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Vacancy ordering in the structure of γ-Al_2O_3

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Abstract

Defect structure of γ-Al_2O_3 prepared by the thermal decomposition of well-crystallized, high purity boehmite (γ-AlOOH) has been studied by HREM. It was shown that the intrinsic feature of γ-alumina structure is a presence of almost hexagonal closed loops formed due to the ordering of cation vacancies over octahedral positions on (110) and (111) planes. These defects are relatively stable; they are preserved, though being changed in shape, in the γ-alumina sample upon its further calcination until the appearance of traces of δ-alumina phase.

Keywords: Al_2O_3; Calcination; Catalysts; Defects; Diffusion

1. Introduction

Transition aluminas, such as γ- and δ-Al_2O_3, are widely used as adsorbents, catalyst supports as well as materials for ceramic production. The structure of γ-Al_2O_3 is treated as closely related to the defect spinel with randomly distributed cation vacancies[1] and interstitial atoms,[2] although there are some publications[3,4] suggesting the presence of well organized defects, e.g. stacking faults, in γ-alumina. The aim of the present work was to obtain information on the configuration of possible defects in the structure of γ-Al_2O_3 prepared from microcrystalline boehmite.

2. Results and discussion

Sample of γ-Al_2O_3 was prepared through topotactic decomposition of boehmite (γ-AlOOH) of high purity at 600°C for 6 h. According to chemical analysis, concentration of Si admixture did not exceed 0.57 wt%. BET surface area of the sample and water content were equal to 90 m^2/g and 0.55 mol of H_2O per mol of Al_2O_3, respectively. High resolution electron microscopy (HREM) was used to determine the real structure of the alumina with a JEM-2010 transmission electron microscope at resolution limit of 0.14 nm and accelerating potential of 200 kV.

X-ray powder diffraction revealed that the structure of the sample under study is that of γ-alumina. According to HREM results, γ-alumina particles are crystallized in the form of regular platelet monocrystals with an average size of 1000 nm. The peculiar feature of γ-alumina microstructure is the presence of the closed loops lying on the (110) well developed plane of the oxide microcrystal. Fig. 1a illustrates the typical view of the loops which tend to be aligned parallel to the definite direction. Such loops are grown into extremely regular, almost hexagonal shape, being bounded by the {111} and {110} type crystal planes as schematically represented in Fig. 1b. We could not consider the observed loops to be voids or pores since they are so large relative to the orientation of the γ-alumina microcrystal with respect to the incident electron beam: tilt of the sample in the microscope for several degrees causes the disappearance of the loops from the image that indicate on their dislocation nature.[5] Loops of more or less regular shapes were often observed in the structure of fcc metals subjected to the radiation damage.[5] Due to the different types of atoms comprising the cationic and anionic sublattices in the spinel structure the formation of the closed loops may occur only if the partial dislocations lying on (110) and (111) planes appear simultaneously in the oxide material. As a result, the octahedra which are usually occupied in the structure of the regular spinel become vacant. So we suggest that the observed loops arise due to the coalescence of cation vacancies located in the octahedral positions in the γ-Al_2O_3 structure.

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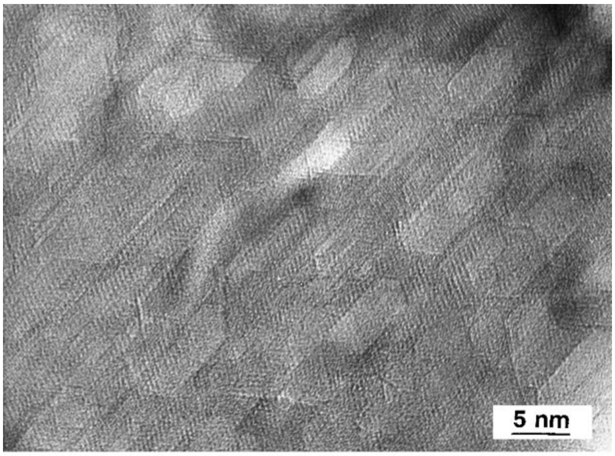
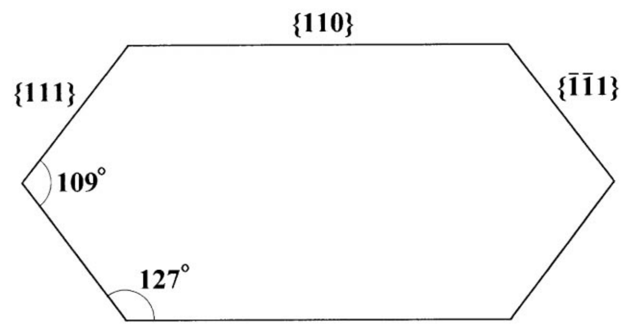


(a)



(b)

Fig. 1. HREM experimental image of the defects in the structure of γ-Al_2O_3 (a) and their schematical representation (b).

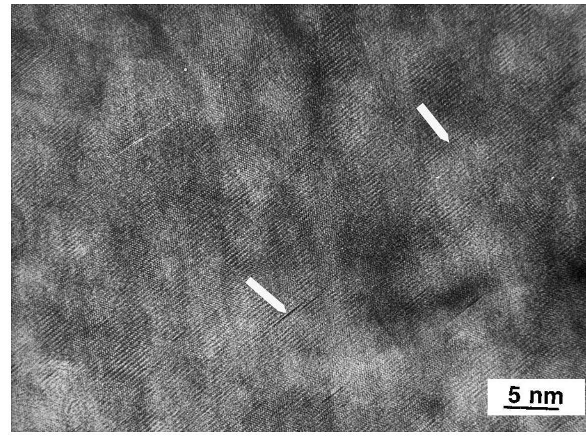


Fig. 2. HREM micrograph of the γ-alumina particle calcinated at 1000°C for 6 h. Defects lying on the (110) plane are arrowed.

After heating of γ-Al_2O_3 sample at 1000°C for 6 h a characteristic crystallographic morphology of the loops changes whereas X-ray powder diffraction indicates on the appearance of δ-Al_2O_3 phase. According to HREM results, the oxide structure of this sample is relatively free of the closed defects with the exception of the chain of ordered vacancies lying on (110) plane. This row of empty octahedra, as shown in Fig. 2 (arrowed), is likely to be a result of the partial disintegration of the loops due to the cation diffusion at the initial step of the structural transformation of γ- into δ-alumina, when at first cations begin to occupy the empty octahedral positions on (111) plane, whereas octahedra on (110) plane remain still vacant.

We should note that there have been several observations which suggest the occurrence of the vacancies in γ-Al_2O_3, but usually preference was given to the case of the random distribution of the vacancies over octahedral[6] or tetrahedral[7] sites in the structure of γ-alumina. Our structural model implies the ordered character of the vacancy distribution over the octahedral sites in the structure of aluminium oxide that leads to the formation of the closed vacancy loops. We observed earlier similar defects, though being lower in concentration, in the structure of magnium–aluminium spinel with the lack of Mg^{2+} cations;[8] this sample was prepared by the low temperature decomposition of boehmite impregnated with the magnium nitrate. The presence of such ordered vacancies organized in the form of closed loops is considered to be the intrinsic feature of γ-Al_2O_3 and other low temperature metastable compounds, based on the structure of γ-alumina that may contribute to their relative stability.

3. Conclusion

Using HREM the presence of the closed hexagonal-shaped defects in the structure of γ-Al_2O_3 prepared from well-crystallized boehmite of high purity has been revealed. A model of the defect based on the regular vacancies emerging in the octahedral cation positions on the (110) and (111) planes has been proposed. We believe that the appearance of such ordered defects is due to the agglomeration of lattice vacancies into relatively large and thermally stable two-dimensional clusters. This defect configuration may be considered as an intrinsic structural feature of the γ-alumina phase.

Acknowledgements

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