

Selective reduction of iron and effective enrichment of vanadium from vanadium slag by carbothermic reduction

Zhi Wang, Shiyuan Liu^{}, Lijun Wang^{*}*

Collaborative Innovation Center of Steel Technology, University of Science and Technology
Beijing, Beijing, 100083 China.

* Corresponding author:

Shiyuan Liu; E-Mail: shiyuanliu126@126.com

Lijun Wang; E-Mail: lijunwang@ustb.edu.cn

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ABSTRACT

In order to avoid production of wastewater and prevent production of highly toxic pentavalent vanadium and hexavalent chromium, a new and cleaner process for the selective chlorination of valuable elements in vanadium slag under argon atmosphere has been proposed. However, a large amount of chlorinating agent was consumed, which was attributed to the high iron content of 37 wt%. In this work, selective reduction of iron and effective enrichment of vanadium from vanadium slag were investigated. The carbothermic reduction of valuable metals (Fe, Mn, V, Cr, Ti) in vanadium slag was calculated by Factsage 8.0 software. On the basis of thermodynamic analysis, the selective reduction of Fe and Cr in vanadium slag was studied. The results show that the iron oxides of the olivine phase were reduced first, and then the spinel phase was reduced. The reduction order of Fe in spinel phase was $\text{Fe}_2\text{TiO}_4 \rightarrow \text{FeV}_2\text{O}_4 \rightarrow \text{FeCr}_2\text{O}_4$. When the reduction temperature is 1400 °C and the amount of graphite added is 12%, the metallization ratio of Fe and Cr in vanadium slag are 90.2%, and 58%, respectively. However, the V reduction ratio is 7%. This process achieves selective reduction of Fe and Cr and enrichment of V.

INTRODUCTION

Vanadium is widely used in metallurgy, materials, and chemical industries due to its unique physical and chemical properties (Moskalyk and Alfantazi, 2003). About 84% of vanadium is used in the steel and metallurgical industry and vanadium is typically added as an additive to carbon steel, alloy steel and tool steel. Vanadium containing alloy steel is widely used in aerospace, oil and gas pipelines, automotive steel, and so on (Pan et al., 2020, Pan et al., 2019, Nan et al., 2005). Grain size can be refined by adding 0.1%–0.5% vanadium to steel in the form of carbides. Adding vanadium to alloy steel can inhibit the bainite development, improve martensitic strength and enhance steel strength, wear resistance, and corrosion resistance of the steel (Taylor et al., 2006, Qin et al., 2013, Hu et al., 2021).

Traditional vanadium extraction processes include sodium roasting and calcium roasting (Xiang et al., 2023, An et al., 2023, Xiang et al., 2020, Xiang et al., 2018). By roasting, the stable spinel structure was destroyed, V^{3+} in vanadium slag can be converted to V^{5+} and formed soluble vanadates (Gao et al., 2022). However, both roasting processes have some environmental pollution issues. In sodium roasting followed water leaching process, a large amount of ammonia nitrogen wastewater was generated, at the same time, Cr in vanadium slag by oxidizing Cr^{3+} to Cr^{6+} , which seriously endangers human health (Kim et al., 2015). In recent years, some scholars have developed many new processes for recovering V from vanadium slag, such as non-salt roasting process. Non-salt roasting process is to recycle V from vanadium slag by oxidizing V^{3+} to V^{5+} directly without any additives. Then V^{5+} ions generated soluble vanadates with Mn, Ca, and Mg in vanadium slag. However, non-salt roasting process does not solve the problem of high valence V, almost V in vanadium slag enrichment in the leaching process, the concentration of leaching solution is too high and the leaching time is too long (He et al., 2008). The Institute of Process Engineering, Chinese Academy of Sciences has proposed a sub-molten salt method for vanadium extraction. The sub-molten salt medium mainly consists of NaOH and KOH. In the oxidizing atmosphere, the spinel in vanadium slag is dissolved into a high alkalinity sub molten salt medium, which is converted into soluble sodium vanadate and sodium chromate (Liu et al., 2013, Chen et al., 2013). Wang et al. (Wang et al., 2014) studied the extraction of vanadium and chromium from vanadium slag using NaOH- NaNO_3 sub-molten salt medium. Compared with traditional processes, the temperature for extracting vanadium from sub-molten salt is 200–400 °C, which is significantly lower than the 800 °C of traditional roasting processes. The recovery ratio of vanadium and chromium reached 95% and 90%, respectively. In the experimental process, the sub-molten salt medium can be recycled without producing toxic gases. However, this method involves using a high concentration alkaline solution as the reaction medium, posing a significant risk of corrosion to the equipment. Additionally, this method results in the oxidation of low-valent vanadium and chromium in vanadium slag to high valence states, posing a significant risk to environmental safety. Liu et al. (Liu et al., 2016, Liu et al., 2024) investigated the extraction of vanadium and chromium from vanadium slag by the original valence state. Thermodynamic calculations showed that AlCl_3 could chlorinate Fe, Mn, V, Cr and Ti in vanadium slag and form the corresponding chlorides. The valence states of vanadium and chromium remained unchanged throughout the chlorination process, which avoids the problem of generating high-valence toxic vanadates and chromates. The electrolysis behavior of VCl_3 - CrCl_3 -

NaCl-KCl system was investigated, revealing that the mass ratio of VCl_3 and $CrCl_3$ was the key factor affecting the final electrolysis product. When the mass ratio of VCl_3 and $CrCl_3$ was 2:1, V-Cr alloy was successfully synthesized (Liu et al., 2019). However, the presence of a significant amount of Fe ions in vanadium slag poses a challenge. During the chlorination process, Fe in vanadium slag will be chlorinated into $FeCl_2$, which not only affects the subsequent extraction of vanadium and chromium, but also consumes a large amount of chlorinating agent. Therefore, it is necessary to remove Fe before the chlorination operation. Graphite is a simple and easily obtainable reducing agent. Vanadium slag oxides can be reduced into metals or metal carbides with the aid of carbothermic reduction, recovering valuable elements from vanadium slag. Yang et al. (Yang et al., 2011) investigated the separation of metallic Fe from vanadium extraction tailings through carbothermic reduction-magnetic separation. The optimized process conditions were as follows: reduction temperature of 1200 °C, lignite addition of 30%, CaO addition of 10%, reduction time of 60 minutes. The metallization rate of Fe can reach 89.76%, and iron concentrate with an iron grade of 90.31% can be separated through magnetic separation. Compared to the traditional roasting methods, the carbothermic reduction method avoids the production of high valence V and Cr. Meanwhile, a significant degree of Fe is removed from the reduced slag, producing vanadium-enriched slag that is advantageous for the future vanadium extraction procedure.

This article explores the reduction of oxides, selective reduction of Fe, and enrichment of vanadium in vanadium slag under different reduction temperatures and graphite addition conditions through carbothermic reduction. Combined with thermodynamic calculation analysis, scanning electron microscopy analysis, and XRD, selective reduction of valuable elements in vanadium slag was achieved.

MATERIALS AND METHOD

MATERIALS

The chemical composition of vanadium slag is shown in Table 1. The composition of the vanadium slag was analyzed by X-ray Fluorescence (XRF, Shimadzu XRF-1800). The X-ray diffraction (XRD) pattern of vanadium slag is shown in Fig. 1, indicating that the main phases are spinel $((Mn,Fe)(Cr,V)_2O_4)$, fayalite (Fe_2SiO_4) and titanomagnetite $(Fe_{2.5}Ti_{0.5}O_4)$. High-purity argon gas (99.999 vol. %) was used as the protective atmosphere. Graphite was used as the reductant in experiments.

TABLE 1 - Chemical composition of vanadium slag used in this work

Fe_2O_3	SiO_2	V_2O_3	Cr_2O_3	TiO_2	MnO	CaO	MgO	Al_2O_3
44.51	15.14	11.47	1.58	13.10	7.80	2.16	1.35	1.86

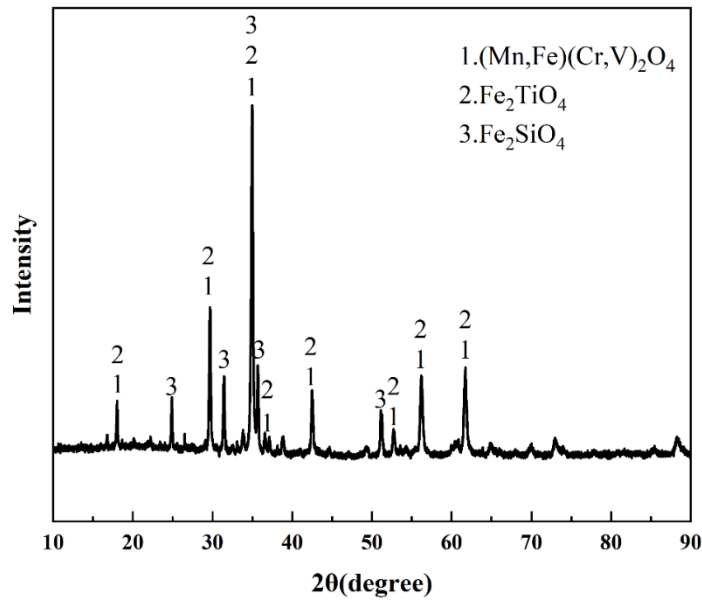


FIG 1 – XRD pattern of vanadium slag

EXPERIMENTAL PROCEDURE

The reduction process of vanadium slag was performed in a vertical tube furnace with a temperature control programmer. In the reduction experiments, 5.0 g vanadium slag and a certain quantity of graphite were mixed evenly. Then the samples were compressed into cylinders under the pressure of 20 MPa. The sample was put into an Al_2O_3 crucible with a size of $\Phi 30\text{mm} \times 30\text{mm}$. After heating the furnace to a required temperature under the argon atmosphere, the crucible was put in the constant temperature zone of the heating furnace. The crucible was connected to an analytical balance with an accuracy of 0.0001g through the iron wire and the analytical balance was connected to a computer. The weight loss of the sample was recorded through the computer. After the experiment was finished, the crucible was withdrawn from the furnace and cooled under the argon atmosphere. The reduction percentage R of vanadium slag is calculated by the following equation (1)

$$R = \frac{W_1 * \frac{16}{28}}{W_0} * 100\% \quad (1)$$

W_1 is the weight loss of vanadium slag, W_0 is the total theoretical weight of oxygen for complete reduction of Fe_2O_3 , V_2O_3 , Cr_2O_3 , TiO_2 and MnO in vanadium slag to the metallic metals Fe, V, Cr, Mn, and Ti.

ANALYSIS

The mineralogical composition of the reduced samples was determined by X-ray diffraction analysis (XRD, M18XHF) using $\text{Cu-K}\alpha$ radiation. The micromorphology and elemental concentrations of the samples were analyzed by scanning electron microscopy (SEM-EDS, Zeiss Ultra 55) ..

RESULTS AND DISCUSSION

THERMODYNAMIC CALCULATIONS

The possible reactions during the carbothermic reduction can be described as reactions (2)-(10). The Gibbs free energy of all the reactions were calculated by a thermodynamic database Factsage 8.0, which is shown in Fig 2. It can be seen that the temperatures at which Fe in FeO , Fe_2SiO_4 , FeV_2O_4 , FeCr_2O_4 and Fe_2TiO_4 are reduced to metallic iron are 727.4 °C, 808.1 °C, 860. 1 °C, 1054.7 °C, and 841.5 °C, respectively. It can be seen that with increasing temperature, the Gibbs free energy of the reaction (2)-(10) change towards a more negative direction and the increase in temperature is conducive to the carbothermic reduction. Normally, Fe ions in iron oxides were

reduced to metallic Fe first. With increasing temperature, the olivine phase was reduced to form Fe and SiO₂. Thermodynamically, the order of spinel phase during reduction process can be described as follows: Fe₂TiO₄→FeV₂O₄→FeCr₂O₄. Meanwhile, the temperature at which Cr in Cr₂O₃ and V in V₂O₃ are reduced to metallic are 1252.9 °C and 1472.1 °C. Thus, based on the thermodynamic, selective reduction of Fe ions and Cr ions can be achieved by controlling the reduction temperature.

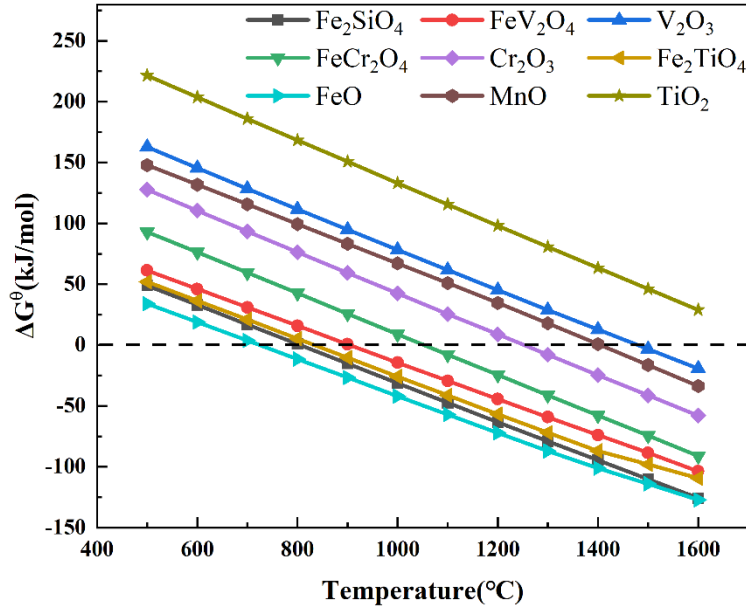


FIG 2 – The relationship between the ΔG^θ and the temperature

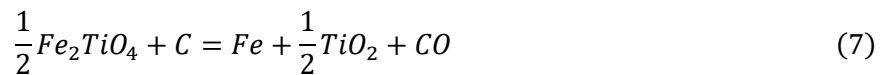
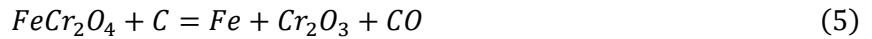
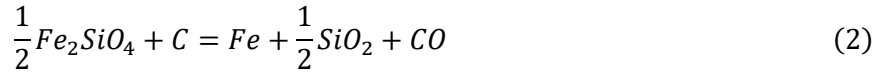


Figure 3 shows the effects of temperature on the thermodynamic equilibrium phase composition of sample during the carbothermic reduction when the graphite content is 12%. The figure 3 shows that with the temperature below 700 °C, only solid slag and gas are present. Solid slag is the rest of the solid phase in vanadium slag. The content of the two phases does not change significantly with temperature, suggesting that the reduction reaction has not yet taken place. The amount of solid slag rapidly decreased and solid iron started to form as the temperature over 700 °C, indicating that the iron oxides in vanadium slag begins to be reduced to metallic iron. Further increasing temperature to 1050 °C, the amount of iron reaches its maximum value, indicating that all iron ions in the vanadium slag are reduced to metallic iron at this temperature, which is consistent with the results in Figure 2. With the temperature went up to 1150 °C, liquid slag begins to appear, with further increasing temperature to 1340 °C, the content of liquid slag rapidly increases to 30%. There is little change in the content of liquid slag with continuing to increase the temperature.

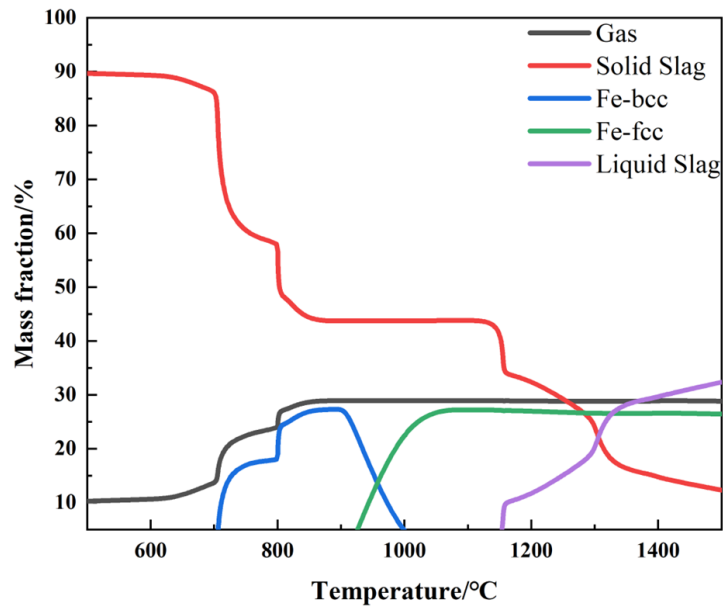
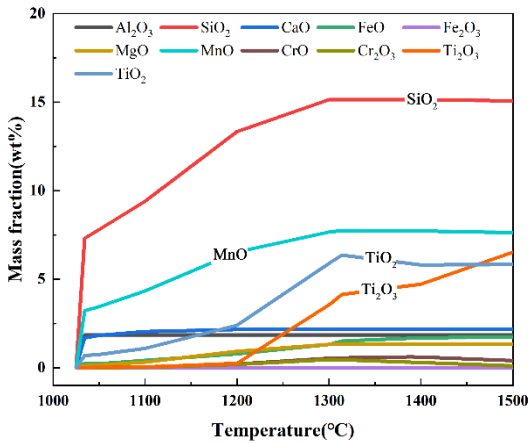
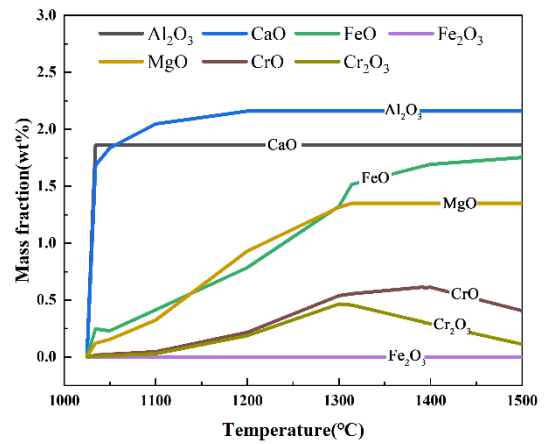


FIG 3 - The effect of temperature on gas, solid slag, liquid slag, and metallic iron

Figure 4 shows the effect of temperatures on the fraction of oxide in liquid slag. It can be seen that increasing the temperature, the fraction of SiO_2 and MnO in liquid slag increases. When the temperature is $1300\text{ }^\circ\text{C}$, the olivine phase is fully decreased and the proportion of SiO_2 and MnO reaches its highest value. The fraction of TiO_2 and Ti_2O_3 in liquid slag increased with increasing the temperature from $1050\text{ }^\circ\text{C}$ to $1340\text{ }^\circ\text{C}$. The fraction of TiO_2 decreased and the fraction of Ti_2O_3 increased with further increasing the temperature, indicated that TiO_2 is reduced to a low valent titanium oxide Ti_2O_3 . The fraction of CrO in the slag decreased with further increasing temperature to above $1400\text{ }^\circ\text{C}$, indicated that Cr ions in the slag was reduced to metallic Cr .



(a)



(b)

FIG 4 - The effect of temperature on the fraction of oxide in liquid slag, (b) Oxides with a content below 3%

CARBOTHERMAL REDUCTION OF VANADIUM SLAG

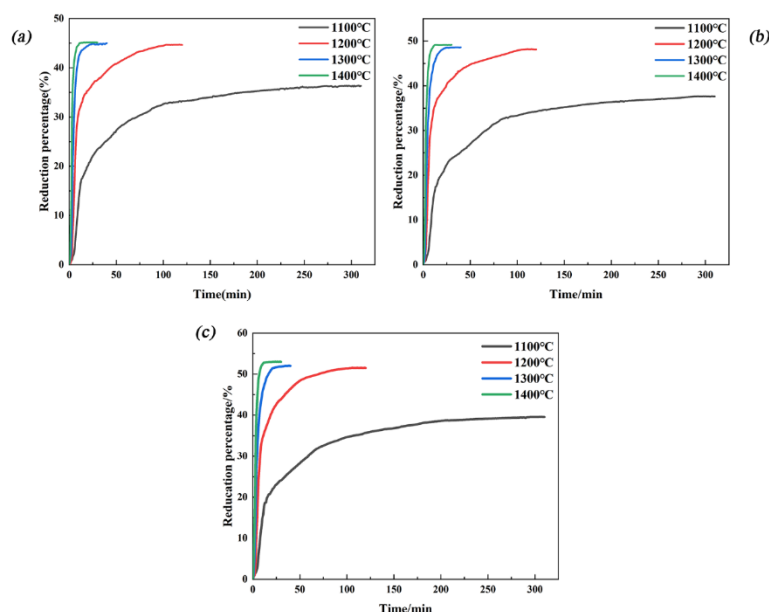


FIG 5 - The effect of temperature on reduction percentage, the content of graphite(a) 10.5%, (b)12%, (c)13.5%

Figure 5 shows the effect of temperature on the reduction percentage of samples with different graphite contents. It can be seen that with increasing temperature, the reduction percentage gradually increases. An essential component of the carbothermic reduction reaction is temperature. The graphite content of all iron oxides reduced to metallic iron in vanadium slag is used as the initial amount of graphite addition. Therefore, the amount of graphite is 10.5%. As can be seen in Figure 5(a), when the carbothermic reduction reaction temperature was 1100 °C, it takes 300 minutes for the reduction percentage to reach the maximum value of 36.3%. The results indicated that it takes 100 minutes for the reduction percentage to reach its maximum value of 44.6% when the temperature is raised from 1100 °C to 1200 °C. With increasing temperature, the reduction percentage remain almost unchanged. This indicated that all the graphite in the sample has been reacted. As the temperature increases from 1100 °C to 1400 °C, the time for the reaction to reach equilibrium has been reduced from 300 minutes to 10 minutes. An increase in temperature is beneficial for improving the rate of carbothermic reduction reaction. Similar phenomena can also be observed in Figures 5 (b) and (c).

The XRD patterns of reduced vanadium slag at different temperatures are shown in Fig. 6. Figure 6 shows the XRD patterns of slag samples at different reduction temperatures when the amount of graphite is 12%. When the reaction temperature was 1100 °C, the main phases of reduced vanadium slag were $(\text{Mn,Fe})(\text{Cr,V})_2\text{O}_4$, $\text{Fe}_{2.5}\text{Ti}_{0.5}\text{O}_4$, Fe, C, SiO_2 . The disappearance of Fe_2SiO_4 phase indicated that Fe_2SiO_4 has been reduced, generating SiO_2 and metallic Fe. The peak of C appeared at 1100 °C, indicated that graphite did not fully react at this temperature, which is consistent with the results observed in Figure 5. The peak of spinel appeared at 1100 °C, indicated that spinel did not react at this temperature. The Fe peak dropped as the reaction temperature rose to 1200 °C. This is because the tiny metal Fe particles in the slag reduce in number as the temperature rises and they combine and grow. The main phases of reduced vanadium slag were Fe, SiO_2 , $(\text{Ti,V})_2\text{O}_3$, Ti_2O_3 , MnO, $(\text{Ca,Mn})_2\text{SiO}_4$. The peak of spinel disappeared, indicated that the spinel phase has been reduced. Some Mn ions exists in the form of oxides, while others combine with Si and Ca to form complex silicates. Ti ions in vanadium slag were reduced, Some Ti ions exists in the form of oxides, while others combine with V to form T-V-O oxide. When the reaction temperature increased to 1300 °C and 1400 °C, the peak of Ti_2O_3 disappeared, indicated that high temperatures are more conducive to the generation of complex oxides.

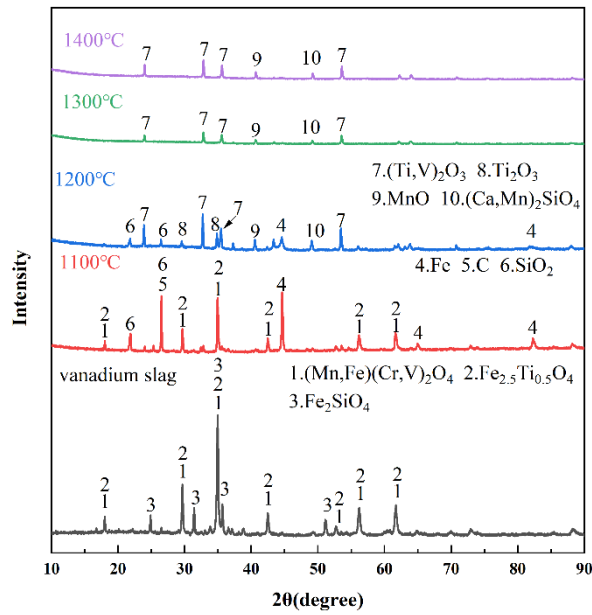


FIG 6 - XRD of reduced vanadium slag at C/slag mass ratio of 0.12

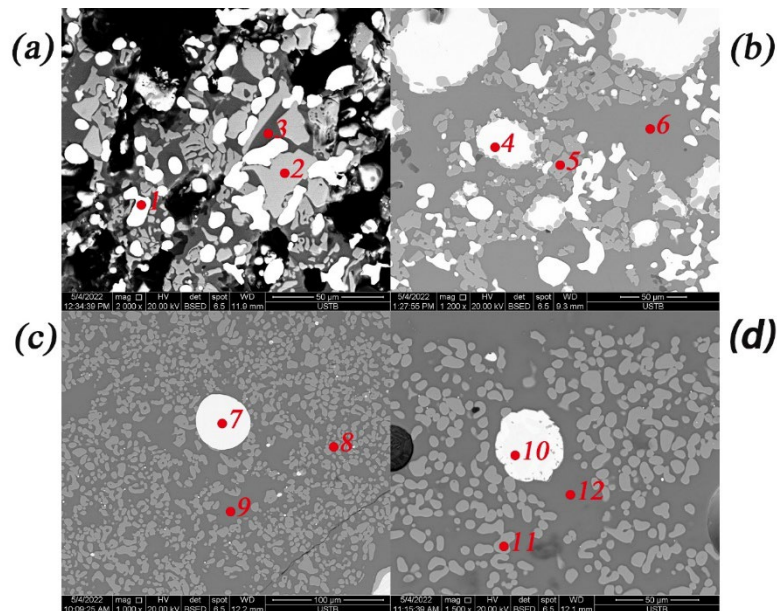


FIG 7 - SEM of reduced vanadium slag at C/slag mass ratio of 0.12 (a)1100 °C, (b)1200 °C, (c)1300 °C, (d)1400 °C

The SEM images of roasted samples under different reduction temperature are shown in Figure 7. The EDS chemical analysis results from regions 1 to 12 are shown in Table 2. From Figure 7, it can be seen that the reduced slag mainly consists of three different phases: bright white, light gray, and dark gray. According to EDS analysis, the main element in the bright white area represented by positions 1, 4, 7, and 10 is Fe (>87%), while the content of other elements is very low, indicated that the bright white area is metallic Fe. The main elements in the light gray area are O (~21%), Ti (17% -40%), and V (23% -35%) presented in regions 2, 5, 8 and 11, indicated that this area is the spinel phase. When the reaction temperature was 1100 °C, the spinel phase contains more than 7% Fe, indicated that the spinel phase has not completely decomposed at this temperature, which is consistent with the results of XRD in Figure 6. Less than 1% of iron is present in the spinel phase at temperatures exceeding 1200 °C. It suggests that at this temperature, the spinel phase can be entirely reduced. Since regions 3, 6, 9, and 12 had measurements of 20% Si, 31% O, and 10%–20% Mn, the dark gray areas are recognized as olivine. With increasing temperature, the manganese content in spinel decreases from 20% to 2.8%. Most of the Mn accumulates in the olivine phase, indicated that Mn combines with Si and O to form complex Mn-Si-O oxides as the temperature increased, consistent with the XRD results in Figure 6.

When the reaction temperature was 1100 °C, most of the metal Fe particles in the reduced sample takes on an irregular elongated shape, while a small amount of metal Fe particles are circular and have a smaller particle size, with a more dispersed distribution and a particle size of 10 μm. The proportion of smaller Fe particles decreased as the reaction temperature rose to 1200 °C, causing the metal Fe particles to combine and grow considerably. As the temperature increases to 1300 °C, the elongated Fe particles disappear. Raising the temperature is beneficial for the aggregation and growth of metal Fe particles, which is beneficial for the separation of slag and iron.

TABLE 2 - EDS analysis of reduced vanadium slag (In Fig. 7).

Region	Elements (wt.%)											Mineral phase
	C	O	Mg	Al	Si	Ca	Ti	V	Cr	Mn	Fe	
1	6.83	1.65	0.09	0	0.19	0.21	0.66	1.41	0.79	0.93	87.24	Iron
2	3.79	20.4	1.92	0.73	0.18	0.12	17.73	23.87	4.11	20.15	7.01	Spinel
3	5.39	30.28	5.86	2.76	24.25	12.25	3.88	3.31	0.37	9.97	1.68	Silicate
4	4.63	1.63	0.16	0.1	0.38	0.19	0.31	1.63	1.5	0.92	88.56	Iron
5	3.57	21.36	1.17	0.65	0.51	0.14	40.23	28.02	0.51	3.35	0.48	V-Ti oxides
6	4.61	31.36	2.68	3.38	25.71	5.08	4.82	0.53	0.51	20.56	0.75	Silicate
7	5.16	1.6	0.05	0.06	0.24	0.16	0.34	1	0.65	0.62	90.12	Iron
8	3.54	21.74	1.18	0.67	0.58	0.25	34.94	32.74	0.73	3.14	0.49	V-Ti oxides
9	4.72	31.77	2.72	3.27	25.91	4.82	4.68	0.87	0.43	20.12	0.69	Silicate
10	6.74	1.65	0.06	0	0.14	0.05	0.21	1.91	1.95	0.36	86.92	Iron
11	3.54	21.57	0.89	2.2	0.45	0.23	30.82	35.42	1.1	2.83	0.95	V-Ti oxides
12	5.18	32.75	2.12	12.56	20.85	3.83	4.5	0.77	0.53	15.77	1.14	Silicate

THE INFLUENCE OF TEMPERATURE ON V AND CR IN METALLIC IRON

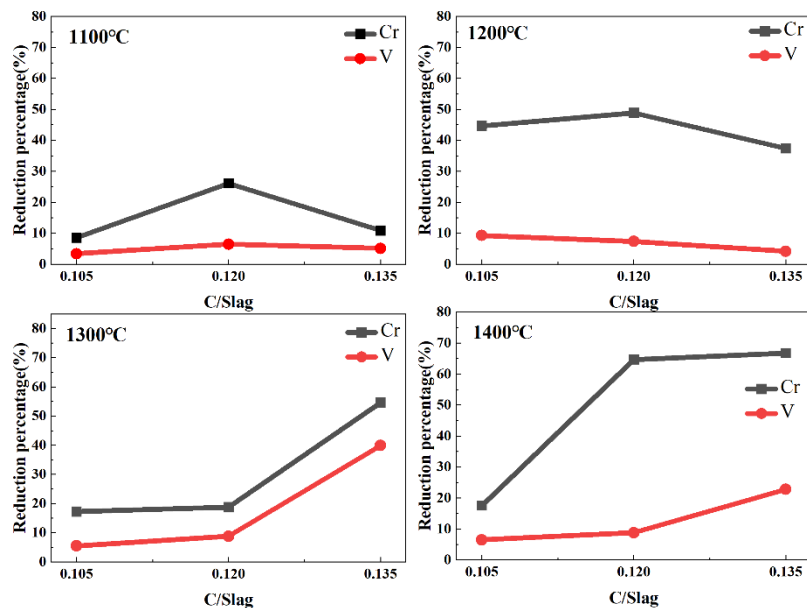


FIG 8 - reduction ratio of V and Cr

Assuming that Fe in vanadium slag is completely reduced to form metallic iron, the effects of different temperatures and graphite content on the reduction ratio of V and Cr were obtained through EDS

analysis of the reduced samples. From Figure 8, it can be seen that the reduction rate of V is basically the same at temperatures from 1100 °C to 1200 °C. When the reaction temperature was 1200 °C, the reduction rate of Cr above 30%. The reduction ratio of V and Cr did not change considerably when the graphite concentration rose from 10.5% to 12% at a reaction temperature of 1300 °C. Continuing to increase the graphite content to 13.5%, the reduction ratio of V and Cr increased to 27% and 78%, respectively. A large amount of V is reduced and enters the metallic iron phase. At a reaction temperature of 1400 °C, the reduction rate of Cr rises from 15% to 58% as the carbon content rises from 10.5% to 12%, whereas the reduction rate of V gradually increases from 5% to 7%. Continuing to increase the carbon content to 13.5%, the reduction rate of Cr remains basically unchanged, while the reduction rate of V rapidly increases to 18%. Thus, when the reaction temperature was 1400 °C, the reduction rate of Cr is 58%, and the reduction rate of V is 7%, achieving the selective reduction of Fe ions and Cr ions.

CONCLUSIONS

In this work, selective reduction of iron and enrichment of vanadium from vanadium slag by carbothermic reduction were investigated. The following conclusions could be obtained:

- (1) The theoretical calculation results show that temperature has a significant impact on the selective reduction of Fe and Cr. When the temperature exceeds 1054.7 °C, the iron in vanadium slag can be reduced to metallic Fe. As the temperature increases, the Fe in olivine phase is first reduced, and the reduction order of Fe in the spinel phase is: $\text{Fe}_2\text{TiO}_4 \rightarrow \text{FeV}_2\text{O}_4 \rightarrow \text{FeCr}_2\text{O}_4$. The temperatures for reducing Cr_2O_3 and V_2O_3 to metals are 1252.9 °C and 1472.1 °C, respectively
- (2) When the reaction temperature was 1100 °C, the olivine phase was reduced. When the temperature exceeds 1200 °C, the spinel phase was reduced.
- (3) SEM and EDS analysis indicated that the reduction of vanadium was influenced by temperature and graphite content. When the graphite addition amount was 13.5% and the temperature was higher than 1300 °C, a large amount of vanadium in vanadium slag entered the metal Fe.
- (4) The metallization ratio of Fe and Cr at 1400 °C and C/slag mass ratio of 0.12 are 90.2%, and 58%. The content of vanadium in iron was 1.91%, which means that only 7% of the vanadium was reduced.

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