Article

Reduction and Nitridation of Iron/Vanadium Oxides by Ammonia Gas: Mechanism and Preparation of FeV45N Alloy

Yongjie Liu ¹, Yue Wang ¹, Zhixiong You ^{1,2,*} and Xuewei Lv ^{1,2}

¹ College of Materials Science and Engineering, Chongqing University, Chongqing 400044, China; liuyongjie@cqu.edu.cn (Y.L.); wangyue_cqu@163.com (Y.W.); lvxuewei@163.com (X.L.)

² Chongqing Key Laboratory of Vanadium-Titanium Metallurgy and Advanced Materials, Chongqing University, Chongqing 400044, China

* Correspondence: youzx@cqu.edu.cn; Tel.: +86-183-0608-9886

Received: 16 January 2020; Accepted: 6 March 2020; Published: 9 March 2020

Abstract: The steel micro-alloyed with ferrovanadium nitride has extremely superior properties that make it widely utilized in structural components, construction and aircraft. The conventional methods for synthesizing ferrovanadium nitride include nitridation of pure ferrovanadium alloy or carbothermal nitridation of metallic oxides, using nitrogen or ammonia gas as nitrogen sources. In this study, ferrovanadium nitride (FeV45N) was prepared by direct reduction and nitridation of the corresponding metal oxides with ammonia as the reductant and nitrogen source. This method avoids the introduction of other impurity elements, except the negligible trace elements accompanied with the raw materials. The thermodynamics of the reduction and nitridation process were initially analyzed. During the subsequent ammonia reduction process, the FeV45N powders were successfully obtained at 1273 K for 6 h. The obtained powders were pressed into cylindrical briquettes by hot pressing (HP) at 1473 K for 1 h in vacuum. In the investigation, the X-ray diffraction and morphological analysis of the products was also carried out, and the reaction mechanisms were discussed in detail. The nitrogen content of the final product can reach 11.85 wt. %, and the residual oxygen content can be reduced to 0.25 wt. %. By sintering, the density of the alloy can reach 5.92 g/cm³.

Keywords: ferrovanadium nitride; ammonia gas; reduction; nitridation; mechanism

1. Introduction

Recently, high-strength low-alloy (HSLA) steel has attracted much attention in industry due to its superior properties and economic benefits [1–3]. The superior performance of HSLA steel mainly accounts for microalloying with carbide- and nitride-forming metals (V, Nb, Al, Ti, etc.). The advantages of nitrogen are related to grain refinement, austenite stabilization, formation of nitrides and carbonitrides with extremely high structural hardness and significant increasing of strength, without restriction of ductility [3,4]. Among these microalloying additives, HSLA steel microalloyed with vanadium and nitrogen exhibits particular economic superiority.

During steel making, vanadium can be added by means of V-bearing compounds—ferrovanadium (FeV), vanadium carbide (VC), vanadium silicide (V₃Si), etc. However, the drawback of these additives is the absence of nitrogen. Although nitrogen is capable of being introduced into the melt by blowing N-bearing gases, the final composition of the melt is generally corrected by adding N-bearing alloys. Up to now, various alloys, including vanadium nitride (VN), vanadium carbonitride (V(C, N)) and ferrovanadium nitride (FeVN), have been proposed for the combined introduction of vanadium and nitrogen into the molten steel [5–9]. Vanadium carbonitride has been researched for many years; however, its practical use is inhibited by its low briquette density (≈ 3 g/cm³) and high melting point

(>2673 K). Compared with vanadium nitride, ferrovanadium nitride has better affinity and higher density (>5 g/cm³), which makes it more easily absorbed by molten steel and can increase the recovery of vanadium and nitrogen, thereby reducing the production cost and improving the mechanical properties of the steel [10,11].

Traditionally, ferrovanadium nitride could be synthesized by direct nitridation of ferrovanadium alloy, carbothermal reduction–nitridation or hydrogen-based reduction–nitridation of corresponding metallic oxides, using nitrogen or ammonia gas as nitrogen sources. The current methods are classified as solid nitridation, liquid nitridation, sintering processes, plasma smelting and carbothermal reduction–nitridation [1,12–21]. Grishchenko et al. have synthesized ferrovanadium nitride using ferrovanadium as raw material via roasting at 1327 K in a vacuum furnace for about 17 h [12]. Nevertheless, the nitrogen content of the final product was 5.0–6.6% and was characterized as heterogeneous. Franke et al. conducted similar experiments, whose results also proved that the N content could not meet the requirements of industrial production [13]. The study by Krastev indicated that the nitrogen content could be improved with the increase of temperature and reaction time, and by using a finer particle size [14]. Preparation of ferrovanadium nitride by liquid nitridation greatly shortened the reaction time [15]. However, the nitridation of liquid alloys has not been industrially adopted due to the high viscosity of nitrides-bearing ferrovanadium melts, which resulted in low nitrogen content in the melts. Ziatdinov et al. also synthesized ferrovanadium nitride from ferrovanadium powders by the self-propagation high-temperature synthesis (SHS) method [16]. Ferrovanadium nitride can also be prepared by the plasma smelting method using ferrovanadium alloys under a nitrogen atmosphere [17]. With respect to the above four methods, ferrovanadium was used as the raw material, which not only contained impurities (Al, Si) but also consumed relatively more money and energy. Carbothermal reduction–nitridation of iron and vanadium oxides has also been investigated to prepare ferrovanadium nitride [19,20]. During the process, although Al, Si impurities were not introduced, there was still some residual carbon in the final product, and the roasting temperature was very high (more than 1823 K). Excessive reducing agent was always added to enhance the deoxidation process, which inevitably increased the residual carbon content and correspondingly decreased the nitrogen content in the product.

In recent decades, transition metal nitrides (TiN, VN, CrN, etc.) have been prepared from corresponding oxides using ammonia as nitrogen source and reducing agent [22–29]. Ammonia gas is proved to be more effective in the nitridation process than high-purity N₂ gas [30]. In view of that superiority, ferrovanadium nitride was also expected to be synthesized by reduction and nitridation of a mixture of vanadium and iron oxides [31]. In the present study, ferrovanadium nitride (FeV45N) was prepared by the specified process with ammonia gas. A systematic study on the thermodynamics of the NH₃–VO₂–Fe₂O₃ system was performed first. The phase transformation of vanadium and iron dioxides was studied using X-ray diffraction. Subsequently, the obtained powders were sintered into bulk ferrovanadium nitride by hot pressing (HP). Morphological analysis of the product was also carried out, allowing the study to be concluded with a discussion of the applicable reaction mechanisms. Compared with the carbothermal reduction nitridation method, this method, using ammonia as the reductant and nitrogen source, avoided the introduction of carbon. Furthermore, the final product contained a relatively high nitrogen content and a low residual oxygen content.

2. Experimental

2.1. Experimental Procedure

Vanadium dioxide powder (Tiantian Chemical Reagent Company, Jiangsu, China, VO₂, >99.7 wt. %) and Fe₂O₃ (Aladdin Industrial Corporation, Shanghai, China, >99.7 wt. %) were used as raw materials to synthesis FeV45N. The particle sizes of these two materials were less than 74 µm. Theoretically, the iron and vanadium contents in FeV45N are about 45 wt. % and 45 wt. %, respectively. Thus, in order to synthesize FeV45N, 200 mg of Fe₂O₃ and 220 mg of VO₂ were uniformly mixed and loaded onto an

ultra-fine stainless steel mesh, which was supported by a corundum crucible. The steel mesh was used to obtain a porous structure, to ensure that ammonia gas was able to flow through the bottom of the anatase powder. Before the experiment, argon gas (99.999 vol.%) flow of 150 mL/min was introduced into an electric tube furnace to expel oxygen and moisture. This gas flow was maintained until the furnace was heated to the required temperature, through steps of 10 K/min. The crucible loading with the mixture was then placed in the roasting zone of the horizontal furnace tube, and the gas was switched to NH_3 (99.999 vol.%), which was also maintained at 150 mL/min. The sample was reduced and nitrided isothermally at temperatures of 873–1273 K for 1–6 h. Once roasting was completed, the furnace was allowed to cool down under flowing argon gas. After that, the obtained powders were pressed into a cylindrical briquette (10 mm in diameter, 4 mm in thickness) by hot pressing (HP) at 1473 K for 1 h in vacuum.

2.2. Analytical Method

Thermodynamic analysis was conducted by using FactSage 6.2 based on the pure substances database [32,33]. After reaction, the cooled powders were examined by X-ray powder diffraction (Rigaku D/max 2500, Rigaku, Tokyo, Japan) under the conditions as follows: $\text{Cu K}\alpha$, tube current and voltage: 250 mA, 40 kV, scanning range: $10\text{--}90^\circ$ (2θ), step size: 0.02° (2θ) and scanning speed: $8^\circ/\text{min}$. The oxygen and nitrogen contents of powders was tested by the German Eltra On-900 (German Eltra, Shanghai, China) N/O elemental analyzer. The sample was heated and fused in an ink crucible. The oxygen in the sample reacted with carbon to form carbon monoxide, and nitrogen was released in the elemental state. Scanning electron microscopy (JSM-7800F, Tokyo, Japan) was carried out to monitor overall powder morphology, and the microstructure of bulk ferrovandium nitride. The density of the FeV45N briquette was measured using the Archimedes method (GB/T1423-1996).

3. Thermodynamic Analysis

In this work, NH_3 contributed simultaneously as the reduction and the nitridation agent to react with the mixture of Fe_2O_3 and VO_2 . To predict the predominant field of various products, the equilibrium calculations of the $\text{Fe}_2\text{O}_3\text{--NH}_3$ system and the $\text{VO}_2\text{--NH}_3$ system were performed, respectively. Figure 1 shows the solid phase fields calculated in the temperature range of 673–1573 K at a pressure of 1 bar. The input NH_3 mole fraction was given as $n_{\text{NH}_3}/(n_{\text{NH}_3}+n_{\text{Fe}_2\text{O}_3})$ and $n_{\text{NH}_3}/(n_{\text{NH}_3}+n_{\text{VO}_2})$, where n_{NH_3} , $n_{\text{Fe}_2\text{O}_3}$ and n_{VO_2} represent the input mole numbers of NH_3 , Fe_2O_3 and VO_2 , respectively.

As shown in Figure 1a, the solid phases, including Fe_2O_3 , Fe_3O_4 , FeO and Fe , were mainly dependent on temperature and input NH_3 fraction. The condition for the occurrence of Fe was that the temperature was about 823 K and the input NH_3 fraction was about 0.5. Thermodynamically, Fe_2O_3 can be easily reduced even at very low temperature and NH_3 fraction. The reaction path of Fe_2O_3 varied as $\text{Fe}_2\text{O}_3 \rightarrow \text{Fe}_3\text{O}_4 \rightarrow \text{FeO} \rightarrow \text{Fe}$ or $\text{Fe}_2\text{O}_3 \rightarrow \text{Fe}_3\text{O}_4 \rightarrow \text{Fe}$, which depended on the temperature. It is worthy to note that iron nitride was not observed in Figure 1a under the calculated conditions. As shown in Figure 1b, VO_2 can be easily reduced to V_2O_3 at a temperature above 973 K, regardless of NH_3 fraction. When the temperature was lower than 973 K, some V_3O_5 would have appeared and then been reduced to V_2O_3 . It meant the reaction path of VO_2 followed $\text{VO}_2 \rightarrow \text{V}_2\text{O}_3 \rightarrow \text{VN}$ or $\text{VO}_2 \rightarrow \text{V}_3\text{O}_5 \rightarrow \text{V}_2\text{O}_3 \rightarrow \text{VN}$ at a different temperature range. However, the NH_3 fraction required for reduction and nitridation of V_2O_3 was relatively higher, which should be greater than 0.98. Thus, compared with Figure 1a, when Fe_2O_3 was converted to Fe , VO_2 oxide was converted to VN . At the same time, the generated iron can promote the decomposition of ammonia and affect the formation of vanadium nitride [34].

In order to predict the phase composition of $\text{NH}_3\text{--Fe}_2\text{O}_3\text{--VO}_2$ system, the solid phase composition as a function of input NH_3 mole fraction at 1273 K was calculated. The calculation was carried out at a pressure of 1 bar by fixing Fe_2O_3 at 1 mol and VO_2 at 2.2 mol. The input NH_3 mole fraction was given as $n_{\text{NH}_3}/(n_{\text{NH}_3}+n_{\text{Solid}})$, where n_{Solid} represents the input mole numbers of Fe_2O_3 and VO_2 . The results in Figure 2 show the absolute mole numbers of solid phases during the reaction process. It can be seen from Figure 2 that Fe_2O_3 undergoes the transformation process of forming Fe step by step. The NH_3

fraction required for generating Fe is around 0.78. However, the reduction and nitridation of VO_2 to form VN required NH_3 fractions to reach above 1, which was much higher than the formation of Fe. It can be seen from Equations (1) and (2) that, at 1273 K, the $\Delta G^\ominus$ of Fe generated by FeO reduction was far less than the $\Delta G^\ominus$ needed for VN formation. From the perspective of thermodynamics, the reaction condition for VN generation was extremely harsh.

Figure 1. Predominant phase diagram of solid phases as functions of temperature and input NH_3 fraction: (a) $\text{NH}_3\text{-Fe}_2\text{O}_3$ system; (b) $\text{NH}_3\text{-VO}_2$ system.

Figure 2. Equilibrium composition of solid products at 1273 K: $\text{NH}_3\text{-Fe}_2\text{O}_3\text{-VO}_2$ system (fixed 1.0 mol Fe_2O_3 and 2.2 mol VO_2).

4. Results and Discussion

4.1. Phase Evolution during Reduction with Ammonia

The phase compositions of the reduced and nitrided products were investigated, and the results are shown in Figure 3. Reduction roasting was conducted as a function of temperature (4 h) and duration (1273 K).

Figure 3. XRD patterns of products roasted for different durations at different temperatures: (a) 837–1273 K for 4 h, (b) 1273 K for 1–6 h.

Figure 3a shows the phase composition with temperature in the range of 873–1273 K for 4 h, respectively. As can be seen from the Figure 3a, three different phases, including VN, Fe and Fe_4N , existed in the roasted samples. It indicated that VO_2 and Fe_2O_3 have already been completely reduced or nitrided after 4 h. When the reaction temperature was 873 K, VN, Fe and Fe_4N were present in the sample. The diffraction peaks were still assigned to VN, Fe and Fe_4N with an increase of reaction temperature to 1073 K. However, when the reaction temperature increased to 1173 K, the diffraction peak of Fe_4N disappeared. This is because Fe_4N is unstable at high temperature and would decompose to Fe and N_2 . As can be seen from Equations (3) and (4), under standard conditions, the initial

temperatures for reactions (3) and (4) are 595 K and 429 K, respectively. It can be deduced that Fe_4N is easily converted to Fe under the experimental conditions. Meanwhile, as can be seen from Figure 3a, the relative strength of the diffraction peak of Fe_4N was relatively low, which also indicated that Fe_4N was unstable in ammonia atmosphere.

The phase transformation of VO_2 and Fe_2O_3 as a function of duration is also compared. Figure 3b shows the X-ray diffraction (XRD) patterns of samples roasted for different hours at 1273 K. It was found that metallic Fe had already been formed after reacting for 1 h. At the same time, VO_2 has also been reduced. Both V_2O_3 and VN were observed after roasting for 1 h, indicating VO_2 was not completely converted to VN. This is because Fe_2O_3 was easier to be reduced than VO_2 under an ammonia atmosphere. The diffraction peak of Fe_4N was not present because the formed iron nitride was unstable at high temperature. As the duration increased to 4 h and 6 h, only Fe and VN were observed. The results of phase transformation were in agreement with the thermodynamic analysis to some extent. As can be seen from Figure 2, Fe_2O_3 was initially reduced and metallic iron can coexist with V_2O_3 . The phase of V_2O_3 will be finally reduced and nitride into VN.

4.2. Morphological Analysis

The micromorphologies of the products obtained under different reaction conditions were investigated by scanning electron microscopy (SEM), and the results are plotted in Figure 4. It can be seen from Figure 4a that when reducing at 1073 K for 4 h, the powder particles of the reduced samples were still dispersive. The bright phase and the gray phase were mainly metallic Fe and VN, respectively, and a sintering phenomenon was negligible at 1073 K. The morphology feature of VN was more obvious due to its face centered cubic crystal structure. By reducing at 1273 K for 6 h, the powder particles of the samples accumulated to a larger size and showed an obvious sintering phenomenon, as shown in Figure 4b and the energy dispersive spectrometer (EDS) results of points 3 and 4.

4.3. Characterization of the Products

In order to determine whether a prepared sample meets commercial application standards, the sample needs to be tested for oxygen and nitrogen contents. Table 1 shows the experimental results of nitrogen and oxygen measurements of FeV45N prepared under different conditions. It can be seen from Table 1 that as the reaction time and the reaction temperature increased, the O content of the product decreased and the nitrogen content increased, correspondingly. After reacting at 1273 K for 6 h, the O content was as low as 0.25%, and the N content was increased to 11.85%, which meets the requirement of FeV45N that the elemental content of N is in the range of 9–12% (National Standard of China, GB/T 30896-2014, Beijing, China). Meanwhile, no impurities are introduced into the powder, such as C, Al or S. Additionally, compared to the products obtained by solid or liquid nitridation methods, whose N contents were less than 10% and whose density was 4.0–4.5 g/cm³, the N content and density in the present were obviously higher [14,15]. The FeVN alloy obtained by high-temperature synthesis method also had high density (5.5–6.5 g/cm³), while the N content was in the range of 9–11% [16].

Figure 4. SEM micrographs and EDS patterns of products roasted at different temperatures: (a) 1073 K for 4 h, (b) 1273 K for 6 h.

Table 1. O and N contents of FeV45N.

Temperature (K)	Reaction time (h)	O content (wt. %)	N content (wt. %)
1073	6	1.16	11.74
1173	4	1.11	11.75
1273	4	0.74	11.79
1273	6	0.25	11.85

4.4. Microstructure of the Alloy after Sintering

In order to increase the density of ferrovanadium nitride alloy, the obtained powders after reduction and nitridation were pressed into a bulk alloy (cylindrical briquette, 10 mm in diameter, 4 mm in thickness) by hot pressing (HP) at 1473 K for 1 h in vacuum. The density of the FeV45N alloy after sintering was determined as 5.92 g/cm³, which was beneficial to increasing its utilization efficiency during the steel making process. The SEM micrograph and its corresponding area scanning results of the bulk alloy are presented in Figure 5. It can be seen that there were two main phases in the alloy, named metallic iron (Fe) and vanadium nitride (VN), respectively. There was an obvious boundary between the metallic iron and VN phases. The area scanning results also demonstrated that vanadium mainly existed in the form of VN, because the region of vanadium overlapped with that of nitrogen.

Figure 5. Microstructure of FeV45N alloy after sintering. (a) SEM micrograph: (b–d) the elemental distributions of V, Fe and N, respectively.

4.5. Reaction Mechanism

Although synthesizing vanadium nitride by ammonia reduction has been investigated [30,35]. The study by Vaidhyanathan et al. proved that high-purity N_2 gas was less effective in the nitridation process than ammonia gas [30]. It is difficult to form vanadium nitride by reacting vanadium oxide with N_2 and H_2 . Thermodynamically, NH_3 would easily decompose to form N_2 and H_2 upon heating. However, the behavior of NH_3 was rarely studied, and the components decomposed from ammonia gas were the actual reaction agents which would contact the raw materials. The actual H_2 concentration in off-gas was detected by gas analyzer and the results are shown in Figure 6. It can be observed that the H_2 concentration increased with an increase in temperature, and it remained almost unchanged after 1373 K. The equilibrium H_2 concentration increased from 12.5 vol.% to 53.5 vol.%, which revealed that the pyrolysis of ammonia gas was enhanced by increasing the temperature. However, the experimental pyrolysis ratio was still less than the theoretical value, which can be reflected by $\ln K$. The theoretical and experimental values of $\ln K$ can be calculated according to Equations (6) and (7), respectively. The difference in the pyrolysis ratio may be attributed to the kinetic factors. Based on the above results, it can be deduced that ammonia gas was not completely decomposed, even at temperatures above 1373 K, leaving the possibility of reacting by NH_3 . A wide range of molecular or radical N-containing intermediates of ammonia pyrolysis, such as N, NH, NH_2 and N_2H_x ($x = 1-4$) may also be formed for nitridation process [27].

$$\ln K = -\frac{\Delta G^\ominus}{RT} = -\frac{18082.75}{T} + 27.74 \quad (6)$$

$$\ln K = \ln \frac{P_{N_2} \times P_{H_2}^3}{P_{NH_3}^2} \quad (7)$$

where K is the equilibrium constant; P_{N_2} , P_{H_2} and P_{NH_3} are the partial pressures of N_2 , H_2 and NH_3 , respectively.

Figure 6. The pyrolysis of ammonia gas under different temperatures.

Thus, the reaction mechanisms can be described by the schematic diagram illustrated in Figure 7. NH_3 may also react with VO_2 and Fe_2O_3 , even though it was easily decomposed during heating. When the temperature was lower than 1073 K, NH_3 reacted with Fe_2O_3 to form Fe and Fe_4N directly. The phase transformation during the entire reaction process proceeded in the following order: $Fe_2O_3 \rightarrow Fe \rightarrow Fe_4N$. However, when the temperature was higher than 1073 K, the transition path of Fe_2O_3 was $Fe_2O_3 \rightarrow Fe$. Fe_4N disappeared at higher temperatures. The difference may be ascribed to the kinetic factors. During the reaction process, the phase transformation of VO_2 follows the order: $VO_2 \rightarrow V_2O_3 \rightarrow VN$. According to the above results, it can be concluded that ammonia gas is an effective reduction and nitridation agent for preparing FeVN alloy with iron and vanadium oxides as the raw material. Although FeV45N alloy has been prepared and the reaction mechanisms were preliminarily revealed in this paper, there are still lots of things that need to be studied further, such as the effect of precursor, gas composition, etc., on the preparation of FeVN alloy. Moreover, scaling up experiments are still on the way for future industrial production on the basis of the studied process.

Figure 7. Schematic of the reaction mechanism of the formation of FeV45N.

5. Conclusions

This study describes the synthesis of FeV45N alloy by the reduction and nitridation of iron, and vanadium oxides mixture with ammonia gas. Thermodynamically, it was feasible to form metallic iron and vanadium nitride using ammonia gas as the reduction and nitridation agent. The experimental results indicated that the reaction temperature and time had significant effects on the reduction and nitridation process. With the increase of reaction temperature and time, the oxygen content was decreased gradually in the product. The maximum nitrogen and minimum oxygen content of FeV45N reached 11.85% and 0.25%, respectively, by roasting at 1273 K for 6 h. During the reaction process, the phase transformation of VO_2 follows the order: $\text{VO}_2 \rightarrow \text{V}_2\text{O}_3 \rightarrow \text{VN}$. When the temperature was lower than 1073 K, NH_3 reacted with Fe_2O_3 to form Fe and Fe_4N directly. Fe could not form Fe_4N when the temperature was over 1073 K. After sintering the composite powders at 1473 K for 1 h, it is possible to obtain a bulk of FeV45N alloy with a density of up to 5.92 g/cm^3 .

Author Contributions: Methodology, Y.L. and Z.Y.; software, Y.L. and Y.W.; validation, Y.L. and Y.W.; formal analysis, Y.L.; investigation, Y.L.; data curation, Y.L.; writing—original draft preparation, Y.L.; writing—review and editing, Z.Y. and X.L. All authors have read and agreed to the published version of the manuscript.

Funding: The authors wish to express their thanks to the National Key R&D Program of China (2018YFC1900500) for the financial support of this research.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Baker, T.N. Processes, microstructure and properties of vanadium microalloyed steels. *J. Mater. Sci. Technol.* **2009**, *25*, 1083–1107. [\[CrossRef\]](#)
2. Vervynckt, S.; Verbeken, K.; Lopez, B.; Jonas, J.J. Modern HSLA steels and role of non-recrystallisation temperature. *Int. Mater. Rev.* **2012**, *57*, 187–207. [\[CrossRef\]](#)
3. Baker, T.N. Microalloyed steels. *Ironmaking Steelmaking* **2016**, *43*, 264–307. [\[CrossRef\]](#)

4. Vdovin, K.; Pesin, A.; Feoktistov, N.; Gorlenko, D. Surface wear in hadfield steel castings DOPED with nitrided vanadium. *Metals* **2018**, *8*, 845. [\[CrossRef\]](#)
5. Li, H.Z.; Tong, W.P.; Cui, J.J.; Zhang, H.; Chen, L.Q.; Zuo, L. The influence of deep cryogenic treatment on the properties of high-vanadium alloy steel. *Mater. Sci. Eng. A* **2016**, *662*, 356–362. [\[CrossRef\]](#)
6. MacKenzie, M.; Craven, A.J.; Collins, C.L. Nanoanalysis of very fine VN precipitates in steel. *Scr. Mater.* **2006**, *54*, 1–5. [\[CrossRef\]](#)
7. Crooks, M.J.; Garratt, R.A.J.; Vander, S.J.B.; Owen, W.S. The isothermal austenite–ferrite transformation in some deformed vanadium steels. *Metall. Trans. A* **1982**, *13*, 1347–1353. [\[CrossRef\]](#)
8. Yücel, O.; Cinar, F.; Addemir, O.; Tekin, A. The preparation of ferrobore and ferrovanadium by aluminothermic reduction. *High Temp. Mater. Processes (London)* **1996**, *15*, 103–110.
9. Han, J.L.; Zhang, Y.M.; Liu, T.; Huang, J.; Xue, N.N.; Hu, P.C. Preparation of vanadium nitride using a thermally processed precursor with coating structure. *Metals* **2017**, *7*, 360. [\[CrossRef\]](#)
10. Zajac, S.; Siwecki, T.; Hutchinson, W.B.; Lagneborg, R. Strengthening mechanisms in vanadium microalloyed steels intended for long products. *ISIJ Int.* **1998**, *38*, 1130–1139. [\[CrossRef\]](#)
11. Cai, Z.; Mao, X.P.; Bao, S.Q.; Zhao, G.; Xu, Y.W. Influence of vanadium microalloying on deformation-induced pearlite transformation of eutectoid steel. *Metals* **2019**, *9*, 268. [\[CrossRef\]](#)
12. Grishchenko, S.G.; Matvienko, V.A.; Sarankin, V.A. Development and introduction of the production of nitrided ferrovanadium at zaporozhe ferroalloy plant. *Stal* **1982**, *7*, 42–44.
13. Franke, H.; Breuer, F.; Fuchs, A. Nitrogen-bearing sintering products and melted alloys. *NEUE HUTTE* **1966**, *11*, 604–606.
14. Krastev, D. Nitriding of ferroalloys. In Proceedings of the VI-th International Metallurgical Congress, Ohrid, Macedonia, 29 May–1 June 2014.
15. Liu, W.; Dong, K.; Zhu, R. Preparation of Nitrogenous Ferrovanadium by Gaseous Nitriding in the Liquid Phase Ferrovanadium. Proceeding of the 5th International Symposium on High-Temperature Metallurgical Processing, San Diego, CA, USA, 3 March 2014; pp. 185–192.
16. Ziatdinov, M.K.; Sha tokhin, I.M. Self-propagating high-temperature synthesis of ferrovanadium nitride for use in smelting high-strength low-alloy steels. *Steel Transl.* **2009**, *39*, 1005–1011. [\[CrossRef\]](#)
17. Pomarin, Y.M.; Grigorenko, G.M.; Lakomskiy, V.I. Solubility of nitrogen in iron alloys with vanadium and niobium. *Russ. Metall.* **1975**, *5*, 61–65.
18. Cheng, J.; Shen, H. Research on Nitrogen Solubility of Fe–Cr–Mn–V–N System Alloys in Liquid and Solid Phases. *Trans. Indian Inst. Met.* **2018**, *71*, 2433–2442. [\[CrossRef\]](#)
19. Wu, Y.D.; Zhang, G.H.; Chou, K.C. A novel process to synthesize high-quality ferrovanadium nitride. *Metall. Mater. Trans. B* **2016**, *47*, 3405–3412. [\[CrossRef\]](#)
20. Wu, Y.D.; Zhang, G.H.; Chou, K.C. Synthesis of high-quality FeV55N alloy by carbonitrothermic reduction of vanadium pentoxide–ferric oxide mixture. *JOM* **2017**, *69*, 676–681. [\[CrossRef\]](#)
21. Claridge, J.B.; York, A.P.E.; Brungs, A.J.; Green, M.L.H. Study of the temperature-programmed reaction synthesis of early transition metal carbide and nitride catalyst materials from oxide precursors. *Chem. Mater.* **2000**, *12*, 132–142. [\[CrossRef\]](#)
22. Glushenkov, A.M.; Jurcakova, D.H.; Llewellyn, D.; Lu, G.Q.; Chen, Y. Structure and capacitive properties of porous nanocrystalline VN prepared by temperature-programmed ammonia reduction of V₂O₅. *Chem. Mater.* **2009**, *22*, 914–921. [\[CrossRef\]](#)
23. Dong, S.M.; Chen, X.; Gu, L.; Zhou, X.H.; Wang, H.B.; Liu, Z.H.; Han, P.X.; Yao, J.H.; Wang, L.; Cui, G.L.; et al. TiN/VN composites with core/shell structure for supercapacitors. *Mater. Res. Bull.* **2011**, *46*, 835–839. [\[CrossRef\]](#)
24. Colling, C.W.; Choi, J.G.; Thompson, L.T. Molybdenum nitride catalysts: II. H₂ temperature programmed reduction and NH₃ temperature programmed desorption. *J. Catal.* **1996**, *160*, 35–42. [\[CrossRef\]](#)
25. Galesic, I.; Reusch, U.; Angelkort, C.; Lewalter, H.; Berendes, A.; Schweda, E.; Kolbesen, B.O. Nitridation of vanadium in molecular nitrogen: a comparison of rapid thermal processing (RTP) and conventional furnace annealing. *Vacuum* **2001**, *61*, 479–484. [\[CrossRef\]](#)
26. Wexler, D.; Calka, A.; Mosbah, A.Y. Ti–TiN hard metals prepared by in situ formation of TiN during reactive ball milling of Ti in ammonia. *J. Alloy. Compd.* **2000**, *309*, 201–207. [\[CrossRef\]](#)

27. Chen, H.Y.; Nambu, A.; Wen, W.; Graciani, J.; Zhong, Z.; Hanson, J.C.; Fujita, E.; Rodriguez, J.A. Reaction of NH_3 with titania: N-doping of the oxide and TiN formation. *J. Phys. Chem. C* **2007**, *111*, 1366–1372. [[CrossRef](#)]
28. Li, Y.G.; Gao, L.; Li, J.G.; Yan, D.S. Synthesis of nanocrystalline chromium nitride powders by direct nitridation of chromium oxide. *J. Am. Ceram. Soc.* **2002**, *85*, 1294–1296. [[CrossRef](#)]
29. Liu, Y.J.; Wang, Y.; Zhang, Y.; You, Z.X.; Lv, X.W. Mechanism on Reduction and Nitridation of Micron-Sized Titania with Ammonia Gas. *J. Am. Ceram. Soc.* **2020**. [[CrossRef](#)]
30. Vaidhyanathan, B.; Rao, K.J. Synthesis of Ti, Ga, and V nitrides: Microwave-assisted carbothermal reduction and nitridation. *Chem. Mater.* **1997**, *9*, 1196–1200. [[CrossRef](#)]
31. Wu, Y.D.; Zhang, G.H.; Chou, K.C. Preparation of high-quality FeV55N using ammonia as a reductant and nitrogen source. *JOM* **2018**, *70*, 2493–2498. [[CrossRef](#)]
32. Barin, I.; Knacke, O.; Kubaschewski, O. *Thermochemical Properties of Inorganic Substances*; Springer: Berlin, Germany, 1977.
33. Stull, D.R.; Prophet, H. *JANAF Thermochemical Tables*; U.S. Department of Commerce: Washington, DC, USA, 1985.
34. Arabczyk, W.; Rafat, P. Studies of the kinetics of two parallel reactions: ammonia decomposition and nitriding of iron catalyst. *J. Phys. Chem. A* **2008**, *113*, 411–416. [[CrossRef](#)]
35. Qin, M.L.; Wu, H.Y.; Cao, Z.Q.; Zhang, D.Y.; Qu, X.H. A novel method to synthesize vanadium nitride nanopowders by ammonia reduction from combustion precursors. *J. Alloy. Compd.* **2019**, *772*, 808–813. [[CrossRef](#)]

© 2020 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<http://creativecommons.org/licenses/by/4.0/>).