The Pennsylvania State University
The Graduate School
College of Earth and Mineral Sciences

MECHANISMS OF SINTERING AND SECOND PHASE FORMATION IN BAYER ALUMINA

A Dissertation in
Materials Science and Engineering
by
Tobias Frueh

Submitted in Partial Fulfillment
of the Requirements
for the Degree of

Doctor of Philosophy

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The dissertation of Tobias Frueh was reviewed and approved* by the following:

Gary Messing
Distinguished Professor of Ceramic Science and Engineering
Thesis Advisor, Chair of Committee

James Adair
Professor of Materials Science and Engineering, Biomedical Engineering and Pharmacology
Optional Title Here

John Hellmann
Professor of Materials Science and Engineering
Associate Dean for Graduate Education and Research

Dogulas Wolfe
Associate Professor of Materials Science and Engineering
Department Head, Advanced Coatings at the Applied Research Laboratory
Senior Scientist

*Signatures are on file in the Graduate School.

Abstract

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Acknowledgments

Dedication

Chapter 1
Statement of Problem

1.1 section1.1

Pestorius [200] developed an algorithm to investigate propagation of finite-amplitude noise in pipes. His algorithm, based on weak shock theory, includes the effects of nonlinearity and tube wall boundary layer attenuation and dispersion. The hybrid time-frequency domain algorithm applies nonlinearity in the time domain, applies a fast Fourier transform (FFT), and then applies attenuation and dispersion in the frequency domain. Then an inverse FFT is taken to return to the time domain to propagate to the next step.

1.1.1 subsection1.1.1

Chapter 2 Introduction

2.1 section2.1

When in the Course of human events, it becomes necessary for one people to dissolve the political bands which have connected them with another, and to assume among the powers of the earth, the separate and equal station to which the Laws of Nature and of Nature's God entitle them, a decent respect to the opinions of mankind requires that they should declare the causes which impel them to the separation.

2.2 section2.2

Chapter 3 | The Effects of Na_2O and SiO_2 on Liquid Phase Sintering of Bayer Al_2O_3

3.1 Introduction

Al_2O_3 is arguably the most extensively used and researched ceramic material because it is used in many large volume applications such as high temperature refractories, technical ceramics, high voltage insulators, and functional fillers. The majority of Al_2O_3 applications use synthetic or specialty aluminas derived from Bayer feedstocks, such as aluminum trihydrate ($Al(OH)_3$), smelter grade Al_2O_3 and others. Bayer process aluminas are typically 99.0 - 99.9% pure and contain Na_2O, CaO, Fe_2O_3, and SiO_2 impurities that originate from the bauxite ore and/or Bayer process reagents (e.g., NaOH). The vast majority of research on the sintering of Al_2O_3, however, focuses on ultra-high purity (âĽě 99.99%) aluminas derived from specialty feedstocks, such as ammonium alum ($NH_4Al(SO_4)_2{\cdot}12H_2O$), boehmite ($\gamma$-AlOOH) and aluminum chloride ($AlCl_3$). While ultra-high purity aluminas provide the purest platform from which to conduct fundamental sintering research, that research does not usually explore the types and amounts of impurities typical of Bayer aluminas. Commercial Bayer Al_2O_3 powders exist in a range of reactive grades that differ in the amount and types of these impurities. Therefore, the evaluation of specialty reactive aluminas, within the context of previous work on ultra-high purity aluminas, is a valuable contribution to industrial users and bridges fundamental sintering research with ultra-high purity aluminas.

3.2 Experimental

A chemically purified 0.4Âăμm median particle size Bayer process Al_2O_3 powder (Almatis, Inc., Leetsdale, PA, USA) with only 2 ppm MgO was used to study the sintering of near MgO-free Bayer Al_2O_3 (Figure 3.1). The powder was chemically purified by the manufacturer so that impurity levels similar to commercial high purity Bayer process aluminas were obtained after doping with Na_2O and/or SiO_2. The physical and chemical characteristics of the as-received powder are shown in Table 3.1. Chemical analysis of the as-received Al_2O_3 was performed by inductively coupled plasma (ICP) emission spectroscopy (iCap 6000, Thermo Fischer Scientific, Inc., Waltham, MA, USA) after Al_2O_3 samples were acid digested in a microwave digestion unit in a Teflon^{TM} sample holder. It should be noted that the as-received Bayer Al_2O_3 contained impurity levels of 90 ppm Fe_2O_3, 62 CaO, and 22 ppm TiO_2. The Na2O and SiO_2 reported after doping include the impurity concentrations in the as-received powder (29 ppm Na_2O and 103 ppm SiO_2).

The Al_2O_3 powders were doped with up to 1000 ppm Na_2O using sodium acetate ($NaC_2H_3O_2{\cdot}3H_2O$, ACS grade, BDH, West Chester, PA, USA), based on the procedure reported by Louet et al. [1]. The Al_2O_3 powders were dispersed in a solution of sodium acetate dissolved in de-ionized water. The suspension was stirred on a magnetic stir plate for 5 h at room temperature, and held at 80°C for 24 h while stirring until the mixture was too viscous to stir, and then dried at 100°C for 24 h.

Samples were doped with up to 500 ppm SiO_2 by first dissolving tetraethyl orthosilicate (TEOS, $Si(OC_2H_5)_4$, 98%, Aldrich Chemical Company, Inc., Milwaukee, WI, USA) in 200 proof ethanol with a few drops of de-ionized water to hydrolyze the TEOS and immediately mixed at room temperature for 5 h with either the as-received or Na_2O-doped Al_2O_3 powder. The mixture was subsequently stirred at 70°C for an additional 12 h. The powder was then dried at 100°C for 2 h, followed by crushing in a mortar and pestle, and sieving to -106 μm (US Standard 140 mesh).

Samples were prepared for sintering studies by uniaxially dry pressing the powders at 170 MPa and then cold isostatic pressing at 200 MPa (CIP, Autoclave

Engineers, Erie, PA, USA) to obtain cylindrical samples (3.0-3.5 mm long by 12.7 mm diameter or 8.5-10 mm long by 6 mm diameter) with green densities of 59.0% ± 0.5% of theoretical density. To investigate the sintering process, dry pressed 8.5-10 mm long by 6 mm diameter cylinders were heated at 10°C/min to 1525°C in a thermomechanical analyzer (TMA, Linseis PT1600, Robbinsville, NJ, USA). The kinetics of sintering and grain growth were evaluated on 3.0-3.5 mm long by 12.7 mm diameter samples heated at 10°C/min to 1200 °C then 5°C/min to 1525°C followed by sintering at 1525°C for up to 8 h. The density of three samples of each condition was measured by the Archimedes method according to ASTM standard B962-15 [2] and the average density reported for each sintering time and temperature. For microstructure analysis, samples were first polished to a surface finish of 1 μm and then thermally etched in air at 1425°C for 40 min. Average grain sizes were measured on SEM (ESEM, Quanta 200, FEI Company, Hillsboro, OR, USA) micrographs using a linear intercept method (ASTM Standard E112-96) [3].

3.3 Results

3.3.1 Effects of Na_2O-doping

The doping experiments were designed to uniformly distribute $Na-2O$ and SiO_2 on the surfaces of the Al_2O_3 particles. Upon heating the dopant $NaC_2H_3O_2{\cdot}3H_2O$ first dehydrates and then decomposes to form Na_2CO_3 above 385°C [4]. Using a video recorder, we observed that anhydrous sodium acetate melts and rapidly spreads on the surface of an Al_2O_3 substrate at ∼420°C. Na_2CO_3 melts at 851°C and subsequently decomposes to Na_2O [4]. As a result of the rapid wetting of the Na_2O precursor on the Al_2O_3 substrate we conclude that Na_2O is uniformly distributed on the powder surface by the acetate doping process.

Figure 3.2 shows the shrinkage behavior of Bayer Al_2O_3 doped with different Na_2O concentrations during heating to 1525°C at 10°C/min. The as-received Al_2O_3 (intrinsic impurities: 29 ppm Na_2O, 103 ppm SiO_2) begins to shrink at ∼1050 °C, whereas shrinkage begins at 1100°C for samples doped with 1029 ppm Na_2O. The difference in density at the beginning of densification continues throughout the heating cycle. However, above ∼1350°C the densification rate of the Na_2O doped samples surpasses that of the as-received sample. Overall, the Na_2O-doped samples are 2.5% less dense than the as-received Al_2O_3 after heating to 1525°C.

Table 3.1. Physical and chemical characteristics of the as-received Bayer Al2O3 powder used in this study.

BET (m^2/g)	7.4
D_{50} (μm)	0.4
D_{90} (μm)	1.5
	ICP (ppm)
Al_2O_3	99.96 %
SiO_2	103
Na_2O (total)	29
Fe_2O_3	90
CaO	62
TiO_2	22
MgO	2

Table 3.2. Calculated compositions and amounts of liquid in as-received, singly doped and co-doped samples at 1525°C (α = α-Al2O3, β = β-Al2O3, LÂă= liquid, M = mullite).

Global dopant concentration		Global $Na_2O:SiO_2$ ratio	$Na_2O:SiO_2$ ratio in Liquid	Composition of liquid (mol %)			Amount of liquid (vol. %)	Stable phases
ppm (wt.) Na_2O/SiO_2	ppm (mol) Na_2O/SiO_2			Na_2O	SiO_2	Al_2O_3		
As-received 29/103	48/175	0.27	0.25	17.9	63.4	19.7	0.03%	α+L
154/103-1029/103	253/175-1693/175	1.45-9.67	0.5	26.1	52.3	21.6	0.03%	α+L+β
29/603	48/1023	0.05	0.25	16.3	65.3	18.4	0.03%	α+L+M
154/603	253/1023	0.25	0.25	16.3	65.3	18.4	0.16%	α+L
279/603	459/1023	0.45	0.45	24.5	54.6	20.8	0.19%	α+L
529/603	870/1023	0.85	0.5	26.1	52.3	21.6	0.22%	α+L+β
1029/603	1693/1023	1.65	0.5	26.1	52.3	21.6	0.22%	α+L+β

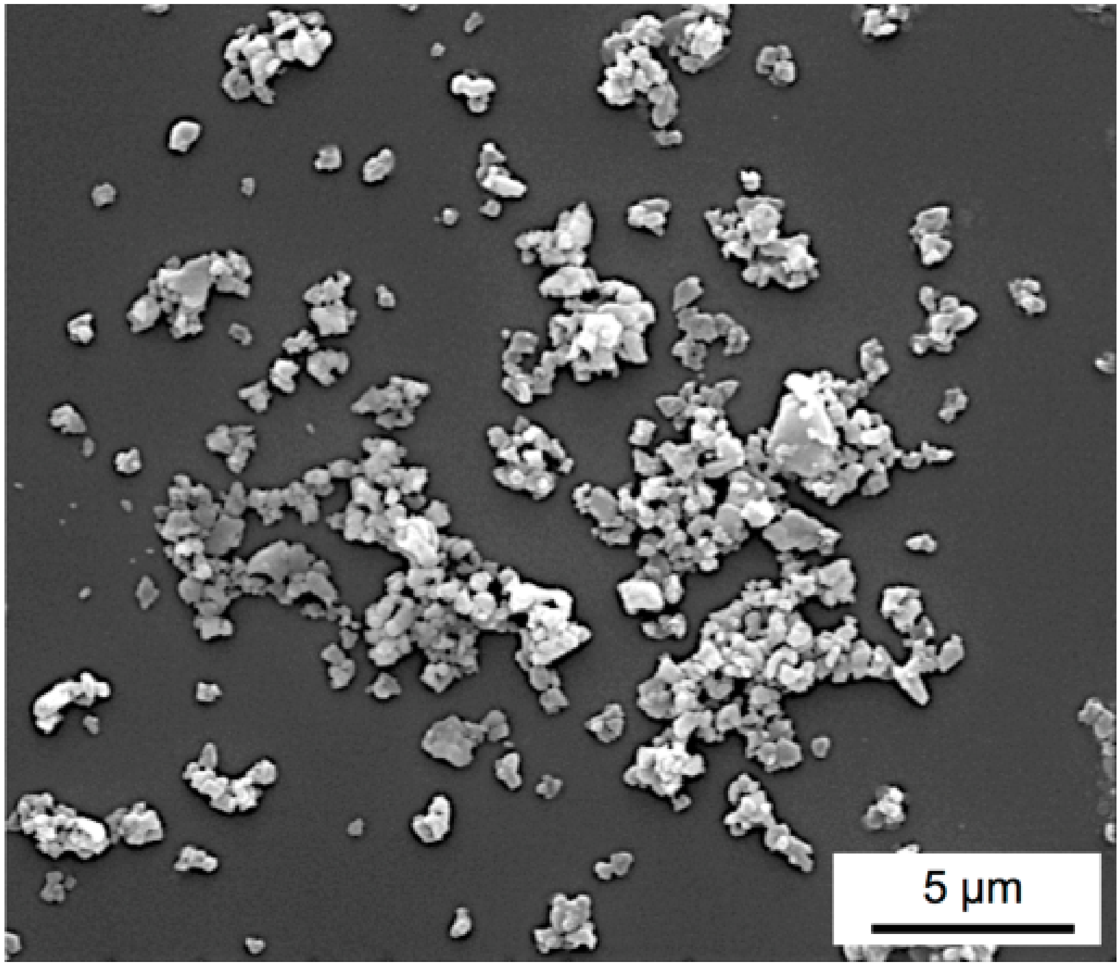

Figure 3.1. SEM image of as-received chemically purified Bayer Al_2O_3 powder used in this study.

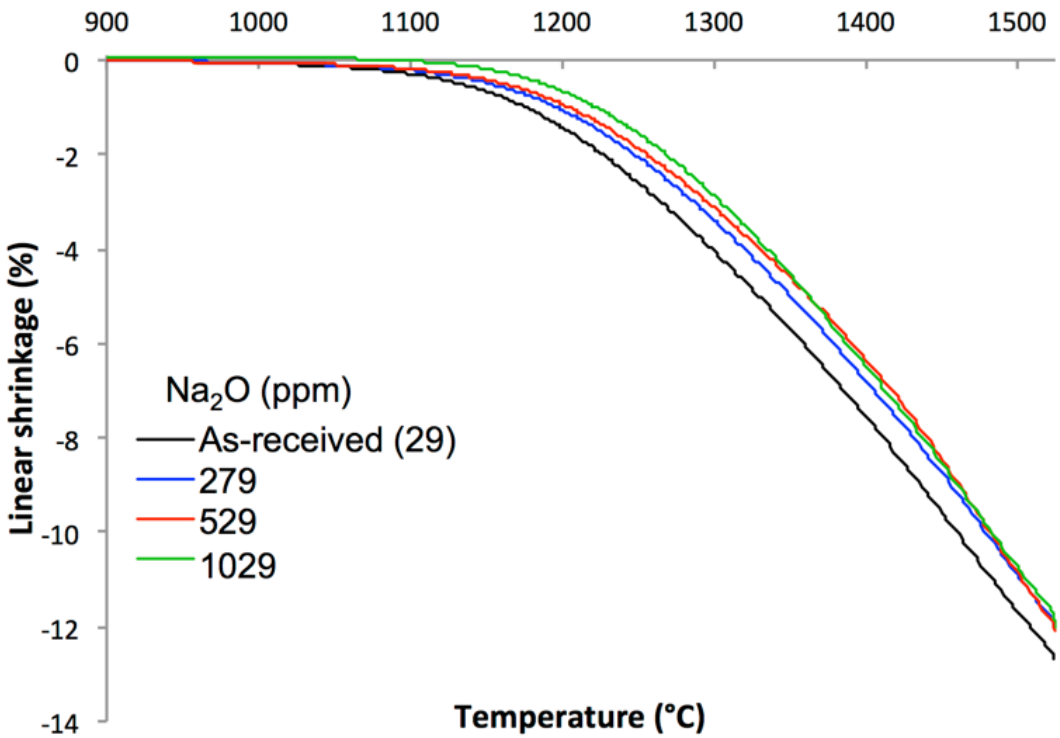

Figure 3.2. Dilatometer curves of as-received and singly Na_2O-doped samples heated at 10°C/min to 1525°C.

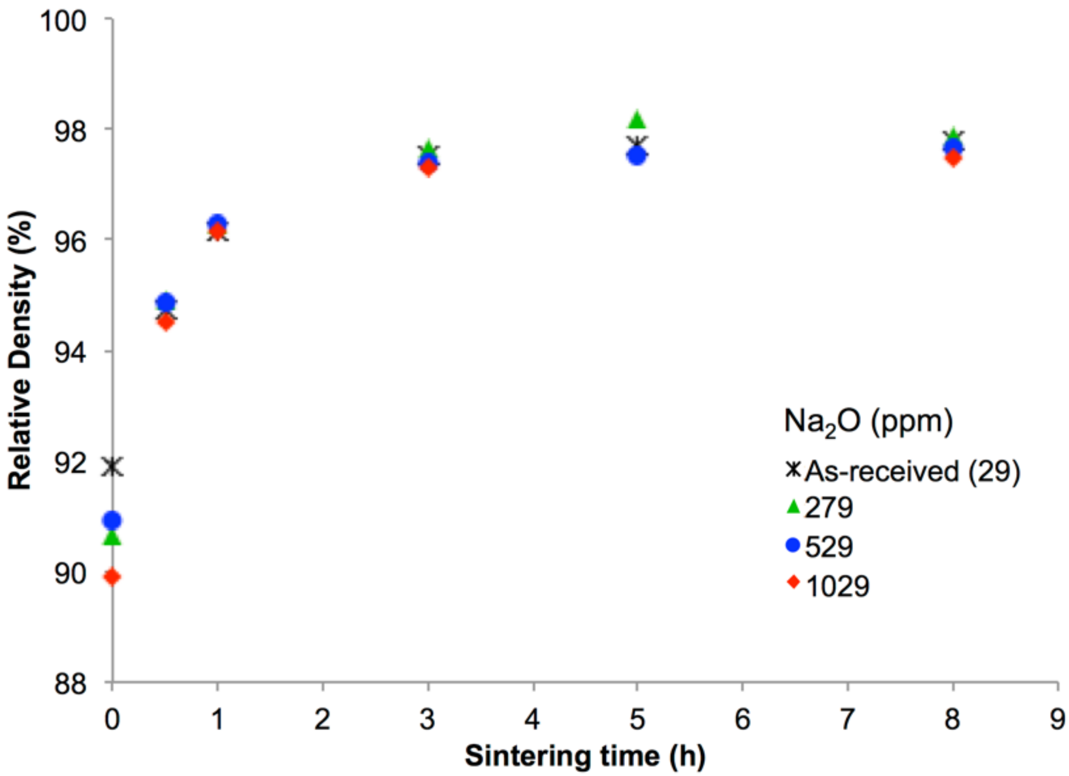

Figure 3.3. Densification kinetics of Bayer Al_2O_3 doped with different Na_2O concentrations and sintered at 1525°C.

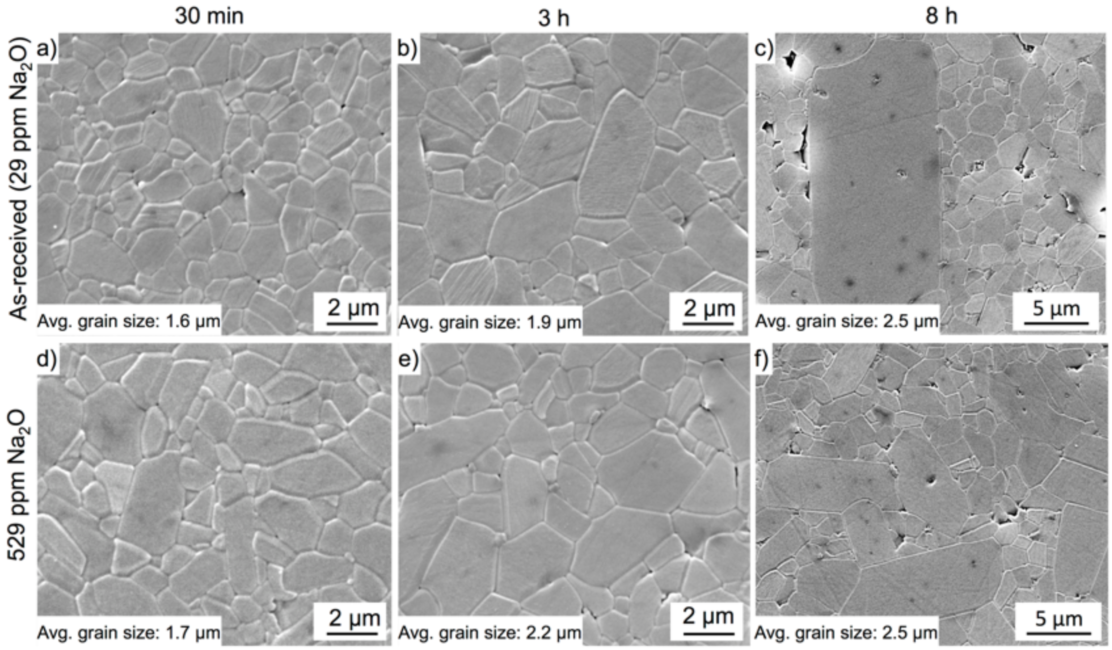

Figure 3.4. Microstructures of as-received and singly 529 ppm Na_2O doped samples after 30 min, 3 h and 8 h at 1525°C.

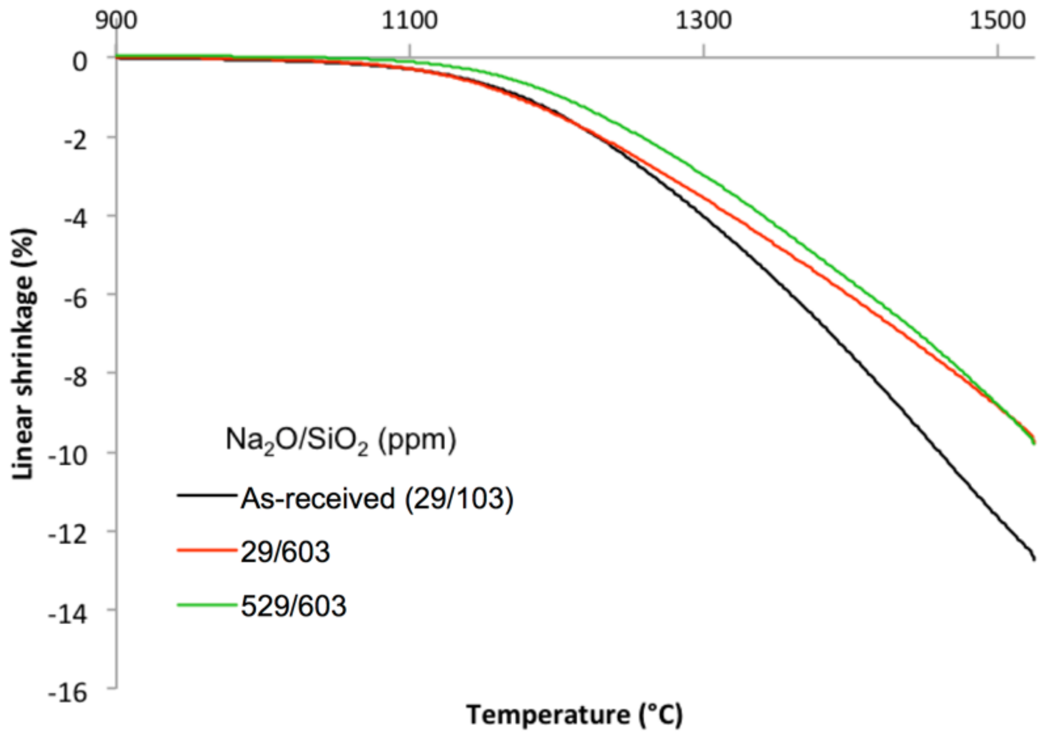

Figure 3.5. Dilatometer curves of as-received, singly SiO_2-doped, and Na_2O/SiO_2-doped Bayer Al_2O_3 heated at 10°C/min to 1525°C.

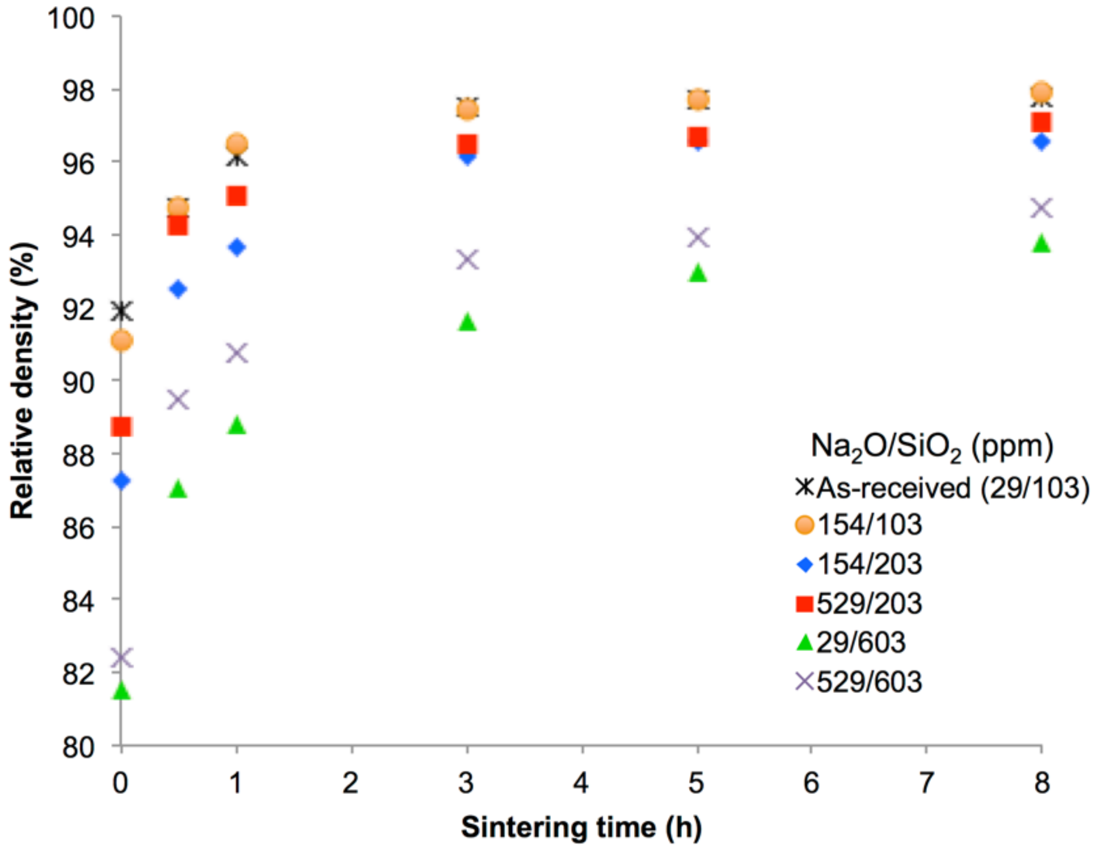

Figure 3.6. Densification kinetics of Bayer Al_2O_3 doped with different concentrations of Na_2O and SiO_2 at 1525°C.

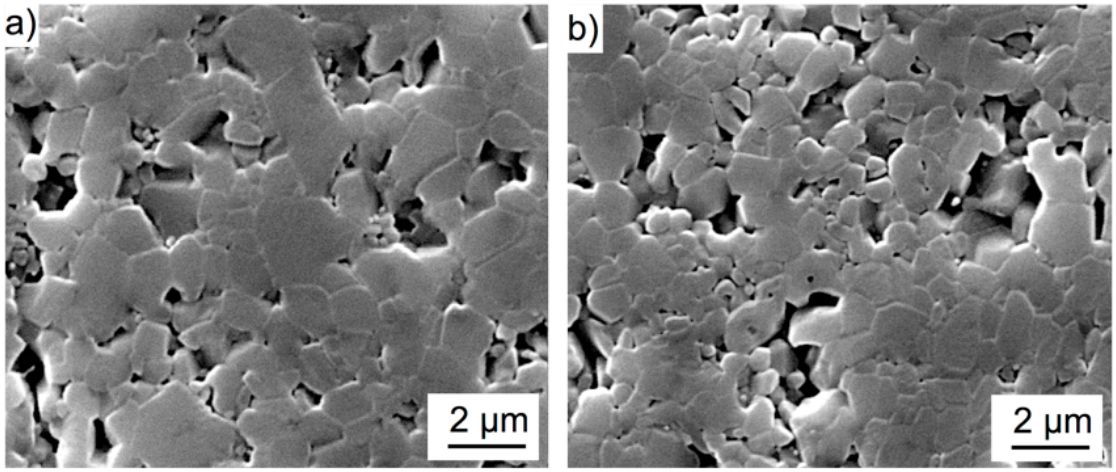

Figure 3.7. Microstructures of Bayer Al_2O_3 doped with a) 603 ppm SiO_2 and b) 529 ppm Na_2O and 603 ppm SiO_2 after heating at 1525°C for 8h.

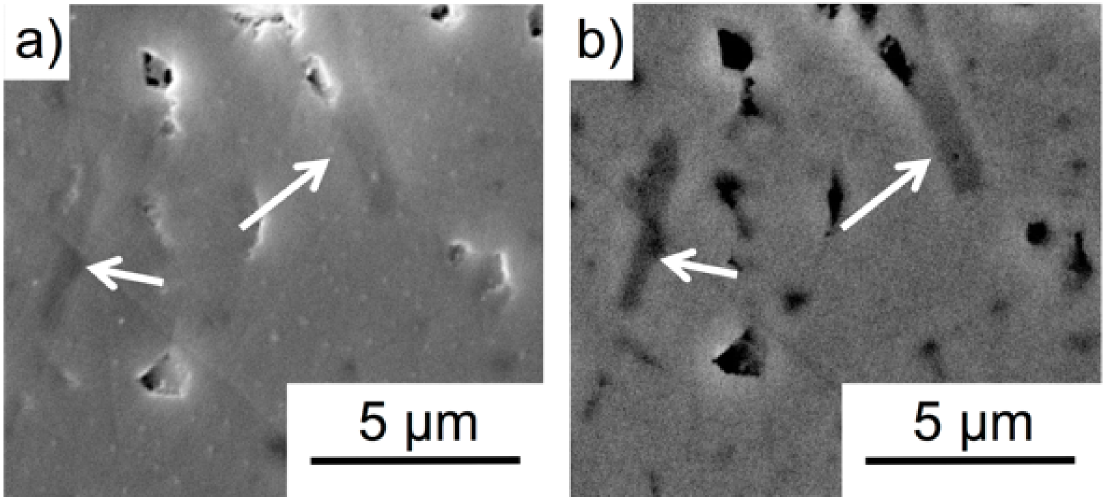

Figure 3.8. Micrographs of a sample doped with 1029 ppm Na_2O after sintering at 1525°C for 3Ââh. The micrographs were recorded using a) a secondary electron detector and b) a backscattered electron detector. The arrows point at the platelet shaped beta alumina grains that form in samples doped with Na_2O. The samples were not thermally etched.

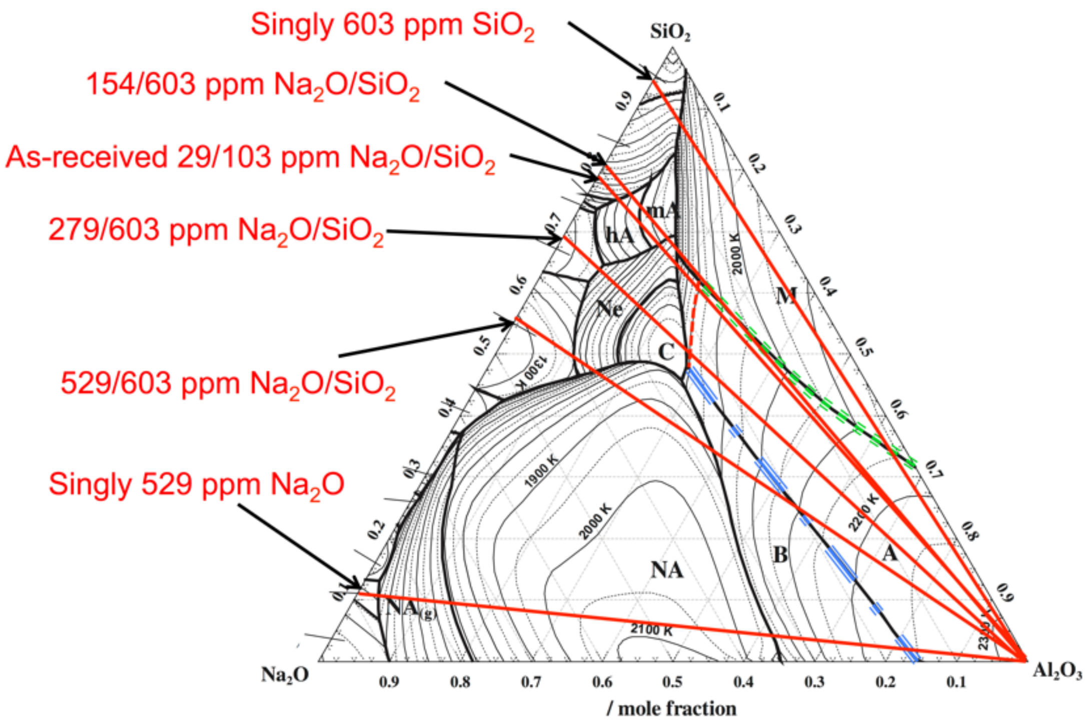

Figure 3.9. Liquidus projection of the Al_2O_3-SiO_2-Na_2O ternary phase diagram. The red solid lines are isoplethal cuts representing the samples investigated in this study. The red dashed line is the 1525°C isotherm where α-Al_2O_3 and liquid are in equilibrium. The blue dash-dot line and green dotted line are eutectic lines at which α-Al_2O_3 and liquid is in equilibrium with β-Al_2O_3 or mullite, respectively.

Chapter 4
Powder Chemistry Effects on the Sintering Behavior of MgO-doped Bayer Alumina

4.1 Introduction

When in the Course of human events, it becomes necessary for one people to dissolve the political bands which have connected them with another, and to assume among the powers of the earth, the separate and equal station to which the Laws of Nature and of Nature's God entitle them, a decent respect to the opinions of mankind requires that they should declare the causes which impel them to the separation.

4.2 More Declaration

We hold these truths to be self-evident, that all men are created equal, that they are endowed by their Creator with certain unalienable Rights, that among these are Life, Liberty and the pursuit of Happiness. –That to secure these rights, Governments are instituted among Men, deriving their just powers from the consent of the governed, –That whenever any Form of Government becomes destructive of these ends, it is the Right of the People to alter or to abolish it, and to institute new Government, laying its foundation on such principles and organizing its powers in such form, as to them shall seem most likely to effect their Safety and Happiness. Prudence, indeed, will dictate that Governments long established should not be

changed for light and transient causes; and accordingly all experience hath shewn, that mankind are more disposed to suffer, while evils are sufferable, than to right themselves by abolishing the forms to which they are accustomed.

4.2.1 Some nonsense here

But when a long train of abuses and usurpations, pursuing invariably the same Object evinces a design to reduce them under absolute Despotism, it is their right, it is their duty, to throw off such Government, and to provide new Guards for their future security. –Such has been the patient sufferance of these Colonies; and such is now the necessity which constrains them to alter their former Systems of Government.

4.2.2 Some additional nonsense here

The history of the present King of Great Britain [George III] is a history of repeated injuries and usurpations, all having in direct object the establishment of an absolute Tyranny over these States. To prove this, let Facts be submitted to a candid world.

Chapter 5
Powder Chemistry Effects on Grain Boundaries During Densification of Bayer Alumina

5.1 Introduction

When in the Course of human events, it becomes necessary for one people to dissolve the political bands which have connected them with another, and to assume among the powers of the earth, the separate and equal station to which the Laws of Nature and of Nature's God entitle them, a decent respect to the opinions of mankind requires that they should declare the causes which impel them to the separation.

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Chapter 6

β-Al_2O_3: A Model System for the Formation of Second Phases in Al_2O_3

6.1 Introduction

When in the Course of human events, it becomes necessary for one people to dissolve the political bands which have connected them with another, and to assume among the powers of the earth, the separate and equal station to which the Laws of Nature and of Nature's God entitle them, a decent respect to the opinions of mankind requires that they should declare the causes which impel them to the separation.

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Chapter 7
Summary and Future Work

7.1 Introduction

When in the Course of human events, it becomes necessary for one people to dissolve the political bands which have connected them with another, and to assume among the powers of the earth, the separate and equal station to which the Laws of Nature and of Nature's God entitle them, a decent respect to the opinions of mankind requires that they should declare the causes which impel them to the separation.

7.2 More Declaration

We hold these truths to be self-evident, that all men are created equal, that they are endowed by their Creator with certain unalienable Rights, that among these are Life, Liberty and the pursuit of Happiness. –That to secure these rights, Governments are instituted among Men, deriving their just powers from the consent of the governed, –That whenever any Form of Government becomes destructive of these ends, it is the Right of the People to alter or to abolish it, and to institute new Government, laying its foundation on such principles and organizing its powers in such form, as to them shall seem most likely to effect their Safety and Happiness. Prudence, indeed, will dictate that Governments long established should not be changed for light and transient causes; and accordingly all experience hath shewn, that mankind are more disposed to suffer, while evils are sufferable, than to right themselves by abolishing the forms to which they are accustomed. But when a long train of abuses and usurpations, pursuing invariably the same Object evinces a design to reduce them under absolute Despotism, it is their right, it is their duty, to throw off such Government, and to provide new Guards for their future security. –Such has been the patient sufferance of these Colonies; and such is now the necessity which constrains them to alter their former Systems of Government. The history of the present King of Great Britain [George III] is a history of repeated injuries and usurpations, all having in direct object the establishment of an absolute Tyranny over these States. To prove this, let Facts be submitted to a candid world.

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Vita

Tobias Frueh

The details of my childhood are inconsequential.