

Preparation of V–Ti–Fe master alloys by metallothermic reduction method

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Abstract: V–Ti–Fe master alloys were prepared by metallothermic reduction method, and the influences of the mass ratio of V_2O_5 to TiO_2 , Al and Al–Mg alloy addition amounts on the metal recovery rates and alloy compositions were investigated. The results show that appropriate technological parameters are: the mass ratio of V_2O_5 to TiO_2 is 0.5:1, Al addition represents 95% of the theoretical value, and the Al–Mg alloy addition amount is one third that of the Al addition. The results from energy spectrum analysis show that V and Fe distribute uniformly in the prepared alloy, while the segregation for Ti, i.e. Ti-rich phase is detected. A spray refining process was carried out to reduce the impurity contents of Al and O in the prepared alloys. The Al content drops from 4.27% to 1.86%, and the O content drops from 2.10% to 0.91% after the refining process.

Key words: V–Ti–Fe master alloys; metallothermic reduction method; recovery rates; refining process

1 Introduction

As a kind of clean energy, hydrogen has attracted a significant attention in recent years due to its high energy efficiency and environmental safety. To utilize hydrogen as a energy carrier in large scale, a severe challenge that must be overcome is how to store it. Many investigations have been performed to solve this problem. The storage of hydrogen in metal hydrides is considered to be one of the most attractive solutions for characteristics of large bulk density and safety. Among various kinds of hydrogen storage alloys, V-based solid solution alloys show a large hydrogen capacity of 3.8% (mass fraction), although the efficient capacity is 1.9% (mass fraction), which is higher than that of the $LaNi_5$ -based and $ZrMn_2$ -based hydrogen storage alloys [1–4].

Ternary V-based solid solutions of Ti–V–Ni [5], Ti–V–Fe [6], Ti–V–Cr [7], Ti–V–Mn [8] and quaternary alloys of Ti–V–Cr–Fe [9] and Ti–V–Cr–Mn [10] have been widely investigated. In the reseraches, the hydrogen storage alloys are generally prepared by smelting pure metals in a induction furnace or electric arc furnace. Some proper heat treatments are executed after the remlting process to improve the hydrogen storage

properties of the alloy. Because V and Ti have high melting posints and V is expensive, the manufacturing cost of V-based solid solutions is very high. If the alloys can be acquired from the metal oxides directly, the manufacturing cost would be reduced markedly.

Alloys prepared by metallothermic reduction method usually contain some Al, O and Si inclusions, which is attributed to the selection of raw materials. For the V-based alloys, Al and Si impurities are harmful for the hydrogen storage [11–14]. Research shows [15] that the argon blowing process could remove inclusions from molten steel well. However, there is less study on the effects of argon blowing process on diminishing impurities in V–Ti–Fe alloys. In this work, the master V–Ti–Fe alloys were prepared by reducing metal oxides by a metallothermic reduction method, and the target composition was $Ti_{46}V_{44}Fe_{10}$ which had a good overall property [16]. Spray refining process was carried out to reduce the impurities of the prepared alloys.

2 Experimental

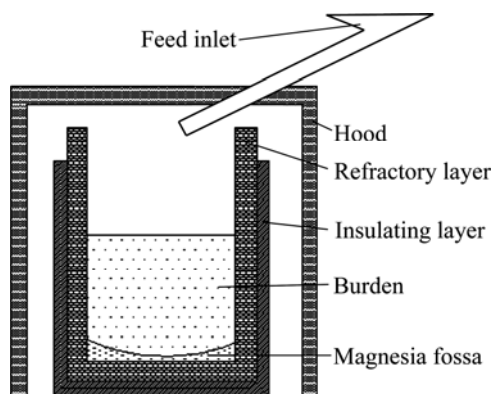
The purities and grain size of the main raw materials for alloy preparation are listed in Table 1. Scrap iron, cryolite, analytical pure CaO , CaF_2 and $KClO_3$ were

Table 1 Specification of materials

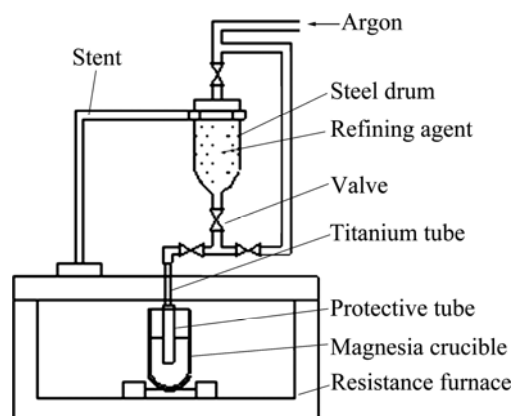
Material	Purity/%	Grain size/mm
Vanadium pentoxide	≥ 95	≤ 1
Titanium white	≥98	≤ 0.1
Al powder	≥99	0.5~2
Al–Mg alloy powder	–	≤1

also used in this experiment.

The alloy samples were prepared in a metal bucket with refractory liner, and the heat was 3100 kJ/kg. The schematic diagram of the smelting device is shown in Fig. 1. Because the reduction process of TiO_2 is difficult to conduct, besides Al powder, the combined reducing agent (Al–Mg alloy) was also used as the reducing agent to increase the metal recovery rates. In addition, some CaO and CaF_2 powders were added for inhibiting the formation of Ti suboxides and promoting the separation of slag-steel. The amounts of CaO and CaF_2 were 90% and 35% (mass fraction) of the Al addition amount, respectively. Raw materials without KClO_3 were first mixed in a mixing barrel for 1 h, and then KClO_3 was introduced into the mixture. After the mixing process, partial burden was first charged into the reactor for ignition. The residual burden was continuously filled into the reactor through the feed inlet during the preparation of target alloys.

**Fig. 1** Schematic diagram of smelting device used for production of V–Ti–Fe master alloys

The refining process was carried out in a YFX12/160–Y6 MoSi_2 resistance furnace in argon atmosphere. The refining temperature was 1600 °C, and the refining time was 10 min. The slag system 50% CaF_2 –25% CaO –25% Na_3AlF_6 (mass fraction) was served as the refining agent. The slag materials were injected in the alloy melt by a self-made powder-spraying device, and the argon flow was controlled at 10 L/min. The schematic diagram of the refining device is presented in Fig. 2.

**Fig. 2** Schematic diagram of refining device used for reducing impurities in alloys obtained by metallothermic reduction method

The content of oxygen was detected by a TC-436 oxygen and nitrogen analyzer, and the contents of other elements in these alloys were detected by chemical analysis. The crystalline phases of the prepared alloys were identified by a D/max-2500PC X-ray diffractometer (Japan) with $\text{Cu K}\alpha$ radiation at a pip voltage of 40 kV and a current of 100 mA. The microstructure and chemical compositions were characterized by scanning electron microscope (SEM, SSX-550, Japan).

3 Results and discussion

3.1 Influences of mass ratio of V_2O_5 to TiO_2 on metal recovery rates and compositions of prepared alloys

It is well known that the activity of V_2O_5 is different from that of TiO_2 , so the mass ratio of V_2O_5 to TiO_2 should not be designed according to the theoretical value absolutely. The influence of the mass ratio of V_2O_5 to TiO_2 on the metal recovery rates and the compositions of the alloys was investigated, and the results are shown in Table 2 and Fig. 3. With decreasing mass ratio of V_2O_5 to TiO_2 , the recovery rates of Ti and V decrease along with an increase in the contents of Al and O impurity. When the mass ratio is 0.3, the alloy does not separate with slag well, and most of the alloy inlays in the slag as the granular form. The recovery rates of Ti and V are very low, just 31.7% and 35.0%, respectively. Simultaneously, the contents of Al and O are also much higher than those obtained from other comparative experiments. The reasonable explanation is that with reducing mass ratio of V_2O_5 to TiO_2 , more Ti is reduced out from TiO_2 ; however, the excessive Ti could not form alloy with V or Fe efficiently. The density of Ti (4.5 g/cm³) is close to that of the slag (3.2–3.6 g/cm³), therefore, part of Ti metal fails to separate from slag before the solidification

process. When the mass ratio of V_2O_5 to TiO_2 rises up to 0.5:1, the slag-metal separation process proceeds smoothly, the recovery rates of V and Ti reach 81% and 55.8%, respectively, and the alloy composition is close to the target composition. When the mass ratio of V_2O_5 to TiO_2 is higher than 0.5:1, although the recovery rates are higher, the alloy composition drifts far from the target composition.

Table 2 Influence of mass ratio of V_2O_5 to TiO_2 on composition of prepared alloys (mass fraction)

Mass ratio of V_2O_5 to TiO_2	Molar ratio of V to Ti to Fe	Composition of alloy/%		
		Al	Si	O
0.9:1	58.4:30.1:11.5	3.77	0.51	2.2
0.7:1	51.0:37.5:11.5	4.13	0.51	2.2
0.5:1	44.3:44.2:11.5	4.59	0.55	2.3
0.3:1	34.7:51.5:13.8	7.17	0.53	3.6

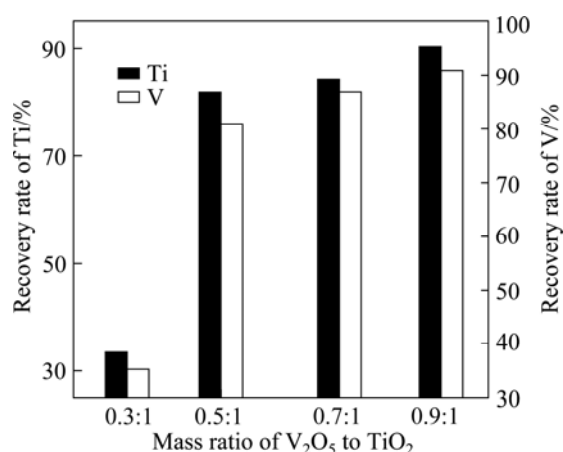


Fig. 3 Influences of mass ratio of V_2O_5 to TiO_2 on recovery rates of V and Ti

The Si content in these alloys is about 0.5% (mass fraction) with a good reproducibility, and no obvious change tendency for Si content can be found, as seen from Table 2. It can be confirmed that a considerable proportion of Si impurity is derived from refractory materials.

3.2 Influences of Al addition amount on metal recovery rates and compositions of prepared alloys

As the main reducing agent, the amount of Al addition directly affects the recovery rate of metals and the impurity content. If the Al amount is not enough, residual Al impurity in the alloy would be less, resulting in insufficient reactions. On the other hand, Al impurity increases if the Al addition amount is high.

The influence of the ratio (n) of actual Al dosage to

theoretical Al dosage on the metal recovery rates and alloying constituents was also studied. The results are shown in Table 3 and Fig. 4. It can be seen that the Al contents in the alloys are high, with the values of n higher than 0.95. When the n value is 0.85, the slag-iron separation process almost disappears for the lack of reductant, and the recovery rates of V and Ti are only 50.1% and 35.0%, respectively. The alloys are acquired close to the target alloy when the n values reach 0.95 and 0.9. But the Ti recovery rate is higher when the n value is 0.95.

Table 3 Influence of Al addition amount on composition of prepared alloys (mass fraction)

n	Molar ratio of V to Ti to Fe	Composition of alloy/%		
		Al	Si	O
1.05	45.1:43.7:11.2	6.51	0.49	2.8
1.00	44.3:44.2:11.5	4.59	0.55	2.3
0.95	44.2:45.2:10.6	4.27	0.56	2.1
0.90	44.5:44.6:10.9	4.37	0.48	2.3
0.85	50.6:36.8:12.6	6.92	0.53	3.1

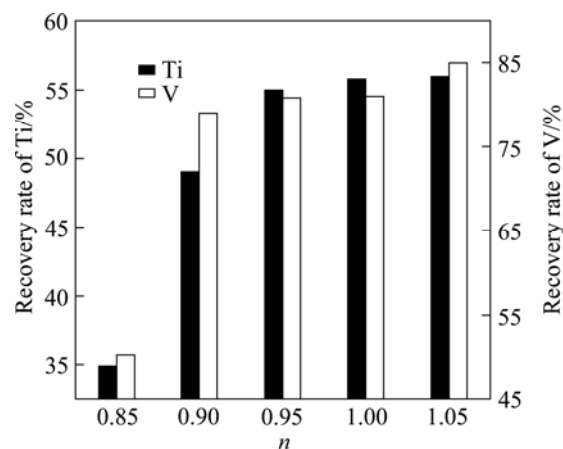


Fig. 4 Influences of Al addition amounts on recovery rates of V and Ti

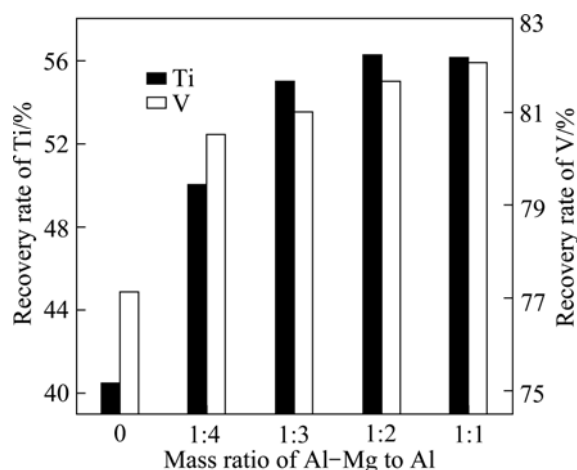
3.3 Influences of Al–Mg alloy addition amount on metal recovery rates and compositions of prepared alloys

As a common reducing agent, pure Al has a limited reducibility. Moreover, the reduction process of TiO_2 is difficult to conduct. So, some combined reducing agent (Al–Mg alloy) should be adopted during the preparation of the alloys. The effect of the mass ratio of Al–Mg alloy to Al was studied, and the results are shown in Table 4 and Fig. 5.

It is clearly observed from Fig. 5 that the V recovery rate increases slightly with an increase in the mass ratio of Al–Mg to Al. When the mass ratio of Al–

Table 4 Influence of Al–Mg addition amount on composition of prepared alloys (mass fraction)

Mass ratio of Al–Mg to Al	Molar ratio of V to Ti to Fe	Composition of alloy/%		
		Al	Si	O
0	54.2:30.9:14.9	5.27	0.51	2.7
1:4	45.8:43.7:10.5	4.98	0.45	2.5
1:3	44.2:45.2:10.6	4.27	0.56	2.1
1:2	44.6:44.8:10.6	4.29	0.58	2.0
1:1	43.4:43.7:12.9	4.19	0.51	2.0

**Fig. 5** Influences of Al–Mg addition amounts on recovery rates of V and Ti

Mg to Al is larger than 1/4, the V recovery rate basically reaches a stable value of about 80%. Therefore, it can be assumed that the V_2O_5 reduction process does not require too much strong reductant.

Comparing with the recovery rate of V, the recovery rate of Ti varies obviously. When the reductant just consists of Al, the recovery rate of Ti is only 40.5%. With increasing mass ratio of Al–Mg to Al up to 1:3, the recovery rate of Ti is improved, and the reaction process is carried on smoothly. According to the results listed in Table 4, the composition of the alloy is also close to the target composition. When the mass ratio of Al–Mg to Al value is up to 1:2 and 1:1, the reaction process proceeds fiercely, but the recovery rate of Ti does not increase any more. The possible reason is that the Al–Mg alloy is wasted seriously in the smelting process for its high activity. In addition, considering the factor of economic cost, the mass ratio of Al–Mg to Al should not be too high.

When the mass ratio of V_2O_5 to TiO_2 is 0.5:1, Al addition represents 95% of the theoretical values, and the Al–Mg addition amount is one third of the Al addition amount, the composition of the obtained alloy is close to the target composition. Detecting means of XRD, SEM

and EDS were applied to characterize the microstructure and further identify the phases of impurities in the obtained alloys.

Figure 6 shows the XRD pattern of the alloy sample obtained by metallothermic reduction method. V-based alloys and Ti-based alloys are the primary phases. Partial Al impurity is detected also in the alloy, existing in the form of V_5Al_8 .

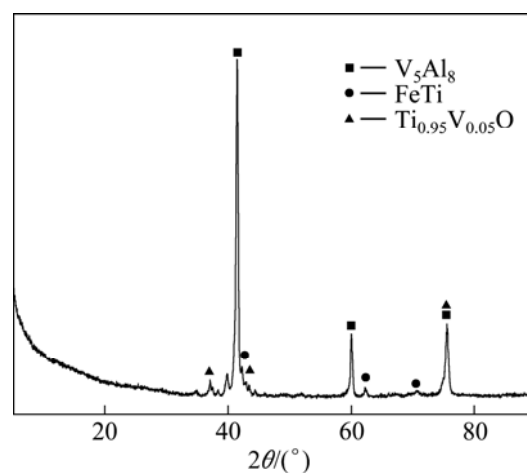
**Fig. 6** XRD pattern of alloy obtained by metallothermic reduction method

Figure 7 and Table 5 show the microstructure and chemical compositions of the alloy acquired by metallothermic reduction method. The results of EDS analysis reveal that the grey phase (Area 1) and the dark grey phase (Area 2) are V–Ti-based solid solution. Fe element distributes uniformly in the solid solution. However, the segregation for Ti can be observed obviously in the form of dendrite morphologies (Area 3) in the alloys. The reason for the uneven compositions can be derived from the given analysis above. During the cooling process, the temperature of furnace decreases quickly resulting in the solidification of some Ti before diffusing homogeneously. Thus, the control of holding

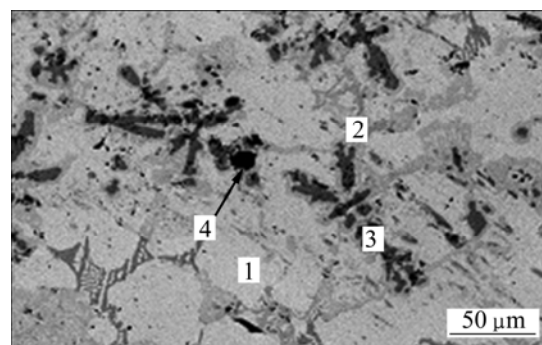
**Fig. 7** SEM image of alloy obtained by metallothermic reduction method

Table 5 EDS analysis result of alloy obtained by metallothermic reduction method shown in Fig. 7 (mass fraction, %)

Area	V	Ti	Fe	Al	Si	O
1	51.57	29.68	11.31	5.11	0.20	2.13
2	16.85	61.42	12.42	3.36	5.27	0.71
3	2.18	97.82	—	—	—	—
4	—	—	—	50.64	—	49.36

time seems important in the experiment. Meanwhile, further work should be carried out to improve the heat resistant property of furnace, and new heat sources should be introduced into the preparation of alloys. The deep dark phase (Area 4) is Al–O phase, according to the mass ratio of Al to O, it can be concluded that some Al_2O_3 inclusions also exist in the alloy.

In order to reduce the impurities in the prepared alloy, a refining process was performed. The refining agent is CaF_2 – CaO – Na_3AlF_6 slag, because CaO and Na_3AlF_6 have a good dissolving ability to oxide inclusion, and CaF_2 can improve the fluidity of slag. The Al, O and Si contents of the alloy reach 1.86%, 0.91% and 0.43% (mass fraction), respectively, after the refining treatment. The Al and O contents decline obviously, therefore, it can be confirmed that the preliminary refining process can remove oxide inclusions effectively. The content of Si just decreases from 0.56% to 0.43% (mass fraction), the change range is smaller. It is probably because most of the Si impurity exists in the form of V–Ti–Fe–Si alloy, and this part of Si cannot dissolve into the refining slag easily. Figure 8 shows the XRD pattern of the alloy sample after refining process. V-based alloys and Ti are the primary phases, and the oxide phase disappears in the alloy.

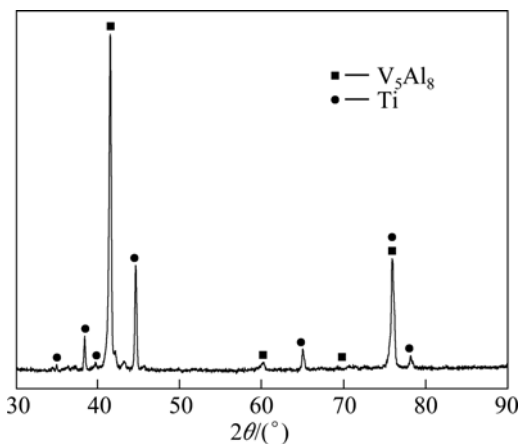
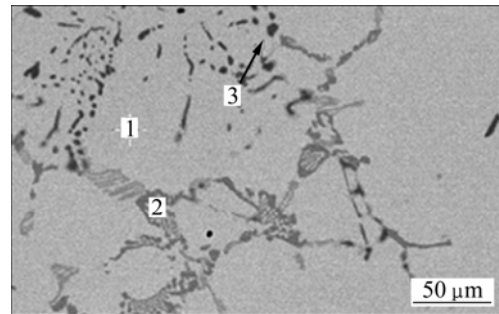
**Fig. 8** XRD pattern of V–Ti–Fe master alloy after refinement

Figure 9 and Table 6 show the microstructure and chemical compositions of the refined alloy, respectively. Compared with Fig. 7, the Al–O phase cannot be

detected again, and moreover, the Ti-rich phase decreases obviously. Therefore, it can be concluded that the refining process also plays a role in heat treatment.

**Fig. 9** SEM image of V–Ti–Fe master alloy after refinement**Table 6** EDS analysis result of V–Ti–Fe master alloy after refinement shown in Fig. 9 (mass fraction, %)

Area	V	Ti	Fe	Al	Si	O
1	50.62	33.58	12.30	2.12	—	1.38
2	13.66	67.27	13.03	1.81	3.72	0.51
3	7.43	85.32	6.51	0.21	0.17	0.36

4 Conclusions

1) The V–Ti–Fe master alloys can be obtained by metallothermic reduction method, and the appropriate technological conditions are: the mass ratio of V_2O_5 to TiO_2 is 0.5:1, Al addition represents 95% of the theoretical values, and the combined reducing agent amount is 1/3 that of the Al addition amount.

2) The compositions of the alloys obtained by metallothermic reduction method are inhomogeneous. V and Fe distribute uniformly, while Ti segregates in the alloys.

3) The oxide inclusions in the V–Ti–Fe master alloys can be removed effectively by the spray refining process.

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金属热还原法制备 V–Ti–Fe 中间合金

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摘 要: 采用金属热还原法制备 V–Ti–Fe 中间合金, 考察 V₂O₅ 与 TiO₂ 的加入比例、用铝量和 Al–Mg 合金用量对金属回收率和合金成分的影响。结果表明: 最佳工艺参数为原料中 V₂O₅ 和 TiO₂ 的质量比为 0.5:1, 实际用铝量为理论值的 95%, Al–Mg 合金用量为铝量的 1/3。能谱分析结果表明, 合金中的 V 和 Fe 元素分布比较均匀, Ti 则存在一定偏析。为降低合金中 Al 和 O 的杂质含量, 进行喷吹造渣精炼。精炼后, 合金中的铝含量由 4.27% 降为 1.86%, 氧含量由 2.10% 降为 0.91%。

关键词: V–Ti–Fe 中间合金; 金属热还原法; 回收率; 精炼

(Edited by FANG Jing-hua)