

Article

The Effect of Chromium on the Roasting Process of Vanadium Extraction

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Abstract: We simulated the roasting process of chromium by mixing Cr_2O_3 and Na_2CO_3 to analyze the influence of chromium on roasting vanadium slag. Samples were characterized by XRD, thermal analysis and SEM at different temperatures: Cr_2O_3 and Na_2CO_3 began to react at 500 °C. When the chromium oxide content was about 3.2%, the conversion rate of V reached the maximum value of 95%.

Keywords: vanadium slag; roasting; chromium

1. Introduction

Vanadium is an important metal used almost exclusively in ferrous and non-ferrous alloys due to its physicochemical and mechanical properties such as grain refinement, high tensile strength, hardness and fatigue resistance; it has a wide range of uses in the metallurgical and chemical sectors [1–3]. There are mainly three kinds of raw materials, bone coal, vanadium slag and waste vanadium catalyst, used to produce vanadium pentoxide in China. In addition, few foreign countries extract vanadium from petroleum residue, including the United States, Japan and others [4]. Vanadium slag is one of the most important sources of vanadium, which accounts for 58% of the production of vanadium [5].

The vanadium slag mixed with salt roasts in an oxidizing atmosphere, vanadium precipitates from the mineral structure and oxidizes to pentavalent vanadium oxide, and then vanadium pentoxide reacts with sodium oxide decomposed from sodium to form soluble sodium vanadate [6–8]. There is a lot of literature on the extraction of vanadium pentoxide from vanadium-containing material using NaCl , Na_2SO_4 , and Na_2CO_3 as additives [9–13]. The representative vanadium extraction route mainly consists of the following procedures: sodium salt roasting, water leaching, solution purification and V precipitation [5].

However, vanadium slag usually contains 3%–6% chromium (III) oxide in the form of chromium spinel, which is thermodynamically more stable than vanadium spinel and cannot be recovered at vanadium roasting temperatures [14].

Chromium is an important strategic resource, but hexavalent chromium is a highly toxic and carcinogenic substance, and it can corrode and damage the organism [14,15]. Hexavalent chromium is one of the key pollutants [14] that creates air, soil, surface and groundwater pollution [16], causes geological disasters, and is a long-term environmental pollution [17]. Chromium slag is one of the important sources of chromium pollution. Vanadium slag is a source of chromium slag, so it is a difficult problem to extract chromium from vanadium slag.

However, there are only a few studies of elements' effects on the salt roast vanadium process with the addition of calcium (every 1% increase of CaO in slag would cause a 4.7%–9.0% V_2O_5 loss [18]). This study will investigate the effect of chromium on salt roasting to provide a theoretical basis for the separation of chromium and vanadium in the future. The change in the mineralogy of vanadium slag

was studied by XRD, SEM/EDS and TG-DSC techniques; the effect of the roasting temperature on vanadium extraction and the characterization of leach residues are also discussed.

2. Experimental Materials and Experimental Procedure

2.1. Materials

Vanadium slag before roasting was obtained from a steel production site in Chengde, China. Vanadium slag after roasting was obtained after extracting vanadium from vanadium slag.

Figure 1 shows that the main mineral phases in vanadium slag are mainly vanadium spinel FeV_2O_4 , chromium spinel FeCr_2O_4 , olivine Fe_2SiO_4 , quartz SiO_2 and so on. Figure 2 depicts the XRD pattern of vanadium slag after roasting; the main phases are iron oxide Fe_2O_3 , magnetic iron oxide Fe_3O_4 , quartz SiO_2 , diopside $(\text{Ca}, \text{Mn})(\text{Mg}, \text{Fe}, \text{Mn})\text{Si}_2\text{O}_6$, and sodium salt $\text{NaCrSi}_2\text{O}_6$, NaFeO_2 . The chemical compositions of vanadium slag before roasting and vanadium slag after roasting are given in Tables 1 and 2.

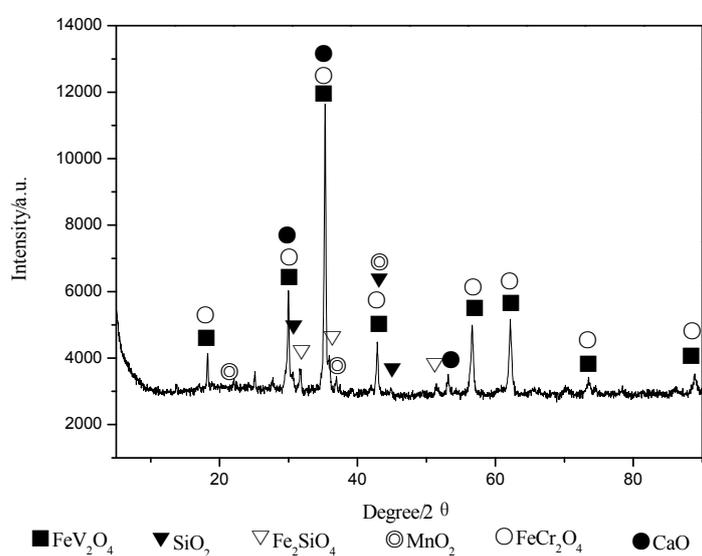


Figure 1. The XRD pattern of vanadium slag before roasting.

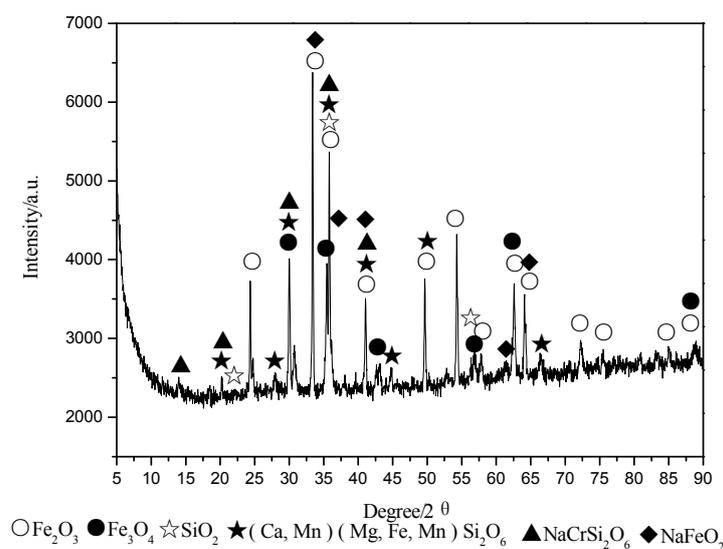


Figure 2. The XRD pattern of vanadium slag after roasting.

Table 1. Chemical compositions of vanadium slag before roasting (wt. %).

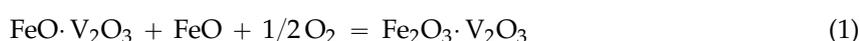
Component	TFe	V	SiO ₂	CaO	Mn	MgO	TiO ₂	Cr ₂ O ₃	P
wt. %	31.12	7.68	16.65	2.04	5.4	3.07	8.49	8.8	0.089

Table 2. Chemical compositions of vanadium slag after roasting (wt. %).

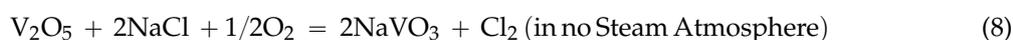
Component	TFe	V	SiO ₂	CaO	Mn	MgO	TiO ₂	Cr ₂ O ₃	P
wt. %	33.36	0.935	15.83	2.16	5.77	2.84	8.82	6.58	0.087

We used sodium roasting technology to extract vanadium pentoxide from slag. It is the most mature technology, and domestic and foreign scholars have done a lot of related research [1,9,18–26].

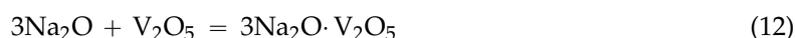
Oxidative decomposition of spinel



Vanadium pentoxide reacts with the sodium salt to form water-soluble sodium vanadate



The reactions of chromium or vanadium in slag are:



2.2. Experimentation

Sample pretreatment: With the raw materials in proportion (vanadium slag before roasting, vanadium slag after roasting, anhydrous sodium carbonate, sodium chloride), mixed ingredients into the blender for 3 h, roasted into the vertical muffle furnace, stirred raw when roasting. A temperature controller was used to maintain the predetermined furnace temperature, with the furnace door kept open to maintain an oxidizing atmosphere. After roasting was completed, cooled the sample in water according to the ratio of liquid poured. The liquid was heated at 80 °C, and stirred 40 min at the rate of 200 revolutions/min. Then the liquid was collected by filtration. The slurry was separated via vacuum filtration, and the residue was washed several times with distilled water. Ammonium ferrous sulfate titration was used to determine the concentration of vanadium in the solution.

Conversion of vanadium in sodium roasting stage was calculated with:

$$\% \text{Conversion} = \frac{[V]_s}{[V]_0} \times 100\%$$

where $[V]_0$ is the mass of M in the V-Cr slag for the stage before roasting; $[V]_s$ is the mass of vanadium after roasting. The conversions were calculated with concentration data in the leaching liquor instead of content data in the leaching residue due to the fact that it is difficult to determine the mass of all residues accurately and estimation of the mass will significantly increase the error. Parallel experiments were conducted three times and average extractions were obtained to ensure the validity of results.

3. Effect of Cr_2O_3 on Vanadium Conversion Rate

The controlled vanadium content in the mixture was 4.7% in this experiment, the alkali/vanadium ratio was 1.2, and the alkali salt/vanadium ratio was 3.5/1; it was insulated for 100 min at 780 °C as shown in Table 3. Each set of experiments was repeated three times, average value was obtained to ensure the validity of results.

Table 3. Scheme of the influence of chrome oxide on the vanadium conversion experiment.

No.	$\text{Cr}_2\text{O}_3\%$	Temperature/°C	Time/min	Alkali Vanadium Ratio	Alkali Salt Ratio
1	8.39	780	100	1.2	3.5/1
2	7.00	780	100	1.2	3.5/1
3	5.25	780	100	1.2	3.5/1
4	4.42	780	100	1.2	3.5/1
5	4.00	780	100	1.2	3.5/1
6	3.80	780	100	1.2	3.5/1
7	3.23	780	100	1.2	3.5/1
8	2.54	780	100	1.2	3.5/1

As the Figure 3 shows, when the chromium oxide content was about 3.2%, the conversion rate of V reached the maximum value of 95%. When the chromium content was less than 3.2%, Cr and spinel would react to form Cr-Mn spinel, which increased the conversion rate of vanadium, but when the chromium content was more than 3.2%, the Cr-Mn spinel content would not increase, and the excess chromium would compete with the vanadium to react with the sodium carbonate, resulting in a reduced vanadium conversion rate. When the chromium content was more than 5.24%, the conversion rate of vanadium was gradually increased, and the reaction of Cr further decomposed the silicate and then increased the conversion rate of the vanadium. When the content of Cr_2O_3 in the mixture was between 3.229%–5.246%, the conversion rate decreased 0.74% for each increase of 0.1% Cr_2O_3 . The maximum conversion rate is higher than that of Li [27] ($\text{V}_2\text{O}_5 = 7.8\%$, $\text{Cr}_2\text{O}_3 = 2\%$) at 90% and Li [28] ($\text{V}_2\text{O}_5 = 8.93\%$, $\text{Cr}_2\text{O}_3 = 8.67\%$) at 88.6%.

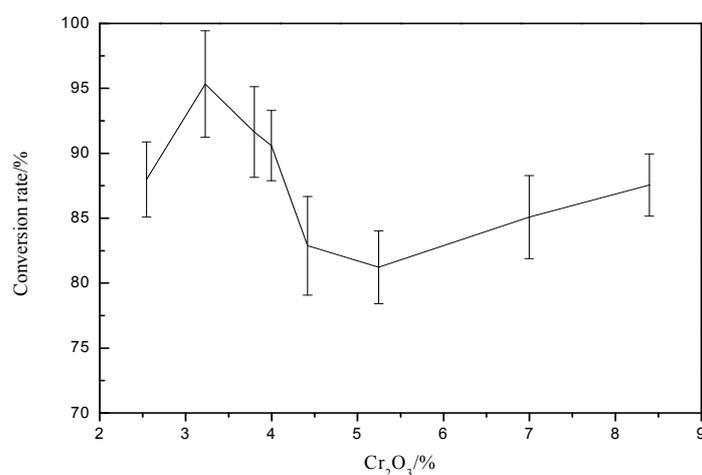


Figure 3. Effect of Cr_2O_3 content on vanadium conversion rate.

Literature [29] indicates that the main components of the spinel central portion are Cr_2O_3 , V_2O_5 , MgO , and FeO , of which Cr_2O_3 and V_2O_5 are the nucleation of monomer spinel. The chemical composition of the chromium-rich vanadium spinel central portion can be approximated considering $(\text{Fe}^{2+}\text{Mg}^{2+})(\text{Cr}^{3+}\text{V}^{3+})\text{O}_4$. The optimum vanadium extraction temperature for transforming Cr_2O_3 to CrO_4^{2-} was around $1200\text{ }^\circ\text{C}$ by chromite FeCr_2O_4 , and the first roasting conversion rate of Cr_2O_3 was usually less than 20% in slag at the optimum calcination temperature ($<850\text{ }^\circ\text{C}$). Thus, the chemical stability of the chromium-rich vanadium spinel is higher, which makes the crystal structure of the central portion of the vanadium-containing spinels remain more complete under calcination conditions, and a relatively complete crystal structure will restrict the soluble transforming of part of V_2O_5 in the crystal. With greater content of Cr_2O_3 and a larger size of the vanadium slag, this phenomenon is more obvious. Therefore, it is very unfavorable for the realization of disposable roasting vanadium when there is a great deal of Cr_2O_3 in the vanadium slag.

4. The Mechanism of Chromium on in the Roasting of Vanadium Slag

4.1. XRD Analysis

The XRD pattern (Figure 4) shows that in the initial low-temperature sintering conditions (300 , $400\text{ }^\circ\text{C}$), the sample phases are Na_2CO_3 and Cr_2O_3 and sodium chromate does not appear, which indicates that Cr_2O_3 and Na_2CO_3 do not react at a low temperature. When the temperature reaches $500\text{ }^\circ\text{C}$, there is a small amount of the Na_2CrO_4 phase in addition to Na_2CO_3 and Cr_2O_3 , indicating that the reaction of Cr_2O_3 and Na_2CO_3 starts at a low temperature of $400\text{--}500\text{ }^\circ\text{C}$.

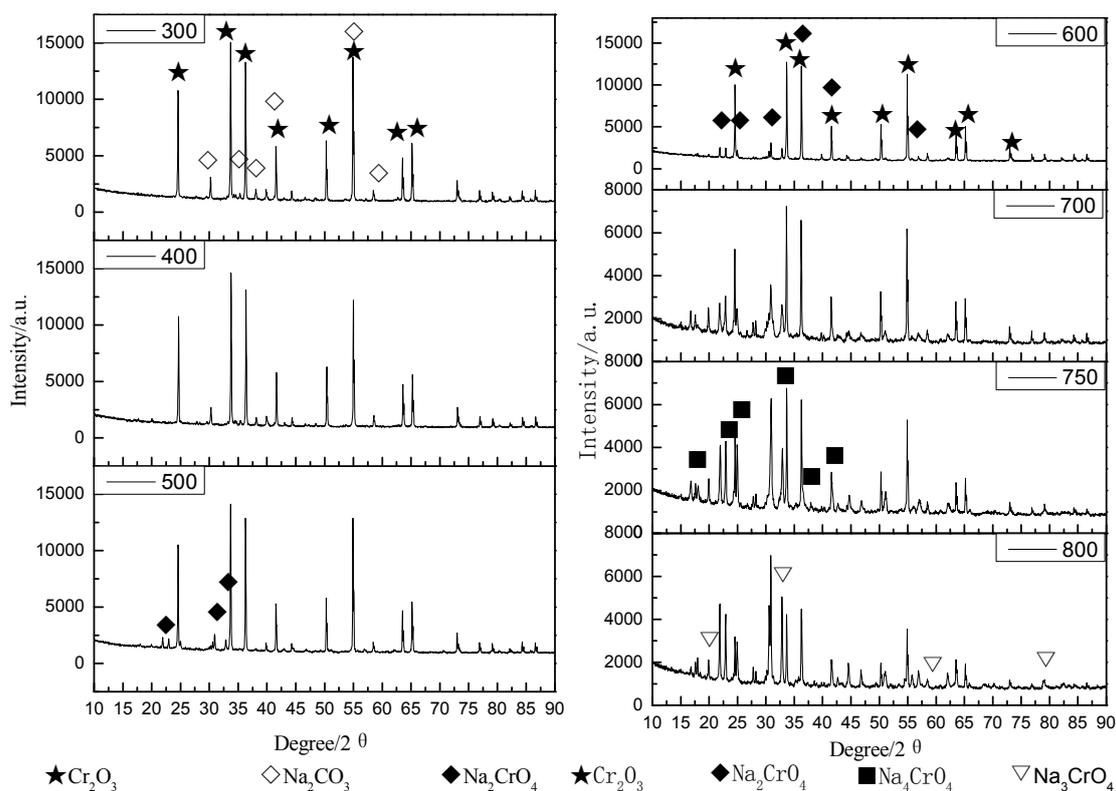


Figure 4. The XRD pattern of a sample of mixed Na_2CO_3 and Cr_2O_3 in a 1:1 ratio, at $300\text{--}800\text{ }^\circ\text{C}$ for 1 h.

At 600 and $700\text{ }^\circ\text{C}$, the sample phase is still Na_2CO_3 , Cr_2O_3 and Na_2CrO_4 , but the peak intensity of Na_2CO_3 and Cr_2O_3 becomes weak, while the phase diffraction peak intensity of Na_2CrO_4 increases. In the sintering condition of $750\text{ }^\circ\text{C}$, diffraction peaks of Na_2CO_3 disappear, the peak intensity of

Cr_2O_3 continues to weaken, and the peak intensity of Na_2CrO_4 increases again while the new phase of Na_4CrO_4 appears. At 800 °C, the peak intensity of Cr_2O_3 continues to decrease, while the peak intensity of Na_2CrO_4 enhances again and becomes the primary phase, and characteristic peaks of Na_4CrO_4 disappear and a new phase of Na_3CrO_4 is observed.

4.2. Comprehensive Thermal Analysis

Figure 5 is a TG-DTA curve of a sample of mixed Cr_2O_3 and Na_2CO_3 in a 1:1 ratio. Combined with XRD, the figure shows the first weight loss is due to the removal of adsorbed water between room temperature to 200 °C; the second weight loss is due to the decomposed Na_2CO_3 powders and liberated CO_2 gas between 200–700 °C; the endothermic peak around 100 °C is a removal reaction of the adsorbed water; and endothermic peak around 800 °C is due to the reaction of Na_4CrO_4 by DTA (Differential Thermal Analysis).

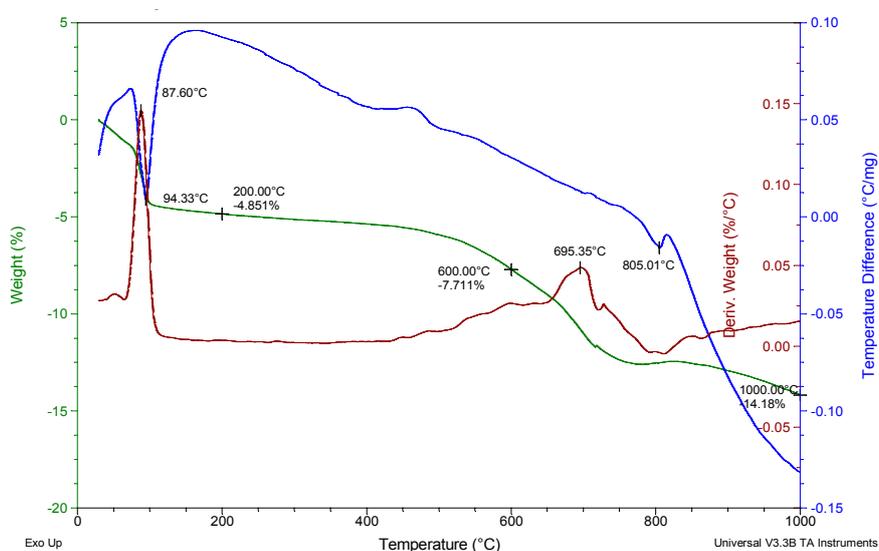


Figure 5. TG-DTA curve of sample mixed Cr_2O_3 and Na_2CO_3 in a 1:1 ratio.

4.3. SEM Analysis

Figure 6 shows the SEM image of a sample of mixed Cr_2O_3 and Na_2CO_3 in a 1:1 ratio, at different temperatures for one hour. The sample at 300 °C is composed of the irregular large blocky particles and uniform elliptical small particles, and the elliptical small particles enrich on the surface of the larger block particles. The two kinds of particles are substantially independent of each other. According to XRD analysis, there is no reaction substantially occurring in the sample at 300 °C, so the product is still composed of Cr_2O_3 and Na_2CO_3 . However, the sample begins to cohere together. The apparent morphology and characteristics of the sample at 400 °C are similar to the sample at 300 °C, but the blocky particle size decreases, while the elliptical-shaped particles appear slightly larger, and small particles show further agglomeration. According to XRD analysis results, the sample has no substantial reaction at 400 °C, and the product is still composed of Cr_2O_3 and Na_2CO_3 powder. The figure shows that, compared with the sample at 300 and 400 °C, blocky large particles in the sample at 500 °C basically disappear. According to XRD analysis results, the sample begins to react at 500 °C and is composed of Na_2CO_3 , Cr_2O_3 and Na_2CrO_4 . The product at 600 °C is similar to the sample at 500 °C and mainly consists of a 1 μm powder composition, approximately elliptical, but some particles start to fuse together. Combined with XRD analysis results, the sample at 600 °C is also composed of Na_2CO_3 , Cr_2O_3 and Na_2CrO_4 . At the temperature of 700 °C, the sample consists of smaller particles, with obvious agglomeration, but the small particles melt together to form larger particles of different shapes and different sizes. Combined with XRD analysis results, the sample at 700 °C is also composed

of Na_2CO_3 , Cr_2O_3 and Na_2CrO_4 , similar to the sample at 500 and 600 °C. The sample at 750 °C consists of a small number of small particles of 1–2 μm and large particles of different shapes; all the different-sized particles get together, and compared with the sample at 700 °C, more particles fuse together. Combined with XRD analysis results, the sample at 750 °C is composed of Cr_2O_3 , Na_2CrO_4 and Na_4CrO_4 . The sample at 800 °C basic melts completely, with only a small part of the small particles enriching on the surface of large particles or getting together; the sample mainly consists of melted large particles and adsorbed or aggregated small particles. Combined with XRD analysis results at 800 °C, the sample is composed of Cr_2O_3 , Na_2CrO_4 and Na_3CrO_4 .

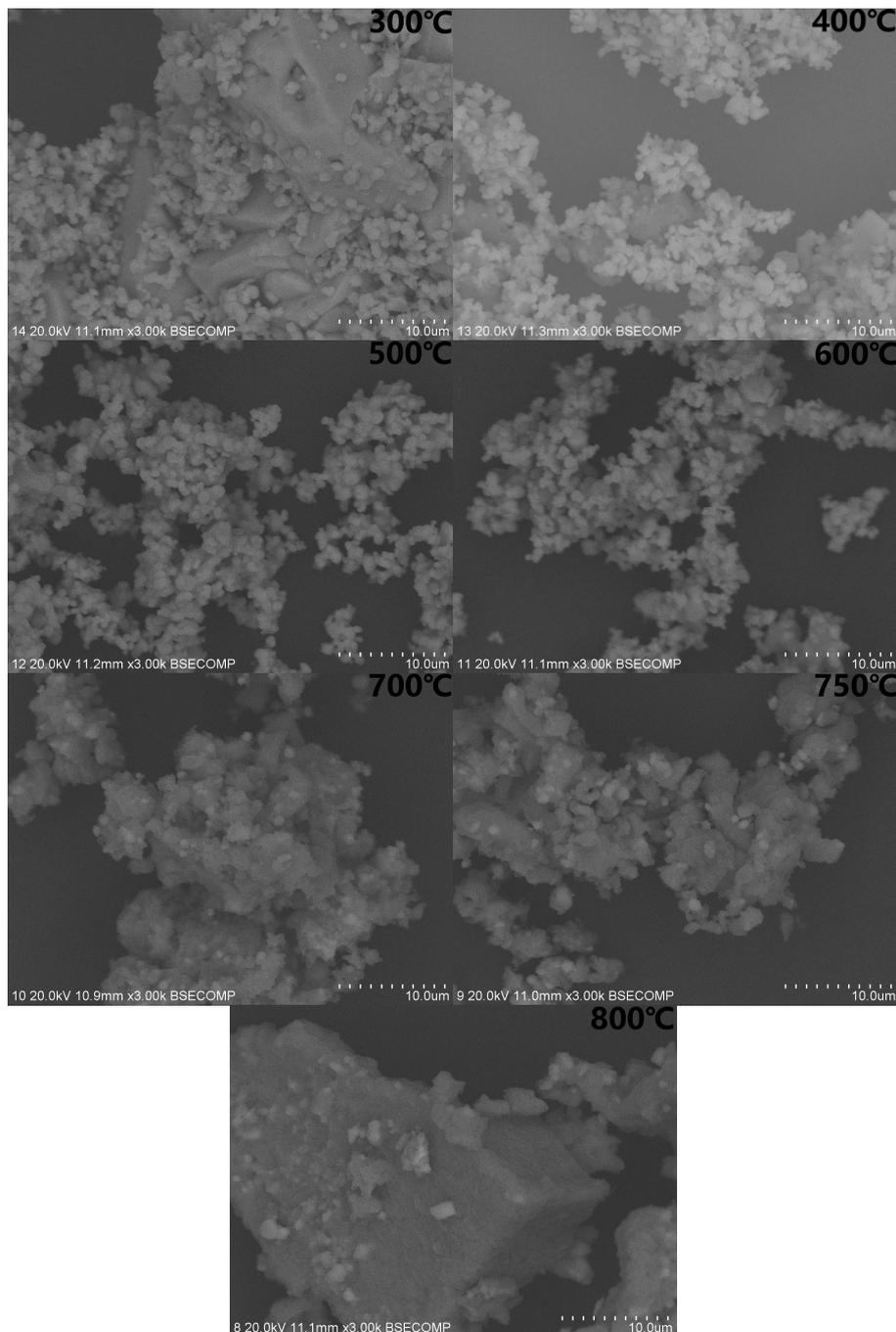


Figure 6. The SEM images of a sample of mixed Cr_2O_3 and Na_2CO_3 in a 1:1 ratio, at different temperatures for 1 h.

5. Conclusions

The mechanism of chromium on the roasting of vanadium slag has been given, and the effect of different contents of chromium on the conversion rate of vanadium in vanadium slag sodium-roasting has been studied.

1. Cr_2O_3 and Na_2CO_3 start the reaction at $500\text{ }^\circ\text{C}$ and generate Na_2CrO_4 , and the sample generates a new phase of Na_4CrO_4 at $750\text{ }^\circ\text{C}$; when heating up to $800\text{ }^\circ\text{C}$, Na_4CrO_4 decomposes to Na_3CrO_4 . There are two weight loss intervals and one endothermic peak and one exothermic peak between room temperature to $1000\text{ }^\circ\text{C}$. Seen from the SEM, the particles begin to melt at $600\text{ }^\circ\text{C}$.

2. When the chromium oxide content is about 3.2%, the conversion rate of V reaches the maximum value of 95%.

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Conflicts of Interest: The authors state that they have no conflict of interest.

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