

PREPARATION OF HIGH QUALITY FERROVANADIUM NITRIDE BY CARBOTHERMAL REDUCTION NITRIDATION PROCESS

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Abstract

High quality ferrovanadium nitride was prepared successfully by carbothermal reduction nitridation process by using V_2O_5 and Fe as the raw materials. The effects of reaction temperature and C/O molar ratio (content of O is defined as the oxygen in V_2O_5) on the quality of ferrovanadium nitride were investigated in detail. It was demonstrated that C/O molar ratio had a great influence on the residue carbon, as well as the nitrogen content in the final products. It was found that the nitrogen content of the final product achieved 11.52% when the C/O molar ratio was 90% of the stoichiometric value. However, the nitrogen contents of the final products decreased with the further increase of C/O molar ratio. For the temperature higher than 1773 K, Fe became liquid phase and surrounded the solid V(C, N, O) particles tightly. The formation of liquid Fe was beneficial for the further removal of oxygen atoms left in the V(C, N, O) lattice, since it provided a liquid tunnel for carbon diffusion which greatly enhanced the reaction kinetics. From the results of X-ray diffraction (XRD) and thermodynamic calculations, phase evolution sequence of V_2O_5 can be obtained as: $V_2O_5 \rightarrow VO_2 \rightarrow V_2O_3 \rightarrow V(C, N, O)$. Moreover, the kinetic process from V_2O_3 to VN was studied and the results shown that the reaction rate can be described by Jander diffusion model with the extracted activation energy of 188.173 kJ/mol.

Keywords: Ferrovanadium nitride; High-strength low-alloy steel; V_2O_5 ; Kinetics

1. Introduction

High-strength low-alloy (HSLA) steel has emerged as a promising advanced material owing to its superior performance such as high strength, high toughness, good corrosion resistance and good abrasive resistance. During the recent years, HSLA steel has been widely used in the auto industry, ship building, railroad and pipeline manufacture. The high performance of HSLA steel is resulted from micro-alloying with carbide- and nitride-forming metals (Al, Ti, V, Nb, etc.) [1-4]. Among them, HSLA steel micro-alloyed with vanadium and nitrogen is of particular economic importance. On the process of cooling and heat treatment, vanadium nitride formed in the steel has the functions of deposition strengthening and grain refining. The combination action can improve overall mechanical characteristics of the steel [5-6]. During the past years, various techniques have been employed to improve the vanadium and nitrogen contents in the steel. Generally, special alloying composites, including vanadium nitride and ferrovanadium nitride, are the widely materials to improve the vanadium and nitrogen contents. Compared with vanadium nitride, ferrovanadium nitride has more

performance advantages such as higher yields of vanadium and nitrogen, higher abilities of grain refining and strength promotion, lower composition fluctuation and higher purity. Moreover, the apparent density of ferrovanadium nitride is more than 5.0 g/cm³, which is almost double of the density of vanadium nitride (2.5-3.0 g/cm³). The large density is favor to enhance the yield of vanadium and nitride since it can penetrate the slag layer very easy.

Generally, ferrovanadium nitride is synthesized by two routes, including solid nitration and liquid nitration [3,7-11]. Solid nitration is the direct nitridation of ferrovanadium powders. However, this method has the disadvantages of low nitrogen content, long reaction time and heterogeneous composition. Zharnitskii [10] synthesized the ferrovanadium nitride at high temperature using plasma technology, which is widely used to improve the nitriding capacity [11]. For the case of the liquid nitridation process by blowing nitrogen gas into the liquid ferrovanadium, it is very hard to obtain high nitrogen content, and normally the content is less than 1.5mass%. Furthermore, the high viscosity of melts after the generation of vanadium nitride in the liquid

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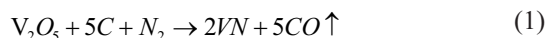


ferrovanadium is also a big problem. For both of two methods, the used raw material ferrovanadium is prepared by aluminothermic or silico-thermic reduction of vanadium pentoxide, which can lead to high cost and energy consumption.

In the present work, a novel process to prepare high quality ferrovanadium nitride has been introduced. V_2O_5 , Fe and graphite are used as the raw materials. Compared with the traditional methods, this method is a short process, which avoids the production of ferrovanadium powders. Carbothermal reduction and nitriding processes are combined together in this method, which can result in a low energy consumption and low cost. Moreover, the residual oxygen and carbon contents of ferrovanadium nitride prepared by this method can be controlled to very low levels. The detailed formation mechanism and reaction kinetics will be given in the following sections.

2. Material and experimental procedures

Vanadium pentoxide (>99.6 mass%), graphite (>99.85 mass%), and Fe (>99 mass%) were used as the raw materials to prepare high quality ferrovanadium nitride. All reagents were supplied by Sinopharm Chemical Reagent Beijing Co., Ltd. By using a temperature programmed reaction (TPR) technique, ferrovanadium nitride can be prepared by reduction and nitridation of V_2O_5 according to the stoichiometric proportion of Eq. (1).



According to the standard chemical composition of FeV45N10 (Strictly, the vanadium and nitrogen contents of FeV45N are 45mass% and 10mass%, respectively, considering the existence of VN, and the others are iron), V_2O_5 , Fe and graphite were mixed in a blender to ensure the starting materials homogeneously. Then, the mixtures were pressed into cylindrical briquettes (diameter 18 mm, thickness 4 mm) by utilizing a stainless steel mold under a pressure of 250 MPa. The total weight of one cylindrical briquette was around 25 g. The cylindrical samples were accommodated in an alumina crucible and placed in the hot zone of the furnace with the heating elements of $MoSi_2$ rods. Due to the volatilization loss of V_2O_5 , the temperature of the system was raised to 923 K with the heating rate of 5 K/s and held for 2 h firstly. Then, the temperature was continued to rise with the rate of 5 K/s until the desired temperatures (1573 K, 1673 K, 1773 K and 1873 K) and held for 3 h. After that, the sample was taken out quickly and cooled down to the room temperature under the protection of argon gas. Throughout the whole experiment, a flowing N_2 atmosphere (>99.995 wt%) was introduced into the

furnace with the flow rate of 500 ml/min. The different conditions of each experiment, including C/O molar ratio, reaction temperature and sampling method, were shown in Table 1. In addition, in order to further study the kinetics of this high temperature reaction process, a series of isothermal experiments at 1473 K, 1523 K, 1573 K, and 1623 K were carried out. During these experiments, V_2O_3 (>95 mass%) was used instead of V_2O_5 and mixed with Fe and graphite, due to the quick reaction of V_2O_5 to V_2O_3 at the high temperature. The mixtures were also pressed into cylindrical briquettes, which were placed in an alumina crucible. When the temperature of the tube furnace reached the desired values, the crucible was put into the constant temperature zone in a flowing nitrogen atmosphere (500 ml/min). After various reaction time, such as 3 min, 10 min, 20 min, 40 min, 60 min and 90 min, the crucibles were taken out from the furnace quickly and cooled down in a flowing argon atmosphere.

The structure of the powders was examined at room temperature via XRD using Cu K α radiation in the range of $2\theta=10-90^\circ$. Scanning electron microscope (SEM, Mineral Liberation Analyzer 250, voltage 200V-30KV) equipped with an Energy Disperse Spectroscopy (EDS) was used to capture the morphologies of products. The contents of oxygen and nitrogen in the final products were examined by thermal conductimetric method after fusion in an inert gas (GB/T 24583.2-2009). The content of carbon was obtained by the infrared absorption method (GB/T 8704.1-1997).

Table 1. The different conditions of each experiment

No.	Reaction Temperature (K)	C/O molar ratio (%)	Sampling Method
1	1573	75	A
2	1573	80	A
3	1573	85	A
4	1573	90	A
5	1573	95	A
6	1573	100	A
7	1673	90	A
8	1773	90	A
9	1873	90	A
10	1773	90	B

Note: A- product was taken out quickly at reaction temperature and cooled to the room temperature under the protection of argon gas; B- product was taken out at room temperature after decreasing to room temperature with the rate of 5 K/s.



3. Results

3.1. Influence of C/O molar ratio on the nitrogen, carbon contents and phase transitions of the products

Fig. 1 shows XRD patterns of the products obtained at 1573 K for 3 h with the various C/O molar ratios. In Fig. 1, it is evident that the sample obtained with the C/O molar ratio of 80% of the stoichiometric value at 1573K consists of peaks corresponding to V_2O_3 (JCPDS 34-0187), VN (JCPDS 35-0768, $a=4.139\text{\AA}$) and Fe. With the increase of C/O molar ratio, the peaks of V_2O_3 disappear, and only VN and Fe phases exist in the products. It indicates that carbon is enough to reduce V_2O_5 completely when the C/O molar ratio is higher than 80% of the stoichiometric value. Strictly speaking, due to that fact VO, VC and VN have the same crystalline structures and the atomic radius difference of O, C and N are small, they can form a continuous solid solution easily. Considering the difficulty to completely remove oxygen and carbon atoms, the products prepared by this method should be V(C, N, O).

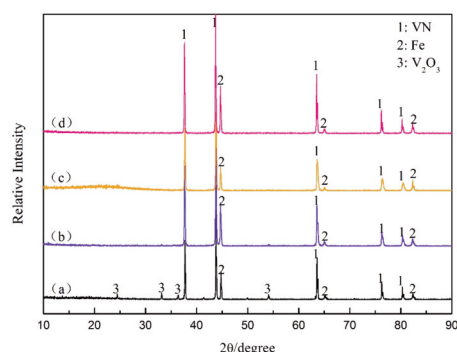


Figure 1. XRD patterns of the products prepared at 1573 K for 3 h with different C/O molar ratios under N_2 atmosphere: a) 80%; b) 85%; c) 90%; d) 95%

In order to ascertain the optimum C/O molar ratio, the variation of the nitrogen, carbon contents left in the products, which are produced at 1573 K for 3 h with different C/O molar ratios, are analyzed and shown in Fig. 2. It is obvious to find that the residual carbon content of the product is very small when C/O molar ratio is lower than 90% of the stoichiometric value, but it starts to increase with the further increase of the C/O molar ratio. The nitrogen content keeps increasing until the C/O molar ratio achieve 95% of the stoichiometric value. Although the nitrogen content is 12mass% when the C/O molar ratio is 95% of the stoichiometric value, the residual carbon content can up to 0.49mass%. This may result in the increase of carbon content of liquid steel during the process of alloying. Considering this factor, the C/O molar ratio of 90% of the stoichiometric value is

chosen to be the optimum molar ratio. When the C/O molar ratio achieves 90% of the stoichiometric value, the nitrogen, carbon contents of the product are 11.52mass%, 0.049mass%, respectively.

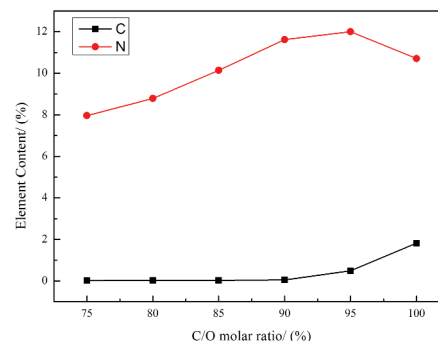


Figure 2. Influence of C/O molar ratio on the carbon and nitrogen contents left in the products

3.2 Influence of reaction temperature on the nitrogen, carbon contents and morphology evolutions of products

For a C/O molar ratio of 90% of the stoichiometric value, the nitrogen and carbon contents of the products prepared at different temperatures for 3 h are shown in Table 2. It can be found that the carbon content is very low and the nitrogen content keeps constant as the increasing temperature from 1573 K to 1873 K. It demonstrates that the higher reaction temperature has no influence on the nitrogen and carbon contents of the products prepared with a C/O molar ratio of 90%.

Table 2. The nitrogen, carbon contents of the products prepared with a C/O molar ratio of 90% of the stoichiometric value at different temperatures for 3 h

No.	Temperature (K)	C/O molar ratio (%)	mass%C	mass%N
4	1573	90	0.049	11.52
7	1673	90	0.082	11.55
8	1773	90	0.063	11.66
9	1873	90	0.066	11.72

SEM photographs in Fig. 3 show the morphology evolutions of the products, which prepared with the C/O molar ratio of 90% of the stoichiometric value at different temperatures for 3 h. It can be seen that there are two phases in the fields. The light gray area is made up of Fe phase and the dark gray area is VN phase. In addition, the black area is pore, which is filled with resin. In Fig. 3(a) and (b), a large area is occupied by numerous pores and most of VN and Fe particles are dispersed. Nevertheless, for the reaction temperature higher than 1773 K, Fe particles are

connected together and VN particles are distributed uniformly and surrounded by Fe phase. Most of the pores existed at the low reaction temperatures disappear. It demonstrates that the density of the products is improved significantly when the reaction temperature is higher than 1773 K. In order to further study the element distribution of the product prepared at 1873 K under nitrogen atmosphere for 3 h, the EDS maps of cross-sections are used and the results are shown in Fig. 4. It is obvious that the distribution of vanadium and nitrogen are almost overlapped. Meanwhile, there is a clear boundary between the distribution of Fe and V. It can be also concluded that carbon and oxygen are distributed uniformly in the field. Considering the dispersed oxygen shown in Fig. 4, it is necessary to measure the oxygen content of the product prepared at 1873 K under nitrogen atmosphere for 3 h and the result is 0.65mass%.

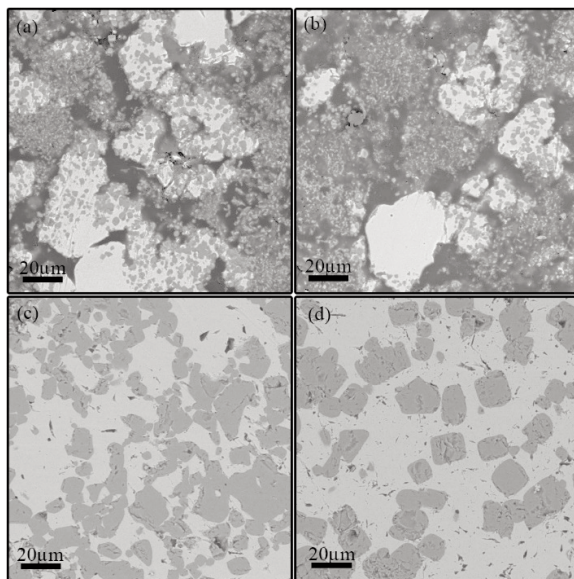


Figure 3. SEM photographs of the products prepared at different temperatures under nitrogen atmosphere for 3h: (a) 1573 K, (b) 1673 K, (c) 1773 K, (d) 1873 K

3.3 Influence of the heat treatment on the nitrogen contents of products

In order to study the influence of the heat treatment on the nitrogen contents, the nitrogen contents of the products prepared with different sampling methods are detected and shown in Fig. 5. It is easy to demonstrate that the nitrogen content of the furnace-cooling product, is close to the product which taken out quickly at 1773 K after reacting at 1773 K for 3 h. It indicates that the furnace-cooling process has no effect on the further increase of the nitrogen content of ferrovanadium nitride.

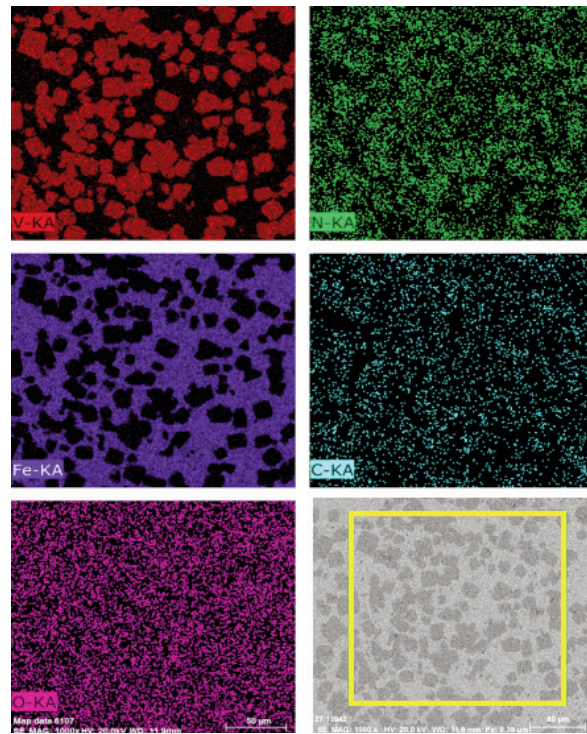


Figure 4. EDS maps of the cross-sections of the product prepared at 1873 K under nitrogen atmosphere for 3 h

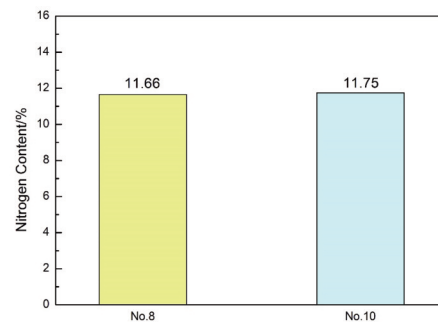


Figure 5. Influence of heat treatment on the nitrogen content of the products

3.4 Isothermal Experiment

Due to the vaporization of V_2O_5 at the high temperature, V_2O_5 cannot be placed into high temperature zone directly to perform the isothermal experiment. According to the previous studies [12-13], V_2O_5 and VO_2 disappear and V_2O_3 can be obtained easily at low temperature during the carbothermal reduction process of V_2O_5 . The reaction kinetics from V_2O_5 to V_2O_3 is too quick to study at high temperature. Therefore, it is meaningful to study the reaction kinetics from V_2O_3 to VN. V_2O_3 is used to perform isothermal experiment instead of V_2O_5 . Isothermal reaction of the mixture of V_2O_3 , Fe and

graphite is studied in the temperature range of 1473 K to 1623 K. The time dependences of the mass loss at four temperatures are presented in Fig. 6. The weight loss ratio (W_t) of the mixture is calculated by the following equation:

$$W_t = \frac{m_0 - m_t}{m_0} \times 100\% \quad (2)$$

where m_0 and m_t are the weights of initial sample and that reacted for a period of time (t), respectively.

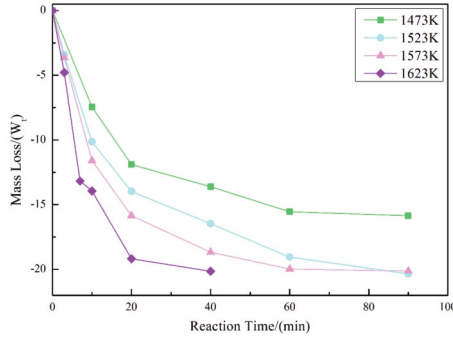


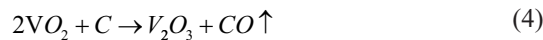
Figure 6. Isothermal mass-loss curves of the samples reacted in the temperature range of 1473 K to 1623 K under nitrogen atmosphere

It can be seen that the total mass losses of the mixture reacted at 1523 K, 1573 K and 1623 K, are similar and maintain at about 20%, which is closed to the theoretical maximum mass loss. However, the sample cannot be reacted completely when the reaction temperature is 1473 K.

4. Discussion

4.1 Thermodynamic analysis

According to the XRD results and the conclusions from the related literatures [13-14], carbothermal reduction and nitriding processes are combined together during the whole reaction process. Firstly, V_2O_5 was reduced to VO_2 firstly and then to V_2O_3 in the low temperature reduction stage. The reaction can be described as:



As shown in Fig. 7, the changes of standard Gibbs free energy of Eqs. (3) and (4) as a function of temperature were calculated by FactSage 6.4. It demonstrated that the reduction of V_2O_5 and VO_2 can be taken place easily at low temperatures. Therefore, the cylindrical samples were preliminary reacted at 923 K for 2 h to avoid the volatilization of V_2O_5 at high temperatures. Moreover, the vanadium oxide was reduced to V_2O_3 after pre-treatment.

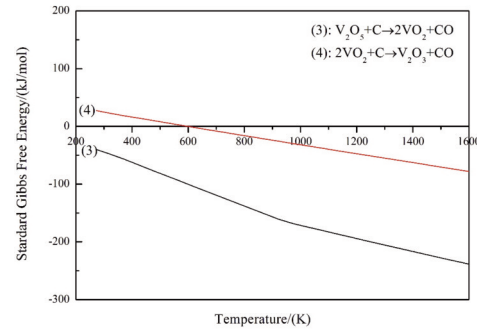
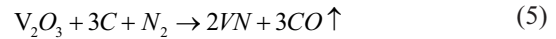


Figure 7. Change of the standard Gibbs free energy as a function of temperature for different reactions

With increasing temperature, the reaction of Eq. (5) started to happen. V_2O_3 was reduced and nitrided to VN directly. The corresponding standard Gibbs free energy change was also calculated and shown in Eq. (7), in which K_N is the equilibrium constant for Eq. (5); P_{N_2} is nitrogen partial pressure during the reaction process, atm; P_{CO} is CO partial pressure during the reaction process, atm. When the furnace temperature started to rise, the N_2 gas was introduced all the time. If the formation of CO_2 gas was ignored, the gas phases during carbonitrothermic reduction process consisted of CO and N_2 . Thus, Eq. (9) can be obtained.



$$\Delta G = \Delta G^\theta + RT \ln K_N \quad (6)$$

$$\Delta G^\theta = 439320 - 337.6T \quad (7)$$

$$K_N = \frac{P_{CO}^3}{P_{N_2}} \quad (8)$$

$$P_{N_2} = 1 - P_{CO} \quad (9)$$

As substituting Eqs. (7), (8) and (9) into Eq. (6), the Gibbs free energy change of Eq. (5) can be obtained as follow:

$$\Delta G = 439320 - 337.6T + RT \ln \frac{P_{CO}^3}{1 - P_{CO}} \quad (10)$$

When $\Delta G=0$, the relations between reaction temperature and equilibrium pressure of CO or N_2 can be obtained and described in Fig. 8. The Eqs. (11) and (12) also can be described in the same way and shown in Fig. 8.

In Fig. 8, it can be seen that the figure was divided into the predominance of V_2O_3 , VN and VC by two solid lines. Two solid lines represented the reactions of Eqs. (5) and (11), respectively. Due to the continuous introduction of N_2 , the partial pressure of CO kept in a low level all the time. When the temperature was closed to 1050 K, V_2O_3 started to transform into VN. Then, VN can be reacted to VC by

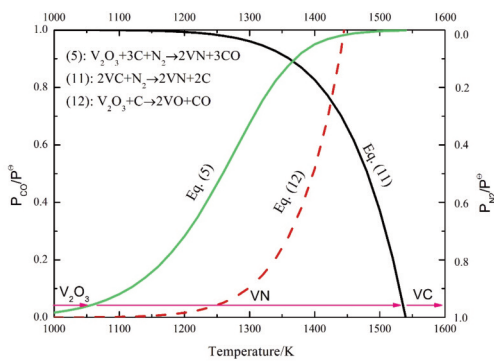


Figure 8. The relations between reaction temperature and equilibrium pressure of CO or N₂ in the carburizing and nitriding process of V₂O₅

residual carbon when the temperature was higher than 1530 K. However, Tripathy et al. [13] considered that V₂O₅ was reduced to VO and then reacted to VN during the process of carbonitrothermic reduction. The relations between reaction temperature and equilibrium pressure of CO or N₂ in Eq. (12) were also shown in Fig. 8. It can be seen that the initial reaction temperature of Eq. (5) was lower than Eq. (12) when the CO partial pressure was in low level. It indicated that V₂O₅ can be transformed to VN easily rather than VO during the reaction process.



During the process, the carburizing and nitriding reaction were performed at the same time. Most carbon atoms diffused into the lattice of V₂O₅ were reacted with oxygen atoms to form CO gas. The others remained in the lattice and formed the solid solution of V(C, N, O). With increasing the reaction degree, oxygen and carbon atoms were further removed by forming CO and the lattice positions of carbon and oxygen atoms were taken up by nitrogen atoms gradually. With the further increase of C/O molar ratio, oxygen atoms almost disappeared but the residual carbon started to occupy the lattice positions of nitrogen atoms according to the inverse reaction of Eq. (11). This was the reason that the nitrogen content decreased when the C/O molar ratio increased from 95% to 100% of the stoichiometric value. In addition,

the oxygen contents of the products prepared with the C/O molar ratio of 85%, 90%, 95% and 100% at 1573K were measured, and were 3.26mass%, 1.84 mass%, 0.39 mass%, 0.24 mass%, respectively. With the further increase of C/O molar ratio, the oxygen content can be decreased to 0.24 mass%. Compared with the oxygen content of the products prepared with the C/O molar ratio of 85% and 90%, the oxygen content was significant decreased. Therefore, the phase transformation of the samples during the whole reaction process can be described in Fig. 9.

4.2 Reaction mechanism

According to the chemical analysis, the composition of the final products prepared with the C/O molar ratio of 90% at 1873K for 3h was obtained and shown in Table 3. Moreover, the composition of FeV45N10 according to the national standard of China GB/T 30896-2014, were also listed in Table 3. It can be seen that the nitrogen content of the product prepared by the present carbothermal reduction nitridation process was in a high level but the carbon content was as low as 0.066mass%. According to the requirement in GB/T 30896-2014, the content of Si and Al should be lower than 3mass% and 2.5mass%, respectively. The requirements for Si and Al were because most ferrovanadium nitride was prepared by using the raw material of ferrovanadium, which was produced by the aluminothermic or silicothermic reduction of V₂O₅. During this process, some Al and Si will be introduced into ferrovanadium. However, during carbothermal reduction nitridation process,

Table 3. The composition of standard FeV45N10 and the final product obtained with the C/O molar ratio of 90% of the stoichiometric value at 1873K for 3h (mass%)

	N	C	O	Si	Al
National standard of China GB/T 30896-2014	9-12	<0.5	Not given	<3	<2.5
Present Product	11.72	0.066	0.65	-	-

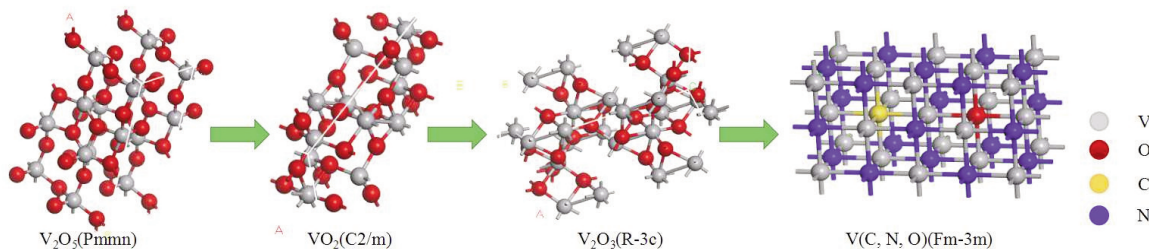


Figure 9. The phase transformation of the products during the whole reaction process

V_2O_5 was used as the raw materials directly. There was no residue of Si and Al. In addition, the oxygen content was also controlled to a low level in the present study. Therefore, compared with traditional methods, ferrovanadium nitride with a higher quality can be prepared by carbothermal reduction nitridation process. Meanwhile, considering the short process and the use of V_2O_5 direct as raw materials, the present process also had a low cost.

During the carbothermal reduction nitridation process, the reaction mechanism was investigated by analyzing the phase transformation and microstructure evolution. To simplify the analyses, the particle shapes of all phases were assumed to be spherical. With the increase of reaction temperature, the phase transitions and morphology evolutions during the production of ferrovanadium nitride can be described by the schematic diagram shown in Fig. 10 and explained as follows.

(a) After mixing and pressing the raw materials, vanadium source, iron source and carbon source were well- proportioned and contacted with each other closely. For the temperature lower than 823 K, V_2O_5 can be reduced to VO_2 and V_2O_3 easily. The vanadium source was reduced to V_2O_3 after low temperature pre-treatment. During the process, a great deal of CO and CO_2 gas was formed in the system.

(b) With the increase of reaction degree, a large amount of carbon atoms diffused into the lattice of V_2O_3 . Most of them were reacted with oxygen atoms and escaped from the system by forming CO gas. The others remained in the lattice and occupied the lattice positions of oxygen atoms. At the same time, nitrogen atoms also diffused into the lattice and occupied most of the lattice positions of oxygen atoms to form the solid solution phase of V(C, N, O).

(c) When the temperature increased to the desired temperatures (1773 K, 1873 K), Fe became liquid phase and surrounded V(C,N,O) particles. It indicated that the density of the products improved significantly. Although higher reaction temperature had no influence on the nitrogen, carbon contents of the products, it can improve the density and strength

of the products obviously, which were required during the alloying process in order to penetrate the slag layer. This was the reason that the reaction temperature was increased to 1773 K, 1873 K. As shown in Fig. 4, it can be found that the carbon atoms also exited in Fe phase. The residual carbon was dissolved in liquid phase and then diffused into V(C, N,O) particles to further remove the oxygen atoms remained in the lattice. Compared with the preparation of VN in other literatures [13, 15-16], the oxygen and carbon contents of the final samples can be controlled to very low levels. For the temperature higher than 1773 K, Fe became liquid phase and the carbothermic reduction reaction changed from solid-solid reaction to solid-liquid reaction, which greatly enhanced the reaction kinetics.

4.3 Reaction kinetics

In order to further study the kinetics of high temperature reaction process, a serial of isothermal experiments were carried out in the temperatures range of 1523 K to 1623 K and the results were shown in Fig. 6. Herein, the model fitting method was used to analyze the reaction kinetics. The reaction extent (α) was calculated as the ratio of weight loss ratio W_t to the theoretical maximum weight loss W_{max} as shown in Eq. (13):

$$\alpha = \frac{W_t}{W_{max}} \times 100\% \quad (13)$$

A diffusion-controlled model was proposed by Jander [17] to correlate the reacted fraction with time. The explicit form of Jander diffusion model were widely applied for the kinetic analysis and shown in Eq. (14) [18]. In Eq. (14), k is the rate constant, the temperature dependence of which is described as the Arrhenius equation (Eq. (15)):

$$\alpha = 1 - (1 - \sqrt{kt})^2 \quad (14)$$

$$k = A \exp\left(-\frac{\Delta E}{RT}\right) \quad (15)$$

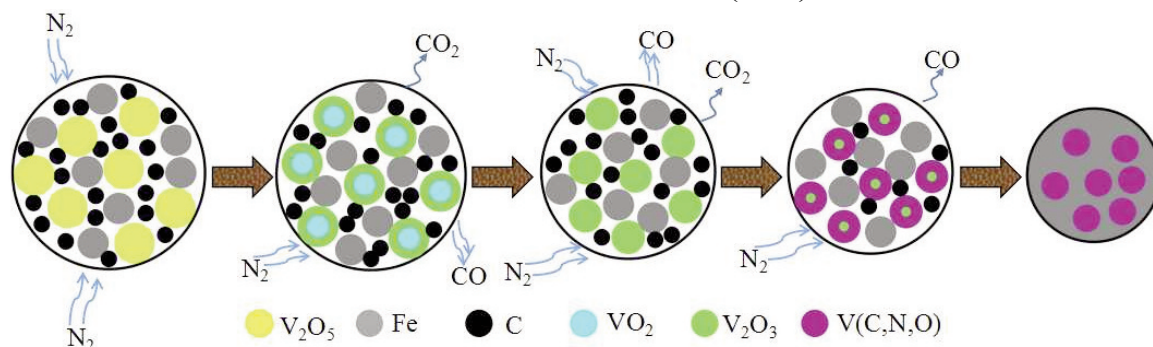


Figure 10. The schematic diagram of the preparation of ferrovanadium nitride when the reaction temperature is higher than 1773 K

where A is the pre-exponential factor (frequency factor), ΔE is the activation energy, R is the gas constant and T is the absolute temperature.

Substituting Eq. (15) into Eq. (14), the total reaction extent α can be written as

$$\alpha = 1 - \left[1 - \sqrt{A t \exp\left(-\frac{\Delta E}{RT}\right)} \right]^2 \quad (16)$$

Fig. 11 shows the comparisons of the experimental results and calculated results with Eq. (16). It can be seen that Jander diffusion model can give a good fitting and the data obtained in the experiments agreed well with the calculated results. Moreover, the measured values, which reacted for 3 min, were lower than the calculated values at all temperatures. This may be because of the retarded heat diffusion when the sample was just put into the hot temperature zone. The extracted activation energy is 188.173 kJ/mol. Thus, the corresponding kinetic equation can be given as shown in Eq. (17).

$$\alpha = 1 - \left[1 - \sqrt{2.6387 \times 10^4 t \exp\left(-\frac{188173}{RT}\right)} \right]^2 \quad (17)$$

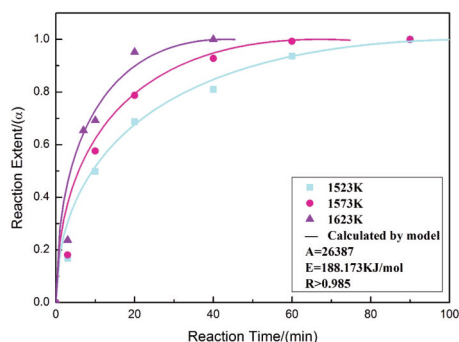


Figure 11. Comparisons of calculated and experimental reaction extent vs reaction time curves for the carburizing and nitriding process of V_2O_5 at 1523 K, 1573 K and 1623 K (R represents the correlation coefficient)

5. Conclusions

In this study, a novel method was proposed to synthesize the high quality of ferrovanadium nitride by temperature programmed reaction among V_2O_5 , Fe and graphite. Compared with the traditional methods, this method can shorten the production period sharply. Moreover, the oxygen and carbon contents of ferrovanadium nitride can be controlled to very low levels. According to the results of XRD patterns and thermodynamic calculations, phase evolution sequences of V_2O_5 were $V_2O_5 \rightarrow VO_2 \rightarrow V_2O_3 \rightarrow V(C, N, O)$, during the reduction and carbonization process.

The optimum ratio of C/O was found to be 90% of the stoichiometric value, and it was demonstrated that the nitrogen content decreased as further increasing the C/O molar ratio. With the increase of temperature, Fe phase became liquid state and surrounded the solid $V(C, N, O)$ particles tightly. It can form a liquid diffusion tunnel of carbon to further remove the oxygen atoms remained in the lattice and improve the density of final products significantly. The reaction rate of V_2O_5 to VN was controlled by Jander diffusion model with the extracted activation energy of 188.173 kJ/mol.

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