

# SPECTRAL STUDY OF CARBONIZATION PROCESS IN ALUMINA PRODUCTION<sup>①</sup>

Hong, Mei Liu, Miaoxiu Zhang, Weiming Zhao, Peifang Chen, Nianyi  
*Shanghai Institute of Metallurgy, Academia Sinica, Shanghai 200050*

## ABSTRACT

The UV spectra of sodium aluminate solutions in the carbonization process exhibit complex change, while the change of Raman spectra is not so evident. Based on the regularity of intensity change of UV and Raman spectra of solutions in the carbonization process, the mechanism of sodium aluminate solution in the carbonization process was discussed.

**Key words:** carbonization spectra reaction mechanism

## 1 INTRODUCTION

The carbonization process is one of the important steps of the sintering method for alumina production. This process affects the recovery and quality of alumina. UV, UV time-scanning and Raman spectra of sodium aluminate solution in the carbonization process were detected so as to study the change of sodium aluminate solution in carbonization process (especially in the early period of carbonization process).

## 2 EXPERIMENTAL METHODS

High-purity aluminium metal was dissolved into sodium hydroxide solution (prepared by dissolving C. P grade NaOH into deionized water) to obtain sodium aluminate solution containing  $\text{Al}_2\text{O}_3$  306 g/L and  $\text{Na}_2\text{O}$  279 g/L. After a lengthy storage in an air-tight polyethylene bottle, the sodium aluminate solution was diluted to a solution containing  $\text{Al}_2\text{O}_3$  102 g/L and  $\text{Na}_2\text{O}$  93 g/L. This diluted solution was used as the raw material of carbonization process.

Two kinds of carbonization methods of sodium aluminate solution were used. One was inletting  $\text{CO}_2$  gas into newly diluted solution with vigorous

stirring, which was relatively similar to the practical process in industry production. The other was adding 1 mol/L  $\text{NaHCO}_3$  into the newly diluted solution with vigorous stirring, which could be exactly controlled the degree of carbonization. Two kinds of carbonization methods were used in the meantime so as to compare their result of spectral measurements.

UV, UV time-scanning spectra at wavelength 2800 Å of sodium aluminate solution in the carbonization process were measured with Shimadzu 2100 S type UV spectrometer. RAMALOG SPEX 1103 type Raman spectrometer was used for the Raman spectra measurement of sodium aluminate solution in the carbonization process. The Ar laser light source with power 200 mW and wavelength 5145 Å was used.

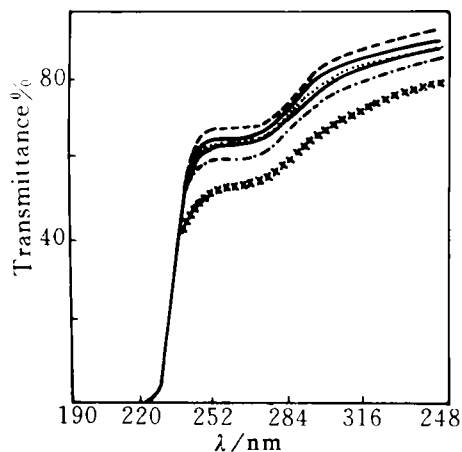
## 3 EXPERIMENTAL RESULTS

### 3.1 *The Change of UV Spectra in the Carbonization Process*

The  $\text{CO}_2$  gas was inletted into the newly diluted sodium aluminate solution containing  $\text{Al}_2\text{O}_3$  102 g/L and  $\text{Na}_2\text{O}$  93 g/L, and vigorously stirring by magnetoelectric stirrer. Then UV spectra began to be

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measured after every other minute for every 10 min until gibbsite precipitation occurred, as shown in Fig. 1.



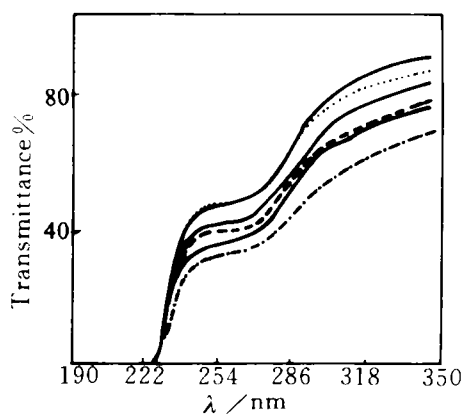
**Fig. 1** The UV spectra change of sodium aluminate solutions in the carbonization process (inletting  $\text{CO}_2$  gas) was measured after each other for every 10 min.

Then 1 mol/L  $\text{NaHCO}_3$  was added to newly diluted sodium aluminate solutions until the total volume of solutions increased to 1.1 ~ 1.6 times of the original dilute solutions. UV spectra of the solutions were then measured after each other minute for every 10 min until gibbsite precipitation occurred. It is found that the UV spectra of every solution exhibit oscillatory changes. Fig. 2. represents one of the example of the UV spectra change in this process. It is seen that the spectra shape of Fig. 1 and Fig. 2 are similar, and transmittance vs time exhibits oscillatory change.

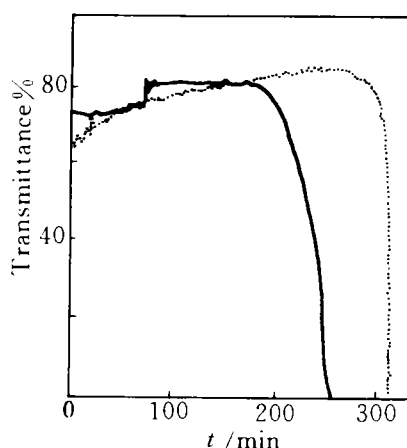
### 3.2 The UV Transmittance Change at Wavelength 2800 Å in Carbonization Process

At the same stirring condition and same adding rate, 1 mol/L  $\text{NaHCO}_3$  was added to two samples of sodium aluminate solution with same composition, same concentration and same preparative histories. Then the UV time-scanning spectra at wavelength 2800 Å were measured, as shown in Fig. 3. It is interesting that the UV transmittance curves of two samples exhibit obvious difference, though the general tendency of transmittance change show similarity, such experiments were re-

peated many times. It is confirmed that the UV transmittance change of sodium aluminate exhibits non-reproducibility.



**Fig. 2** The UV spectra change of sodium aluminate solution (adding 1 mol/L  $\text{NaHCO}_3$ ) was measured after each other for every 10 min

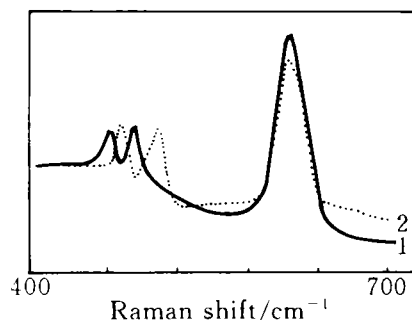


**Fig. 3** The UV transmittance changes at wavelength 2800 Å and non-reproducibility of sodium aluminate solution in the carbonization process (adding 1 mol/L  $\text{NaHCO}_3$  till the volume of solution was increased 1.6 times)

### 3.3 The Raman Spectra Change of Sodium Aluminate Solution in the Carbonization Process

Fig. 4 illustrates the change of Raman spectra of newly diluted sodium aluminate solution after addition of 1 mol/L  $\text{NaHCO}_3$  until the total volume of

solution increased to 1.6 times of the originally dilute solution. It is shown in Fig. 4 that Raman spectra exhibit less evident change as compared with UV spectra at the same condition. The 625 cm<sup>-1</sup> chief peak, implying the existence of Al(OH)<sub>4</sub><sup>-</sup>, shows less change, while the peaks in the range of 460 cm<sup>-1</sup> to 480 cm<sup>-1</sup> exhibit some changes. It means that Al(OH)<sub>4</sub><sup>-</sup> is still the major anionic species at the early period of carbonization process.



**Fig. 4 The Raman spectra of sodium aluminate solution in carbonization process**

Curve 1—5 min after addition of NaHCO<sub>3</sub> into newly diluted sodium aluminate solution;  
Curve 2—25 min after addition of NaHCO<sub>3</sub> into newly diluted sodium aluminate solution

**4 DISCUSSION**

In our previous work, it was noted that UV spectra of sodium aluminate solutions (containing Al(OH)<sub>4</sub><sup>-</sup> as major anion species and different concentration of Al(OH)<sub>6</sub><sup>3-</sup> and its polymeric anions such as Al<sub>2</sub>(OH)<sub>10</sub><sup>4-</sup>) exhibit great change. According to the mechanism of decomposition or carboniza-

tion of sodium aluminate solutions proposed by Назынич, Al(OH)<sub>6</sub><sup>3-</sup> and polymeric anions are reaction intermediate products, whose formation and further polymeration may induce UV spectra change in carbonization process.

It is found that transformation of HCO<sub>3</sub><sup>-</sup> and CO<sub>3</sub><sup>2-</sup> is not the dominant factors of UV spectra change in the carbonization process, because their transmittance in the range of our measurement wavelength is very high.

It was found in our previous work that UV spectra of sodium aluminate solution in the decomposition process of diluted solution also exhibit similar complicated change, implying the similarity between the decomposition and carbonization process.

With pattern recognition (PCA method) of the spectra change, the number of anionic species, occurring the spectra change, can be confirmed. The results of PCA analysis of the UV spectra of sodium aluminate solution in carbonization process with two above-mentioned methods are shown in Table 1 and Table 2.

It can be seen in Table 1 and Table 2 that the first eigenvalue is 98% and 96.8% of the total values respectively, implying that only one kind of anionic species is responsible to the UV spectra change in carbonization process. This anionic species may be Al(OH)<sub>6</sub><sup>3-</sup> or its polymeric anions.

In our previous works, it was found that the chaotic phenomenon occurs in the decomposition process of sodium aluminate solutions. In this work, the non-reproducibility of the reaction kinetics in the decomposition and carbonization of sodium aluminate solutions was found. All these facts

**Table 1 PCA analysis of UV spectra of sodium aluminate solution in the carbonization process (adding NaHCO<sub>3</sub>)**

No	1	2	3	4	5	6	7	8	9	10	11	12	13	14
λ <sub>i</sub>	26.96705	0.32251	0.13167	0.04170	0.01719	0.0131	0.00826	0.00625	0.00525	0.00397	0.00191	0.00116	0.00058	0.00039
λ <sub>i</sub> /∑λ <sub>i</sub> (%)	98.0	1.17	0.48	0.16	0.06	0.05	0.03	0.02	0.02	0.01	0.007	0.005	0.002	0.001

**Table 2 PCA analysis of UV spectra of sodium aluminate solution in the carbonization process (inletting CO<sub>2</sub>)**

No	1	2	3	4	5	6	7	8	9	10	11	12	13	14
λ <sub>i</sub>	25.84505	0.40393	0.21286	0.10156	0.04397	0.02908	0.01512	0.01192	0.00820	0.00521	0.00436	0.00311	0.00089	0.00023
λ <sub>i</sub> /∑λ <sub>i</sub> (%)	96.8	0.15	0.80	0.39	0.16	0.11	0.06	0.04	0.03	0.02	0.02	0.01	0.003	0.0009

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tallines will be free from matrices. This is the reason why the dendritic  $\gamma$ - $\text{Al}_2\text{O}_3$  powders is more disperse than the porous  $\gamma$ - $\text{AlOOH}$  powders.

When the calcination temperature is up to 1200 °C, the atom of alumina intermediate phase being activated by heating, could rearrange into  $\gamma$ - $\text{Al}_2\text{O}_3$  lattice in order to reduce the lattice energy. On the other hand, the rearrangement of atom and a tendency to cut down the surface energy of powder, could urge the dendrite to shrink into spherical powders. That the spheroidization of ultrafine powders means the accelerating growth of powders, is one of difficulties for preparing ultrafine  $\alpha$ - $\text{Al}_2\text{O}_3$  powder. There is a tendency for powders in Fig. 4 (d) to spheroidize, but this tendency is not so distinct because the amount of reagent A added was controlled suitably. So the spheroidization of  $\text{Al}_2\text{O}_3$  powders could be controlled by the amount of reagent A added. This is significant for preparation of nanocrystalline alumina ceramic. As for the mechanism of reagent A in the spheroidization, it needs to be studied extensively.

#### 4.4 Determination of Apparent Density

The apparent density of powder obtained under different test conditions and percentage of apparent density to theoretical density were measured, as shown in Table 1. (The theoretical density of  $\gamma$ - and  $\alpha$ - $\text{Al}_2\text{O}_3$  are 3.5 and 4.0 g/cm<sup>3</sup> respectively).

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imply the non-linear characteristics of these chemical processes. Both the decomposition and carbonization involve complex anionic polymerization process with autocatalytic amplification mechanism. In the mixing and dilution process, the local instantaneous composition of solution is different. After autocatalytic amplification, these very small difference may induce the non-reproducibility of the reaction kinetics.

**Table 1 Apparent density of alumina powders prepared under different test conditions**

test condition	600 °C, 3h	800 °C, 3h	1200 °C, 3h
apparent density	0.0864	0.0923	0.1444
percentage to theoretical density, %	2.47	2.64	3.61

## 5 CONCLUSIONS

(1) The porous  $\gamma$ - $\text{AlOOH}$  powders were obtained by hydrolysis of aluminum isopropoxide.

(2) After calcination of  $\gamma$ - $\text{AlOOH}$  powders, disperse dendritic  $\gamma$ - $\text{Al}_2\text{O}_3$  powders with mean length less than 70 nm and width about 10 nm were produced. The apparent density of  $\gamma$ - $\text{Al}_2\text{O}_3$  at 600 °C and 800 °C were 0.086 and 0.092 g/cm<sup>3</sup>, respectively.

(3)  $\gamma$ - $\text{Al}_2\text{O}_3$  powders transformed into  $\alpha$ - $\text{Al}_2\text{O}_3$  with mean particle size of 70 nm and apparent density about 0.14 g/cm<sup>3</sup> after calcination at 1200 °C for 1 h.

## REFERENCES

- 1 Guo, Jinkun *et al.* Guisuanyan Xuebao, 1992, 20(3): 286.
- 2 Yoldas, B E. In: Mackerzie, J D, Ulrich D R (eds), Ultrastructure Processing of Advanced Ceramics, New York, John Wiley & Sons, 1988.
- 3 Chan-ching, J Y *et al.* J Am Ceram Soc, 1986, 69 (8): C-174.
- 4 Farelli, A J *et al.* J Am Ceram Soc, 1981, 71(1): 83.
- 5 Hardy, A B *et al.* J Am Ceram Soc, 1993, 76(1): 97.
- 6 Wakakuwa, M *et al.* J Mater Sci Lett, 1990, 9: 1304.

## REFERENCE

- 1 Пафнер А П. Производство глинозема. Металлургиздат, Москва 1961.
- 2 Istvan Nagypal; Irving R; Epstein. J Phys Chem 1986, 90:6285—6292.
- 3 Chen, Nianyi; Liu, Miauxio; Hong, Mei; Tang, Bo; Cao Yilin. Scientia Sinica, 1993, B36, 32.
- 4 Chen, Nianyi. Physical Chemistry in Alumina Production. Shanghai: Shanghai Science and Technology Press, 1962.