

Chapter Two

STRUCTURE OF ALUMINA PHASES

The remarkable range of properties of the hydrous and non-hydrous crystalline phases of alumina has induced much scientific curiosity about their structures. The properties of the aluminous are determined by crystal structure. The crystal structures of the alumina phases are shown in Table 1³⁵.

Table 1: Crystal Structure of the Aluminas

Phase	Formula	Crystal system	Unit Cell Parameters			Angle
			Angstroms			
			a	b	c	
Hydrated Aluminas						
Gibbsite	$\alpha\text{-Al}_2\text{O}_3\cdot 3\text{H}_2\text{O}$	Monoclinic	8.64	4.07	9.72	84°26'
Bayerite	$\beta\text{-Al}_2\text{O}_3\cdot 3\text{H}_2\text{O}$	Monoclinic	4.72	8.68	4.06	90°07'
Nordstrandite	$\text{Al}_2\text{O}_3\cdot 3\text{H}_2\text{O}$	Monoclinic	8.63	4.01	19.12	92°00'
Boehmite	$\alpha\text{-Al}_2\text{O}_3\cdot \text{H}_2\text{O}$	Orthorhombic	2.87	12.22	3.7	
Diaspore	$\beta\text{-Al}_2\text{O}_3\cdot \text{H}_2\text{O}$	Orthorhombic	4.4	9.43	2.84	
Transition Aluminas						
Chi		Cubic	7.94			
Eta		Cubic (spinel)	7.9			
Gamma		Tetragonal	7.94	7.94	7.79	
Delta		Tetragonal	7.97	7.97	23.47	
Iota		Orthorhombic	7.73	7.78	2.92	
Theta		Monoclinic	4.63	2.94	11.86	103°42'
Kappa		Orthorhombic	8.49	12.73	13.39	
Corundum	$\alpha\text{-Al}_2\text{O}_3$	Rhombohedral	4.76		12.99	
	Al_2O_3	Cubic	4.68			
			(1100°C)			
			4.67			
			(1700°C)			

2.1. Structure of Gibbsite

Gibbsite has been the most precisely determined of the trihydroxide phases because of the availability of well crystallized coarse specimens. Gibbsite is designated as

monoclinic by Dana³⁶. It usually occurs both in native and in commercial production as twinned pseudo-hexagonal tablets. Saalfeld³⁷ observed triclinic crystals dispersed in the monoclinic structure of the native form.

Pauling³⁸ first proposed the concept of gibbsite structure consisting of double layers of OH ions with aluminum ions occupying two-thirds of octahedral interstices within the layers, form the basic structural element. The hydroxyls of adjacent layers are situated, directly opposite to each other i.e. in a cubic packing. Thus the sequence of OH ions in the direction perpendicular to the planes is A-A-B-B (fig.1). This superposition of layers and the hexagonal arrangement of Al ions lead to channels through the lattice parallel to the c-axis. Hydrogen bridges OH groups of adjacent double layers. From proton magnetic resonance measurements, Kroon *et al*³⁹ has deduced a model of spatial distribution of these H-bonds.

2.2. Structure of Boehmite

The structure of boehmite consists of double layers in which oxygen ions are in cubic packing (fig.2). These layers are composed of chains formed by double molecules of AlOOH which extends in the direction of the a-axis. The double layers are linked by hydrogen bonds between hydroxyl ions in neighboring planes. Average O-O distance of the hydrogen bridges is 0.27 nm. If the excess water is very high (typically >14wt% excess water) a,b,c distances in three dimensional directions of crystallographic dimension become longer and produce pseudo-boehmite. X ray diffraction patterns of pseudo-Boehmite are similar to boehmite with a broad peak. Papee *et al*⁴⁰ postulated that the excess water is not only merely absorbed on crystalline surface but also located

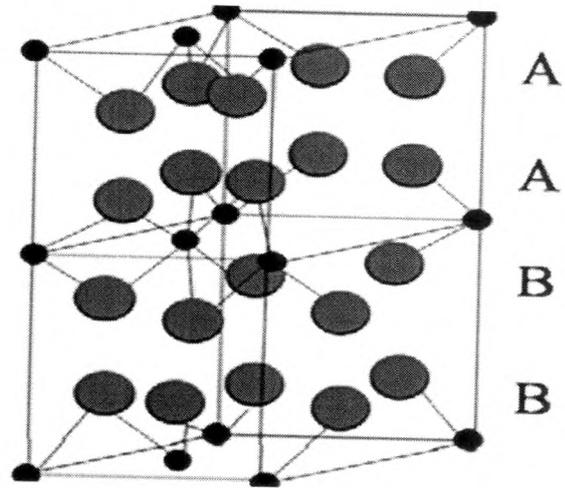


Fig.1: Structure of Gibbsite

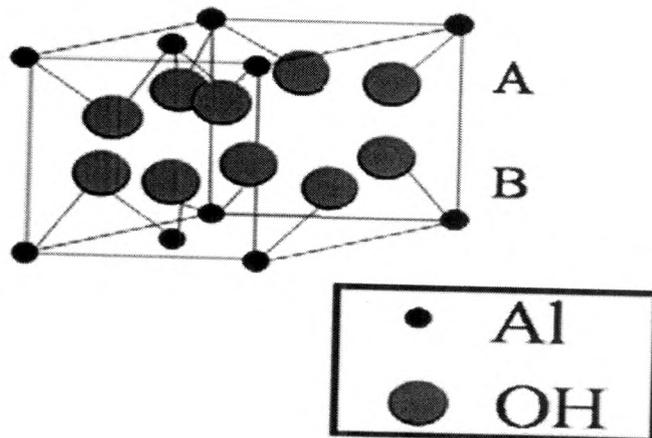


Fig.2: Structure of Boehmite

between boehmite-like layers as molecular water. Heating of pseudo-boehmite results in the formation of transition alumina in a sequence similar to that associated with bayerite.

Tettenhorst *et al*⁴¹ synthesized boehmite at temperatures ranging from room temperature to 300°C. They examined boehmite by scanning electron microscopy, transmission electron microscopy, electron diffraction, X-ray powder diffraction, differential thermal analysis, and infrared spectroscopy. The results showed that boehmite exhibits a continuous gradation in crystallite size ranging from single octahedral layers or a few unit cells to about 64 unit cells in the y-direction. This conclusion suggested that the term pseudo-boehmite is inappropriate for finely crystalline boehmite.

2.3. Structure of Diaspore

The structure of diaspore was first investigated by Deflandre⁴². The basic elements of the structure are chains of double molecules. The chains are arranged in a nearly hexagonal close packing. Refinements of the diaspore structure were published by Ewing⁴³ and Hopp⁴⁴. Busing and Levy⁴⁵ established more precise hydrogen positions by neutron diffraction. There is agreement among investigators that the AlO_6 coordination octahedra are distorted resulting in two Al-O bond length of 0.184 and 0.198 nm respectively. Busing and Levy's results indicated the presence of hydroxyl ions and structure calculations by Giese *et al*⁴⁶ favor a more ionic proton.

Experimental analysis of Li *et al*⁴⁷ established that the a axial direction is more compressible than the b and c axial directions in the low pressure range(13.4-18 GPa) at

1900K whereas all three direction are showing the similar behaviors in the high pressure range (18-27.8 GPa). Friedrich *et al*⁴⁸ explained the fact that the structural response to pressure is due to the shortening of the hydrogen bond which is oriented nearly parallel to the a axis.

2.4. Structure of Bayerite

Bayerite is rarely found in nature and produced commercially for catalysts or other applications requiring high quality for products. According to Fricke *et al*⁴⁹ bayerite is obtained by hydrolyzing aluminum alcoholates at temperature below 40°C.

The structure of bayerite is similar to gibbsite which is built by basic layers of Al-OH octahedral. The layers are arranged in A-B-A-B-A-B sequence (fig.3).

Bentor *et al*⁵⁰ reported the first occurrence of the structure verified by X-ray analysis. The structure of bayerite is similar to gibbsite which is built by basic layers of Al-OH octahedra. The layers are arranged in A-B-A-B-A-B sequence.

2.5. Structure of Transition Alumina

Transition Al₂O₃ crystallizes in spinel or similar to it with effective lattice. In the spinel structure, the oxygen ions form face centered cubic lattice and Al⁺³ ions occupy tetrahedral interstitial sites (fig.4). FCC lattice is also formed by close packed plane but the stacking sequence is A-B-C-A-B-C-. Since Al ions favors octahedral coordination under normal circumstances.

Saalfeld *et al*⁵¹ assumed that all octahedral sites are to be occupied and the cation vacancies being confined to the tetrahedral sites. John *et al*⁵² used solid state

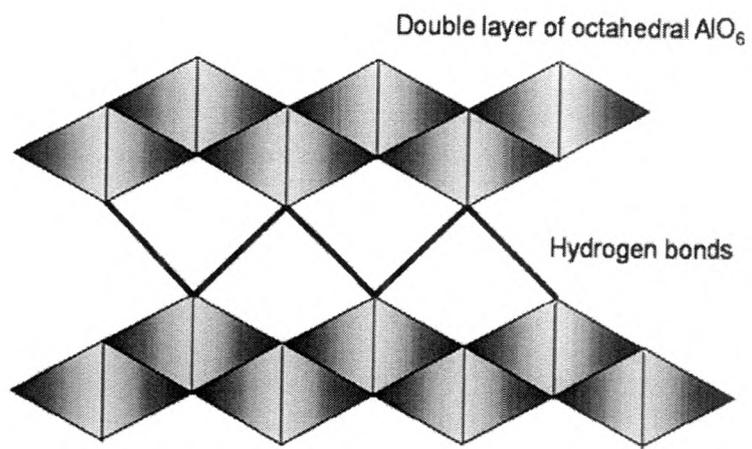


Fig.3: Structure of Bayerite

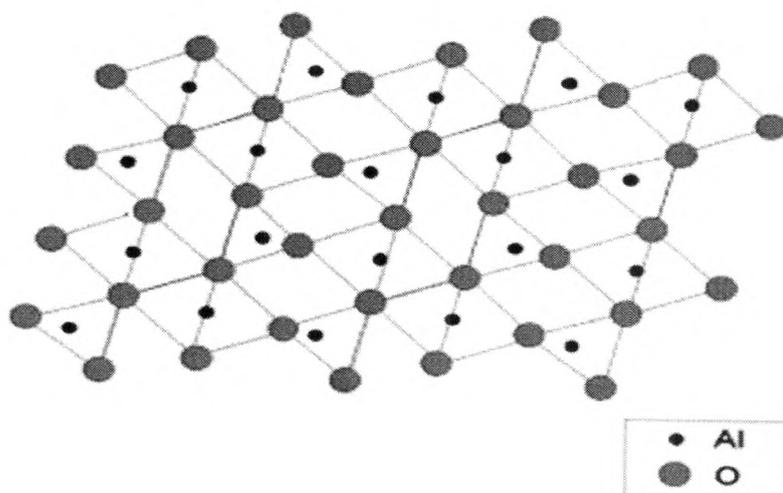


Fig.4: Structure of Transition Alumina

NMR study to determine the co-ordination of Al ions in the transition alumina. They focused that 64% and 74% of the Al ions are in the octahedral sites in η and γ alumina respectively. The cation vacancies, therefore, favor octahedral sites in η -Al₂O₃ but tetrahedral sites in γ -Al₂O₃ which is in agreement with X-ray powder diffraction pattern reported by Shirasuka *et al*⁵³.

2.6. Structure of Alpha Alumina

Unlike the transition aluminas, the crystal structure of alpha alumina is well known. Alpha alumina crystallizes in the corundum structure (mineralogical term) to form sapphire mono crystals. The corundum structure belongs to the rhombohedral system space group R 3 C, the lattice parameter at room temperature being in hexagonal axes, $a=0.4749$ nm and $c=1.299$ nm, with $Z=6$. The crystal can be described as a compact hexagonal stacking of O²⁻ anions, in which the two-thirds of the octahedral interstices are occupied by Al³⁺ cations⁵⁴. The anions and cations consists rather misleading on the ionicity of the bond:- it is considered that the alumina bond is ionic for two-thirds and covalent for the remaining third part. The empty sites of the cation sub lattice are used to define the corner of the unit cell (fig 5 & 6). The use of these sites to define the cell means there is a 30° rotation of the a-axes about the c-axes when compare to HCP metal so that the close-packed planes in the anion sublattice lie along $\langle 1010 \rangle$, whereas in HCP metals the close-packed directions lie along $\langle 1120 \rangle$.

The considerable amount of formation enthalpy ($\approx 1,600$ KJ mole⁻¹), which explains the absence of natural deposits of metal aluminum, makes alumina one of the most tightly bonded compounds, resulting in very high hardness (9 in the Mohs scale)

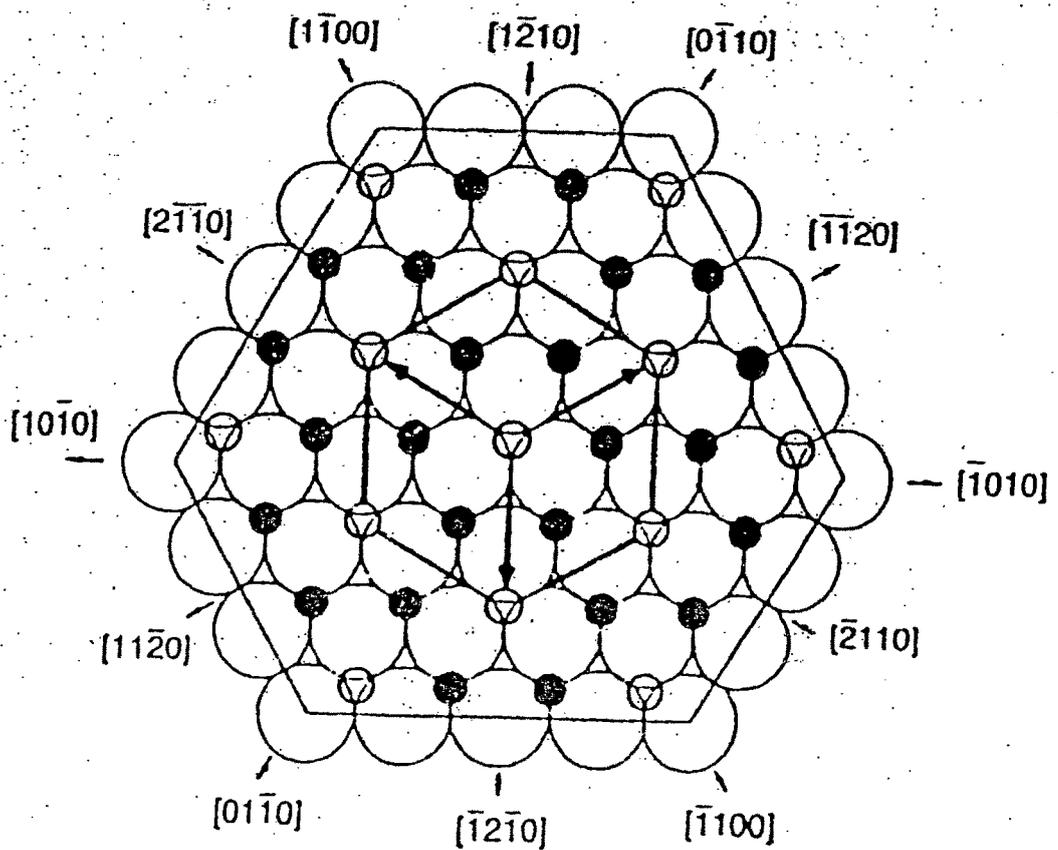


Fig. 5. The basal plane of α -alumina showing the hexagonal close packed anion sublattice (large open circles) and the cations occupying two-thirds of the octahedral interstices (small filled circles); small open circles are empty octahedral interstices (after Kronberg, 1957).

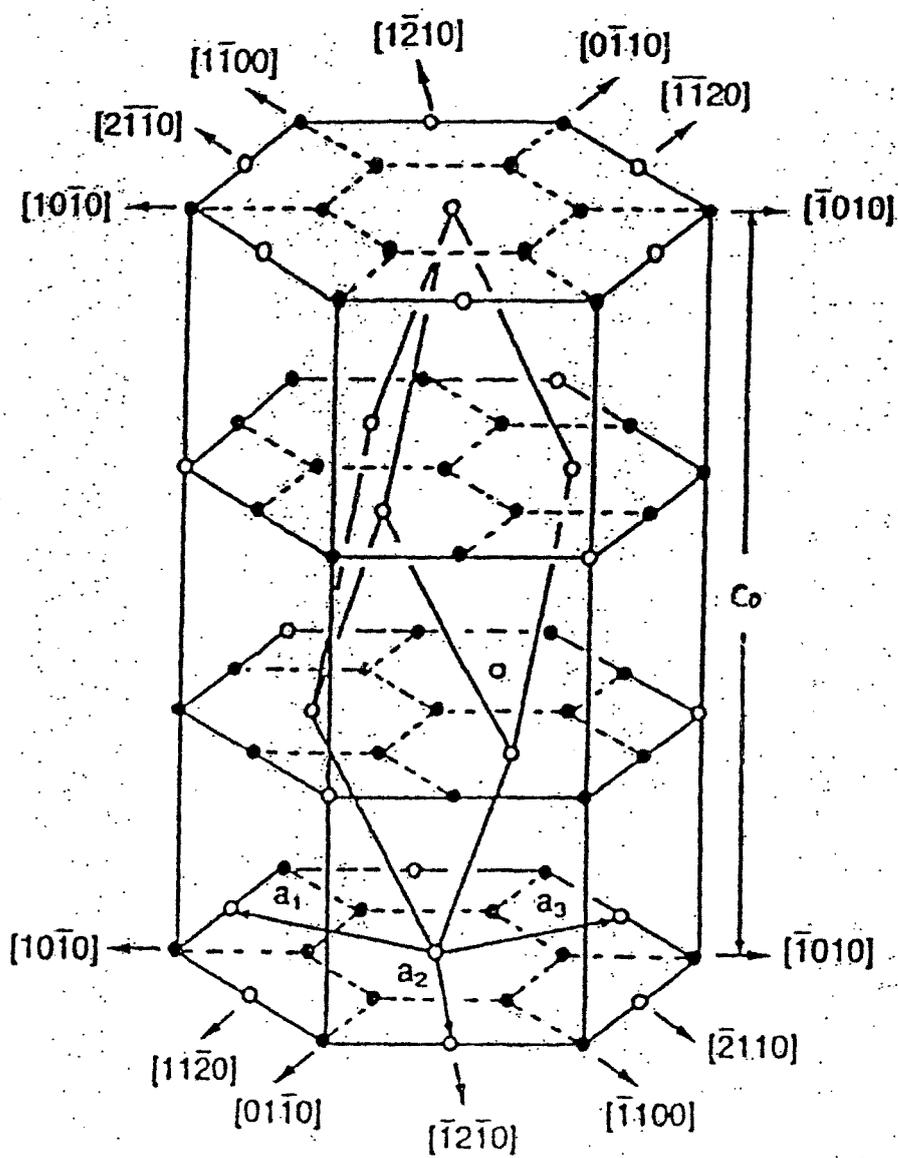


Fig. 6. The cation sublattice in α -alumina. Filled circles are Al, open circles are empty octahedral interstices (after Kronberg, 1957).

and high melting point (2040°C) and density of sapphire very close to 4.0 g.cm³. The strong ion-covalent bonds and the rhombohedral structure combine to restrict the dislocation movement. The sapphire monocrystal remains brittle until very high temperature and the basal slip (0001) $\langle 11\ 20 \rangle$ is only possible beyond 900°C. The plasticity of the polycrystal comes primarily from the effects of intergranular diffusion or flow of vitreous phases. These are mechanisms that depend on the purity of the material and whose occurrence temperature thresholds are lower than 800°C for impure alumina and higher than 1100°C for aluminas with purity exceeding 99%⁵⁵.