



Preparation of potassium chromate by roasting of carbon ferrochrome



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Abstract: The oxidizing roasting process of carbon ferrochrome to prepare potassium chromate in the presence of potassium carbonate and air was investigated. The effects of reaction temperature, reaction time, mole ratio of potassium carbonate to carbon ferrochrome were studied, and thermodynamics and kinetics were also discussed. It was observed that the reaction temperature and reaction time had a significant influence on the roasting reaction of carbon ferrochrome. The reaction mechanism changed greatly as the temperature varied. A two-stage roasting process was favorable for the roasting reaction, and a chromium recovery rate of 97.06% was obtained through this two-stage roasting method. The chromium residue yielded from this method was only 1/3 of the product. Moreover, the component of Fe in the residue was as high as 55.04%. Therefore, it can be easily recovered to produce sponge iron, realizing complete detoxication and zero-emission of chromium residue.

Key words: carbon ferrochrome; potassium chromate; two-stage roasting; chromium residue; zero-emission

1 Introduction

Chromate compounds are important chemical products, which have been widely used in metallurgy, chemistry, material, leather-making, etc. Normally, the chromate products are achieved via a soda-ash roasting process, which is now under enormous pressure due to the environmental problems [1]. In this soda-ash roasting process, lime with amount of about 100% of the chromite ore was incorporated in the charge to control the siliceous and acid gangue minerals in the ore. But the addition of lime generates a large quantity of highly alkaline chromite ore processing residue (COPR), which contains hexavalent chromium of about 1%–2%. It also results in the generation of CaCrO_4 , which is volatile and can be easily airborne, causing a major threat to human, animal, and plant health. The remediation of the COPR is either too expensive or not thorough [2,3]. Although, the lime-free roasting process can reduce the generation of COPR and restrict the generation of CaCrO_4 , the necessity for high grade chromite ores with a silica content of less than 1% restricts its wide application [4].

Carbon ferrochrome (CrFeC) is a kind of intermediate product of chromium metallurgy, which is mainly used for producing stainless steel, tool steel,

ball-bearing steel, heat resistant steel, and so on [5]. Because the factories for producing CrFeC are always built in areas where electric power and mineral resources are rich, there are only fewer economic disadvantages using CrFeC as raw material than chromite. Accordingly, a novel method to produce K_2CrO_4 from CrFeC through an oxidizing roasting process has been proposed. The residue emitted from this process was very little, and it mainly consisted of iron oxides, which could be easily recovered to produce sponge iron. Therefore, it can realize the target of zero-emission of chromium residue, and resolve the chromium residue pollution problem completely.

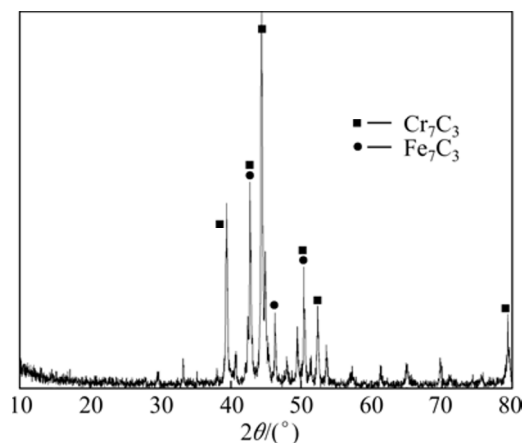
2 Experimental

The CrFeC specimen originated from Africa is provided by Jiafei New Material Co., Ltd., in Hunan Province, China. The particle size of the CrFeC specimen is $12.6 \mu\text{m}$ (D_{50}). The brief chemical components and the phase compositions are shown in Table 1 and Fig. 1, respectively, indicating that, CrFeC mainly consists of Cr, Fe and C in forms of Cr_7C_3 and Fe_7C_3 .

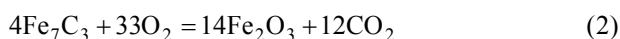
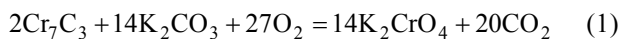
According to the chemical analysis results in Table 1 and the XRD pattern in Fig. 1, the main components of

Table 1 Brief chemical components of CrFeC (mass fraction, %)

Cr	Na	Fe	S	C	Mn	V
60.6	1.3×10^{-2}	27.9	5.0×10^{-3}	8.7	1.9	6.0×10^{-2}
Mg	Pb	Co	Si	Ni	Al	Ti
1.2×10^{-1}	3.2×10^{-3}	1.4×10^{-1}	2.4×10^{-1}	1.1×10^{-1}	1.4×10^{-1}	9.5×10^{-2}

**Fig. 1** XRD pattern of CrFeC

CrFeC are Cr_7C_3 and Fe_7C_3 . During the roasting process, Cr_7C_3 is oxidized to K_2CrO_4 in the presence of O_2 and K_2CO_3 , while the component of Fe_7C_3 is converted to Fe_2O_3 . The reaction equations of the main reactions are as follows [6]:



The experiments were carried out in a muffle furnace. The temperature was precisely controlled by a programming temperature controller. CrFeC was mixed homogeneously with a certain amount of K_2CO_3 in a porcelain mortar. Then, the mixture was loaded in a corundum boat and put into the muffle furnace when the temperature of the muffle furnace rose to the specified value. When time was up, the roasted product was taken out and cooled quickly. The roasted product was leached in distilled water at 313 K with the liquid-to-solid ratio of 5:1, and then it was washed three times under the same condition. At last, it was filtered to get a chromate solution and a solid residue. The solution was analyzed for Cr and other impurities. The conversion rate was calculated according to the following formula:

$$r = \frac{m_r}{m_o} \times 100\% \quad (3)$$

where r is the conversion rate of Cr; m_r is the total quantity of Cr in the solution and m_o is the total quantity of Cr in CrFeC. While the residue was analyzed for Cr(VI) to determine the quantity of Cr(VI) remaining in

the residue.

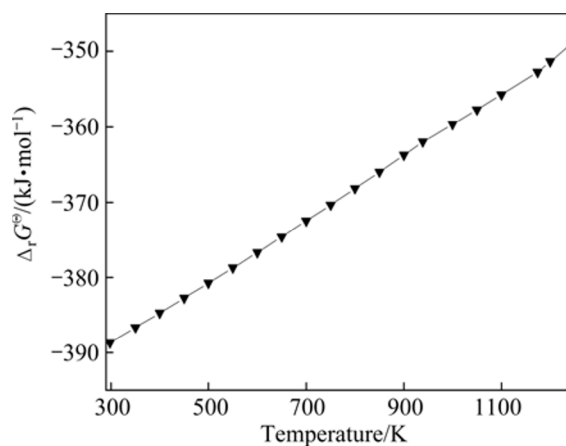
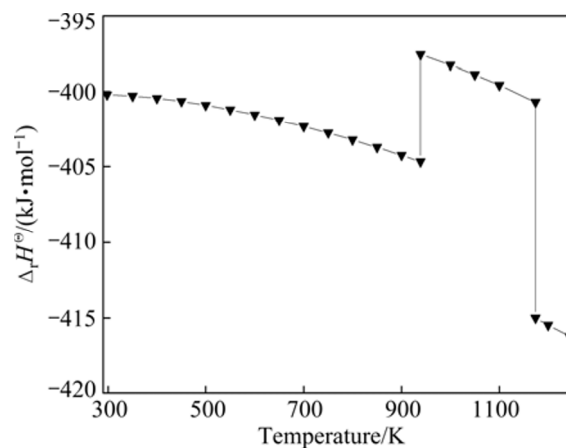
The leaching solution was analyzed by inductively coupled plasma-optical emission spectrometer (ICP-OES, PE Optima 5300DV, Perkin Elmer), and the residues were analyzed with a volumetric titration method. The phase identification was on an X-ray diffraction (XRD, Phillips PW223/30). The particle size distribution was measured by a particle size analyzer (LS230, Beckman, Coulter). SEM (scanning electron microscopy) images were taken by a JSM-35CF SEM equipment (Japan Electron Optics Laboratory Co., Ltd.). Thermoanalysis was performed on a universal V4.0C TA instrument (SDT Q600 V8.0 Build 95).

3 Results and discussion

3.1 Thermodynamical analysis

The standard Gibbs energy changes ($\Delta_r G^\ominus$) and standard enthalpy changes ($\Delta_r H^\ominus$) of Reaction (1) are shown in Figs. 2 and 3, respectively. They are calculated by using the method from Ref. [7] following the assumptions below:

1) All the components in Reaction (2) are pure substances.

**Fig. 2** $\Delta_r G^\ominus$ of Reaction (1) at 298–1244 K**Fig. 3** $\Delta_r H^\ominus$ of Reaction (1) at 298–1244 K

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