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# New Preparation Method for Ti6AI4V Powder by Multistage Depth Reduction Process

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**Abstract:** Using  $\text{TiO}_2$ ,  $\text{V}_2\text{O}_5$ , and Al as raw materials and Mg and Ca as reducing agents, a novel method for preparing Ti6Al4V alloy powder through multistage deep reduction process was introduced. This new process has higher productivity and less pollution than traditional metallurgical process does. The results of self-propagating primary reduction experiments show that Mg is a more suitable reducing agent than Ca in the specific stage, and the porous Ti-Al-V-O precursor material with 6.74wt%~16.4wt% oxygen can be obtained when the amount of reducing agent Mg is appropriate. The Ti6Al4V powder with 0.24wt% oxygen can be obtained after the further calciothermic deep reduction (holding at 1173 K for 3.5 h).

Key words: multistage depth reduction process; self-propagating; acid leaching; Ti6Al4V alloy powder

Titanium alloys are commonly used in aerospace, medical industry, nuclear industry, and other fields because of their superior properties<sup>[1-3]</sup>. At present, Ti6Al4V alloy is the most widely used titanium alloy. With the rapid development of powder metallurgy and 3D printing industries, the demand for titanium alloy powder is increased significantly. However, the high cost of production restricts its application. Modifications for low cost, such as Ti-5Al-2.5Sn, and Ti-2Al-2.5Zr, have been considered and investigated. But none of them can share the equal performance of Ti6Al4V.

Currently, the main production methods of titanium alloy powders are atomization and hydrogenation-dehydrogenation which are all based on the Kroll process. Although the atomization method has the advantages of narrow particle size distribution and high sphericity, its production cost is high. The hydrogenation-dehydrogenation method can reduce the cost, but it has disadvantages such as excessive hydrogen content and difficult controlling of oxygen content. For example, Azevedo et al<sup>[4]</sup> prepared Ti6Al4V powder by hydrogenation-dehydrogenation method, but the hydrogen content was as high as 0.027wt%.

Various new processes have been investigated to replace the Kroll process. Chen et al<sup>[5,6]</sup> used the molten metal electrolysis

method (proposed by Fray, Farthing, and Chen, namely FFC method), which used graphite, TiO<sub>2</sub>, and molten CaCl<sub>2</sub> as the anode, cathode, and electrolyte, respectively, to produce titanium. Shi<sup>[7]</sup> and Du<sup>[8]</sup> et al also prepared TiV and TiFe alloy powders by FFC process. However, due to the low efficiency of the molten-salt process and the poor quality of products, FFC method still remains in the experimental research stage. To overcome the technical difficulties of FFC process, Suzuki<sup>[9]</sup> and Park<sup>[10]</sup> et al used the Ono-Suzuki (OS) method and electronically mediated reaction method, respectively. But none of the methods can be used for industrial production. Jiao et al<sup>[11]</sup> used the method proposed by researchers of University of Science and Technology Beijing, namely USTB method. Firstly, TiO, is reduced and sintered into Ti-C-O composite material of good conductivity, and then it is used as an anode in an electrolysis process. The technique overcomes the problems of low current density and low current efficiency which commonly exist in FFC and OS method. The experimental current efficiency of USTB method is generally about 90%, and the purity of metal titanium is over 99.90%. The method has a huge advancement in current electrolytic titanium process. In addition to electrolytic preparation of titanium, metallothermic reduction (MRC) is another

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promising low-cost method to prepare titanium. MRC method aims to reduce titanium oxide or titanium chloride by alkali sodium salt or alkaline earth metal, such as Mg and Ca, to obtain titanium and titanium alloy powders. Chen<sup>[12]</sup> and Weil<sup>[13]</sup> et al used TiCl<sub>4</sub>, AlCl<sub>3</sub>, and VCl<sub>4</sub> as raw materials, and sprayed the materials into molten Na or Mg for reduction to obtain Ti6Al4V powder. However, this kind of method is based on the preparation of TiCl<sub>4</sub> by Kroll method. Froes<sup>[14]</sup> and Wei<sup>[15]</sup> et al studied the reduction of TiO<sub>2</sub> with H<sub>2</sub> and CaH<sub>2</sub> to obtain titanium powder. Titanium alloy powders are synthesized by adding alloying elements. These methods need to solve some technical problems, such as difficult deoxidation of titanium oxide and control of trace impurities.

The preparation process of Ti and TiAlV alloys using Mg and Ca as reducing agents in different reduction stages was proposed by Nersisyan<sup>[16,17]</sup>, but AlCl<sub>3</sub> and a large amount of Ca(OH)<sub>2</sub> as additive agent were used in the process. According to the thermodynamic characteristics of step-by-step reduction of high valent metal oxides and the thermodynamic transmutation of different equilibrium phases in the reduction process<sup>[18,19]</sup>, a novel method of preparing Ti6Al4V alloy powder by multistage reduction of metal oxides (TiO<sub>2</sub>, V<sub>2</sub>O<sub>3</sub>) was proposed in this research. A high productivity and pollution-free metallurgical method for preparing Ti6Al4V powder was introduced. The law of phase transformation in the reduction process was studied. The products were characterized and some important experimental parameters were investigated.

#### **1** Experiment

Raw materials used in this research were listed as follows: titanium dioxide (TiO<sub>2</sub>, purity>98.5%, particle size: 200~500 nm, Kemiou, China), vanadium pentoxide (V<sub>2</sub>O<sub>5</sub>, purity>99%, particle size: <10  $\mu$ m, Macklin, China), aluminum powder (Al, purity>99%, particle size: <200  $\mu$ m, Macklin, China), magnesium powder (Mg, purity>99%, particle size: 74~1500  $\mu$ m, Sinopharm, China), calcium granules (Ca, purity>99%, particle size: <200  $\mu$ m, Sinopharm, China), hydrochloric acid (HCl, 36vol%, Sinopharm, China). TiO<sub>2</sub> and V<sub>2</sub>O<sub>5</sub> were dried at 373~423 K for 24 h in order to remove water and some volatile impurities before experiment.

Firstly, TiO<sub>2</sub>, V<sub>2</sub>O<sub>5</sub>, Al, and Mg (Ca was used to replace Mg for investigating the effect of different reducing agents during the self-propagating primary reduction process) were mixed evenly according to the molar ratio of TiO<sub>2</sub>:V<sub>2</sub>O<sub>5</sub>:Mg (or Ca):Al =1.88: 0.0393: 3.96 $\alpha$ : 0.222 ( $\alpha$  =1 indicates the theoretical addition of Mg). Then the mixture was pressed into a billet of  $\Phi$ 33 mm×40~50 mm. The pressed specimen was put into the self-propagating reactor, and high-purity argon was inflated into the reactor and the inner pressure was kept at 0.5 MPa. Then the 0Cr21Al6Nb resistance wire was heated and reaction began. The obtained products were leached with dilute HCl solution (2 mol/L) to remove the by-products and to obtain the primary reduction products. Then the primary reduction products were reduced by Ca at different temperatures for different time under high-purity argon atmosphere. Then the calciothermic reduction products were leached with acid to remove CaO by-products, washed, and vacuum dried. Finally, the Ti6Al4V alloy powder was obtained. The experiment process is shown in Fig.1.

Factsage 7.05 software package was used to calculate the equilibrium phase and adiabatic temperature according to the principle of minimum Gibbs free energy variation. The phase of the reaction products was characterized using a copper target X-ray diffractometer (XRD, Bruker, D8, Germany). The microstructure of the products was characterized by field emission scanning electron microscopy (SEM, SU8010, Hitachi, Japan) coupled with energy disperse spectroscopy (EDS). The particle size of the products was characterized using a laser particle size analyzer (Mastersizer, 2000, UK). The specific surface area (SSA) of the products was characterized by a SSA analyzer (ASAP2020M, US). The oxygen content of the products was analyzed using an oxygennitrogen analyzer (Bruker, D8, Germany). Other chemical components were analyzed by inductively coupled plasma spectrometry (ICP-AES, Leeman, Prodigy XP, US).

#### 2 Results and Discussion

#### 2.1 Thermodynamic analysis

The calculated phase equilibria of the self-propagating reaction systems are as follows: (1)  $\text{TiO}_2$ :  $V_2O_5$ : Mg: Al=1.88: 0.0393: 3.96: 0.222; (2)  $\text{TiO}_2$ :  $V_2O_5$ : Ca: Al=1.88: 0.0393: 3.96: 0.222 (the ratio of reactants is designed according to the composition of Ti6Al4V). Assuming that the starting temperature of the reaction is 298.15 K, the equilibrium pressure in the system at the end of the reaction is P(Mg/Ca)=0.01, 0.1, 0.2, 0.3, and 0.4 MPa, and the enthalpy change of the chemical reaction is  $\Delta H=0$ , the phase of the products at equilibrium and the reaction temperature of the system are calculated according to the Gibbs free energy minimum principle. The results are shown in Fig.2.

As shown in Fig.2, when Mg is used as the reducing agent in the self-propagating reaction systems, the main phases of the reaction products are Ti, TiO, by-products MgO, and



Fig.1 Schematic diagram of experiment process



Fig.2 Adiabatic combustion temperature and equilibrium phases in Mg-TiO<sub>2</sub>-V<sub>2</sub>O<sub>5</sub>-Al (a) and Ca-TiO<sub>2</sub>-V<sub>2</sub>O<sub>5</sub>-Al (b) systems

Mg (g). The titanium sub-oxide phase TiO in the reduction products disappears when Ca is used as the reducing agent, whreras the by-product phase  $Ca_3Ti_2O_6$  is formed. Whether Mg or Ca is used as the reducing agent, almost all metal Al in the compound is combined with Ti and transformed into TiAl intermetallic compound, and  $V_2O_5$  is completely reduced to V.

It is known from Fig.2a that when the equilibrium pressure of Mg vapor in the reaction system increases from 0.01 MPa to 0.4 MPa, the TiO content in the reduced products decreases from ~20mol% to ~10mol%, indicating that it is difficult to completely break through the thermodynamic bottleneck of TiO→Ti by Mg as the reducing agent. Compared with the results shown in Fig.2b, it is known that when Ca is used as the reducing agent, TiO<sub>2</sub> can be completely reduced to Ti. However, the by-product phase Ca<sub>3</sub>Ti<sub>2</sub>O<sub>6</sub> exists in all systems of different vapor pressures. Because of the significant difference between CaO and titanium oxides in acidity and basicity, once CaO and Ti<sub>2</sub>O<sub>3</sub> are formed during the reduction process, Ca<sub>3</sub>Ti<sub>2</sub>O<sub>6</sub> can be formed in the reduction in hightemperature environment. The Ca<sub>2</sub>Ti<sub>2</sub>O<sub>6</sub> can deteriorate the mass transfer conditions and decrease the reduction efficiency of the reduction reaction, and it is difficult to completely remove in the subsequent purification process. When Mg is used as the reducing agent, the composite oxide by-product phases (MgTiO<sub>3</sub>, MgTi<sub>2</sub>O<sub>5</sub>, etc.) are not formed. Because the alkalinity of MgO is much weaker than that of CaO, the thermodynamic and kinetic conditions are insufficient for the formation of MgTiO<sub>3</sub> and MgTi<sub>2</sub>O<sub>5</sub> in the transient large gradient temperature field of the self-propagating rapid reduction.

#### 2.2 Self-propagating primary reduction process

The raw materials of  $TiO_2$ :  $V_2O_3$ : Ca: Al=1.88: 0.0393: 3.96: 0.222 were used in the experiment of primary reduction process. The XRD patterns of the products before and after acid leaching are shown in Fig. 3. When Ca is used as the reducing agent, CaTiO<sub>3</sub>, unreduced TiO<sub>2</sub>, and a small amount of titanium sub-oxide phase Ti<sub>2</sub>O can be detected. However, a distinct metal Ti phase appears, which is different from the product results when Mg is used as the reducing agent under the same experiment conditions. Besides, Mg cannot completely reduce TiO<sub>2</sub> to Ti (as shown in Fig.4). This result is consistent with the thermodynamic theory predicted in Fig. 2. The existence of the TiO<sub>2</sub> phase in the reduction products is due to the deterioration of mass transfer kinetics of the reaction caused by the appearance of CaTiO<sub>3</sub> during the reduction process. CaTiO<sub>3</sub> appears, as shown in Fig. 3, and Ca<sub>2</sub>Ti<sub>2</sub>O<sub>6</sub> appears in the thermodynamic calculation results, because the instantaneous high temperature formed by the selfpropagating rapid reaction causes local excess of TiO<sub>2</sub> and the preferential combination of TiO<sub>2</sub> with CaO is more obvious. To obtain high-purity titanium powder, the Ca reduction of CaTiO, requires that the system temperature increases to 1273 K with holding for 6 h<sup>[20]</sup>. Setting the system temperature at 1173 K for 3.5 h shows an obvious energy-saving effect. Therefore, Mg is selected as the reducing agent in the selfpropagating primary reduction process.

The raw materials of TiO<sub>2</sub>:V<sub>2</sub>O<sub>5</sub>:Mg:Al=1.88:0.0393:3.96 $\alpha$ : 0.222 were used for the experiment of primary reduction in order to investigate the influence of Mg dosage. Fig.4a and 4b show the XRD patterns of the reduction products before and after acid leaching. It can be seen from Fig.4a that phases of the products before acid leaching are composed of MgO, TiO, and Ti<sub>2</sub>O phases, and there is no significant difference among the results of products of different Mg ratios, indicating that the primary reduction processes are consistent under different Mg dosages. As shown in Fig.4b, when  $\alpha$  increases from 0.8 to 1, the TiO diffraction peak gradually weakens, while the Ti<sub>2</sub>O diffraction peak gradually increases; Both Ti<sub>2</sub>O and Ti<sub>6</sub>O phases have the hexagonal crystal form,



Fig.3 XRD patterns of calciothermic self-propagating primary reduction products before and after acid leaching



Fig.4 XRD patterns of magnesiothermic self-propagating primary reduction products before (a) and after (b) acid leaching; TiO phase content (c), oxygen content (d), and Ti, Al, and V element contents (e) of products of different Mg ratios after acid leaching

but TiO has the cubic crystal form. The diffusion rate of O<sup>2-</sup> ions in the hexagonal crystal form is much lower than that in the cubic crystal form. Fig. 4c and 4d show the TiO phase content calculated by JADE 7.0 software and oxygen content of products of different Mg ratios after acid leaching, respectively. The curves in Fig. 4c and 4d have the similar trend and can be divided into two stages:  $\alpha \leq 1$  and  $\alpha \geq 1$ . When  $\alpha \leq 1$ , the decline trend is obvious. But when  $\alpha \geq 1$ , the curve tends to be gently fluctuant around a stable value. This is because the magnesiothermic self-propagating reaction has the characteristics of fast reaction speed, which deviates reaction greatly from the theoretical reaction equilibrium. Therefore, when  $\alpha$  increases to a certain degree, the oxygen content in the product tends to be stable. The porous Ti-Al-V-O precursor material with 6.74wt% ~16.4wt% oxygen content can be obtained, as shown in Fig.4d. The thermodynamic bottleneck in the TiO<sub>2</sub> reduction process of TiO→Ti has not been completely overcome, which is consistent with the thermodynamic calculation results shown in Fig.2. Fig.4e shows the element contents of Ti, Al, and V. It is worth noting that as Mg ratio increases, the proportion of Ti in the product also increases. Although different researches reported nearly opposite conclusions<sup>[21,22]</sup>, this phenomenon is probably due to different acid solubility of different types of titanium oxides.

XRD analysis shows that no substance contains V and Al elements, which can be explained by two reasons: (1) the amount of added  $V_2O_5$  and Al is small; (2) V and Al elements are dissolved in Ti oxides, as shown in Fig.5.

In order to better observe the original morphology of the magnesiothermic self-propagating products, the products

 $(\alpha=1, before acid leaching)$  were embedded in an industrial gel and then polished. The dark colored part in Fig. 5a is the industrial gel, and the bright colored areas are the products. Through the EDS results of point A, unreacted Mg can be found in Fig. 5a. Fig. 5b also shows the light and dark areas. According to the EDS results of area B (Fig. 5c), it can be found that the distribution regions of Mg and O are basically the same, and the distribution regions of Ti, Al, and V are basically the same. It shows that Ti-Al-V-O precursor material was obtained by the self-propagating primary reduction process. Fig. 6 shows the porous morphology of magnesiothermic self-propagating products after acid leaching. These pore sizes are 3~5 µm, which is consistent with the morphology in Fig. 5b, indicating that these voids are caused by the reaction of MgO and hydrochloric acid. The porous particles provide abundant channels for the mass transfer of Ca reductant in the next calciothermic deep reduction process, and the reduction reaction can only occur gradually from the outmost surface to the interior of the particles.

### 2.3 Calciothermic deep reduction process

As it was difficult for magnesiothermic self-propagating primary reduction to reduce oxygen content in the products, calcium with stronger metallic properties was used to continuously reduce the oxygen. Because the proportion of alloy elements (Ti, Al, V) in the magnesiothermic selfpropagating products meets the requirement of Ti6Al4V alloy when  $\alpha=1\sim1.2$  and their oxygen contents are not much different, the products of  $\alpha=1$  was selected to conduct the further experiment.



Fig.5 SEM image of magnesiothermic self-propagating products (α=1) before acid leaching (a); enlarged SEM image (b) and EDS mapping (c) of area B in Fig.5a



Fig.6 SEM image of magnesiothermic self-propagating products ( $\alpha$ = 1) after acid leaching

The magnesiothermic self-propagating primary reduction products were mixed with Ca according to the mass ratio of 1:1. The reaction was conducted at different reduction temperatures (973~1373 K) for different durations (1~5 h). Fig. 7 shows the oxygen content and XRD patterns of the products at different conditions. The oxygen content in the products after reduction for 3.5 h is decreased firstly and then increased with increasing the reduction temperature, reaching a minimum value of 0.24wt% at 1173 K. The oxygen content in the products after reduction at 1173 K is decreased firstly and then remains stable with increasing the reduction time, reaching a minimum value at 3.5 h. These results are the consequence of the interaction between thermodynamics and



Fig.7 Oxygen content of products (α =1) after acid leaching at different calciothermic deep reduction temperatures for different durations (a); XRD patterns of products (α=1) after acid leaching at 1173 K (b)

kinetics. The calciothermic deep reduction process is an exothermic reaction, and increasing the reduction temperature is not conducive to the production. However, increasing the reduction temperature can change the crystal form of the titanium sub-oxides (Ti<sub>2</sub>O, Ti<sub>6</sub>O) from hexagonal to cubic, which is conducive to the migration of O<sup>2-</sup> ions. In addition, a higher reduction temperature can increase the kinetics of the consumption of titanium sub-oxides. The cell parameters of products after acid leaching at different calciothermic deep reduction temperatures for different durations were calculated by JADE 7.0 software: *a*=0.292 26 nm, *b*=0.466 03 nm. The elements Al and V enter *a*-Ti, resulting in the smaller *a*-Ti unit cell parameters. Therefore, the phase peak of products (6.2wt% Al, 3.64wt% V, 0.24wt% O, 0.01wt% Mg, <0.01wt% Ca) shifts to a higher angle, as shown in Fig.7b.

Fig. 8 shows the analysis results of the particle size



Fig.8 Particle size distribution of different magnesiothermic selfpropagating primary reduction products and calciothermic deep reduction products

distribution of the products at different stages during the preparation of Ti6Al4V alloy powders. The magnesiothermic self-propagating primary reduction products before and after leaching and the calciothermic deep reduction products after leaching at 1173 K are marked as product A, B, and C, respectively. The average particle size of product B and C does not change significantly, indicating that the calciothermic deep reduction process does not cause excessive growth of the final products. The  $D_{10}$ ,  $D_{50}$ , and  $D_{90}$  values of the calciothermic deep reduction products after acid leaching are 7.52, 34.6 and 81.0 µm, respectively. SSA of product A, B, and C is 0.173, 0.461, 0.328 m<sup>2</sup>·g<sup>-1</sup>, respectively.

Fig.9 shows the SEM morphologies of calciothermic deep reduction products. The products before acid leaching were embedded in an industrial gel and then polished, as shown in Fig. 9a and 9b. Table 1 is EDS analysis results of different points in Fig. 9. According to Table 1, the lightest part in Fig. 9a and 9b is the TiAlV alloy. The cross-section of the products exhibits an irregular shape, and the product is embedded in the substrate formed by the condensation of excess molten Ca. The internal filling of TiAlV alloy is CaO and a small amount of Ca. Combined with the morphology of the products in Fig. 6, it can be determined that when the calciothermic deep reduction temperature is 900 °C, Ca penetrates the void of the titanium sub-oxides in a liquid form, and deoxidation occurs after the contact between liquid Ca and titanium sub-oxides. The generated CaO is precipitated as a solid phase. Excess Ca remains in the voids of TiAlV alloy phase. The final products form a dense contracted smooth morphology. Fig. 9c shows the microstructure of TiAlV alloy powder after acid leaching, which is a typical porous hollow shape. Fig.9d distinctly shows an incompletely sintered diffusion phase. From the results of EDS analysis in Table 1, it can



Fig.9 SEM morphologies of cross-section of calciothermic deep reduction products at 1173 K before (a, b) and after (c, d) acid leaching

Point	Ti	Al	V	Mg	Ca	0	
1	2.94	0.47	0.18	-	96.41	-	
2	91.93	4.14	1.64	-	2.29	-	
3	3.38	0.1	0.25	-	71.24	25.03	
4	77.65	0.86	19.26	-	0.23	-	
5	92.90	6.82	0.04	0.25	-	-	

Table 1 EDS analysis results of of point 1~5 in Fig.9 (wt%)

 Table 2
 Process duration of main production processes (h)

Process	Duration
Self-propagating primary reduction	5~6
Deep reduction	15
Acid leaching and drying	12

be concluded that V and Al elements in the calciothermic deep reduction products are not evenly distributed in Ti, but form Ti-V-rich phase and Ti-Al-rich phase.

#### 2.4 Production cycle assessment

The new method proposed in this research involves four main production steps: self-propagating primary reduction process, deep reduction process, and two times of acid leaching and drying processes, as shown in Fig. 1. The required time for each process is shown in Table 2. This method makes full use of the huge chemical energy contained in the raw materials. In the self-propagating primary reduction stage, only a small amount of electrical energy is required to initiate the reaction. The deep reduction stage consumes electric energy, but the energy consumption is not large.

Therefore, this novel method can complete a production cycle within 48 h, which has huge industrial production potential and is much shorter than the production cycle of Kroll process<sup>[23]</sup>.

## **3** Conclusions

1) A multistage depth reduction process, i. e., magnesiothermic self-propagation primary reduction and calciothermic deep reduction can obtain low-oxygen Ti6Al4V alloy powder using TiO<sub>2</sub>,  $V_2O_5$ , and Al as raw materials.

2) During the magnesiothermic self-propagating primary reduction process, as the Mg content increases, the TiO content in the products gradually decreases, indicating that the deoxidation reaction becomes more difficult. The porous Ti-Al-V-O precursor material with 6.74wt%~16.4wt% oxygen content can be obtained, and no composite metal oxide appears in this process.

3) After reduction at 1173 K for 3.5 h in the calciothermic deep reduction process, high-purity Ti6Al4V alloy powder can be obtained.

4) This novel method has the characteristics of short

production cycle and non-pollution, and is expected to be used for industrial production.

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# 通过多级深度还原制备Ti6Al4V合金粉体的新工艺

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摘 要:介绍了一种以TiO<sub>2</sub>、V<sub>2</sub>O<sub>5</sub>和Al为原料,Mg和Ca作为还原剂的通过多级深度还原法制备Ti6Al4V合金粉体的新方法。与传统的冶金方法制备Ti6Al4V粉末相比,该方法具有更高的生产效率和更少的环境污染。自蔓延初级还原实验的结果表明,Mg比Ca更适合在此阶段作为还原剂,当使用Mg作为还原剂时可以得到氧含量为6.74%~16.4%(质量分数,下同)的多孔Ti-Al-V-O前驱体。通过进一步的钙热深度还原(1173K下保持3.5h)可以得到含氧量为0.24%的Ti6Al4V粉体。 关键词:多级深度还原;自蔓延;酸洗;Ti6Al4V合金粉体

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