Research Article

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Preparation of vanadium by the magnesiothermic self-propagating reduction and process control

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Abstract: A new process for preparing vanadium by direct reduction of V₂O₅ from the Mg–V₂O₅ self-propagating system is proposed in this article. The reaction behavior and path of V₂O₅ in the magnesiothermic reduction process were investigated using the XRD, SEM-EDS, laser particle size analyzer, and specific surface area analyzer. The experimental results show that the reaction of the V₂O₅–Mg system is a solid-solid reaction, and the initial reaction temperature is 570°C. Although the formation of MgV₂O₄ spinel cannot be predicted via the calculation of thermodynamics, the presence of MgV₂O₄ spinel is of great significance to the V₂O₅ reduction process. Taking into account the characteristics of the gradual reduction of V₂O₅ by Mg and the appearance of the MgV₂O₄ spinel phase, the limiting link of the reaction may be the transition from MgV₂O₄ to V. A reduction path of V₂O₅ beyond the thermodynamic prediction is proposed: V₂O₅ → V₁O₃ → MgV₂O₄ → V. The reaction temperature and the phase transformation process can be effectively controlled by adjusting the ratio of reactants and additives, and element V can be obtained by a one-step rapid self-propagating reaction and breaking through the reaction restriction link. In this experiment, the vanadium powder with a porous structure, a specific surface area of 3.44 m² g⁻¹, and the oxygen content of 4.86 wt% were obtained.

Keywords: self-propagating reaction, metallic V, adiabatic temperature, MgV₂O₄

1 Introduction

Vanadium is commonly used as an additive in the iron and steel industry, which can refine the microscopic grains of steel and improve the strength, toughness, and corrosion resistance of steel [1–3]. Vanadium is also used as a stable element of the β phase in titanium alloys, which significantly improves the ductility and plasticity of titanium alloys. In addition, vanadium is an important component of superconducting materials, battery materials, phosphors, catalysts, photosensitive materials, and hydrogen storage alloys [4–7]. Therefore, vanadium has become a strategic material that countries around the world are competing to reserve [8–10].

Metal V and Ti–V alloys were obtained by electrolyzing V₂O₅ in the CaO–CaCl₂ molten salt system based on the principle of the “OS” method [11–15]. Wu et al. studied the electrochemical behavior during the electrolysis of V₂O₅ and achieved satisfactory results in controlling the current efficiency and energy consumption index [16], Gussone et al. used the LiCl–KCl molten salt system to electrolyze VCl₃ and TiCl₂ to prepare Ti–V alloy [17]. Weng et al. electrolyzed NaVO₃ from the CaCl₂–NaCl molten salt to obtain V [18,19]. Cai et al. improved the FFC process, studied the electrochemical behavior of V₂O₅ in the CaCl₂–NaCl electrolyte system, and found that V₂O₅ was first reduced to V₂O₃ and finally reduced to V [20–23]. However, the defect of low current efficiency still remained in this method. High-purity metallic vanadium is currently mainly prepared by reducing vanadium chloride with Mg. This idea is derived from the Kroll method to produce sponge titanium, but the inherent problems of the Kroll method such as high energy consumption and high pollution still need to be overcome [24,25]. Inazu et al. [26] proposed a new idea on the production of V, that is, V₂O₅ and MgO were sintered to obtain the MgV₂O₄ precursor, and then the MgV₂O₄ precursor was reduced by the Mg steam in a microwave field to obtain V. In the decomposition method, VN is first obtained by reducing V₂O₅/V₂O₃ with carbon/magnesium in nitrogen, and then VN is decomposed at high
temperature to obtain the metal V [27–29]. In the silico-
thermic method, V₂O₅ is reduced with Si to obtain the primary product, and then high-purity metal V is produced by the deep deoxidation of molten salt electrolysis [30]. Xu used V₂O₃ as raw material and CaCl₂ as a pore-forming agent, and reduced V₂O₃ with Ca steam under vacuum to obtain metal V [31]. Lee et al. used hydrogen to reduce V₂O₅ to obtain V₂O₃ and then reduced V₂O₃ at 1,073 K for 48 h with magnesium to obtain metal V [32].

Although metallic vanadium was successfully prepared in the above processes, the intermediate such as VCl₃, MgV₂O₄, V₂O₃, or VN were also produced in the preparation process, and the research on the preparation of metals and their alloys by direct reduction has gradually matured. For example, Ti, TiAlV, etc. have been successfully prepared by using TiO₂ as raw material and using magnesium thermal self-propagation [35,36].

### 2 Experimental

In this study, the raw materials were chosen with chemical reagents of vanadium pentoxide (V₂O₅, >99%, Macklin, China), magnesium powder (Mg, >99%, Sinopharm, China), sodium chloride (NaCl, >99%, Sinopharm, China), and hydrochloric acid (HCl, 36%, Sinopharm, China). The ratio of raw materials is listed in Table 1. The raw materials were weighed precisely and mixed thoroughly according to the ingredient ratio shown in Table 1, and then pressed into a cylindrical parison sample. The sample was placed in a self-propagating reactor and performed a self-propagating reaction in a vacuum to obtain a self-propagating reaction product. The reaction product was taken out and pulverized, and then soaked in a dilute hydrochloric acid solution for 3 h. After soaking, the solution was filtered. The filtered product was washed to neutrality, and finally, dried in a vacuum to obtain the reduced product.

The product phase was analyzed by X-ray diffraction (XRD, copper target, Bruke, D8, Germany). The micro-

| No. | Molar ratio (V₂O₅:Mg:NaCl) | Raw materials (g) |
|-----|---------------------------|-------------------|
|     | V₂O₅ | Mg | NaCl |
| 1#  | 1:1:-- | 36.4 | 4.8 | 0 |
| 2#  | 1:2:-- | 36.4 | 9.6 | 0 |
| 3#  | 1:3:-- | 36.4 | 14.4 | 0 |
| 4#  | 1:4:-- | 36.4 | 19.2 | 0 |
| 5#  | 1:5:-- | 36.4 | 24 | 0 |
| 6#  | 1:8:3.5 | 36.4 | 38.4 | 41 |
| 7#  | 1:8:-- | 36.4 | 38.4 | 0 |
| 8#  | 1:10:-- | 36.4 | 48 | 0 |

*: not detected.

morphology of the product was characterized by field emis-

scanning electron microscopy (SEM-EDS, Hitachi, su8010, Japan). The specific surface area of the product was obtained using a specific surface area analyzer (ASAP2020 m, U.S.A.). The oxygen content of the product was detected with an oxygen nitrogen hydrogen analyzer (LECO onh836). The particle size distribution of the product was characterized with a laser particle size analyzer (Mastersizer, 2000, UK).

### 3 Results and discussion

#### 3.1 Analysis of the reaction kinetics of the V₂O₅–Mg system

The TG–DTA curve of the V₂O₅–Mg system is presented in Figure 1(a). A sharp exothermic peak appeared near 570°C on the DTA curve, indicating that the reduction reaction was initiated at low temperatures, and the sharp exothermic peak indicated that the reaction was rapid and violent. Simultaneously, the obvious weight loss occurred near 570°C in the TG curve, which may be caused by splashing during the violent reaction and the volatilization loss of the metal magnesium in a high-temp-

erature environment. The melting point of Mg is 651°C and that of vanadium pentoxide is 690°C, but the actual reaction temperature was around 570°C, which suggested that the self-propagating reaction was a solid-solid reac-
tion. The DTA curve shown in Figure 1(a) was analyzed using the Freeman–Carroll differential method [37]. It can be seen that the reaction order $n = 0.14$ and the apparent activation energy $E = 1816.227$ kJ mol⁻¹.
3.2 Evolution of the theoretical equilibrium phase during the reduction reaction

Based on the minimum Gibbs free energy principle, the equilibrium phase evolution law of the Mg–V₂O₅ system with different molar ratios of Mg/V₂O₅ at different temperatures was calculated, as shown in Figure 2. When the molar ratio of Mg/V₂O₅ (replaced by Mg:V₂O₅) was 1:1 (Figure 2a), the Mg₂V₂O₇ composite oxide phase was formed in the reduction process, and there were also a large number of intermediate oxides and Magnéli phases such as VO₂, V₂O₃, and V₃O₅ in the system. When the Mg:V₂O₅ ratio was 2:1 (Figure 2b), in the reduction process, the Mg₂V₂O₇ compound disappeared, the content of V₂O₅ decreased, and the contents of V₂O₅ and VO increased, indicating that the degree of reduction of V₂O₅ increased. When the Mg:V₂O₅ ratio was 3:1 (Figure 2c), only two phases MgO and VO existed in the reduction products. When the Mg:V₂O₅ ratio reached 4:1 (Figure 2d), metal V appeared in the reduction products, and a large amount of VO and unreacted Mg also existed. Especially with the increase of the reaction temperature, the content of unreacted Mg and VO increased, even if the Mg:V₂O₅ ratio exceeded 5:1 to 10:1 (Figure 2d–g); there was still an unreduced VO phase in the products. This change rule of the equilibrium phase with the temperature showed that high temperatures were not conducive to completing the reduction reaction thoroughly, which was consistent with the strong exothermic thermodynamic properties of the self-propagating reaction system; in other words, increasing the amount of the reducing agent cannot promote the complete reduction reaction. It can be theoretically speculated that the composite oxide phase may be formed in the self-propagating rapid reaction process, and then the composite oxide phase was reduced.

Therefore, the phase evolution path during the reduction process was V₂O₅ → Mg₃V₂O₇ → V₂O₃ → VO → V.

3.3 Product phase analysis

Figure 3(a) shows the XRD pattern of the self-propagating product before acid leaching. When the Mg:V₂O₅ ratio was 1:1 (1#), the diffraction peaks of Mg₃V₂O₇, MgO, V₃O₅, and MgV₂O₆ phases emerged. When the Mg:V₂O₅ molar ratios increased to 2, 3, and 4 (2#, 3#, and 4#), the phases of the reaction products were only MgV₂O₆ and MgO, indicating that the actual self-propagating reaction was in the thermodynamical nonequilibrium and free escape system state, and there was a certain lag in the evolution of phases in the actual reaction process. When the ratio of Mg:V₂O₅ was 8:1 (7#), the diffraction peak intensity of Mg₂V₂O₇ decreased, and the diffraction peak of V appeared. After adding NaCl, the diffraction peak of MgV₂O₆ basically disappeared (6#). When the Mg:V₂O₅ ratio was 10:1 (8#), the diffraction peak of Mg₂V₂O₇ also disappeared. The XRD pattern of the pickled product is shown in Figure 3(b). It can be seen that after acid leaching, the by-product phases such as NaCl and MgO in the self-propagating reaction products could be effectively removed, but the by-product phases such as Mg₂V₂O₇ and MgV₂O₆ could not be removed; when the Mg:V₂O₅ ratio was 8:1 (6#) and 10:1 (8#), only the elemental V phase existed, indicating that pure metal V could be prepared by adjusting the material ratio of the self-propagating reaction experiment. The XRD analysis results showed that the evolution path of the product phase in the self-propagating reaction of the Mg–V₂O₅ process was V₂O₅ → V₂O₅ → MgV₂O₆ → V, which was somewhat different from the thermodynamic equilibrium prediction.
Table 2 shows the chemical composition analysis results of the products after pickling. As can be seen, when Mg:V$_2$O$_5$ ratios were 8:1 and 10:1 (6# and 8#), the mass fraction of oxygen in the metal vanadium was about 5%. When the Mg:V$_2$O$_5$ molar ratios were 2, 3, and 4 (2#, 3#, and 4#), although the acid leaching product phase
was only MgV2O4, the contents of Mg and V in products were significantly different. The three main diffraction peaks corresponding to the XRD pattern in the acid leaching product were analyzed, as shown in Table 3. It can be seen from Table 3 that with the increase of the Mg content in the raw material ratio, the diffraction peak of the products tended to shift to a low angle, the intensity of diffraction peaks near 35° and 18° decreased, and the intensity of diffraction peaks near 43° increased. This may be related to the atomic ratio of Mg and V.

### 3.4 Product morphology analysis

From the macro morphology photo of the self-propagating reaction product in Figure 4, it can be seen that when Mg:V2O5 was less than 5:1 (1#, 2#, 3#, 4#, and 5#), the volume of the self-propagating reaction product shrank significantly. When Mg:V2O5 was greater than 8:1 (6#, 7#, and 8#), the volume of the self-propagating reaction product expanded significantly.

Figures 5 and 6 present the SEM images of products before and after pickling, respectively. Table 4 shows the EDS results of the products in Figures 5 and 6. It can be seen that the morphologies of 2# and 4# products before pickling (Figure 5) and after pickling (Figure 6) were basically the same, and they were both dense blocks, and the EDS results (Table 4) indicated that a large amount of Mg element still remained in the 2# and 4# products after pickling, which was consistent with the XRD pattern analyses in Figure 3. The structure of the 5# product was loose after pickling, which was obviously different from the 2# and 4# products (Figure 6). The surface of the 8# product was dense before pickling, while the surface of the 6# product was attached with small particles (NaCl) before pickling (Figure 5). After pickling, both the 8# and 6# products were elementary V, proved by EDS analysis (Table 4), and exhibited porous morphology, which was obviously different from other products (Figure 6). These holes were divided into two types, one was the closing hole formed by interconnecting adjacent metal vanadium particles and the other was the tunnel-type hole formed by a hole and a skeleton together. In addition, it can be seen from the comparison of the morphology of products after pickling (Figure 6) that there were more sintered necks in the 8# product after pickling, indicating that the reaction temperature of the 8# product was higher than that of the 6# product; as the Mg content in the reaction system increased, the structure of the product gradually changed from dense blocky to porous after pickling. When the molar ratio of Mg and V2O5 was low (such as 2# and 4#), Mg was wrapped by liquid V2O5, solid MgO was formed by combining Mg with O2−, and

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**Figure 3:** XRD pattern of the products: (a) before acid leaching and (b) after acid leaching.

**Table 2:** Product composition analyses after acid leaching, mass %

| Sample number | O   | Mg  | V   |
|---------------|-----|-----|-----|
| 1#            | Bal.| 7.36| 52.73|
| 2#            | Bal.| 15.19| 44.24|
| 3#            | Bal.| 20.44| 45.97|
| 4#            | Bal.| 24.82| 47.11|
| 5#            | Bal.| 25.2| 50.2|
| 6#            | 5.02| 0.68| Bal.|
| 7#            | Bal.| 9.52| 78.59|
| 8#            | 4.86| 0.46| Bal.|

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**Table 3:** Diffraction peak analyses of acid leaching products

| No. 1   | No. 2   | No. 3   |
|---------|---------|---------|
| Pos.    | FWHM left | Area | Height | Pos.    | FWHM left | Area | Height | Pos.    | FWHM left | Area | Height |
|---------|-----------|------|--------|---------|-----------|------|--------|---------|-----------|------|--------|
| 5#      | 42.88     | 0.137| 2,728  | 14,955  | 35.34     | 0.114| 685    | 4,509   | 18.3      | 0.114| 675    | 4,454   |
| 4#      | 42.88     | 0.137| 2,736  | 1,500   | 35.51     | 0.114| 2,316  | 15,240  | 18.4      | 0.114| 1,132  | 7,446   |
| 3#      | 43.18     | 0.093| 1,525  | 11,021  | 35.58     | 0.13 | 3,170  | 16,370  | 18.5      | 0.15 | 1,843  | 8,326   |
then the composite MgV$_2$O$_4$ was formed by combining solid MgO with low-valence V oxide. After the reaction, the volume shrank. As the Mg:V$_2$O$_5$ molar ratio increased, the amount of MgO produced after the reaction also gradually increased, and the degree of reduction of V$_2$O$_5$ also gradually increased, but part of the Mg escaped in gaseous form during the reaction. When enough Mg content was involved in the reaction, V$_2$O$_5$ would be wrapped by liquid Mg during the reaction, and then O$^{2-}$ would be continuously transferred from V$_2$O$_5$ to liquid Mg to produce MgO. With the decrease of O atoms in V$_2$O$_5$, the volume of V$_2$O$_5$ continued to shrink, liquid and gaseous Mg would enter the gap of the raw material under the action of the capillary force, and the removal of MgO after pickling would leave a porous morphology (such as 6# and 8#). However, MgO combined with the low-valent
vanadium oxide cannot be removed by pickling. Therefore, the 2# and 4# products after pickling were dense and blocky, and the 5# and 7# products showed a “transition from dense blocky to porous” morphology.

### 3.5 Product particle size and specific surface area analysis

Because 1#–5# and 7# products were relatively hard and difficult to break, only the 6# and 8# products were analyzed for the particle size. Figure 7 shows the particle size distribution curves of 6# and 8# products after pickling. Compared with the particle size distribution curve of 8# product after pickling, the particle size distribution curve of 6# product after pickling was obviously shifted to the left, indicating that the particle size of 6# product after pickling was smaller than that of 8# product. Table 5 shows the particle size characteristics of the 6# and 8# products after pickling. The characteristic values of particle size D10, D50, D90, and D [3,4] of the 6# product after pickling were 7.63, 31.69, 73.23, and 36.99 µm, respectively, which were all smaller than the those of 8# product.

Figure 8 are the adsorption–desorption curves of 6# and 8# products after pickling. According to the IUPAC classification standard, the adsorption–desorption curves conformed to the characteristics of the type II adsorption isotherm. An obvious inflection point occurred in the low-pressure section of the adsorption curve, suggesting that the single-layer adsorption was completed at this time.

Table 4: EDS analysis results of different regions of the product

| Element (at%) | V  | Mg | O  | Na | Cl |
|---------------|----|----|----|----|----|
| A             | 28.2 | 27.99 | 43.81 |    |    |
| B             | 14.68 | 35.25 | 50.6 |    |    |
| C             | 18.22 | 32.40 | 49.37 |    |    |
| D             | 3.04 | 40.51 | 55.48 | 0.49 | 0.46 |
| E             | 9.07 | 53.28 | 37.65 |    |    |
| F             | 0.78 | 41.07 | 58.15 |    |    |
| G             | 41.28 | 19.43 | 39.29 |    |    |
| H             | 27.74 | 32.6 | 39.66 |    |    |
| I             | 22.57 | 32.43 | 44 |    |    |
| J             | 100 |    |    |    |    |
| K             | 39.91 | 17.68 | 39.91 |    |    |
| L             | 100 |    |    |    |    |
Then, multilayer adsorption occurred as the partial pressure increased. Obvious hysteresis appeared in the high-pressure section of the desorption curve because of the occurrence of capillary condensation between the particles and in the macropores. The analysis results of the specific surface area, pore volume, and average pore diameter of the 6# and 8# products after pickling are listed in Table 6. It can be seen that the specific surface areas of the 6# and 8# products were 2.01 and 3.44 m² g⁻¹, respectively. The 8# product had a larger specific surface area and pore volume, which was related to the Mg content in the 8# system and temperature. The higher reaction temperature caused the vaporization of metal Mg, and one part of the gasification Mg escaped from the reaction system, and the other part entered the gap of the raw material to participate in the reduction reaction of V₂O₅ to form metal V. The reduced metal V was sintered together under the action of high temperatures. Therefore, as more Mg was vaporized, the content of gasification Mg that participated in the reduction reaction of V₂O₅ increased, which led to an increase in the specific surface area and pore volume of the product after pickling. In the 6# product, NaCl did not participate in the reduction reaction of V₂O₅ but acted as “pore former,” resulting in larger pore size of 6# product compared with that of the 8# product.

### 3.6 Reaction mechanism analysis

Figure 9(a) shows the temperature–time curves during the reaction of 6# and 8# samples, and the illustration on the lower right of Figure 9(a) is a schematic diagram of the temperature measurement. It can be seen that the maximum combustion temperature and combustion rate of the 8# reaction system were higher than those of the 6# reaction system. The highest reaction temperature of both 6# and 8# reaction systems was much higher than the boiling point of Mg and slightly higher than the boiling point of NaCl, but lower than the melting point of metal V. Therefore, in the XRD analyses of the products before pickling, the phase diffraction peak of NaCl was present but no phase diffraction peak of Mg. The self-propagating exothermic reaction of the V₂O₅–Mg system relied on the flow of liquid/gas Mg and the transfer of heat. During the reaction, NaCl did not participate in the reaction but only played a role in reducing the adiabatic temperature. Since there was no NaCl in the 8# system and the heat release of the system was larger, the production rate of liquid/gas Mg of 8# system was faster than that of the 6# system, resulting in the higher combustion rate of the 8# reaction system than that of the 6# reaction system. The adiabatic temperature of systems with different Mg and

| Sample | Specific surface area/m² g⁻¹ | Pore volume/cm³ g⁻¹ | Average pore size/nm |
|--------|-------------------------------|---------------------|----------------------|
| 8#     | 3.44                          | 0.039               | 45.718               |
| 6#     | 2.01                          | 0.030               | 59.056               |

**Figure 8:** The adsorption–desorption curves of the products after pickling (a) 8# and (b) 6#.
NaCl contents is shown in Figure 9(b). It indicated that NaCl or excessive Mg could reduce the adiabatic temperature of the system as a diluent, and the dilution capacity of NaCl was larger than that of Mg under the same quantity condition. It was assumed that all the V$_2$O$_5$ in the raw materials were converted into the target product V in the process of calculating the adiabatic temperature, that is, no secondary reactions occurred, but only the experimental results of 8# and 6# systems were close to the ideal process in the present research. The adiabatic temperatures of the 8# and 6# samples were 1714.7°C and 1490.6°C, respectively. The highest temperature of 8# and 6# samples during the reaction (Figure 9a) was lower than the adiabatic temperature. This is because the system dissipated heat as it reacted, and there was dissolved oxygen with a mass fraction of 5% in element V obtained by the reduction reaction, which means that the reaction did not proceed completely. The changing trend of the calculated system reaction temperature in Figure 9(b) was basically consistent with the measured temperature in Figure 9(a), suggesting that the addition of NaCl could reduce the adiabatic temperature and the loss of Mg, so as to save the reducing agent. There was no active addition of MgO in this study, and MgV$_2$O$_4$ appeared when the compound of V$_2$O$_5$ and MgO were heated in the air, so the MgV$_2$O$_4$ in this experiment was likely to come from the reduction of V$_2$O$_5$ [26]. The chemical reactions that may occur in this process are shown in formulas (1)–(3).

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\begin{align*}
V_2O_5 + 2Mg &= V_2O_3 + 2MgO, \\
V_2O_3 + MgO &= MgV_2O_4, \\
MgV_2O_4 + 3Mg &= 2V + 4MgO.
\end{align*}
\]

4 Conclusion

In this article, V$_2$O$_5$, Mg, and NaCl were used as raw materials, and ultrafine metal V powder was successfully prepared by the magnesiothermic self-propagating reaction method. The conclusions are as follows:

1) The TG–DTA analysis showed that the reaction temperature of the V$_2$O$_5$–Mg system was around 570°C, so the self-propagating reaction of the V$_2$O$_5$–Mg system was a solid–solid reaction. The reaction order $n$ and the apparent activation energy $E$ calculated by the Freeman–Carroll differential method were 0.14 and 1816.227 kJ mol$^{-1}$, respectively.

2) The change path of phase during the reaction was $V_2O_5 \rightarrow V_3O_5 \rightarrow MgV_2O_4 \rightarrow V$. The formation of the complex MgV$_2$O$_4$ was related to the content of Mg involved in the reaction. MgV$_2$O$_4$ was formed in the case of insufficient Mg content, and MgV$_2$O$_4$ cannot be removed by pickling. With the increase of the Mg content involved in the reaction, the morphology of the product after pickling gradually changed from blocky to porous.

3) The temperature–time curve showed that it was feasible to control the reaction temperature of the system by adding NaCl, and the addition of NaCl could achieve the purpose of reducing the reaction temperature and saving the reducing agent. The finally obtained metal V powder containing oxygen with a mass fraction of 4.86 had a porous network structure with a specific surface area of 3.44 m$^2$ g$^{-1}$ and an average pore diameter of 45.718 nm.
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