International Journal of Recent Development in Engineering and Technology
Website: www.ijrdet.com (ISSN 2347 - 6435 (Online))Volume 3, Issue 2, August 2014)

In-situ X-ray Diffraction Study of Alumina α-Al_2O_3 Thermal Behavior

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***Abstract*—We determined the crystalline characteristics of the hexagonal α-alumina phase by X-ray diffraction at high temperatures between 293 and 2308K under dynamic vacuum. Our experimental values allow us to deduce an anisotropy of the 'c' direction compared to the 'a' direction of approximately 12% in the range of 293K - 1760K: Such an anisotropy is related to internal constraints in the alumina structure which may cause plastic deformation. There is quite a difference in the range 1760K – 2308K : no further anisotropy remains. The perfect isotropic expansion of the alumina cell leads us to conclude the absence of any internal constraint above 1760K. As the anisotropy which characterizes the alumina structure is a direct consequence of the fact that the aluminum atoms occupy two thirds of the octahedral sites in the compact hexagonal subnetwork formed by the oxygen atoms, we believe that the isotropy in question must surely translate an equal occupation for all octahedral sites so that the site contains statistically 2/3 Aluminium atom.**

***Keywords*—Alumina thermal properties, High temperature X-ray diffraction, Evolution of the alumina cell lattice parameters depending on the temperature, Alumina in-situ thermal behavior study, Ceramics, Gas solid reaction, Thermal expansion.**

I. INTRODUCTION

The alumina , with Al_2O_3 formula, exists in nature under several allotropic varieties, including the α variety known as corundum. This latter is distinguished singularly from other forms by a high thermal stability and an exemplary chemical inertia. Thermal expansion of the refractory material, very helpful in industry, was studied very early in laboratory, mainly by dilatometry [1-6].

To our knowledge, the thermal expansion of the α-alumina lattice by in situ X-ray diffraction has been the subject of only one study Baldock et al. in 1968 [7] after which these authors had deducted an anisotropic thermal expansion in a quadratic equation. However, we noted that, this study was made under an atmosphere of helium and concerned a sintered form of small blocks material.

We estimated that it will be interesting to resume the experimental study of the thermal expansion of the α-Al_2O_3 alumina, with X-diffraction at high temperatures, but by using the non-sintered polycrystalline alumina and operating under dynamic vacuum while extending the temperature range compared to the referred study [7].

The x-ray diffraction technique coupled with a high performance furnace that we used to achieve this work, allows the in situ recording of several tens powder diffractograms which exclusively concern the superficial layer of the sample diffracting, layer directly in contact to the reactional environment: in other words which reacts first as well as to the thermal effect than to the residual atmosphere in the furnace.

II. EXPERIMENTAL CONDITIONS

The device implemented has been described elsewhere [8] ; it is essentially constituted of a graphite resistance furnace to work easily up to 2300 K as well as under dynamic vacuum than under controlled pressure.

This furnace is fixed in the axis of a vertical Philips goniometer PW 1050 itself mounted on a Philips diffractometric unit PW 1011 with copper anticathode ($\lambda_1 = 0.15405$ nm).

The furnace enclosure is connected to devices intended for measuring pressure or to the introduction of gas. The temperature of the sample is measured by optical means using a pyrometer MECI PM130, with an accuracy of ± 30 K between 1073 and 2300 K. As the pellet's temperature depends only in the resistor dissipated electric power, the calibration real-temperature/consumed-power was performed using a graphite pellet as emissive surface. The pyrometer being provided calibrated against the blackbody, a correction is needed because of the actual graphite emissivity, of absorption by various optical components crossed and the residual atmosphere of the oven. This correction was determined [14] examining the melting of a thin platinum wire placed on the graphite surface pellet: the temperature read (T_L) at the beginning of the melting is 1973K instead of 2042K, the true platinum melting point. It is then easy to deduce the value of the classical formula's constant ($1/T_L – 1/T_N = A$) by which the temperature of the blackbody T_N is obtained from the read temperature on a graphite surface, whether A= 17,126 10^{-6} K^{-1}. It is also possible, the resistor being in operation, to make the correction real-temperature/consumed-power.

The samples used in this study were made from polycrystalline alumina supplied by Johnson-Matthey (Spécpure quality); the shaping was made by plain axial compression under a 100 MegaPascals to obtain a cylindrical pellet of 8 mm diameter and 3 mm thick.

The pellet thus obtained is then disposed in the graphite sample holder, its surface slightly exceeding the walls of the latter; any contact between the sample and carbon being prevented by a washer and a tungsten jacket. After which, the sample is re-ascended in the heating zone of the furnace. .We proceed systematically to the preliminary degassing of the furnace chamber until the residual pressure reaches to the order of 10^{-4} Pa, the actual test can then be undertaken: its consists of performing a progressive heating under dynamic vacuum such a way that the temperature increase occurs by successive bearings; a diffractogram is systematically registered at each level. The calculation and refinement of crystalline parameters were performed using a calculation based on a least-squares program (Index and Affin programs).

Note that one of the biggest benefits of this experimental setup is the possibility at any time to align the surface of the sample with incident beam axis and thus to eliminate errors of eccentricity which inevitably occur as a result of heating, regardless of the pressure values and temperature which prevail in the furnace chamber.

III. EXPERIMENTAL RESULTS

The study of the thermal expansion of the alumina by in situ X-ray diffraction has required the use of two pellets prepared exclusively from the α-Al_2O_3 polycrystal variety.

The compound crystallizes in a rhombohedral lattice (a_r = 0.513 nm ; α_r = 55.10° [9]) ; the equivalent hexagonal cell has the following lattice parameters : $0.4750 \leq a_h (nm) \leq 0.4759$ and $1.2990 \leq c_h (nm) \leq 1.2992$ [10-14] .

The product we used to make our pellets presents itself in an excellent state of crystallization; its lattice constants deducted from our powder diffractogram which recorded under dynamic vacuum at 293K (a = 0.47608 nm ; c = 1.2997 nm) conformed to the bibliographic data.

A first pellet underwent slow heating cycles up to 2258K while the second sample was heated just once until 2308K more quickly.

A. First pellet

We tested three slow and gradual thermal cycles on the first pellet punctuated by many tempering. A cycle consists of heating the sample from room temperature to a maximum temperature by successive bearings; after the last bearing, the pellet is quenched.

The first cycle, with a total duration around 2h 30min, consists in a slow heating under dynamic vacuum ($10^{-3} \leq P (Pa) \leq 10^{-2}$). It is constituted by four isothermal bearings (323, 773, 1053 et 1278K). Our powder diffractograms exploitation recorded on each of the bearings allowed us to determine the presence of α-Al_2O_3 peaks phase only in which the intensities have revealed to be practically constants : such constancy translate, naturally, the absence of any alumina reactivity.

The second heating cycle, which lasted nearly to 1h 30min, had consisted of six isothermal bearings ($1208 \leq T (K) \leq 1828$ pour $1,3\ 10^{-2} \leq P (Pa) \leq 10^{-1}$). The analysis of in situ diffractograms led us to split the second cycle in two distinct steps:

- First stage ($1208 \leq T (K) \leq 1518$) : The crystallographic analysis allowed us to note the constancy of peaks intensities and therefore the absence of alumina reactivity.

- Second stage ($1613 \leq T (K) \leq 1828$) : The recordings do not reveal any new phase, on the other hand, the intensity of the main diffraction peaks of alumina decreased as the temperature increased: it is a consequence to the alumina sublimation which is attested by the presence of whitish contrails clearly visible on the sample holder and oven walls.

- During the last heat cycle ($1943 \leq T (K) \leq 2258$), we noticed an increase in the sublimation phenomenon.

B. *Second pellet*

This pellet was subjected to one thermal treatment more from 923 to 2308K in an hour, is still an increase of about 20 degrees per minute. That is to say three times faster than previously.

TABLE I

LATTICE PARAMETERS OF THE HEXAGONAL CELL ALUMINA

investigation	**T (K)**	**a (nm)**	**c (nm)**	**10^3V (nm^3)**	**c/a**
			First pellet		
first heating	293	0.47608	1.2997	255.12	2.730
	523	0.47681	1.3019	256.34	2.730
	773	0.47771	1.3047	257.84	2.731
	1050	0.47862	1.3075	259.39	2.732
	1278	0.47952	1.3101	260.88	2.732
quenching 1	293	0.47591	1.2994	254.87	2.730
second heating	1208	0.47925	1.3091	260.39	2.731
	1403	0.48010	1.3120	261.89	2.732
	1518	0.48047	1.3129	262.48	2.732
	1613	0.48094	1.3145	263.32	2.733
	1723	0.48128	1.3155	263.88	2.733
	1828	0.48190	1.3173	265.50	2.733
quenching 2	293	0.47619	1.3003	255.36	2.731
third heating	1943	0.48250	1.3182	265.76	2.732
	2043	0.48282	1.3200	266.49	2.734
	2148	0.48345	1.3218	267.54	2.734
	2258	0.48387	1.3233	268.32	2.735
quenching 3	293	0.47601	1.3000	255.10	2.731
			Second pellet		
One heating	293	0.47608	1.2997	255.12	2.730
	923	0.47840	1.3064	258.99	2.731
	1348	0.48004	1.3114	261.70	2.732
	1668	0.48129	1.3149	263.77	2.732
	1778	0.48175	1.3166	264.62	2.733
	1988	0.48290	1.3198	266.60	2.733
	2308	0.48442	1.3244	269.16	2.734
quenching	293	0.47609	1.3004	255.27	2.731

This vacuum heat treatment maintained ($6,6\ 10^{-3} \leq P (Pa) \leq 2,6\ 10^{-1}$) is composed of six isothermal stepwise (923, 1348, 1668, 1778, 1988 et 2308K).

The exploitation of diffractograms recorded on each bearing allowed us to observe, here again, the absence of any new phase reflecting chemical inertia of alumina and sublimation from 1778K.

We provide, in the Table I, the values of the lattice parameters a and c, as well as the volume of the ratio (c/a) of the hexagonal cell alumina obtained and maintained under vacuum at different temperatures.

IV. EXPLOITATION AND RESULTS

We used our experimental results by following thermal evolution of the lattice parameters of the α-Al_2O_3 alumina hexagonal cell. We have shown in Figures 1, 2 and 3 below, changes, depending on the temperature, respectively lattice parameters (a), (c) and the volume V of the cell.

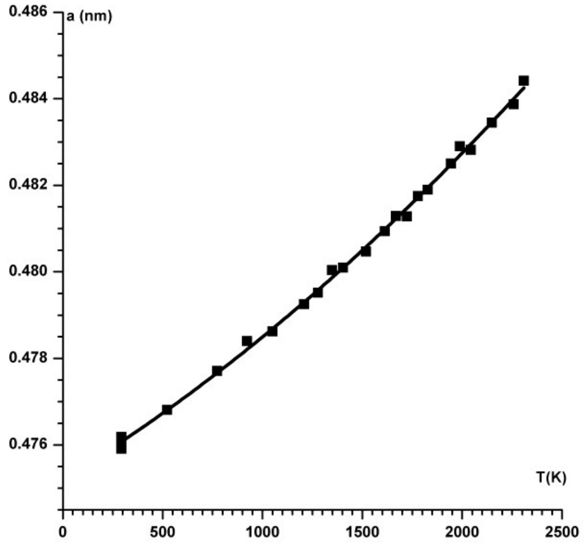

Fig. 1. Variation of the alumina hexagonal cell's lattice parameter a (nm) versus temperature T(K)

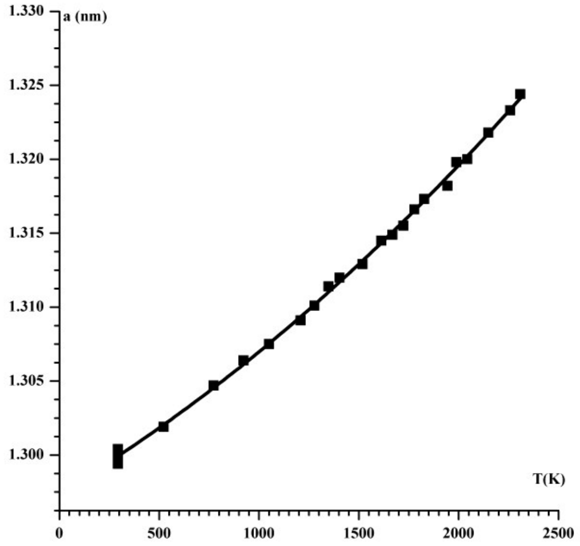

Fig. 2. Variation of the alumina hexagonal cell's lattice parameter c (nm) versus temperature T(K)

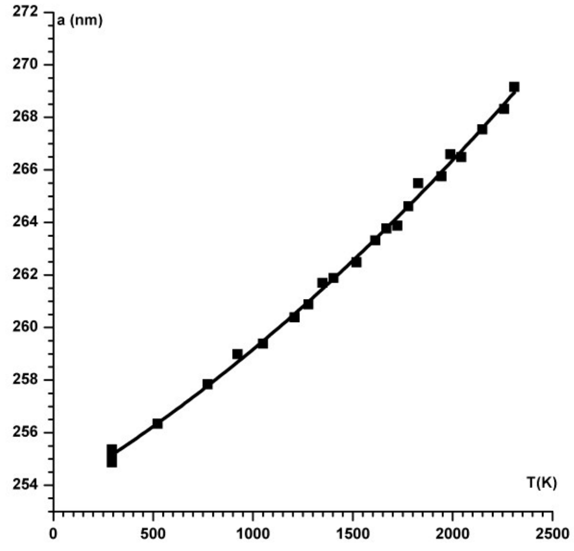

Fig. 3. Variation of the alumina hexagonal cell's Volume versus temperature T(K)

We can observe on each of the three figures that the expansions are done according to curves. Our analysis of these curves led us to propose a second order polynomials :

$a \text{ (nm)} = 0.4753 \, [\, 1 + 5.7 \; 10^{-6}\, T + 1.07 \; 10^{-9}\, T^2 \,]$ equation (1)

$c \text{ (nm)} = 1.2974 \, [\, 1 + 6.3 \; 10^{-6}\, T + 1.17 \; 10^{-9}\, T^2 \,]$ equation (2)

$10^3 V \text{ (nm}^3\text{)} = 253.83 \, [\, 1 + 17.4 \; 10^{-6}\, T + 3.62 \; 10^{-9}\, T^2 \,]$ equation (3)

The equations (1) et (2) (in which the temperature T is given in Kelvin) allow us to infer that the thermal expansion of the hexagonal lattice is anisotropic : the increase according to the direction ‘c’ is higher of about 10 % in comparison to the direction 'a'. Expansions and similar anisotropy to ours have been highlighted in 1968 by Baldock et al. [7] in their study by in situ X-ray diffraction under helium dedicated to the sintered alumina. Their polynomials are as follows:

$a' \text{ (nm)} = 0.4749 \, [\, 1 + 6.7 \; 10^{-6}\, T + 0.80 \; 10^{-9}\, T^2 \,]$ equation (1’)

$c' \text{ (nm)} = 1.2968 \, [\, 1 + 7.4 \; 10^{-6}\, T + 0.80 \; 10^{-9}\, T^2 \,]$ equation (2’)

It must be noted that the polynomials proposed in this study are quite different from those proposed by Baldock et al.. Despite this dissimilarity, the extent of the anisotropy characterizing the hexagonal alumina mesh is absolutely the same!

It seemed to us appropriate to propose an alternative interpretation of our experimental results.

Indeed, the lattice constants of the cell hexagonal α-alumina may also vary according to two distinct straight-line (d_1 et d_2) as clearly shown in the figures 4, 5 et 6 regarding respectively to the lattice parameters (a), (c) and to the cell volume V :

- **The d_1 straight-line in the range** ($293 \leq T \text{ (K)} \leq 1760$)
- **The d_2 straight-line in the range** ($1760 \leq T \text{ (K)} \leq 2308$)

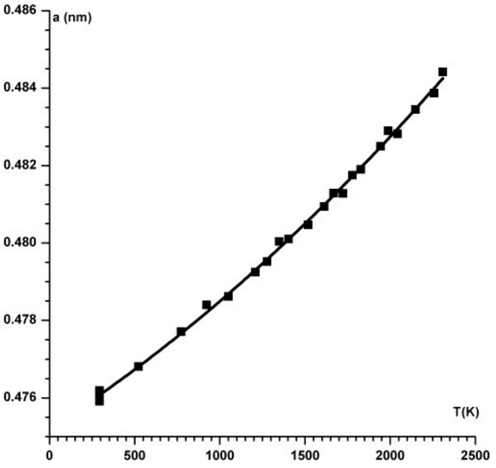

Fig. 4. Variation of the alumina hexagonal cell's lattice parameter a (nm) versus temperature T(K)

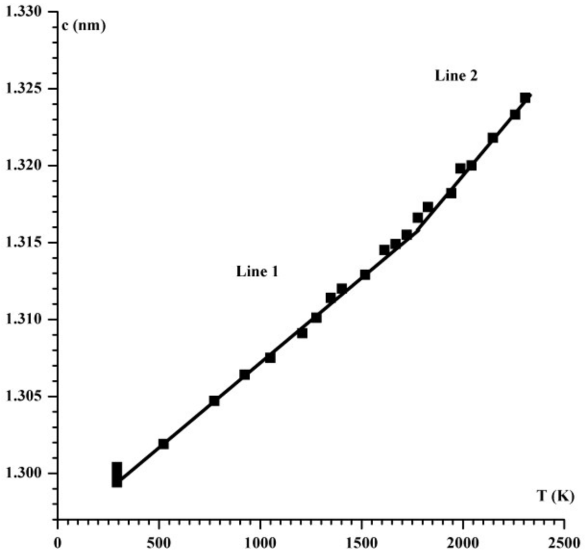

Fig. 5. Variation of the alumina hexagonal cell's lattice parameter c (nm) versus temperature T(K)

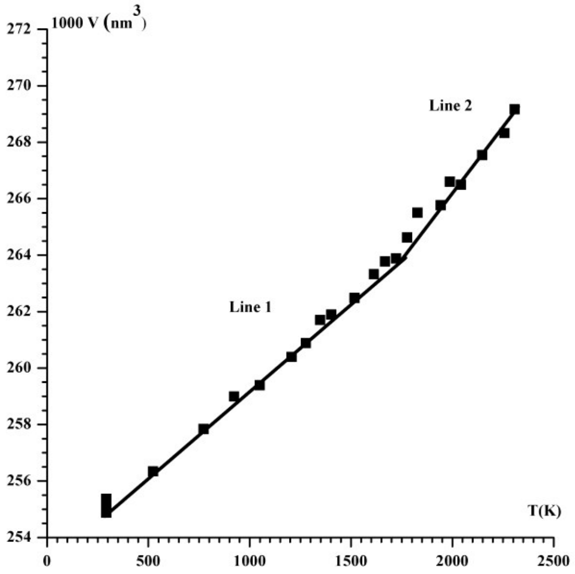

Fig. 6. Variation of the alumina hexagonal cell's Volume versus temperature T(K)

The values of a linear thermal expansion coefficients regarding each parameters are, in these conditions, as follows:

According to the d_1 straight-line in the range ($293 \le T$ (K) ≤ 1760)

$\alpha_a = 7.96\ 10^{-6}\ K^{-1}$ for the parameter (a)

$\alpha_c = 8.89\ 10^{-6}\ K^{-1}$ for the parameter (c)

$\alpha_V = 24.85\ 10^{-6}\ K^{-1}$ to the volume (V)

According to the d_2 straight-line in the range ($1760 \le T$ (K) ≤ 2308)

$\alpha_a = 11.10\ 10^{-6}\ K^{-1}$ for the parameter (a)

$\alpha_c = 11.11\ 10^{-6}\ K^{-1}$ for the parameter (c)

$\alpha_V = 33.31\ 10^{-6}\ K^{-1}$ to the volume (V)

Our experimental values allow us to deduce an anisotropy of the 'c' direction in comparison to the 'a' direction of about 12% in the interval d_1 straight-line: such anisotropy on similar linear expansions to ours was linked by authors [15] to internal constraints in the alumina structure which can generate plastic deformation.

There is quite a difference in the second interval d_2 straight-line: indeed, no further anisotropy remains. The perfectly isotropic expansion of the mesh alumina leads us to conclude to the absence of any internal stress above 1760K.

The change in slope, around 1760K, which characterizes the transition from d_1 to d_2 straight line is therefore the experimental demonstration of the anisotropic transition behavior to an isotropic behavior.

As the the anisotropy which characterizes the structure of the alumina is a direct consequence of the fact that the aluminum atoms occupy two thirds of the octahedral sites in the compact hexagonal subnetwork formed by the oxygen atoms, then we believe that the isotropy in question must surely translate equal occupation of all octahedral sites in order to contain statistically 2/3 aluminum atom per site.

V. CONCLUSION

Our experimental in situ thermal expansion observations of alumina lattice parameters led us to consider two possible interpretations:

- A thermal expansion according to quadratic equations which highlight an anisotropy of about 10% of 'c' direction compared to the direction 'a'.

- Two different linear thermal expansion in two contiguous temperature areas of which reflect a shift from an anisotropic behavior to an isotropic behavior.

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