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STRUCTURE IMPERFECTION OF γ-Al_2O_3

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Abstract—The X-ray diffraction pattern of γ-Al_2O_3 is found to be broadened with every diffraction line being different. This is attributed to the difference of regularity of oxygen ions and aluminium ions. In order to study the structural information shown by this selected broadening, the peak separation processing for the γ-Al_2O_3 X-ray diffraction pattern has been carried out. It is found that the lattice distortion of γ-Al_2O_3 can be neglected and the γ-Al_2O_3 crystallite size is approximately isotropic. Therefore it might be deduced that the selective widening of the diffraction line does not come mainly from the anisotropy of the crystallite shape. According to our result that the diffraction line width with low index (220) is wider than that with high index (440) the selective widening of the diffraction line might come mainly from the structure defect.

This implies the possibility of the existence of the stacking fault in the γ-Al_2O_3 structure and it might be concluded that the diffraction line widening of the γ-Al_2O_3 caused by the stacking fault leads to the crystalline structure imperfection.

Alumina is one of the most widely used inorganic materials. Due to the raw materials and preparation conditions different types of the crystalline aluminas can be obtained, among which the γ-Al_2O_3 is widely used as a catalyst and as a catalyst carrier. There are many research reports on its structure, but their opinions are still very different. In our previous work[1] a new explanation for the phenomenon of broadening of X-ray diffraction lines was proposed. In this paper we further deduce that the imperfection of the microscopic structure for γ-Al_2O_3 is caused by stacking faults. We have therefore studied structure changes reflected by the broadening of the diffraction lines for γ-Al_2O_3, which are obtained under the different dehydration temperatures.

EXPERIMENTAL

Samples

Boehmite (α-AlOOH) (10 g) (Fig. 1) was placed in a blind roaster and the temperature raised at a rate of 200° h^{-1} up to 200°C and held at that temperature for 30 min. Approximately 1 g of the sample was removed and the remainder heated to 300°C and after holding at this temperature for 30 min, another 1 g of the sample was removed and so on. The process was repeated at 450°, 500°, 550°, 600° and 700°C.

Measurement of the X-ray diffraction

The D/max-Rc turnable plate X-ray diffractometer (Rigaku Corporation, Japan) was used to measure the X-ray diffraction. By using a graphite

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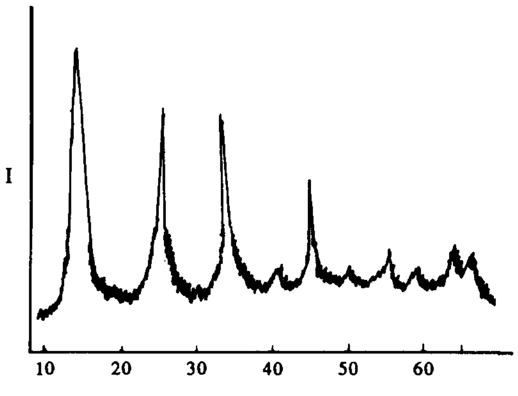

Fig. 1. X-ray diffraction of boehmite.

curved crystal monochromater to get Cu-K_α we can obtain X-ray diffraction pattern of γ-Al_2O_3 with better signal-noise ratio (see Fig. 2) and then the diffraction data with the technique of symmetrical-reflection and scan-step measurement method (angular interval of 0.02°, scan time per step of 10 s) to separate the peaks. The voltage of the X-ray tube was 40 kV and the current 150 mA. The exit slit and receiver slit are 1° and 0.15 mm, respectively. The random and perfectly crystallized silicon powder is taken as the standard sample to determine the width b (the value is 0.130–0.190) of the instrument and then the X-ray diffaction measurement was carried out under the same conditions.

Data processing

By use of a computer program for peak deconvolution based on eq. (1) the collected diffraction data have been processed to obtain the peak deconvolution data. The number of fitted points was 15 and the deviation was smaller than 3%.

X-ray diffraction pattern analysis

The X-ray diffraction patterns of the dehydration products of the boehmite obtained at 200, 300, 400, 450, 500, 550, 600 and 700°C are plotted in Fig. 2. Below 500°C incomplete conversion to γ-Al_2O_3 is observed, but above that temperature conversion is complete. Every X-ray diffraction pattern of γ-Al_2O_3 obtained at different temperature has the characteristic of the typical spinal structure diffraction pattern, but the broadening of every diffraction line is different. We have initially studied this selective X-ray line broadening in our previous work[1] and attributed it to the difference of regularity of oxygen ions and aluminium ions. In order to further study the structural information shown by this selective broadening we used the Gaussian–Cauchy compound function eq. (1) to characterize the crystalline peaks and to make a more rigorous peak separation processing for the γ-Al_2O_3 X-ray diffraction pattern. The peak separation at 500°C is shown in Fig. 3. The parameters of crystalline peaks obtained by peak separation processing are as follows:

$$I_c(2\theta) = \sum_{i=1}^{N} f_i A_i \exp\{-\ln 2[2(2\theta-P_i)/\omega_i]^2\} + \sum_{i=1}^{N} (1-f_i)A_i/\{1+[2(2\theta-P_i)/\omega_i]^2\}, \quad (1)$$

where N is the number of peaks, f_i, A_i, P_i and ω_i are

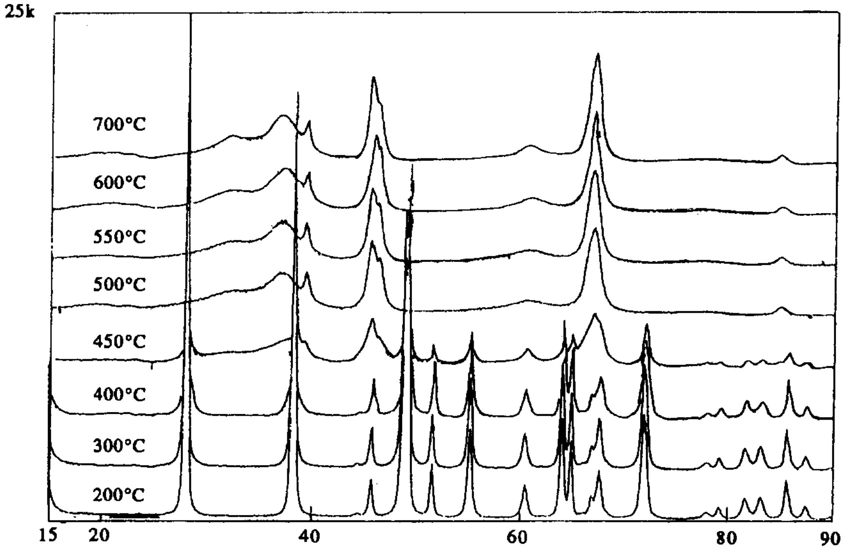

Fig. 2. X-ray diffraction of products obtained by dehydration of boehmite at various temperatures.

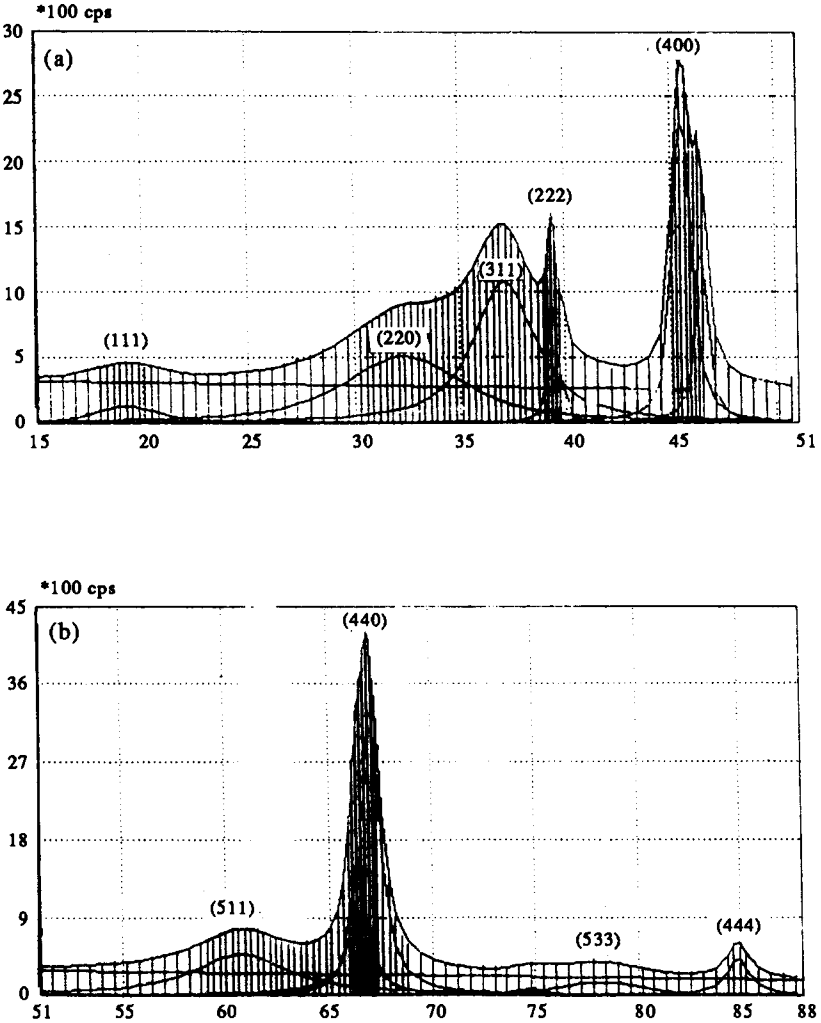

Fig. 3. X-ray diffraction of γ-Al_2O_3 at 500°C and results of peaks separation.

peak form factors, peak height, peak position and half-height width of the i peak, respectively.

These peak parameters can be calculated by using the minimum of the following objective functions:

$$S = \sum_{i=1}^{M} [I_c(2\theta)_j - I_e(2\theta_j)]^2, \qquad (2)$$

where M is the number of the fitting experimental intensity. We often use the deviation to express whether or not the fit is good.

$$E = \left\{ s \Big/ \sum_{j=1}^{M} [I_e(2\theta)_j]^2 \right\}^{1/2}.$$

For the X-ray diffraction pattern of the γ-Al_2O_3 within the range of $2\theta = 15 \sim 90°$, the fitting can be done by using eq. (1) as the characteristic function of each crystalline peak and $E = 2.08\%$ ($E_{max} < 2.7\%$). In Table 1 the diffraction line widening $\beta = B_{hlk} - b$ and the crystal size D are listed. If the diffraction line widening β is caused by the crystal size effect and the lattice distortion e, this gives

$$\beta = 0.9\lambda/(D\cos\theta) + 4e\tan\theta. \qquad (3)$$

So, the broadening of diffraction line for high angles should be lower than that for low angles. But from the data in Table 1, it can be deduced that the width of some diffraction lines with a low angle is lower than that with a high angle. It can be concluded that the lattice distortion of γ-Al_2O_3 can be neglected. By using the well known Scherrer formula $D_{hkl} = 0.9\lambda/\beta_{hkl} \cdot \cos\theta$ the crystalline grain thickness D_{hkl} along the direction which is perpendicular to the crystalline plane (hkl) can be evaluated based on the broadening β_{hkl} of the diffraction line.

γ-Al_2O_3 belongs to the cubic crystal system. According to analysis in the previous paper,[2] the γ-

Table. 1 X-ray diffraction line widening and crystal size of γ-Al_2O_3 obtained by peaks separation for dehydrated products of boehmite at various temperatures

		500°C		550°C		600°C		700°C	
	2θ	β^a	D_{hkl} (Å)	β	D_{hkl} (Å)	β	D_{hkl} (Å)	β	D_{hkl} (Å)
111	19.43	3.588	22.5	3.392	23.8	3.189	25.3	2.611	30.9
220	32.26	6.663	12.4	6.534	12.7	6.347	13.1	5.013	16.5
311	37.30	3.376	24.8	3.106	27.0	2.896	28.9	2.765	30.3
222	39.53	0.412	205.0	0.410	206.0	0.428	197.4	0.405	208.6
400	45.79	0.880	98.0	0.840	102.7	0.832	103.7	0.730	118.1
400	45.79	0.496	174.0	0.503	171.5	0.533	161.9	0.472	182.8
511	61.01	5.370	17.2	4.992	18.5	4.310	21.4	3.736	24.7
440	66.98	0.838	113.8	0.945	100.9	0.916	104.1	0.867	109.9
440	66.98	0.932	103.3	0.919	103.8	0.884	107.9	0.804	118.6
533	79.65	4.611	22.2	4.416	23.4	4.675	22.1	5.046	20.5
444	84.90	1.043	103.4	0.863	125.0	0.826	130.6	0.874	123.4
D_o		131.6		135.0		134.2		143.6	
D_M		19.9		21.3		22.0		24.5	
SF		5.61		5.34		5.10		4.86	

[a] Average error of $\beta \leqslant 0.050°$.

Al_2O_3 crystallite size is approximately isotropic, so it can be considered that the selective widening of diffraction lines does not come mainly from the anisotropy of the crystallite shape. Although there are empty positions in the spinal structure which might cause the X-ray broadening, our experiment shows that sometimes broadening apears and sometimes not. So the X-ray broadening does not arise from these empty positions. The fact that the diffraction line width with a low index (220) is wider than that with a high index (440), shows that the selective widening of the diffraction line comes mainly from the structural defect.

The formula evaluating the structure factor of the defect spinal structure is as follows:

$$\begin{aligned} F_{hkl} = {} & 8F_A \cos\frac{\pi}{4}(h+k+l) \\ & +4\cdot\frac{5}{6}F_B\left[\cos\frac{\pi}{2}(h+k+l)+\cos\frac{\pi}{2}(2h+k+l)\right. \\ & \left.+\cos\frac{\pi}{2}(h+2k+l)+\cos\frac{\pi}{2}(h+k+2l)\right] \\ & +8F_0\left[\cos\frac{\pi}{2}(h+k+l)+\cos\frac{\pi}{2}(h+2k+l)\right. \\ & \left.+\cos\frac{\pi}{2}(2h+k+2l)+\cos\frac{\pi}{2}(2h+2k+l)\right], \end{aligned} \tag{4}$$

where F_A is the scattering factor of Al^{3+} ion in the oxygen tetrahedral gap (position A), F_B the scattering factor of Al^{3+} ion in the oxygen octahedral gap (position B) and F_0 the scattering factor of O^{2-} ion.

As stated before[1] all the structure factors of the sharper diffraction line include the oxygen scattering term F_0, but the structure factor of the more broad diffraction line does not. That means the oxygen sublattice is more regular than the metal ion sublattice. For γ-Fe_2O_3 there is a similar phenomenon which was explained by Nakajima,[3] due to the existence of the stacking fault in γ-Fe_2O_3. Similarly, the widening of the γ-Al_2O_3 diffraction line implies the possibility of the existence of the stacking fault in the γ-Al_2O_3 structure.

Veyssiere[4] made an outstanding theoretical analysis for the stacking fault in the spinal structure. According to his analysis on the fault plane of (110), (100), (111), there is a $d/4 < 110 >$ displacement vector. Because this displacement vector is a lattice vector of the oxygen ions sublattice in the spinals, so the translation of the oxygen ions caused by the stacking fault does not effect the oxygen ion sublattice, but the distribution of the metal ions caused by the stacking fault effects the metal ions sublattice. This is because the fault face is an opposite-phase interface, so the stacking faults cause the metal ion sublattice to separate into some smaller coherent domains. This is due to the diffraction line broadness, which is inversely proportional to size of the coherent domain, therefore the diffraction lines for the sublattice contained metal ions became broader.

It is now impossible to calculate the stacking fault exactly, so we can use the sizes of the metal ion sublattice and the oxygen ion sublattice to estimate the approximate stacking fault index (*SF*):

$$SF = \frac{D_O}{D_M} - 1,$$

$$D_O = \langle 0.9\lambda/\beta\cos\theta \rangle O,$$

$$D_M = \langle 0.9\lambda/\beta\cos\theta \rangle Al, \qquad (5)$$

where D_O and D_M are the average sizes of the oxygen ion sublattice and the metal ion sublattice which are determined by the X-ray diffraction line widening.

From the point of view of physics the meaning of *SF* is that when $D_O = D_M$ the stacking fault (*SF*) is zero. The stacking fault indexes of the γ-Al_2O_3 obtained by dehydration of Boehmite at different temperatures are listed in Table 1. From Table 1 it is shown that when the temperature is increased, the crystalline size of the γ-Al_2O_3 also increases slightly. At the same time the stacking fault reduces slightly, which means that the crystal lattice tends to become a little more regular.

The experiment indicates that it is impossible to dismiss the stacking faults of the γ-Al_2O_3 with increasing temperature and prolonging time (it will turn into δ-Al_2O_3 and θ-Al_2O_3 when the temperature is further increased), so the stacking fault might be an intrinsic structural feature of the γ-Al_2O_3.

As mentioned above, we can conclude that the diffraction line widening of the γ-Al_2O_3 caused by the stacking fault leads to the crystallite structure imperfection.

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