JOURNAL OF OPTOELECTRONICS AND ADVANCED MATERIALS Vol. 10, No. 11, November 2008, p. 3083 - 3085

Mathematical model for uniform huge grains growth (from the polycrystalline systems to the monocrystals)

S. CONSTANTINESCU[a], I. MERCIONIU, N. POPESCU-POGRION[*]
National Institute for Materials Physics, Magurele, Romania

Despite many investigations already performed with respect to sintering stability and grain growth vs. annealing conditions - in low yttrium doped α- Al_2O_3 (150 ppm) - some fundamental questions are still open. These questions concern mainly the influence of small level of impurities at grain boundary in the sintering behavior and grains growth of the materials, i.e. the microstructure function of the annealing time at annealing temperature of 1650^0 C. The low yttrium doped α- Al_2O_3 (150 ppm) samples were sintered and annealed at high temperatures. Besides conventional micro structural studies, such as grain diameter and grain size functions of distribution of the annealing temperature were studied by electron microscopy investigations and statistical measurement. The implications of the different microstructures with respect to micro structural stability have discussed and compared to observations described in the literature.

(Received August 24, 2008; accepted October 30, 2008)

Keywords: Low Y doped α-Al_2O_3, Grain growth vs. annealing, Uniform huge grains, SEM, Modeling of the grain growth

1. Introduction

Impurities (intentional dopants and/or contamination) have drastic effects on the microstructural evolution, sintering and properties of polycrystalline - α- Al_2O_3 (150 ppm)[1].

For sintered materials, the micro-structural evolution (grains growth) depends of the initial powder characteristics (e.g., particle size, size distribution and particle shape, agglomerations); the green compact microstructure; and finally the sintering and coarsening processes. During sintering and annealing the pores are removed from a ceramic body and, grain boundaries (Gabs) are developed between particles. In low yttrium doped α-Al_2O_3, the doping ions may react with the major constituents and may be redistributed for thermodynamic or kinetic reason. The shape, average particle size, homogeneity of particles of the low Y doped α-Al_2O_3 powder will determine the structural characteristics of compact samples, such as shape of grains, size and average size of the grains, grain boundaries, surface and interfaces state, porosity, etc. The physical - chemical state of the powder (especially the microstructure, geometrical shape and average dimension) is a complex criterion, very important, for the: technological parameters, theoretical studies, characterization of the samples after pressing (green body) and, after sintering and annealing the stabilization of chemical composition stoichiometry.

2. Experimental details

Samples preparation. Two different sets of polycrystalline low yttrium doped α-Al_2O_3 (150 ppm), were prepared simultaneously. Both sets were prepared from AKP 3000 high purity powders (with total cation impurity levels < 60 ppm). Yttrium was added to the powders by the stoichiometric component Y (NO3)3.6H2O (Stream Chem. Newburyport, MA). The powders were mixed with amounts of yttrium in 200 proof isopropanol and high purity alumina-milling ball and milled for 2 hour. The mixture was filtered and dried, in high purity conditions; ground powder was compacted by mechanical uniaxial pressing at 20 MPa, using a cylindrical mould, followed by a cold isostatic pressed at 800 MPa, for 1 minute [2].

Sintering and annealing All samples were calcinated and sintered in a bed of their starting powders and closed alumina crucibles in air. The samples were calcinated using two different roads, one of them was adapted for the purpose to obtain porous samples (the Pp set of the samples) and the other was adapted to obtain compact ones (the Pc set samples). The Pp set of samples was calcinated for 7 hours at 1100°C (the heating rate was 5°C/min) and, then, sintered for 2h30' hours at 1550°C (the heating rate was 10°C/min for the interval 1100-1550°C). The cooling rate was of about 38°C/min.

The Pc set of samples were calcined and sintered (2h30') following a complex road (curves, with intermediate steps). The Pp set of samples showed an average porosity of ~ 2 42%. 42 (± 0.014) % and the Pc set of samples showed a residual porosity of ~ 0, 042 (± 0.00188) %.

The both sets of samples were annealed at 1650 ^{0}C in the interval [1 up to 15) hours [3,4].

Scanning electron microscopy investigation For microstructural analysis the samples were cut in half perpendicular to the axial directions and analyses were done in these inner surfaces except where indicated otherwise. Polished and thermally etched (1400 ^{0} C for 1 h) surfaces where coated with aluminium and observed in scanning electron microscopes (SEM). Grain sizes (mean value of the grains and size distribution) were determined by statistical interpretations (around 1000 grains measured for each sample).

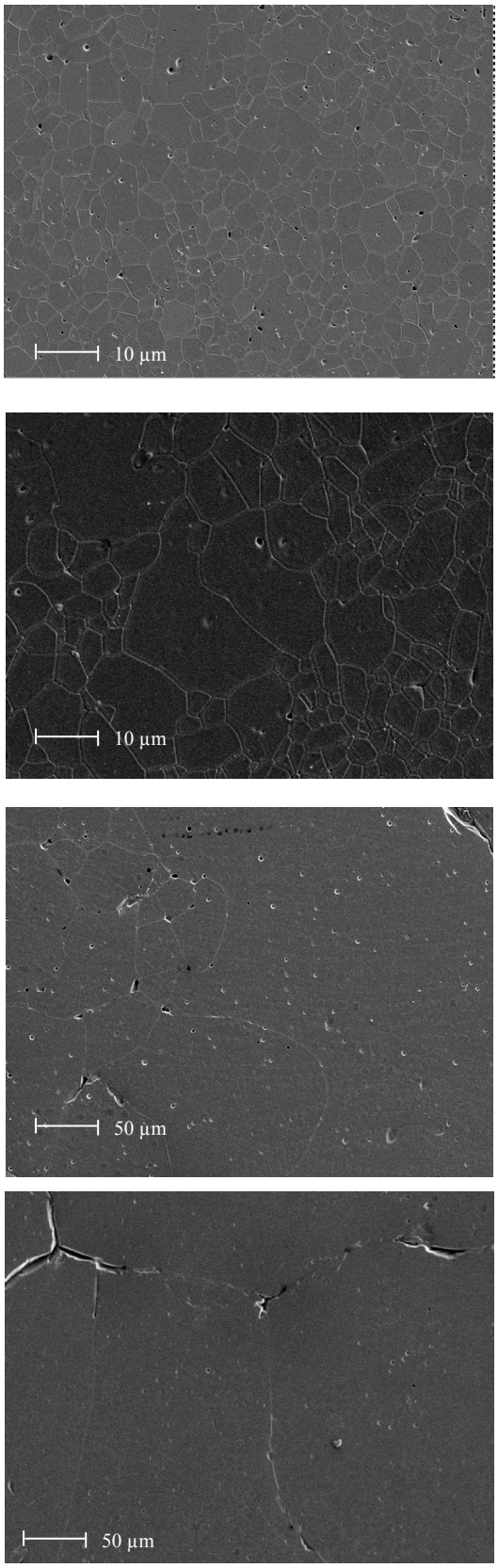

Fig. 1. SEM micrographs of ***Pp*** *(2.42 ± 0.014) % with yttrium content of 150 wt ppm, annealed at 1650^{0}C at following times a) 3h b) 5h , 10h, 15h.*

3. Modeling of grains growth

Frequently, the grains growth (GG) is monitoring by more of the well known three mechanisms, (intrinsic, impurities and pores drag mechanisms). During the solid-solid transformation, the kinetics of GG and of grain boundaries (GBs) are given by: the free energy difference between phases (matrix, matrix + solute ions, solute phase, and pores), the GB's surface curvature during GG and the pores and/or impurities (doped and/or intrinsic impurity). The growing velocity V of the grain size (GS), and respectively of GB, depends on the mobility M and total drag force F_{tot} of GB. They are a superposition of the first, second and the third mechanism contributions (M_o, F_o; M_I, F_I; M_p, NF_p). Generally, the F_{tot} depends on the size (G) and shape of the grain due to the interaction between GB and the pores and/or impurities. The presence of the pores and solute ions in GB diminishes velocity in the case of normal GG.

$$\left.\begin{aligned} \mathbf{V} &= \mathbf{M}\mathbf{F}_{tot} \\ \mathbf{F}_{tot} &= \mathbf{F}_o + \mathbf{F}_I - \mathbf{N}_p\mathbf{F}_p \end{aligned}\right\} \rightarrow \mathbf{V} = \frac{\mathbf{dG}}{\mathbf{dt}} = \frac{\mathbf{F}_{tot}(\mathbf{G})}{\frac{\mathbf{1}}{\mathbf{M}_o} + \frac{\mathbf{1}}{\mathbf{M}_I} + \frac{\mathbf{N}_p}{\mathbf{M}_p}} \Rightarrow \frac{\mathbf{dG}}{\mathbf{F}_{tot}(\mathbf{G})} = \mathbf{M}\mathbf{dt} \tag{1}$$

The solution G(t) of the differential equation (1) can be obtain analytically or numerically, only knowing the drag force vs. grain size. The parabolic solution is obtain for a simple inverse dependence F_{tot}~1/G and corresponds to uniform grain growth [4]. The statistical analysis of GG distribution, determined by electron microscopy, evidenced than, the departure from the uniform polyhedral shape of the grains (departure from the linear grains) around the critical time or presence of pores/impurities, suggest a critical size G_c and a limiting one G_l in drag force [5, 6, 7].

$$F_{tot} \propto \left(\frac{1}{a} - \frac{1}{G}\right) \rightarrow \int_{G_o}^{G(t)} \frac{G'dG'}{G'-a} = \int_0^t KMudt';$$

K = constant depending of grain shape; u = density of energy

$$\frac{G(t)-a}{G_o-a}\exp\frac{G(t)-a}{a} = \exp\left[\int_0^t KMudt\right] \Leftrightarrow \frac{G(t)-a}{G_o-a}\cdot\sum_{n=0}^{\infty}\frac{1}{n!}\cdot\left(\frac{G(t)-a}{a}\right)^n = \exp\left[\int_0^t \frac{KMu}{a^2}dt\right]$$

$$a = \begin{cases} G_c \leftarrow \begin{cases} G > G_c \text{corresponds to growthing grain} \\ G > G_c \text{corresponds to shrinking of the grain} \end{cases} \\ \frac{G_cG_l}{G_c+G_l} \leftarrow \frac{1}{G} < \frac{1}{G_c} + \frac{1}{G_l} \\ \frac{G_cG_l}{G_l-G_c} \leftarrow \frac{1}{G} < \frac{1}{G_c} - \frac{1}{G_l} \end{cases}$$

One can observe:

a. The particular solution, taking into account of the real curvatures and/or the presence of the pores and impurities on GB, is characterized by a time exponential growth, $\exp\left[\frac{K}{a^2}\int_0^t Mudt\right]$, initial ($G_o$), critical ($G_c$) and the limiting ($G_l$) parameters for grains sizes.
b. The pores dynamic on the GBs, their removed from GBs and their insert inside the grains, during the thermal treatments (annealing) can generate the changes in the slope of time-

exponential growing and, can evidence a critical point in GG (t) evolution.

The microstructural investigation of α-Al_2O_3-grain growth evidenced the possibility to obtain huge grain (monocrystals up to 10^{-6}m) of sapphire, for 1650C and a time of ≤ 15h. During of the thermal treatment it revealed a critical thermal treatment time ~10h, where the slope and shape of G_{exp} (t) is changed. Under t=10h medium size data are well fitted by an exponential growth, characterized G_{01}= 0, A_1 =1.0(4) μm and the time-parameter τ_1=1.43(8)h. For t>10h a visible change of the G_{exp}(t) slope is evidencing. The data on the interval (10 - 15) h, the second range have been fitted with another exponential growth, characterized by G_c=1250 μm, A_2=0.03(5) μm and time parameter τ_2=1.4(2)h. The best fit has been obtained with a polynomial function see the fig. 2.

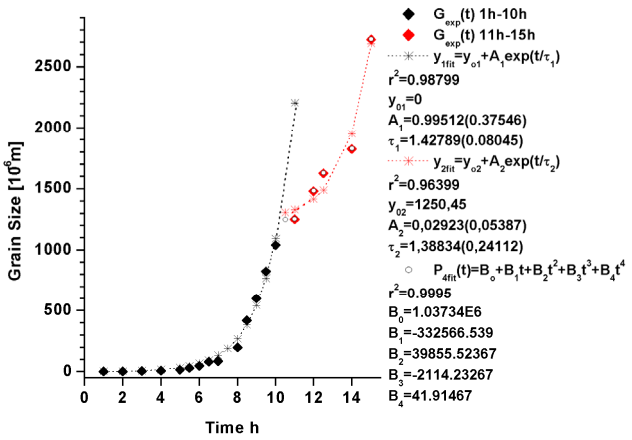

Fig. 2. *The fit of G_{exp}(t) by the two different exponential growths on the t∈[1÷15]h and polynomial function on t∈[10÷15]h.*

The best fit of data evidenced than the mathematical model, describing the GG, is superposition of two time exponential growths or, one exponential growth + a polynomial time dependencies. The polynomial time dependence can be considered as an approximation (truncated Taylor series) of a time exponential growth. Probably, the major role in this particular grains growth type and the GBs mobility are due to: the porosity and the segregation of the doped (Y) and accumulated Si (in the time of annealing) on the some GBs. Y and Si ions are responsible in GBs structural transformation and GG time evolutions.

4. Conclusions

- As previous remarked [4], the compact samples Pc (~ 2. 42 (± 0.014) %) had a normal growth – *parabolic* - in time of the annealing: uniform grains, without AGG, a constant low porosity and a good defined shape of the grains [4].
- The investigated porous samples Pp (~ 2. 42 (± 0.014) %), of low yttrium doped α-alumina reveal a particular grains growth vs. the time of the annealing (uniform – non-uniform /AGG/ *uniform huge grains*, a low increase of the porosity). Indeed, the grain growth evolution *vs*. the time of annealing evidenced two different stages.
- The experimental statistical data are fitted with: an exponential function (G_o= 0, A_1 =1.0(4) μm ,τ_1=1.43(8)h), in the first stage, t∈[1÷10]h, and with another one (G_c=1250 μm, A_2=0.03(5) μm, τ_2=1.4(2)h) or polynomial function for the second stage t∈[10÷15]h.
- The exponential fit parameters and polynomial fit coefficients, of experimental data, depend on the mechanism of pores mobility [4] and synergetic effect of yttria and silica [3] in the huge grain growth. Y and Si ions are responsible in GBs structural transformation and GG time evolutions.

Acknowledgements

We thank Prof. M. Ruhle and Prof. M. Gulgun, for fruitful discussions and Mrs. S. Kuhnemann for SEM assistance. Also, the authors express their gratitude for the financial support of MEC /CEEX 14/2006.

References

[1] M. A. Gulgun, V. Putlayev, M. Ruhle, J. Am. Ceram. Soc., **82**(7),1849 (1999).
[2] M. A.Gulgun, M.Ruhle Key Engineering Materials, pg.171 (2000).
[3] Ian Maclaren, Mehmet Ali Gulgun, Raissa Voythovych, Nicoletta Popescu-Pogrion, Ulrike Taeffner, Rowland Cannon, Manfred Ruhle, J. Am.Ceram. Soc. 86(4). 650 (2003).
[4] N. Popescu-Pogrion*, R. Bercia**, M. Tirnovan** J. Optoelectron. Adv. Mater., 6(3) , 1071 (2004).
[5] M. F. Yan R. M. Cannon, K. Bowen, "Grain Boundary Migration in Ceramics", Report 1, ed. Materials Processing Center, school of Engineering, Massachusetts Institute of Technology Ceramics Processing Research Laboratory, Proceedings of the 6th International Materials Symposium, Ceramics Microstructures '76 , Berkley Aug. 24-27, 1976, California, USA, ed**.** Richard Fulrath and Joseph A. Pask, Westview Press, Boulder, Colorado
[6] J. W. Cahn, Acta. Met. **10**, 789 (1962).
[7] M. Hillert, Acta Met. **13**, 227 (1965).

*Corresponding author: pogrion@infim.ro