STUDY AND APPLICATION ON STEELMAKING PROCESS OF Nb-MICROALLOYED ULTRA-PURIFIED FERRITE STAINLESS STEELS[1]

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Abstract

Impacts of Nb on the properties of ultra-purified ferrite stainless steel and the development of stainless steels in China have been introduced and the behavior of Nb in the steelmaking process as well as the use technology of Nb in TISCO has been analyzed. The existing problems and influences, such as alloy adding methods and times, the yield of Nb, have been studied to enhance the development of Nb alloy and reduce the production cost.

Keywords: Ultra-purified; Ferrite stainless steel; Nb yield; Steelmaking process.

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1 INTRODUCTION

As one of the micro alloying elements, Nb can be used in ferrite stainless steels and austenitic stainless steels. It is important to stabilize the content of Nb, increase the yield and avoid certain quality problems caused by Nb through the study of the behavior and process of Nb during steelmaking process.

1.1 Classification of Stainless Steel

Stainless steels according to their microstructures can be divided into austenitic stainless steels, ferrite stainless steels, martensitic stainless steels, duplex stainless steels and martensite precipitation-hardening stainless steels.(1) The ferrite stainless steels are Ni free or containing a small amount of Ni. Therefore, they represent typical economy stainless steels. In addition to corrosion resistance, ferrite stainless steels also show strong resistance to stress corrosion, pitting corrosion and crevice corrosion.(2)

Ferrite stainless steels can be divided into ordinary ferrite stainless steels, ultra-purified ferrite stainless steels and super ferrite stainless steels,(3)whose Cr are normally 11~15%, 16~20% and 21~30%,respectively.Typical ferrite stainless steel classification and representative grades are shown in Table 1. As one of the micro alloying elements, Nb is used in ultra-purified ferrite stainless steels and super ferrite stainless steels to further improve the corrosion resistance and other properties.

Table 1. Typical ferrite stainless steel classification and representative type

	Ordinary ferrite stainless steels	Ultra-purified ferrite stainless steels	Super ferrite stainless steels
Typical grades	409, 410, 430	436L, 439, 441, 444	446, 447
Stabilizing elements	Nothing or Ti	Nb, Ti	Nb, Ti

2 IMPACT OF Nb ON THE ULTRA-PURIFIED FERRITE STAINLESS PROPERTIES

2.1 Main Factors in the Properties of Ultra-purified Ferrite Stainless Steels

Main performance indicators for ultra-purified ferrite stainless steels include corrosion resistance, formability, welding performance, etc. In addition to the main alloy component Cr and others such as, Ni and Mo, C + N content in the steel plays a very important role in the properties. Fig.1 shows the relationship between C+N content of $Cr_{21}Mo_3$ and corrosion resistant properties in boiling 65% HNO3.(1) The graph indicates that the corrosion rate of steel increases with increasing C+N content, especially above the certain content, the corrosion rate has increased dramatically. The main season is that more $Cr_{23}(C,N)_6$ precipitate around grain boundaries with increasing C+N content, which causes the formation of Cr depletion zone and reduces steel corrosion resistant properties.

2.2 The Main Function of Nb in Ultra-purified Ferrite Stainless Steels

In order to alleviate the impact of C and N on ferrite stainless steel corrosion resistance performance, two methods are adopted: First, using various refining process to reduce the content of C and N in steels; Second, adding Stabilizing elements for C and N (such as Nb or Ti)(5) to avoid the combination of C(N) and Cr, stabilizing methods in real production process by only Nb or Ti or by both Nb and Ti are acceptable.[(6)]

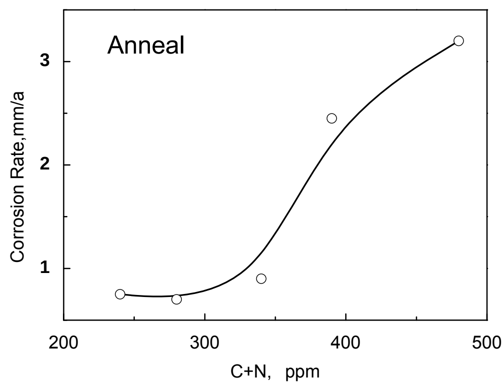

Figure 1. The relationship between C+N content of $Cr_{21}Mo_3$ and corrosion resistant properties in boiling 65% HNO_3.

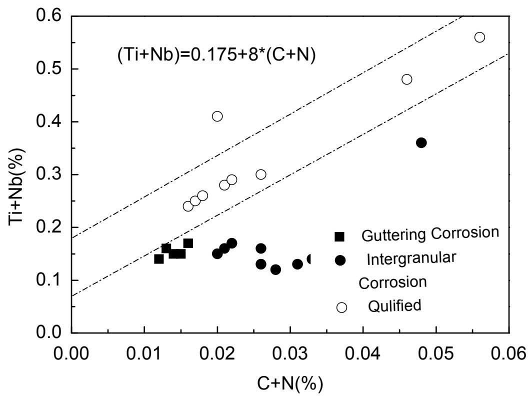

Figure 2. The impact of Ti and Nb on the intergranular corrosion.

Nb and Ti which are added to ultra-purified ferrite stainless steels can refine grain and improve welding property, strength and resistance to high temperature oxidation performance.

2.2.1 Improvement of the steel corrosion resistant property by Nb

Research shows that C and N in the solubility of ferrite is very low,[(7)] even by way of rapid cooling after heat treatment it is also difficult to prevent chromium carbide and nitride formation. In the ultra-purified ferrite stainless steels, the forming of $Cr_{23}(C+N)_6$ can be restrained by adding Nb and Ti which can form compounds such as (Nb,Ti)(C,N). As a result, the corrosion resistance properties of the steel are improved. Fig.2 shows that adding Nb or Ti can improve the corrosion resistance of the ultra-purified ferrite stainless steels.[(1)]

2.2.2 The impact on the steel mechanical properties by Nb

Fig.3 shows the impact on mechanical properties of ultra-purified ferrite stainless steel at high temperatures by adding Nb.[(8)] It is seen that yield strength at high temperature increases with increasing Nb, this kind of steel can be used at higher temperature for a long lifetime, such as in auto exhausting system where temperature can reach 900°C.

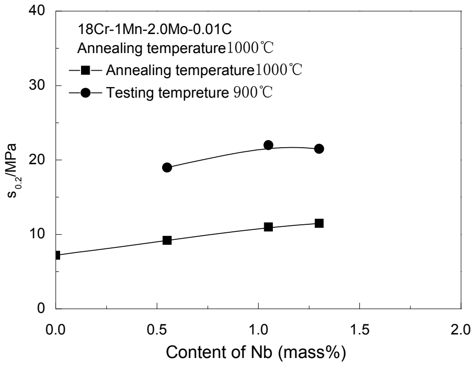

Figure 3. The relationship between Nb content and strength stainless steel at 900°C and 1000°C.

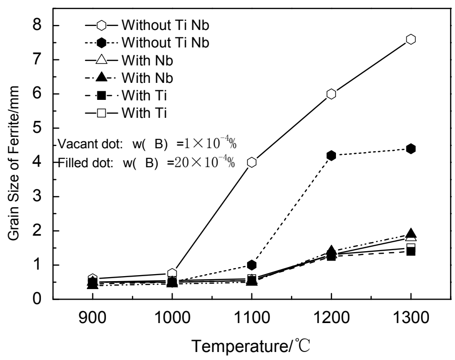

Figure 4. The impact on grain size of ferrite stainless steel by adding microelements of ferrite.

2.2.3 The impact on the steel welding property by Nb

By adding Nb, elements diffusion can be hindered under high temperature in ferrite stainless steels, and recrystallization temperature increases. Thus, the refining grain effect can be obtained and the plasticity after welding will be improved. Fig.4 shows the impact on grain size of ferrite stainless steels by adding micro alloying elements(9) and the grains are refined obviously.

3 STEELMAKING TECHNOLOGY OF ULTRA-PURIFIED FERRITE STAINLESS STEEL WITH Nb

3.1 The Development of Stainless Steels in China

Stainless steel in China started late, just in the 21st century stainless steel get the high speed development, the products cover the main varieties, production of stainless steel has been improved significantly. China has become the world's largest stainless steel producer, stainless steel production accounted for 40% of global output, the production of stainless steels as well as ferrite stainless steels since 2001 in China can be seen in Fig.5. With the striking features of resources saving, lower cost and resistance to stress corrosion, production of ferrite stainless steels accounted for the proportion of stainless steels increases steadily.

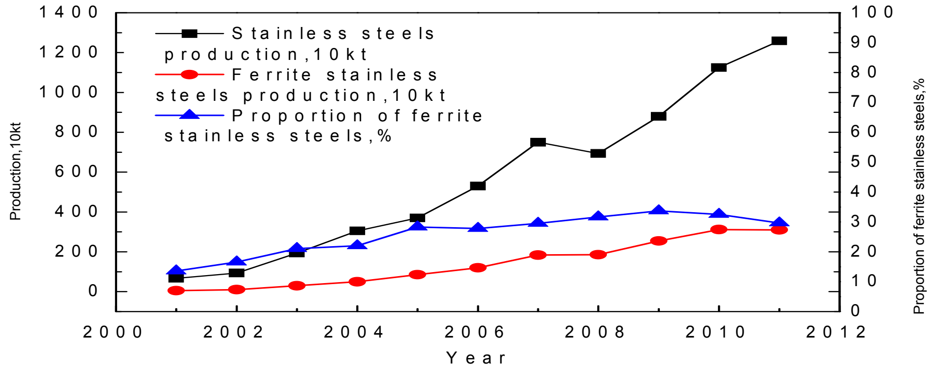

Figure 5. The production of stainless steels and ferrite types in China since 2011.

Ferrite stainless steels, especially ultra-purified ferrite stainless steels, have a high requirement of the purity of C and N. Small cracks tend to appear in slabs, and it is easy to bond on the surface of hot strips. Also the heat treatment conditions are strict. All above led to the situation that at present, only several large scale stainless steel makers (Table 2) in China such as TISCO, BAO STEEL, etc. mastered the key technology and have the ability of mass production.

Table 2. Typical steelmaking process of ultra-purified ferrite stainless steel in China

Enterprises	Technological process	Heat size	Max. Slab size	Start Year	Typical grades
TISCO	DEP→K-OBM-S→VOD→LF→CC	80t	1250mm	2002	Ultra-purified
	BOF /EAF→AOD→LF→CC	180t	2050mm	2006	Common
	BOF /EAF→AOD→VOD→LF→CC	180t	2050mm	2012	Ultra-purified
BAO STEEL	DEP→EAF→AOD→VOD→LF→CC	120t	1500mm	2002	Ultra-purified
JISCO	BOF /EAF→AOD→LF→CC	100t	1600mm	2006	Common

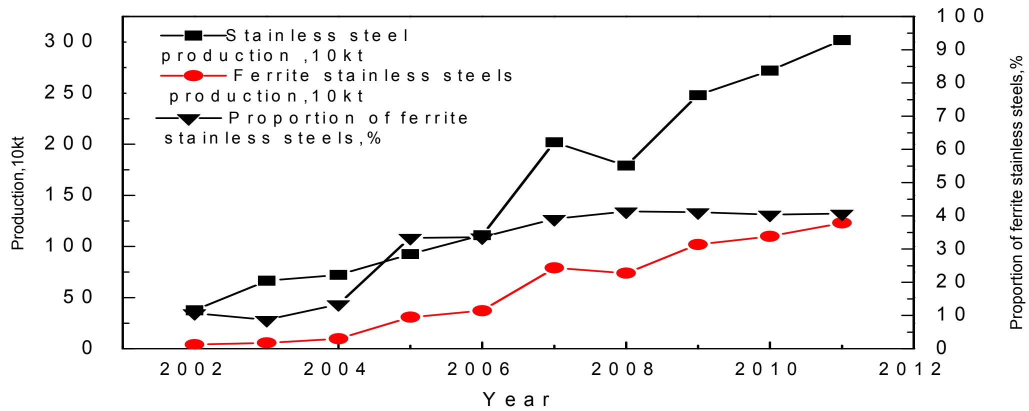

Figure 6. The proportion of ferrite stainless steels and stainless steels in TISCO since 2002.

3.2 Behavior of Nb in the Steelmaking Process

Because of more steelmaking steps, complex technological processes and higher price of ferroniobium, the behavior of Nb in the steelmaking process such as oxidbility, and dissolving speed, adding methods and time of the FeNb alloy should be studied so that the yield of Nb will increase.
Because of the helpful effect caused by Nb in ferrite stainless steels, a number of Nb is added and the content of Nb can be determined according to the application conditions and performance requirements of the steel. The content of Nb can be determined according to the application conditions and performance requirements of the steel. The main principles are as follows:

1. Nb+Ti≥0.08+8（C+N）as improving the corrosion resistance performance;
2. Waste products tend to appear under stabilizing only by Ti and the cost will increase under stabilizing only by Nb. Therefore it is necessary to control the proportion of Nb and Ti according to the controlling level of C+N during steelmaking.
3. In order to further improve the heat-resistant property of ultra-purified ferrite steel, amount of Nb is necessary in the steel, such as the grades of 429 and 441 which is designed for automotive exhaust system at high temperatures contain Nb between 0.40 to 0.60%.

3.2.1 Nb oxidization

Nb, which is an oxidation element, can combine with oxygen to generate oxide. Therefore Nb should be added in reducing conditions to achieve a higher yield. Fig. 7 shows the free energy of forming oxide. It can be seen that Nb is hard to be oxidized compared with Si and Al, as a result the Nb yield will increase with higher Si and Al in the steel.

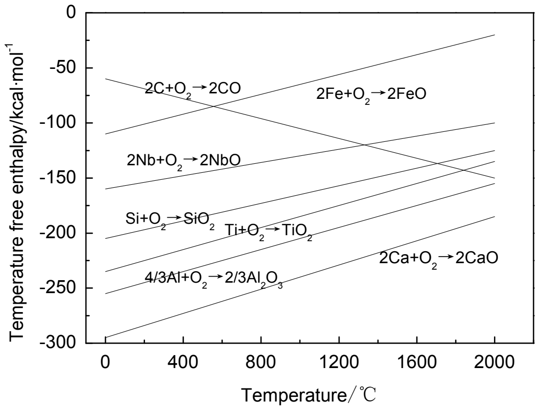

Figure 7. Free energy of the formation of the oxides with Nb.

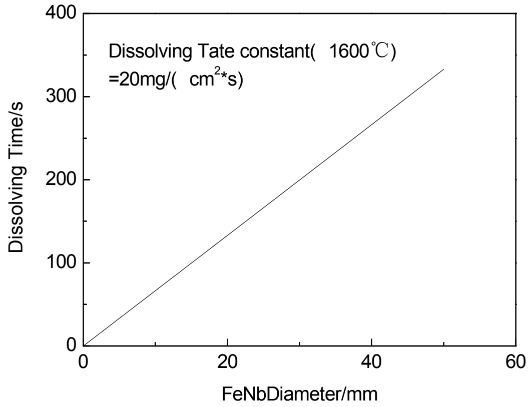

Figure 8. The relationship between particle size and dissolving time.

3.2.2 Melting speed of ferroniobium in the liquid steel

Generally ferroniobium with a 66.5% of Nb is easily crapping. The alloy with a particle size between 2 to 80 mm is the most popular type used in metallurgical production process,[10]. The melting temperature is 1580 ~ 1600^{o}C and it will take certain time to melt. Fig. 8 shows the relationship between different size of ferroniobium and dissolution time. In practical production the mixing time after ferroniobium addition can be determined by the heat size and the particle size of ferroniobium.

3.2.3 The main adding method of ferroniobium

Ferroniobium can be added during tapping, ladle refining and casting process. Adding the alloy during ladle refining process is the most common way.
There are four existence forms of ferroniobium: dust, in ladle slag, on slags shell and dissolved in the liquid steels, as shown in Fig. 9.[10] It is effective only when the alloy entered into liquid steel, and other forms will reduce Nb yield. So in order to improve the yield of Nb, it is important to optimize the adding conditions or improve adding technology to reduce all the loss factors to the minimum level.

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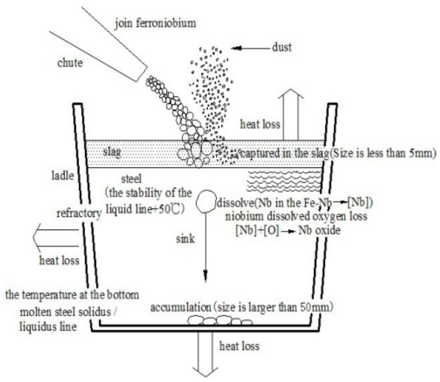

Figure 9. The existence forms of Nb during smelting process.

3.2.4 The increase of Nb yield

According to the characteristics of ferroniobium, different adding tests of Nb in different processes were carried out to improve and stabilize the Nb yield in TISCO. The chart shows that Nb will be oxidized if it is added into the ladle during K-OBM-S tapping and the final yield is 83%. The number will reach 95% if ferroniobium is added after reduction in VOD. The highest Nb yield can hit 100% if added during LF refining process (Fig.10).

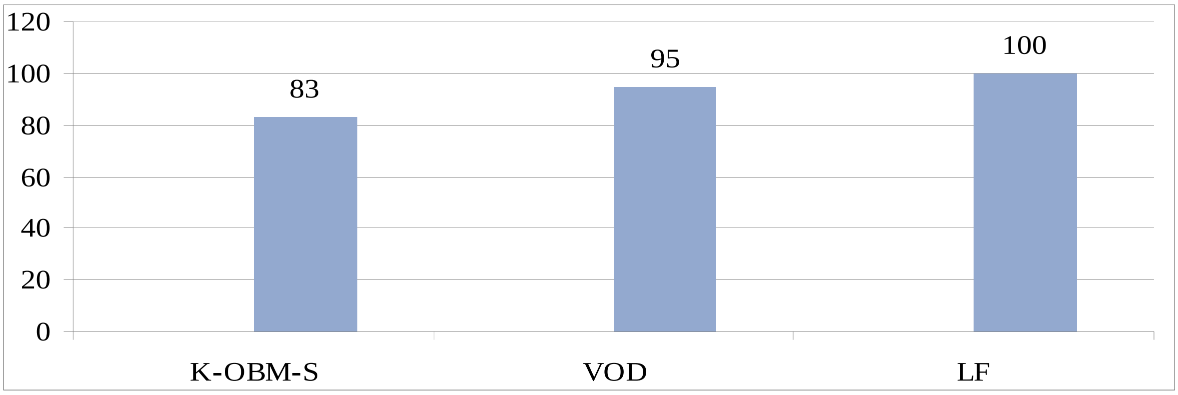

Figure 10. The impact on Nb yield of ferroniobium adding time (%).

4 THE APPLICATION SITUATION OF Nb IN ULTRA-PURIFIED FERRITE STAINLESS STEEL IN TISCO

Since 2004, the manufacture of ultra-purified ferrite stainless steel developed from nothing and the grades increased from a single species to series. Now TISCO has a capacity of 100 thousand and a market share of more than 65% in China. The production of ultra-purified ferrite with Nb and usage of ferroniobium in TISCO since 2007 are shown in Fig.11.

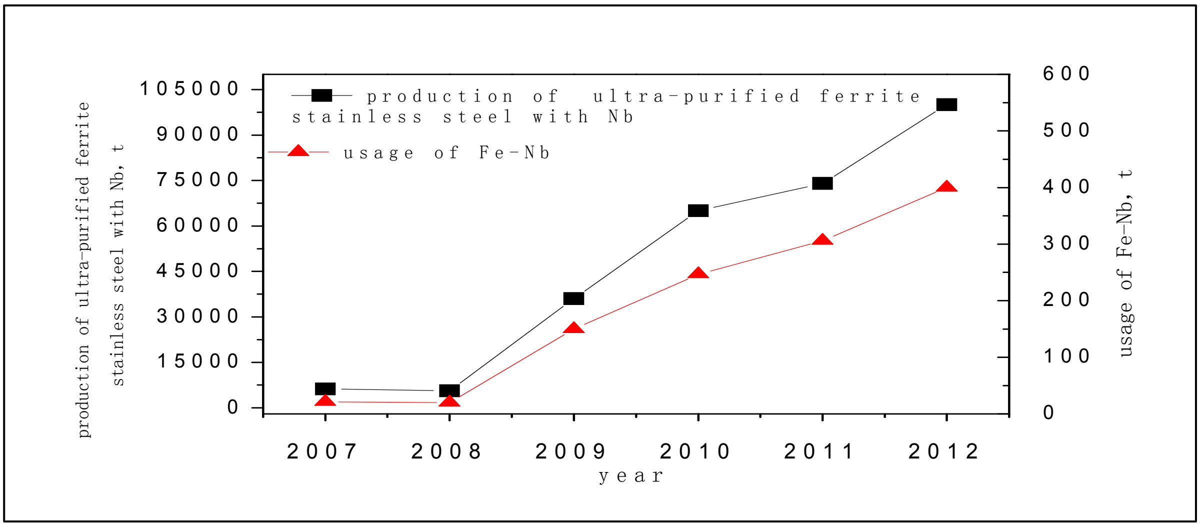

Figure 11. The production of ultra-purified ferrite with Nb and usage of ferroniobium in TISCO.

Ultra-purified ferrite stainless steels, which are produced by TISCO cover all varieties and exhibit wide application, have been applied in the areas of elevators, decoration, automotive exhaust pipe, decoration and coinage, and become the most competitive brand and have broad market prospects. Main varieties and application can be seen in Table 3.

Table 3. Typical ultra-purified ferrite stainless steel grades and composition

type	grade	content：（%）				application
		Cr	Mo	Nb	Ti	
21%Cr	TTS443M	20.8	—	0.15~0.22	0.12~0.18	elevator, decoration
17%Cr with Mo	SUS444, 436L	17.4~18.0	0.96~1.89	0.12~0.24	0.14~0.18	water tank, solar energy,
17 %Cr	439M, 441, TTS429	15.5~18.0	—	0.20~0.60	0.10~0.18	automotive exhaust pipe
High Cr with Mo	TTS445, TTS446	21.5~25	0.8~1.8	0.20~0.30	0.10~0.2	solar energy, electric water heater

5 Problems of Nb in ultra-purified ferrite stainless steels production

It is benefit to steel properties when Nb is applied in the ultra-purified ferrite stainless steels, but there are still some problems during production process, mainly small transverse crack defects (see Fig. 12) exiting on the surface of slabs occasionally.

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Figure 12. Transverse crack of slabs.

Based on transverse crack defect analysis, it is considered that, because of the higher brittleness in casting microstructure of ultra-purified ferrite stainless steels after adding Nb, transverse crack defects tends to appear during slab cast bending, straightening and cooling. Therefore it is necessary to control the caster equipment precision, cooling strength, bending and straightening temperature, storage time and slab grinding method, etc. to prevent small transverse crack formation.

6 CONCLUSIONS

Through the study of Nb and ferroniobium, the steelmaking process of ultra-purified ferrite stainless steels with Nb is determined; the quality of the products has been improved and the foundation is laid for mass production of ultra-purified ferrite stainless steels.
With its good comprehensive performance, ultra-purified ferrite stainless steels with Nb have been gradually accepted and applied to automotives, household appliances, decoration, solar energy heaters and many other fields, and the production increases year by year.

REFERENCES

1 Lu Shiying, Zhang Tingkai. Stainless Steel[M]. Bei Jing：Atomic Energy Press.1995 1~10.

2 Zhang Juhua, Wang Deying，Xu Yourong. Ultra pure ferritic stainless steel in chloride solution of passive film formed on XPS and AES [J]. Journal of Shanghai university of science and technology ,2001 24（4）35~36.

3 You Xiangmi, Jiang Zhouhua, Li Huabing.Development and Application of Super Ferrite Stainless Steel [J]. China Metallurgy 2006 16（11） 2~3.

4 Wei Ming, Wu Dianjie,Zhang Jiaqiu. Production and application of ultra-purified ferrite stainless steel [J].Casting engineering, 2012 (4), 1~2.

5 You Xiangmi, Jiang Zhouhua, Li Huabing. Progress in Grades and Refining Technology of Ultra Purity Ferritic Stainless Steels [J]. Special Steel, 2006, 27（5）1~3.

6 Liu Tao, Cao, Zhao Baolu. The application of Nb in stainless steel [J]. Material review, 2008 3(1)：1~3.

7 Lu Shiying. Super Stainless steel and corrosion resistance alloy with high Nickel [M].Beijing. Chemical Industry Press，2011 4~6.

8 Sun Quanshe,Xu Chun, Zhangxin. The research on the impact of Nb on the recrystallization and mechanical properties of 16%Cr ferrite stainless steel with super low C and N [J].Shanghai Metal, 2011, 33(6)：3~5.

9 Meng Fanmao, Fu Junyan. Modern niobium steel strip material [M].Beijing：Metallurgical Industry Press, 2006, 10~14.

10 Hiroshi Takechi. How to improve the performance of steel with niobium - containing niobium steel production [M].Beijing：Metallurgical Industry Press，2007.