



Preparation of potassium chromate by roasting of carbon ferrochrome

Guo-rong HU, Jia-liang WANG, Zhong-dong PENG, Ke DU, Wei-gang WANG, Qing-lai JIANG

School of Metallurgy and Environment, Central South University, Changsha 410083, China

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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.

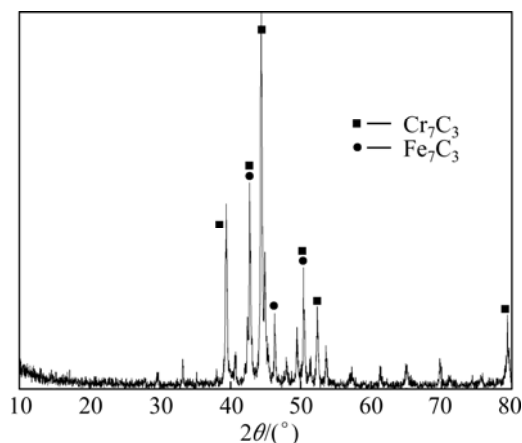
2 Experimental

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 .

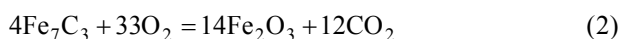
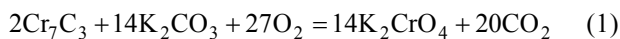
According to the chemical analysis results in Table 1 and the XRD pattern in Fig. 1, the main components of

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.

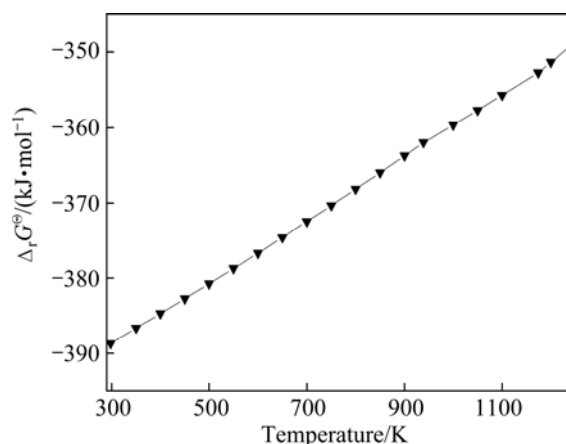
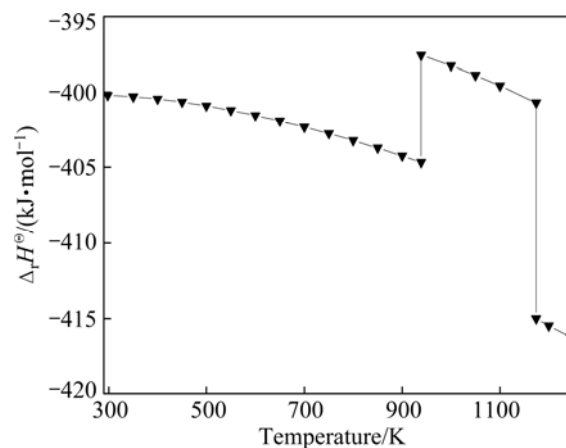
The leaching solution was analyzed by inductively coupled plasma-optical emission spectrometer (ICP-OES, PE Optima 5300DV, Perkin Elmer), and the residues were analyzed with a volumetric titration method. The phase identification was on an X-ray diffraction (XRD, Phillips PW223/30). The particle size 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

2) The gas of oxygen and carbon dioxide are all in standard state.

3) Cr_7C_3 and K_2CrO_4 are all solid, and the activity is 1. K_2CO_3 can be in liquid or solid state, depending on the roasting temperature, and the activity is 1.

The highly negative values of $\Delta_r G^\ominus$ shown in Fig. 2 indicate that Reaction (1) has a very intensive thermodynamic tendency. And the lower the temperature is, the higher the reaction tendency will be. The negative $\Delta_r H^\ominus$ values of Reaction (1) in Fig. 3 show that the oxidizing roasting reaction of CrFeC is an exothermic process, which can contribute to the reduction of energy consumption [7].

A DTA–TG analysis was employed to determine the behaviors of the reactants during the roasting process. CrFeC and K_2CO_3 were mixed in stoichiometric ratio, and then performed in a DTA instrument with a temperature rising rate of 5 K/min in air atmosphere. On the DTA–TG curves in Fig. 4, the first endothermic peak appearing at 363.58 K is caused by the evaporation of the free water, and the corresponding mass loss is 6.54%. Between 930.00 and 1083.38 K, it shows a slight decrease of the slope on the DTA curve, which is induced by the gradually melting of the K_2CO_3 – K_2CrO_4 eutectic. From 1083.38 K, the roasting reaction intensifies suddenly, and a sharp exothermic peak is observed at 1089.66 K, accompanied with a mass loss of 4.90%. With the temperature increasing, K_2CO_3 begins melting rapidly, and the corresponding endothermic peak appears at 1192.21 K. The endothermic peak starting from 1243.65 K is due to the melting of K_2CrO_4 . Because the vapor pressure of K_2CrO_4 will obviously increase after melting to liquid phase, the total mass decreases significantly from 1243.65 to 1478.00 K, and the mass loss reaches 25.11%. This indicates that, K_2CrO_4 of liquid phase is easy to vaporize.

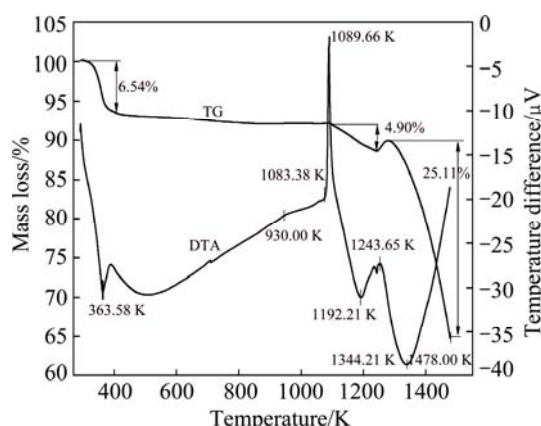


Fig. 4 DTA–TG curves of CrFeC and K_2CO_3 mixture

3.2 Kinetics

The conversion rates as a function of time at different temperatures are compared in Fig. 5. The

reaction regimes are quite different as the temperature changes. The eventual conversion rate increases with the rising of temperature. According to the DTA–TG plots in Fig. 4, there is no melting phenomenon at 873 K. Therefore, the reaction among CrFeC, K_2CO_3 and O_2 is gas–solid–solid reaction at this temperature. From the kinetic curve of the reaction at 873 K (Fig. 5), it can be observed that, the reaction rate is very rapid at the very beginning, but it runs to flat after 60 min. This is because small amount of fine particles existing in the reactant increase the contact area of CrFeC and K_2CO_3 , therefore, accelerating the reaction rate. When the fine particles are exhausted, the contact area will decrease significantly, and the mass transfer between CrFeC and K_2CO_3 will be very difficult. Accordingly, the gas–solid–solid reaction at 873 K is mainly controlled by mass transfer process.

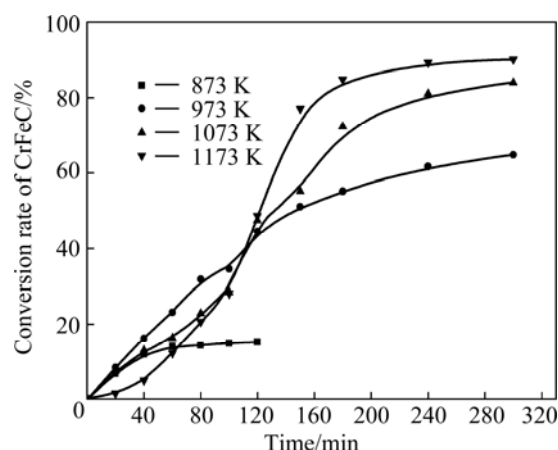


Fig. 5 Conversion rate of CrFeC at various temperatures

According to the DTA–TG plots in Fig. 4 and the SEM image in Fig. 6(a), only small amount of K_2CO_3 – K_2CrO_4 eutectic melt appears at 973 K. But thanks to this slight amount of melt, the contact area of reactants increases dramatically, and the reaction velocity has a greater improvement than that at 873 K. The first half of the kinetic curve fits well with the function $1-(1-r)^{1/3}=kt$ (Fig. 7), which is based on the shrinking un-reacted core model [6,8,9]. Namely, the roasting reaction is controlled by interface chemical reaction at the beginning of 973 K.

It can be observed from the DTA–TG curves that K_2CO_3 will melt down rapidly at 1173 K. The SEM image in Fig. 6(c) also indicates that the reactant has molten thoroughly after roasting at 1173 K for 1 h. So, the reaction among CrFeC, K_2CO_3 and O_2 is gas–liquid–solid reaction. And the S-type kinetic curve fits well with the crystal nucleation controlled Avrami function [10,11], namely, $\ln[-\ln(1-r)]=n\ln t+\ln k$ (Fig. 8). The value of Avrami index n and the crystallization rate constant k calculated by the slope and intercept of the linear plot in Fig. 8 are 1.96 and 3.99×10^{-5} , respectively.

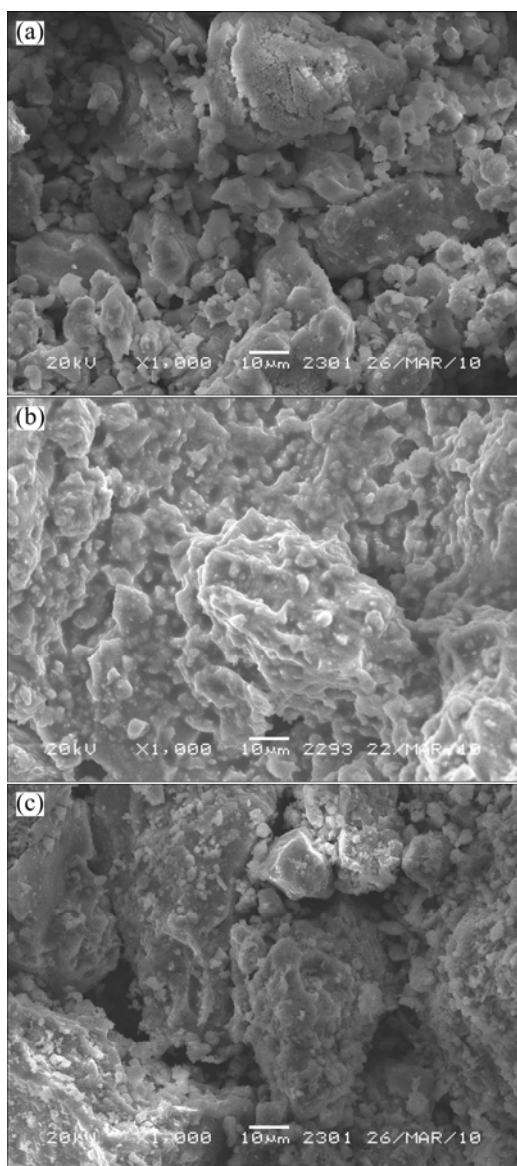


Fig. 6 SEM images of reaction products at various roasting temperatures (All of samples were slightly ground before SEM analysis): (a) Roasting at 973 K for 1 h; (b) Roasting at 1073 K for 1 h; (c) Roasting at 1173 K for 1 h

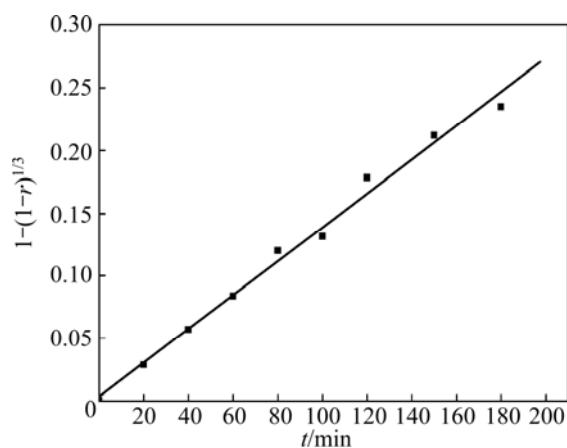


Fig. 7 Plot of $1-(1-r)^{1/3}$ vs t at 973 K

The SEM image in Fig. 6(b) shows that the surface of the reactants has been covered by moderate quantity of melt after roasting at 1073 K for 1 h. Namely, the quantity of melt increases with a moderate speed. In the first stage, when the quantity of the melt is still very small, the kinetic curve shows the same character as that of 973 K. While after 80 min, with the growth of the melt quantity, it changes to S-type curve like that at 1173 K. In conclusion, 973 K is the temperature point where the roasting reaction changes from interface chemical reaction controlled process to crystal nucleation controlled process.

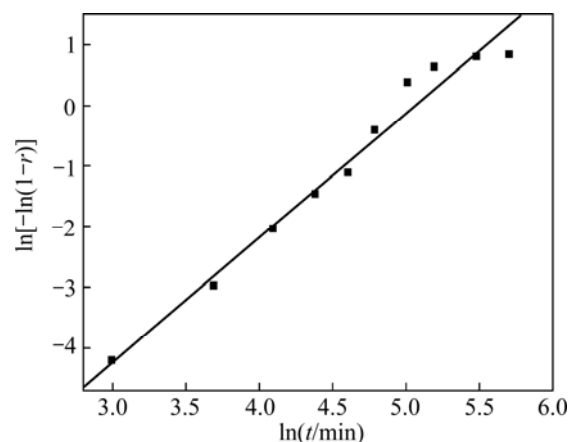


Fig. 8 Plot of $\ln[-\ln(1-r)]$ vs $\ln t$ at 1173 K

Because the eutectic of $\text{K}_2\text{CO}_3\text{--K}_2\text{CrO}_4$ just begins to melt with a very slow velocity at 973 K, even after roasting for 1 h, there is no obvious molten substance observed from the SEM image (Fig. 6(a)). So, when roasted at this temperature, the quantity of molten substance was effectively controlled, which not only increased the contact area between the reactants, but also made the melt quantity not to such an extent as to block the transmission path of O_2 and CO_2 . That is the reason why a more rapid reaction velocity was achieved at the first stage of 973 K. Moreover, the effectively controlling of the molten substance can also avoid the globule formation and kiln choking problems when operating in a rotary kiln in industrial scale. Actually, the products roasted at 973 K were quite porous and fragile, while the sample roasted at 1173 K was consolidated and hard to crush. However, as seen from the kinetic plots in Fig. 5, a higher temperature is essential to gain a higher conversion rate. Accordingly, to finish the roasting reaction thoroughly and rapidly, a two-stage roasting process was proposed. In this process, the mixture of CrFeC and K_2CO_3 was firstly roasted at about 973 K for certain duration, and then temperature increased to about 1173 K to complete the roasting reaction.

3.3 Orthogonal experiment of two-stage roasting

According to the kinetic analysis above, the factors which affect the two-stage roasting process most are the duration of the first stage (t_1), the roasting temperature of the first stage (T_1), the duration of the second stage (t_2), and the roasting temperature of the second stage (T_2). To determine the optimum conditions of the two-stage roasting process, an $L_9(3^4)$ orthogonal experiment was applied [12,13]. The factors and levels for the orthogonal experiment are shown in Table 2.

Table 2 Factors and levels of orthogonal design

Level	Factor			
	t_1/min	t_2/min	T_1/K	T_2/K
1	30	90	1003	1173
2	90	30	973	1213
3	60	60	1033	1193

The experiment results are listed in Table 3. In Table 3, k_1 , k_2 and k_3 are the mean values of the conversion rates, while R is the range of k . As seen from Table 3, the influence on the conversion rate from strong to weak is in the order of $t_2 > T_1 > t_1 > T_2$ according to the R values. This suggests that the roasting time of the second stage has an outstanding influence on the conversion rate, while the temperatures of the second stage almost make no difference in the studied range. We can achieve that a longer roasting duration is favorable at the two stages. Therefore, the optimal parameters of the two-stage roasting process determined by the k and R values are: $t_1=90$ min, $t_2=60$ min, $T_1=1003$ K, $T_2=1213$ K.

Table 3 $L_9(3^4)$ orthogonal experiment results

Experiment No.	t_1/min	t_2/min	T_1/K	T_2/K	Conversion rate/%
1	30	90	1003	1173	92.65
2	30	30	973	1213	75.88
3	30	60	1033	1193	85.46
4	90	90	973	1193	91.85
5	90	30	1033	1173	86.26
6	90	60	1003	1213	95.04
7	60	90	1033	1213	91.85
8	60	30	1003	1193	85.46
9	60	60	973	1173	83.86
k_1	84.66	92.12	91.05	87.46	
k_2	91.05	82.53	83.73	87.59	
k_3	86.92	87.99	87.86	87.59	
R	6.39	9.58	7.32	0.13	

3.4 Effect of mole ratio of K_2CO_3 to CrFeC

The mole ratio of K_2CO_3 to CrFeC being 1:1 (stoichiometry), 1.1:1, 1.2:1, 1.3:1 and 1.4:1 were investigated employing the two-stage roasting process ($t_1=90$ min, $t_2=60$ min, $T_1=1003$ K, $T_2=1213$ K). The experiment results are shown in Fig. 9. It can be seen that when the ratio changes from 1:1 to 1.1:1, the conversion rate of CrFeC has a significant improvement. But it has little variation when the ratio keeps changing to 1.3:1. Moreover, the conversion rate confronts an apparent fall when the ratio reaches 1.4:1. This is because the excess K_2CO_3 induces too much liquid materials, which blocks the transmission path of O_2 and CO_2 during the second roasting stage. Accordingly, a mole ratio of K_2CO_3 to CrFeC of 1.1:1 is optimal for the roasting reaction, of which a conversion rate of 97.06% is achieved.

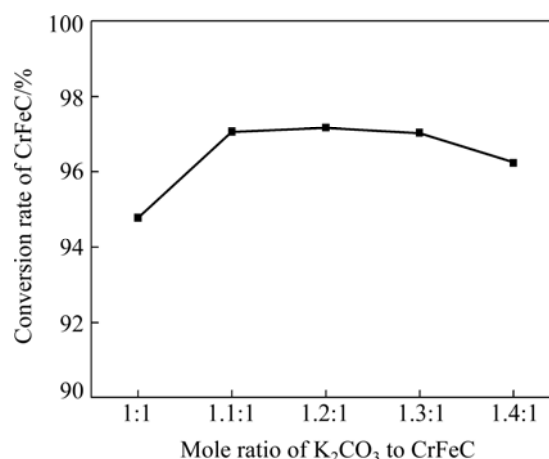


Fig. 9 Effect of mole ratio of K_2CO_3 to CrFeC

3.5 Leaching solution and residue

A roasting product was firstly obtained from the two-stage roasting process, and the XRD pattern of the roasting product is shown in Fig. 10. According to Fig. 10, the roasting product mainly consists of K_2CrO_4 , K_2FeO_4 , Fe_3O_4 and FeCO_3 .

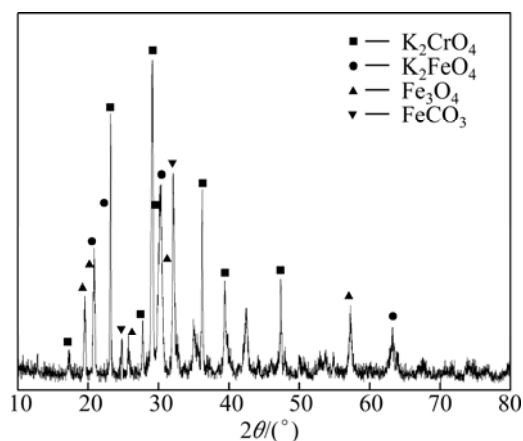


Fig. 10 XRD pattern of roasted product

The roasted product was leached and washed. At last, it was filtered to get a K_2CrO_4 solution and a chromium residue.

The chemical components of the solution are shown in Table 4. The fractions of the impurities in the leaching solution are all quite low, namely, K_2CrO_4 product can be achieved just through a simple refining process.

Table 4 Components of leaching solution (mg/L)

Cr	K	Si	Al	Mn	Co	V	As	Ca
5.13×10^3	8.34×10^3	7.8	9.6	3.3	1.6	3.1	2.4	1.7

According to the XRD pattern in Fig. 11, the residue mainly consists of Fe_3O_4 , and there are no cementitious materials like tricalcium silicate or calcium alluminoferrite in the residue. The particle size distribution of the residue in Table 5 indicates that the particle size of the residue is very small, only tens of microns. So, it is favorable for the high efficient leaching of Cr(VI). Chemical analysis [14,15] shows that Cr(VI) remaining in the chromium residue is only 0.08%, far less than that of the traditional soda-ash roasting process, which is as high as 1%–2% [2]. The quantity of the residue is very low, only about 1/3 of the product, compared with 250% of the product in the soda-ash process. The Fe content in the residue reaches up to 55.04% according to a volumetric analysis. So, the residue can be easily recycled to produce sponge iron from a carbon reduction method, realizing the complete detoxication of chromium residue and the target of clean production [16,17].

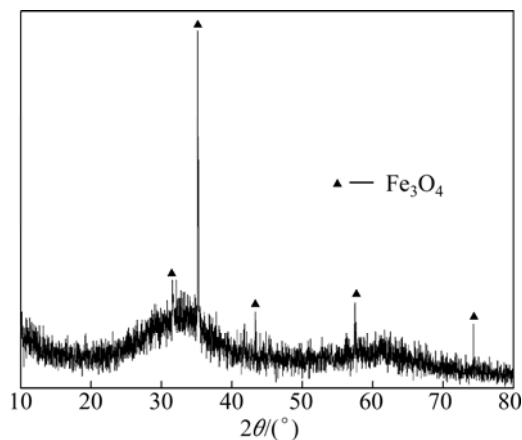


Fig. 11 XRD pattern of residue

Table 5 Particle size distribution of residue

$D_{10}/\mu m$	$D_{50}/\mu m$	$D_{90}/\mu m$
7.3	34.8	82.6

4 Conclusions

1) The kinetic mechanisms are quite different as the temperature varies. A relatively low temperature is beneficial to the first stage of the roasting reaction. But, a higher temperature is essential to a higher conversion rate. The appearance of melt with a proper level can accelerate the oxidizing reaction significantly.

2) The two-stage roasting process can effectively control the quantity of the molten substances, which not only makes the roasting reaction complete thoroughly and rapidly, but also makes it have the potential to operate in a rotary kiln for industrial production.

3) The quantity of the residue is very low, only about 1/8 of that of the traditional soda-ash method. Moreover, this high-iron residue can be easily recycled to produce sponge iron, through which the targets of complete detoxication and zero-emission of chromium residue are realized.

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高碳铬铁氧化焙烧制备铬酸钾

胡国荣, 王家良, 彭忠东, 杜柯, 王伟刚, 蒋庆来

中南大学 冶金与环境学院, 长沙 410083

摘 要: 研究以高碳铬铁为原料在碳酸钾的存在下经氧化焙烧制备铬酸钾的反应过程。考察反应温度、反应时间和碱矿比(碳酸钾与高碳铬铁的摩尔比)对氧化焙烧过程的影响, 并讨论反应的热力学与动力学。结果表明, 反应温度和反应时间对高碳铬铁的氧化焙烧过程影响较大; 反应机理随反应温度发生改变。采用两段焙烧法可以获得较好的反应效果, 碳素铬铁中铬的转化率达到 97.06%; 此工艺产生的铬渣量极少, 仅为所得产品质量的 1/3 左右, 且铬渣中 Fe 含量高达 55.04%, 可用于碳还原法生产海绵铁, 实现铬渣的彻底解毒和零排放。

关键词: 铬铁合金; 铬酸钾; 两步焙烧; 铬渣; 零排放

(Edited by Wei-ping CHEN)