It has excellent hardenability and economic performance which makes it a successful automotive sheet steel. In the future precipitation strengthening effect may be used for the high strength hot formed steel rather than just relying on raising carbon content to increase strength and help improve the ductility and weldability.

3.4 Control of hot work die steel alloy uniformity

Vanadium in the high carbon and medium carbon forms an initial carbide with other alloying elements such as chromium, tungsten, molybdenum, etc. during solidification. These carbides are stable at high temperature and remain partially insoluble in the subsequent forging and heat treatment. They are the basis for wear resistance and high hardness of tool and die steel. In addition to the initial carbide, some vanadium is also dissolved in the matrix for increasing tool and die steel hardenability and toughness.

Vanadium is precipitated in the fine secondary vanadium carbide to further improve the wear resistance.

Most vanadium in the steel is used as micro-alloying elements. However higher content of vanadium in the mold steel and bearing steel can be used as alloying elements. When the vanadium content is over 0.5% in steel such as H13, there will be dendritic segregation of vanadium during solidification, which affects the service performance of the steel. Ma Dangcan studied the technology of H13 steel where the segregation of alloying elements is reduced to achieve the effect of anisotropy of the mold steel[19]. Through controlling the speed of remelting eletroslag, high-temperature diffusion annealing of billets, post-forging refinement and other technologies, segregation of alloying elements in H13 steel like molybdenum, chromium and vanadium is greatly reduced and the anisotropy is substantially improved, thus hot worked mold steel of premium quality is developed for the Northeast Special Steel.

4 Conclusion

In the steel, vanadium is an effective micro-alloying and alloying element. Vanadium mainly strengthens precipitation in the steel. More attention should be paid to the balance between vanadium and other alloying elements for maximizing the effect of vanadium. For example nitrogen is used to promote precipitation of more vanadium in the steel for more performance improvement and lower cost. In addition to improvement of strength through controlling precipitation phases, more advantages of vanadium precipitated from the steel should be identified, such as controlling the hydrogen trap to improve delayed fracture resistance for improvement of performances of steels. In this way vanadium resources can be rationally used so that it can play a greater role in steels.

Acknowledgements

Particular thanks will go to Mr. Yang Xiongfei of Panzhihua Iron and Steel Research Institute for providing useful information and Yong Qi-long, professor of Central Iron and Steel Research Institute for providing meaningful research results.

References

[1] toker, The Metallurgy of Vanadium, John Wiley & Son, Inc., 1958.

[2] P. S. Mitchell, The Use of Vanadium, VANITEC Publications, 2001.

[3] J.H.Woodhead, The Physical Metallurgy of Vanadium Steels, Vanadium in High Strength Steel, 3-10.

[4] Yong Qilong, Second Phase of Iron and Steel Material, Metallurgical Industry Press, Beijing 2006.

[5] Yong Qilong, Study on Roles of vanadium in the steel and mechanism, report of Central Iron and Steel Research Institute, 2010.

[6] C. Bain, Functions of the Alloying elements in Steel, ASM 1939, Cleveland, USA, 256.

[7] Yong Qilong,The Control of Second Phase, report of Central Iron and Steel Research Institute, 2010.

[8] H.Asahi, D.Hirakami and S.Yamasaki, Hydrogen Trapping Behavior in Vanadium added Steel, ISIJ International, 43 (2003) 4, 527–533.

[9] Hui Weijun, Weng Yuqing, Dong Han, High Strength

Steel for Fastening Pieces, Metallurgical Industry Press, Beijing 2009, 79-109.

[10] D.T.Llewellyn, Vanadium in steels, Ironmaking and Steelmaking, 23(1996)5, 397-405.

[11] Lin Huiguo, Lin Gang, Wu Jingwen, Pocket Manual of World Steel Types (third edition)，Mechanical Industry Press, Beijing 2007.

[12] Suggestion made by experts like Zhujing, Ganyong, Tu Mingjing, Gong Shihong, Sheng Guangmin about popularization of Micro-alloying high strength rebars and seismic resistant rebars, 2009.

[13] Cai Qigong, Gan Yong, Zhu Jing, Symposium of Communication Regarding the Seismic resistant Performance, 2009.

[14] Yang Caifu, Research, Production and Application of High Strength Rebars, International Symposium 2003 on the Research and Application of High Strength Reinforcing Bar, Hangzhou, China, 124-132.

[15] Xu Yin, Production, and Applications of 400MPa Grade Hot Rolled Ribbed Bars, International Symposium 2003 on the Research and Application of High Strength Reinforcing Bar, Hangzhou, China, 62-67.

[16] Vanadium Steel for Reinforcing Bars, VANITEC Publications.

[17] A.M.Sage, Effect of Vanadium, Nitrogen, Aluminum on the Mechanical Properties of Reinforcing Bar Steel, Metal Technology, (1976)2, 65-70.

[18] F.Perrard and C.Scott, Vanadium Precipitation During Intercritical Annealing in Cold Rolled TRIP Steels, ISIJ International, 47 (2007) 8, 1168–1177.

[19] Ma Dangcan，Study on Anisotropy Behaviors of H13 Hot Working Model Steel, the Ph.D. doctoral theses of the Central Iron and Steel Institute.