Article ID: 1003－6326(2004)01－0180－04

Temperature dependence of crystal structure and digestibility of roasted diaspore①

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Abstract: Through X-ray diffraction patterns and scanning electronic micrographs, temperature dependence of the crystal structure of roasted diasporic bauxite at different temperatures and the digestibility of roasting production were investigated systematically. The lattice parameters of unit cell for chemically purified diaspore and unequilibrium alumina-contained oxide obtained from the diaspore roasted at different temperatures were determined. It is found that, with roasting temperature increasing, the roasting production changes from the original dense and perfect diaspore crystal into imperfect corundum with many microcracks and small pores on its surface and then into perfect corundum with low digestibility. The optimum roasting temperature with best digestibility is approximately 525 ℃ when residence time is about 25 min. It is thought that the change of crystal structure, formation of microcracks and small pores in the temperature field are the main essential reasons for improving digestibility of diasporic bauxite and its roasting production.

Key words: temperature field; crystal structure; digestibility; diaspore
CLC number: TF 082 **Document code:** A

1 INTRODUCTION

Due to the relatively stable crystal structure and low reaction ability with caustic soda of diaspore, high concentration of caustic soda, high reaction temperature and long reaction time in Bayer process are needed. Furthermore, the caustic ratio of aluminate solution after digestion is high and the mass ratio of alumina to silicon dioxide (A/S) in red mud is also high. Besides requiring equipments with high quality, this also affects all technological and economical parameters in Bayer process. It has been the obstacle and research focus of alumina industry at present, and much attention was paid to the intensifying digestion of diaspore.

So far, several methods for intensifying digestion are proposed[1, 2]. For example, tube digestion technology[3] is used successfully to treat diasporic bauxite in the Great Wall Aluminium Company, China. But this method is not suitable to modify all the traditional digestion technology dominated by vapor heating in China. Another one is to pre-treat the diaspore to improve the reaction ability of diaspore with caustic soda so that it can be digested under relatively relaxed digestion condition. Sweetening process[4] is a new promising technology by adding activated diaspore roasted at certain condition. In the new technology, eighty to ninety percent of total diasporic bauxite was treated by the traditional Bayer process without changing the other digestion conditions. The rest ten to twenty percent of diaspore was added after digestion with high pressure. By this means alumina can completely be reacted with caustic soda in the first digestion stage to reach its theoretical content, as the sodium aluminate solution was not far supersaturation. In the sweetening process (second digestion stage), most of alumina in the activated diaspore can also be extracted into sodium aluminate solution because of the improved digestibility of diaspore by pretreating process with temperature field, so the higher yield of alumina in diaspore can be achieved successfully. Red mud with lower A/S ratio is thrown away.

Although much work was conducted on the roasting pre-treatment and sweetening process technology[5, 6], few work in the literature was reported on the relationship between the change of crystal structure of roasting production from diasporic bauxite roasted under different conditions and its digestibility. In this paper, the influence of temperature field on the crystal structure of roasting production from diasporic bauxite, its digestibility and the relationship between them are studied.

2 EXPERIMENTAL

The diasporic bauxite concentrate was from Henan branch of China Aluminium Corporation. As there were still many impurities in the diasporic bauxite concentrate, which would affect the temperature

① **Foundation item:** Project(G1999064910) supported by the National Key Fundamental Research and Development Program of China
Received date: 2003－03－17; **Accepted date:** 2003－05－20
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field of roasting production, purifying process with chemical method was employed in the experiment to ultimately remove all the present impurities. Firstly, dilute caustic soda was used to remove silicon dioxide. Secondly, dilute hydrogen chloride was adopted to remove iron. At last, hydrogen fluoride was chosen to remove other impurities, which were rather difficult to remove in the previous two processes. The chemical composition of the purified diaspore is listed in Table 1. It shows that diasporic bauxite treated chemically is relatively pure. The content of alumina in diaspore almost reaches its theoretical value 85%.

Table 1 Chemical composition of purified diaspore by chemical method (mass fraction/ %)

Al_2O_3	SiO_2	TiO_2	Fe_2O_3	Impurity	Water
83.23	0.25	0.48	0.82	1.03	14.69

Digestion experiments were carried out in the rotating bomb with mixed nitrate salts as heating medium (XYF—d44 × 6) which was designed by the Alumina & Ceramic Research Institute. Temperature was controlled by TA-641 temperature apparatus with precision of ±1 ℃. In order to intensify agitation, two big steel balls with diameter of 6mm and two small steel balls with diameter of 2 mm were added into the bomb.

Phases and lattice parameters of unit cell for crystal structure of roasting production were determined by Siemens D-500 X-ray diffractometer (Germany). And the morphology of roasted production was observed by JSM 5600LV (Japan).

3 RESULTS AND DISCUSSION

3.1 Temperature dependence of crystal structure of roasting production from chemically purified diasporic bauxite

As we know, if the crystal structure of pure diaspore is changed in temperature field, its digestibility with caustic soda will also be changed. In this paper, we tried to intensify the digestibility of diaspore by pre-treatment with temperature field. X-ray diffraction patterns of roasting production from pure diaspore at 400, 525, 650, 800, 900 and 1000 ℃ for 25 min were conducted. And their lattice parameters of unit cell are calculated and listed in Table 2. Compared with the standard X-ray diffraction patterns of diaspore and corundum, it is indicated that the phase of roasting production at 400 ℃ is still diaspore. But its lattice parameters of unit cell of diaspore were changed a little. The value of c became bigger and the values of a and b became a little smaller. While pure diaspore was roasted at above 525 ℃ for the same time, the phase was changed from diaspore into corundum. The original crystal structure of diaspore was destroyed completely and reconstructed into an imperfect corundum phase. Diaspore belongs to Pbnm AlO(OH) octahedron and corundum belongs to AlO_6 octahedron. With roasting temperature varying from 525 ℃ to 1 000 ℃, the value of a became bigger, the value of c became smaller and the ratio of c/a is more and more closer to its theoretical value. With the temperature rising from 400 ℃ to 1 000 ℃, diaspore was changed from pure and dense crystal structure into imperfect corundum and eventually into perfect corundum phase, so the digestibility with caustic soda might be improved obviously by suitable pre-treatment with temperature field.

Table 2 Lattice parameters of unit cell of roasting production at different temperature for 25 min

Temperature / ℃	Phase	a	b	c	c/a
400	Diaspore	4.326 0	9.417	2.864 0	
525	Corundum	4.749 3		13.015 4	2.740
650	Corundum	4.757 8		13.004 6	2.733
800	Corundum	47 588		13.003 3	2.732
900	Corundum	4.759 4		12.999 5	2.731
1 000	Corundum	4.760 4		12.991 9	2.729
	Pure corundum	4.760 2		12.993 3	2.730

Fig. 1 presents the scanning electronic micrographs of roasting production from pure diaspore roasted at 400, 525 and 650 ℃ respectively for a certain time. It shows that there are many microcracks and small pores on the surface of corundum crystals formed during the roasting pre-treatment process. This greatly increases the specific surface area of roasted diasporic bauxite, which results in better digestibility of roasting production with caustic soda.

3.2 Temperature dependence of digestibility of roasting productions from diaspore under different conditions in synthetic sodium aluminate solution

Concentrations of alumina and sodium oxide in the green liquor used in sweetening process were 242.67 g/L and 224.70 g/L, respectively. The amount of added alumina-contained production was calculated according to the hypothesis that caustic ratio (molar ratio of caustic soda to alumina) of so-

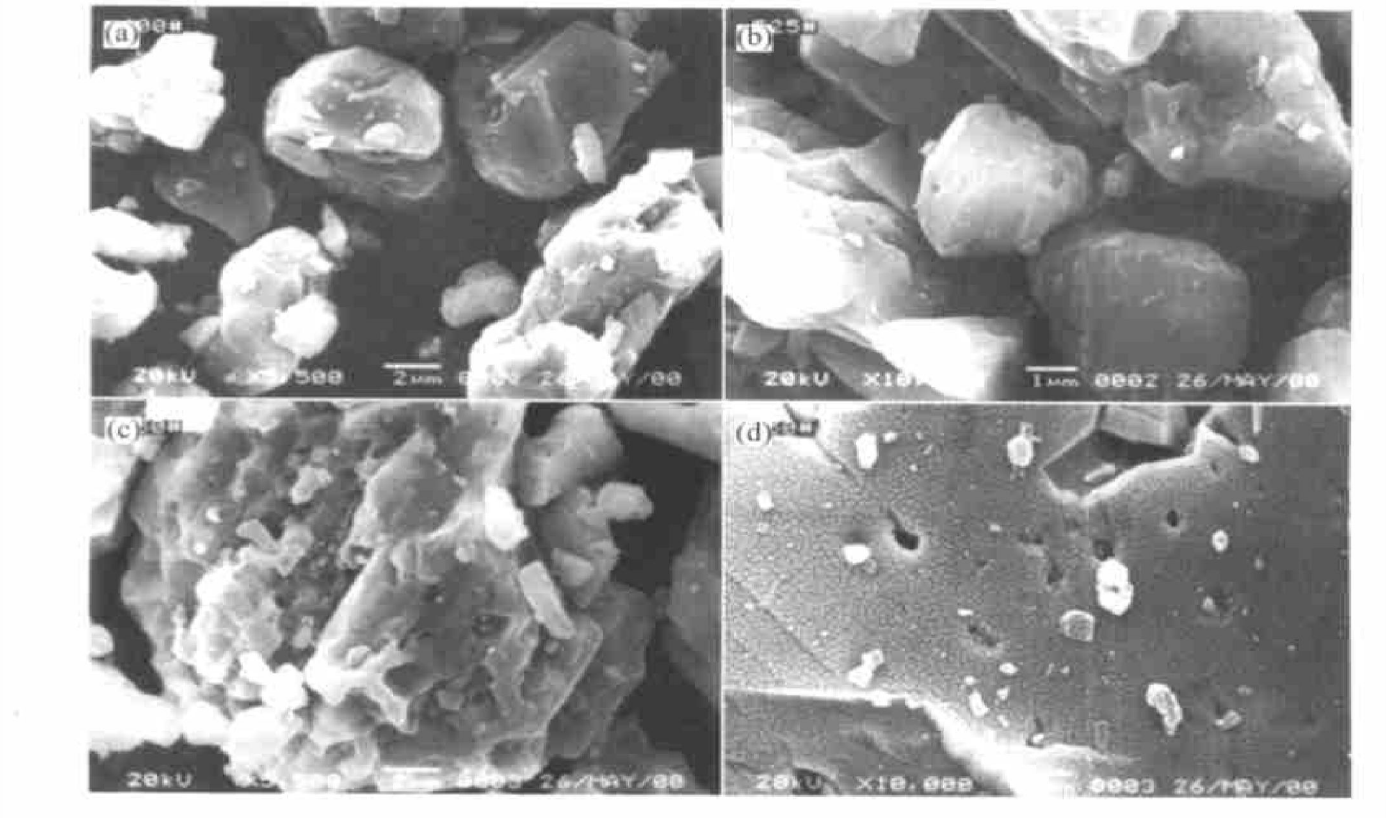

Fig. 1 SEM micrographs of purified diaspore roasted at different temperatures
(a) —400 ℃; (b) —525 ℃; (c) —650 ℃; (d) —1 000 ℃

dium aluminate solution after digestion is 1.30. Purified diaspore was roasted at 400, 525 and 650 ℃, respectively for 25 min. Digestion experiments were conducted at different temperatures during sweetening process. Chemical compositions of roasting production at different temperatures are listed in Table 3. It shows that purified diaspore roasted at 400 ℃ for 25 min is practically not changeable, as the content of alumina in diaspore is almost the same. However, purified diaspore roasted at 525 ℃ and 650 ℃ for the same residence time is decomposed and new phase comes into being, as the content of alumina in roasting production is much higher than the original one. The results agree well with the investigations reported in Refs. [7 − 9].

Table 3 Content of alumina in roasting production (mass fraction, %)

Temperature/ ℃	400	525	650
Content of alumina/ %	84.70	97.56	97.58

The digestion results of activated diaspore by roasting purified diaspore at different temperatures are shown in Figs. 2 − 4. It is shown that 60% of alumina in roasting production can be extracted by roasting purified diaspore at 525 ℃ for 25 min, while the digestion residence time is 6 0 min and digestion

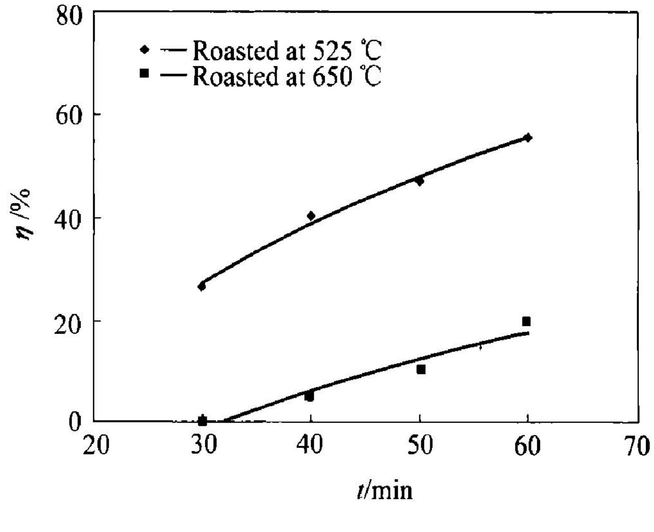

Fig. 2 Digestion curve of roasting production at digestion temperature of 210 ℃

temperature is 210 ℃. When the digestion temperature is 220 ℃ and digestion residence time is 40 min, more than 90% of alumina in bauxite can be extracted. That is to say, almost all of alumina in bauxite can be recovered under this condition. It is also suggested that the digestion ability of imperfect corundum (far to equilibrium phase) was far better than that of the relatively perfect corundum (closer to equilibrium corundum) obtained from roasting temperature of 650 ℃ or even higher temperature and the original diaspore or purified diaspore without roasting.

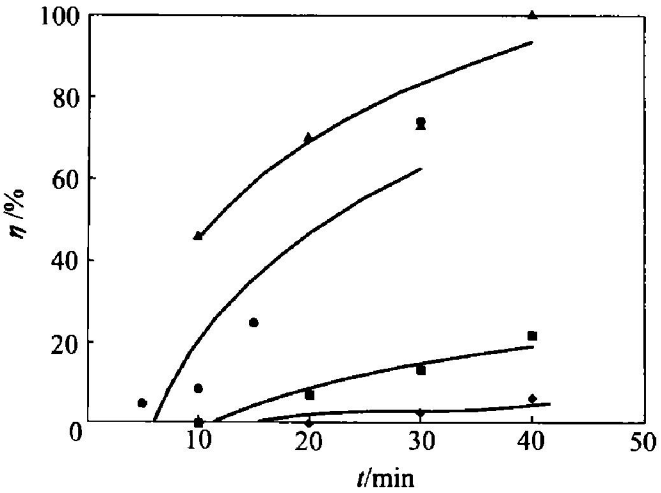

Fig. 3 Digestion curve of roasting production at digestion temperature of 220 ℃

▲—Roasted at 525 ℃; ●—Roasted at 650 ℃; ■—Roasted at 400 ℃; ◆—Original pure diaspore

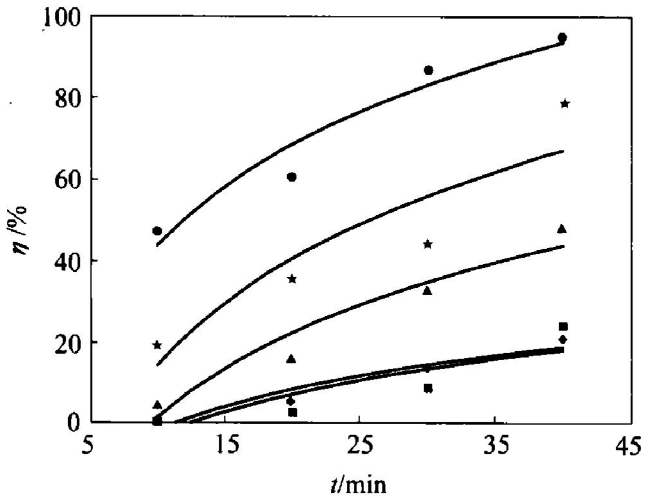

Fig. 4 Curves of alumina extraction for differently treated diaspore at digestion temperature of 230 ℃

●—Purified diaspore roasted at 525 ℃;
★—Purified diaspore roasted at 650 ℃;
▲—Purified diaspore roasted at 400 ℃;
◆—Original diaspore; ■—Purified diaspore

4 CONCLUSIONS

1) The lattice parameters of roasting production of diaspore purified chemically vary with the roasting temperature. The crystal phase of roasting production gradually changes into unequilibrium corundum and eventually into equilibrium and perfect corundum from perfect diaspore when the roasting temperature rises from 400 ℃ to 1 000 ℃ through analysis and calculation of X-ray diffraction patterns.

2) There are two main reasons of improving digestibility of roasting production of purified diaspore. Firstly, in certain roasting temperature range, the crystal structure of diaspore is completely changed from dense and perfect diaspore phase into imperfect and activated corundum by roasting pure diaspore for certain time. Secondly, the specific surface area is greatly increased as there are many microcracks and small pores which form during the roasting process on the surface of the roasting production.

3) The digestibility of alumina-contained un-equilibrium corundum phase is best, which is obtained by roasting pre-treatment of chemically purified diaspore at approximate roasting temperature of 525 ℃ for 25 min.

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(Edited by YANG Bing)