

A Thesis Presented to
The Faculty of Alfred University

Apparent Correlation of Sintering Temperature With the Viscosity of the Grain Boundary Liquid

by
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TABLE OF CONTENTS

	Page
ACKNOWLEDGMENTS.....	ii
TABLE OF CONTENTS.....	iii
LIST OF TABLES	v
LIST OF FIGURES	vi
ABSTRACT	viii
I. INTRODUCTION	1
II. LITERATURE REVIEW	2
A. Liquid Phase Sintering.....	2
1. Stage I – Rearrangement and Liquid Redistribution.....	3
2. Stage II – Solution-Precipitation	4
3. Stage III – Solid State Sintering.....	5
B. Glass Formation Boundary.....	6
C. Fragility	7
D. Sintering High Purity Alumina without a Liquid Phase.....	8
E. Sintering High Purity Alumina with a Liquid Phase	9
III. EXPERIMENTAL PROCEDURE	10
A. Sample Selection.....	10
B. Sample Preparation	11

TABLE OF CONTENTS (CONTINUED)

	Page
1. Milling.....	11
2. Heterocoagulation Process for Coating Alumina with Silica.....	11
3. Slip Casting	14
4. Doping via Salt Solution Infiltration	14
5. Chemistry Verification	15
C. Sintering.....	15
D. Sample Characterization.....	16
1. Density Measurements	16
2. Microstructure	16
IV. RESULTS AND DISCUSSION	17
A. Chemistry	17
B. Density Measurements.....	19
C. Microstructure.....	22
V. EVIDENCE OF DE-SINTERING WITH INVERT GLASSES	25
VI. CONCLUSIONS	26
VII. FUTURE WORK.....	27
IIX. REFERENCES	28
IX. APPENDIX	31

LIST OF TABLES

	Page
Table I. Calcium Chloride Solution Compositions	14
Table II. ICP-ES Results	15
Table III. Average Densities for Invert and Normal Samples.....	19
Table IV. Average Densities and True Densities.....	21
Table V. Complete ICP-ES Analysis Results.....	31

LIST OF FIGURES

	Page
Figure 1. Schematic Drawing Illustrating Fragmentation and Rearrangement.....	3
Figure 2. Two Densification Mechanisms During the Second Stage of Liquid Phase Sintering.....	4
Figure 3. Schematic Diagram for Solid State Sintering.....	5
Figure 4. Proposed Glass Formation Boundaries	6
Figure 5. Fragility Diagram for Typical Melts	7
Figure 6. Grain Structure of Alumina Illustrating Abnormal Grain Growth.....	9
Figure 7. Glass Formation Boundaries with Tested Chemistries Indicated	10
Figure 8. CT-1200 Milled for 8 Hours.....	11
Figure 9. Measured ζ -potential as a Function of pH	12
Figure 10. Schematic of Heterocoagulation Process	13
Figure 11. Uncoated Alumina and Alumina Coated with Silica.....	13
Figure 12. Reaction Paths in the CaO-Al ₂ O ₃ -SiO ₂ ternary phase diagram	17
Figure 13. Percent Alumina Dissolved into the Glass as a Function of Temperature	18
Figure 14. Densification with a Liquid Phase	20
Figure 15. Plot of Measured Density vs. True Density	21
Figure 16. BSE Images of Samples Containing a Normal Liquid.....	23
Figure 17. BSE Images of Samples Containing an Invert Liquid.....	24
Figure 18. Evidence of De-Sintering for Invert Glasses	25
Figure 19. Proposed Future Work.....	27
Figure 20. BSE and SE Images of 15% Invert Glass Samples at Low Magnification ...	32

LIST OF FIGURES (CONTINUED)

	Page
Figure 21. BSE and SE Images of 9% Invert Glass Samples at Low Magnification	33
Figure 22. BSE and SE Images of 7% Normal Glass Samples at Low Magnification ...	34
Figure 23. BSE and SE Images of 4% Normal Glass Samples at Low Magnification ...	35
Figure 24. BSE and SE Images of 15% Invert Glass Samples at High Magnification ..	36
Figure 25. BSE and SE Images of 9% Invert Glass Samples at High Magnification	37
Figure 26. BSE and SE Images of 7% Normal Glass Samples at High Magnification ..	38
Figure 27. BSE and SE Images of 4% Normal Glass Samples at High Magnification ..	39

ABSTRACT

It is common for industrial polycrystalline alumina to contain a significant amount of liquid, but it is unclear what dictates the densification temperature. It is proposed that the viscosity of the grain boundary liquid dictates the densification temperature of polycrystalline alumina. To test this hypothesis two glass chemistries were engineered, one in the invert glass region and one in the normal glass region. In addition, two levels of each chemistry were evaluated to demonstrate that densification is independent of the amount of liquid in the grain boundary. In support of the hypothesis, samples containing a low viscosity liquid densified at 1600°C whereas samples containing a high viscosity liquid densified at 1700°C. These results illustrate an opportunity to tailor the grain boundary chemistry in order to control the densification temperature for industrial sintering systems.

I. INTRODUCTION

Most industrial systems sinter alumina in the presence of a liquid phase. Previous studies done by Lam and DeCarlo et al. have demonstrated information on the sintering of alumina with respect to the glass formation boundary.^{1,2} When sintering alumina, it was observed that the dissolution of alumina into an amorphous silicate grain boundary and the dissolution into a calcia based grain boundary is different and results in different phases present.^{1,2}

In this study, it is proposed that the viscosity of the grain boundary liquid dictates the densification temperature in polycrystalline alumina. In order to obtain different viscosity liquids in the grain boundary, a composition within the normal region and a composition in the invert region were produced. A normal glass is a silicate glass that has a high viscosity and low fragility. An invert glass is a calcium-aluminate based glass that has a low viscosity and high fragility.

Often times a frit may be introduced to an alumina powder in order to form a glassy phase.³ Doping alumina through the use of a glass frit can result in uneven distribution of the glassy phase due to the large size difference between the frit and alumina particles. To alleviate the poor distribution of glass throughout the sample a heterocoagulation process may be utilized.⁴

This allows for an opportunity to modify the grain boundary chemistry and therefore control the densification temperature.

II. LITERATURE REVIEW

A. LIQUID PHASE SINTERING

Today, a majority of ceramic products are fabricated with a liquid phase present during sintering.⁶ Liquid phase sintering is when the formation of a liquid phase is used to assist in sintering and microstructural evolution. The main reason behind using liquid phase sintering is to enhance densification rates, achieve accelerated grain growth, or produce specific grain boundary properties.⁶ The liquid coats each grain, allowing the material to be sintered to a higher density at a lower temperature.⁷ Liquid phase sintering is comprised of three stages: rearrangement and liquid redistribution, solution-precipitation, and solid state sintering.

1. Stage I – Rearrangement and Liquid Redistribution

Experiments have observed considerable redistribution of the liquid during liquid phase sintering. Depending on the volume fraction throughout the system, the low viscosity liquid will distribute itself either in the necks or the pores. If the pores have a narrow distribution of sizes then there will be a homogeneous distribution of the liquid phase. Heterogeneous packing leads to the liquid filling the larger pores later in the firing process. This causes inhomogeneous mixing which results in a lack of driving force for the redistribution of liquid. After the formation of the liquid, particle rearrangement is very rapid and occurs in as little as a few minutes. Initial densification occurs during this step and determines the initial microstructure of the sintering compact. Rearrangement and liquid redistribution is illustrated in Figure 1.

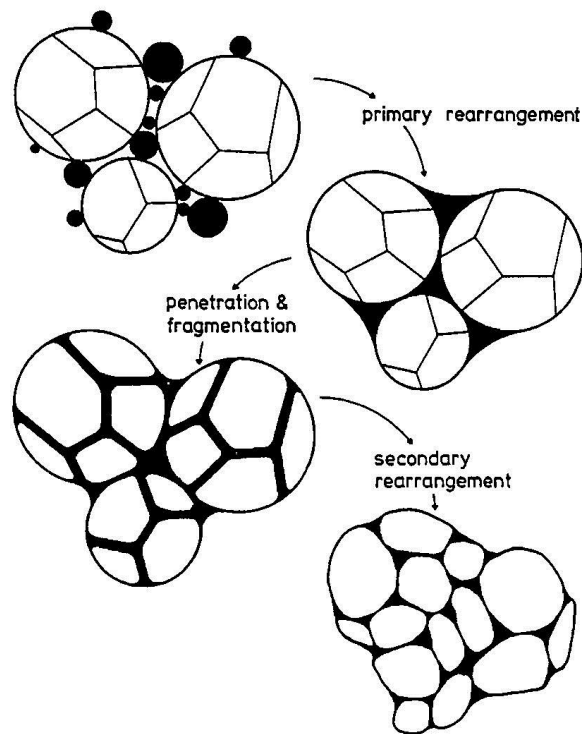


Figure 1. Schematic drawing illustrating fragmentation and rearrangement of polycrystalline particles.⁵

2. Stage II – Solution-Precipitation

Throughout the second stage of liquid phase sintering rearrangement is no longer the main contributor to densification. In this stage the solution-precipitation mechanism becomes dominant. This mechanism is made up of two processes: densification and coarsening.⁷ Densification during this intermediate stage depends on material flow through the liquid. The microstructural changes that occur, such as grain coarsening and shape accommodation, will lower the total system energy by eliminating interfacial area; allowing for pore shrinkage and grain growth.⁶ Two mechanisms of densification through a liquid that utilize solution-precipitation are contact flattening and dissolution of small grains with reprecipitation onto large grains. Both of these mechanisms allow for grain shape accommodation which results in increased packing and density of the material. The controlling step for these mechanisms is diffusion through the liquid. A schematic for contact flattening and Ostwald ripening is shown in Figure 2.

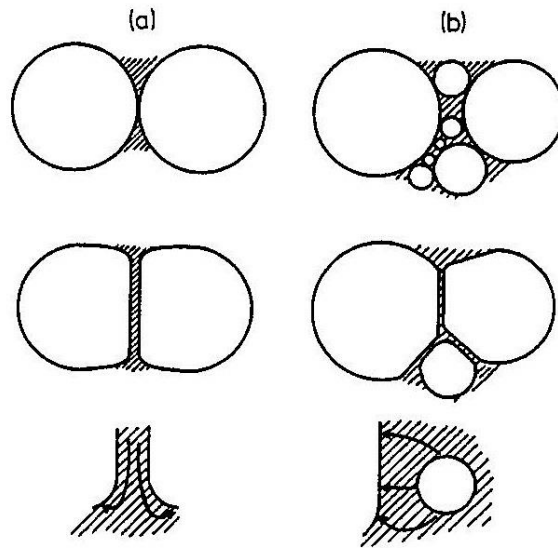


Figure 2. Two mechanisms of shape accommodation and neck growth during the intermediate stage of liquid phase sintering; (a) contact flattening, and (b) dissolution of fine grains.⁵

3. Stage III – Solid State Sintering

Solid state sintering consists of three stages: initial stage, intermediate stage, and final stage. An illustration of these three stages can be seen in Figure 3. The completion of liquid phase sintering follows solid state sintering mechanisms. During this stage the pore volume reduces and grain boundaries increase.⁸

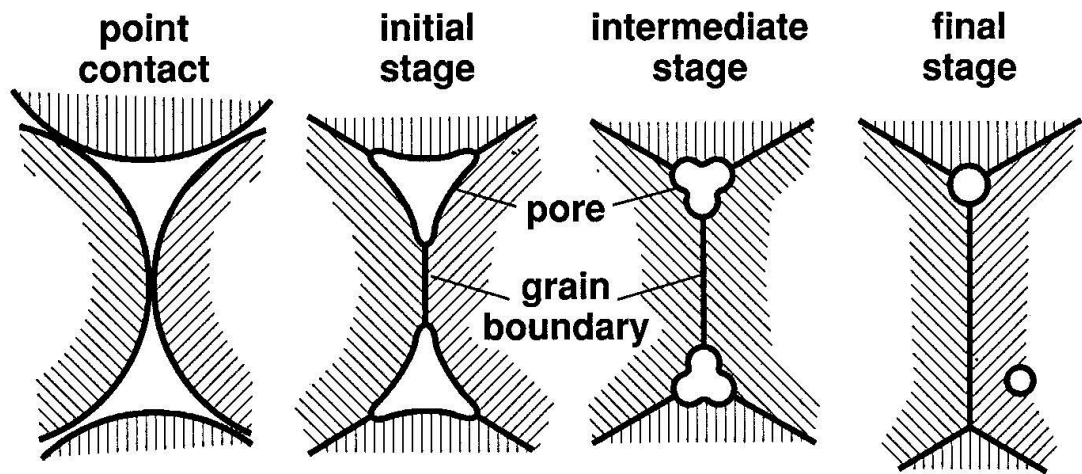


Figure 3. Schematic diagrams of the pore structure changes during sintering, starting with particles in point contact. The pore volume decreases and the pores become smoother. As pore spheroidization occurs, the pores are replaced by grain boundaries.

B. GLASS FORMATION BOUNDARY

The glass formation boundary represents the location where the chemistry prefers to form a glass upon cooling rather than crystallizing. The proposed glass formation boundaries for normal and invert is illustrated in Figure 4. This boundary is independent of cooling rate for industrial heat treatment schedules. Previous work by Lam provides for the prediction of grain boundary evolution in sintered alumina as well as grain boundary chemistry experienced when sintering alumina in the presence of a liquid phase.¹

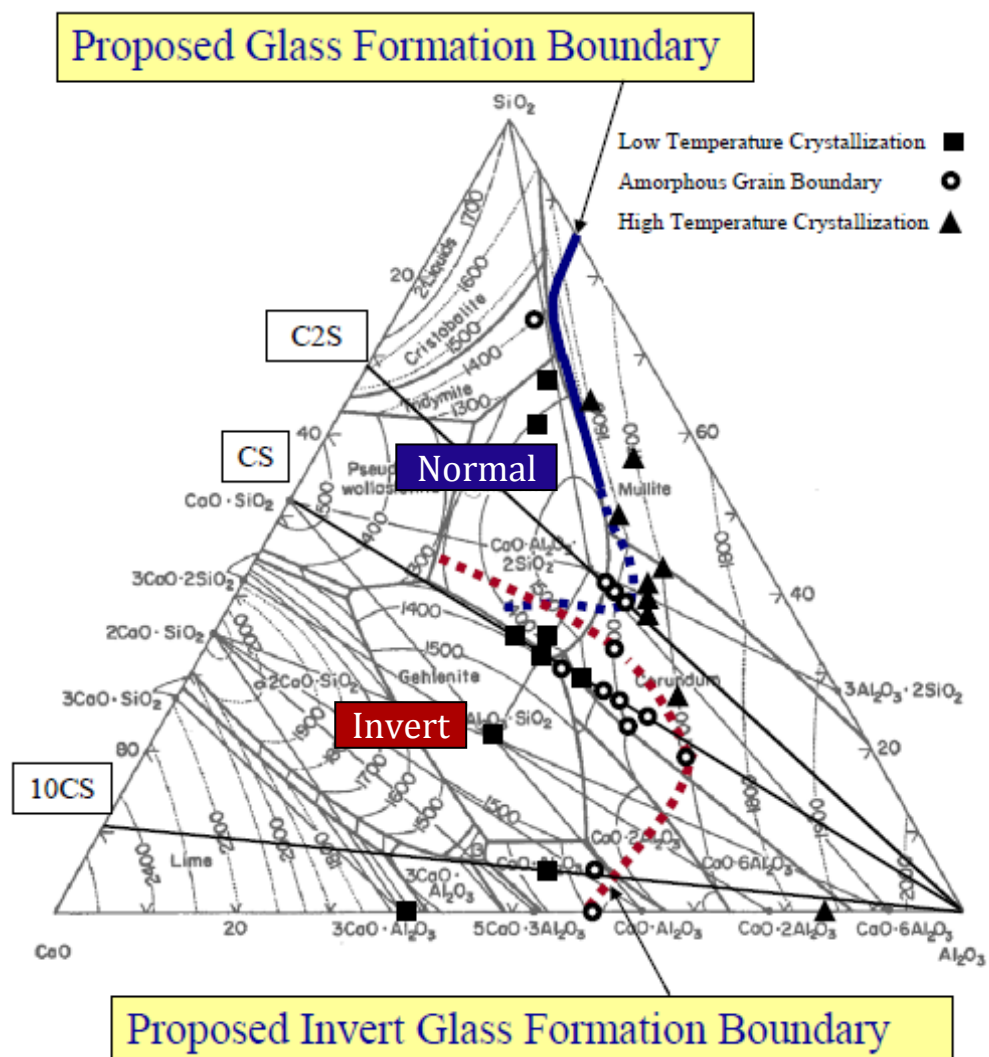


Figure 4. The glass formation boundaries in the sintering of alumina as proposed by Lam.¹

C. FRAGILITY

Generally a strong, normal melt will have a well-developed structural unit with a high degree of short range order, at least partially covalent bonds, and is minimally affected by an increase in temperature. Normal melts usually display only small changes in heat capacity upon passing through the glass transition region.

Fragile melts are characterized by a low degree of short range order, high structural disorder, and ionic bonds. Their structures disintegrate rapidly with an increase in temperature above the glass transition temperature. Fragile melts are usually characterized by large changes in heat capacity at the glass transition temperature.⁹

Overall, melts with a lower fragility will exhibit near-Arrhenian behavior on a log viscosity versus temperature curve. Normal melts will have a broad glass transition temperature range. Fragile melts display an increased curvature which correlates to a narrow glass transition temperature range as illustrated in Figure 5. Using the calculated fragility parameter the viscosity can then be calculated at any temperature.

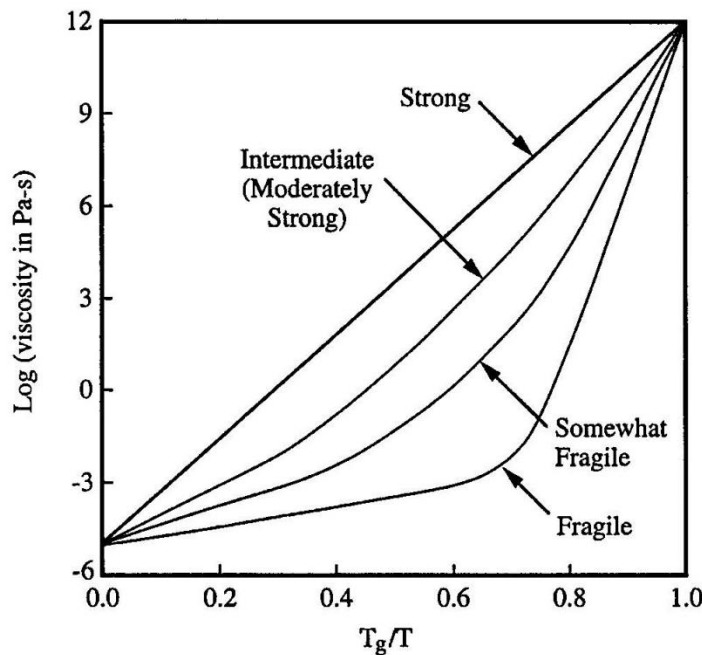


Figure 5. Fragility diagram for typical melts.⁹

Otminski applied the Avramov-Milchev equation with a predicted characteristic temperature at the Littleton softening point, where $\eta=10^{6.6}$ Pa·s, to then calculate the fragility parameter by using the Newton-Raphson algorithm.^{10,11}

For a normal glass composition having a 5:1 molar ratio of SiO₂ to CaO in Al₂O₃ at 1500°C the viscosity is calculated to be 10^{3.66} Pa·s.¹⁰ This composition is approximately the proposed chemistry of the grain boundary in this study. Though there is a lack of Littleton softening point data for invert glasses within the SciGlass database, for a glass composition having a 1:0.37 molar ratio of CaO to SiO₂ at 1500°C the viscosity is calculated to be 10^{1.57} Pa·s.^{10,12,13} This invert glass viscosity predication is consistent with previous experimental observations by Moesgaard and Yue.¹⁴ Based on the structural difference of the glasses, it is speculated that invert glasses will generally exhibit at least two orders of magnitude lower viscosities than normal glasses at 1500°C.¹³ The compositional difference of normal and invert amorphous grain boundaries should influence grain growth and the densification process in the sintering of alumina.

D. SINTERING HIGH PURITY ALUMINA WITHOUT A LIQUID PHASE

Studies have shown that high purity alumina can be sintered to a relatively high density at a low temperature by the incorporation of a trimodal system or by changing the particle size distribution of the powder.^{15,16} One disadvantage of sintering without a liquid phase present seen by Marchlewski was the development of abnormal grain growth. An illustration of abnormal grain growth as a result of sintering without a liquid phase is shown in Figure 6. A study similar to this illustrating the same results was done by McDevitt.¹⁷

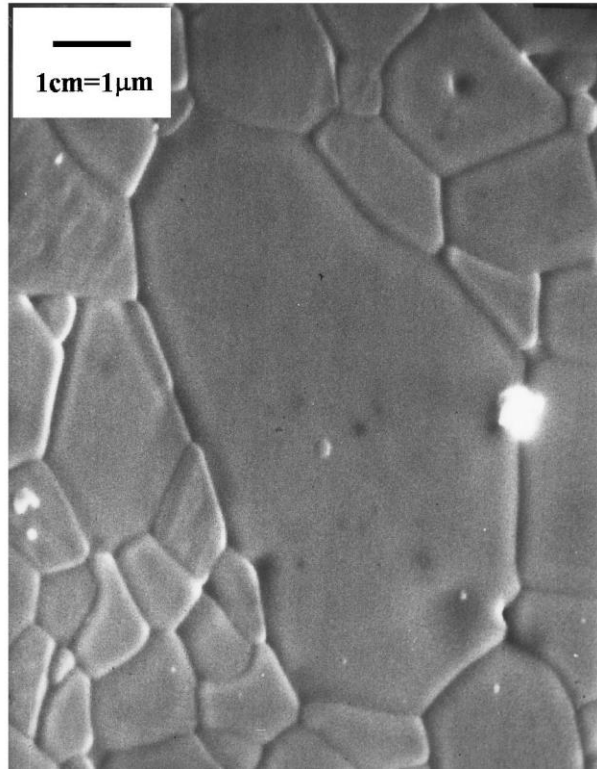


Figure 6. Grain structure of alumina illustrating abnormal grain growth.¹⁵

E. SINTERING HIGH PURITY ALUMINA WITH A LIQUID PHASE

It has been demonstrated throughout studies that the incorporation of a glass phase into high purity alumina can be executed in various ways. One method to combine frit and alumina is through a wet-ball-mill process.³ Another possible technique utilizes heterogeneous precipitation of calcium hydroxide and hydrated silica on to the alumina particles by hydrolysis.¹⁸ Both of these methods resulted in inhomogeneous final distribution of the glass within the alumina. An alternative approach was needed to produce a homogenous dopant chemistry distribution, which resulted in the heterocoagulation process being used.

III. EXPERIMENTAL PROCEDURE

A. SAMPLE SELECTION

Chemistries were chosen based on previous work by Lam (Figure 7).¹ In order to evaluate the effect of glass viscosity on densification, a low viscosity (invert glass) and a high viscosity (normal glass) were selected.

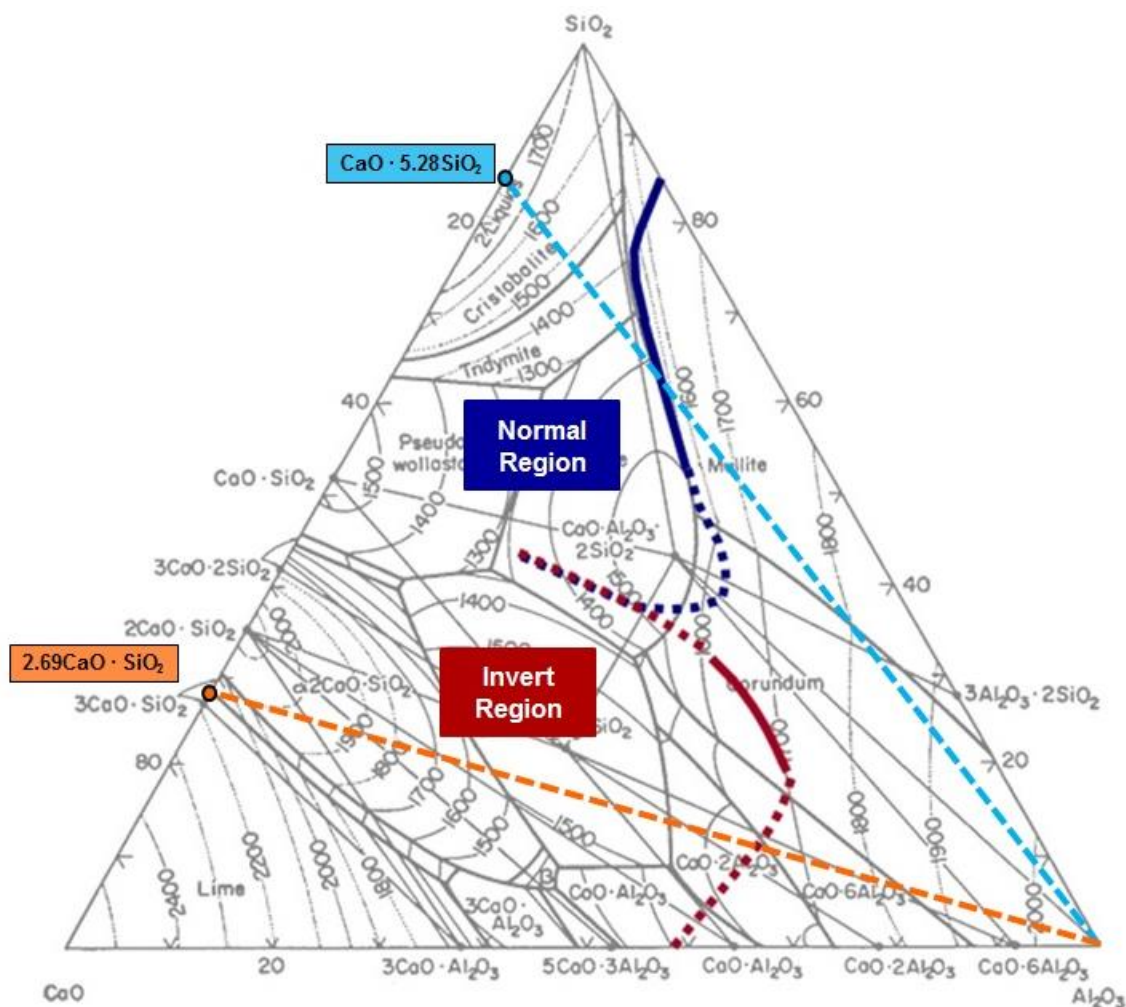


Figure 7. The glass formation boundaries in the sintering of alumina as proposed by Lam.¹

B. SAMPLE PREPARATION

1. Milling

A thermally reactive alumina (CT-1200, Almatiss, Leetsdale, PA), was wet milled for eight hours using a Sweco vibratory mill. After milling, the particle size was determined to be approximately 1-2 μm and the specific surface area was measured to be 4.14 m²/g. The powder after milling can be seen in Figure 8.

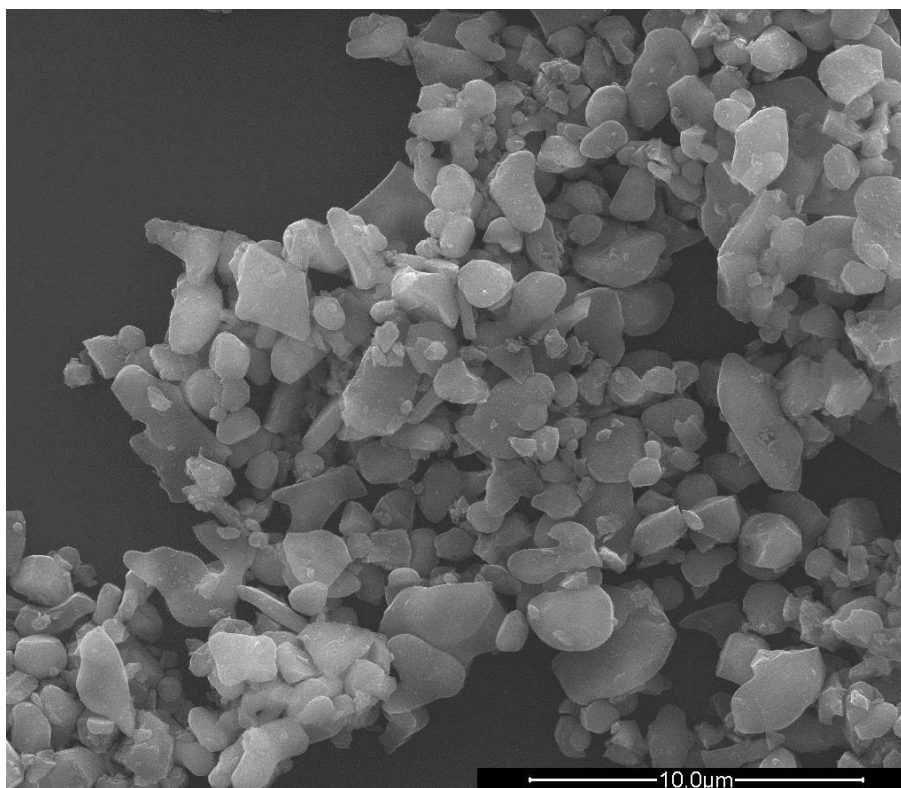


Figure 8. CT-1200 milled for 8 hours. (Size bar = 10 μm .)

2. Heterocoagulation Process for Coating Alumina With Silica

A method for coating relatively large particles (such as alumina) with significantly smaller particles of a different chemistry (such as colloidal silica) in order to create a uniformly distributed nano-scale coating on the primary matrix particles has been successfully demonstrated.⁴ Typically the size of the coating particle should be at least ten times smaller than that of the particle to be coated. In the case of alumina as the primary matrix particle and silica as the coating particle, the difference in

surface chemistry between the two particles can be exploited causing heterocoagulation to occur. As seen in Figure 9, between a pH of 2 and 9 the surface charge on alumina will be positive while silica has a negative surface charge.

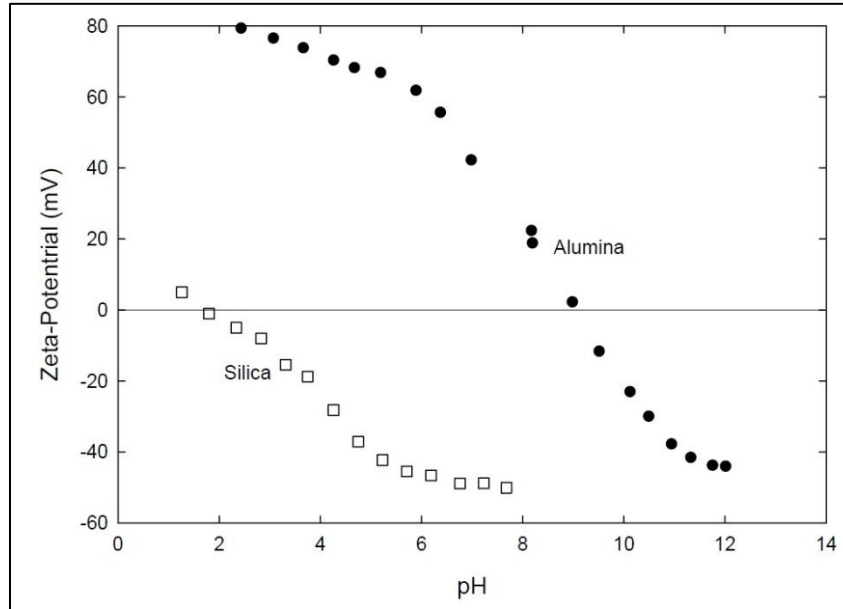


Figure 9. Measured ζ -potential of micron-sized silica and alumina particles as a function of pH in an aqueous medium.⁵

Oppositely charged surfaces between alumina and silica particles allow for heterocoagulation to occur. Individual suspensions of alumina and silica are prepared and adjusted to the desired pH, then mixed together with agitation resulting in heterocoagulation. Figure 10 illustrates the heterocoagulation process between alumina and colloidal silica particles. The amount of silica required to provide a mono-layer of the alumina particles can be calculated based on a hexagonal close-packed array of spheres. However, using excess silica ensures proper coating of the particles and will not result in any long-term instability of the suspension. After the coating process has been completed, excess silica can be removed through centrifugation. This heterocoagulation process allows for a uniform distribution of the glass phase within the alumina.

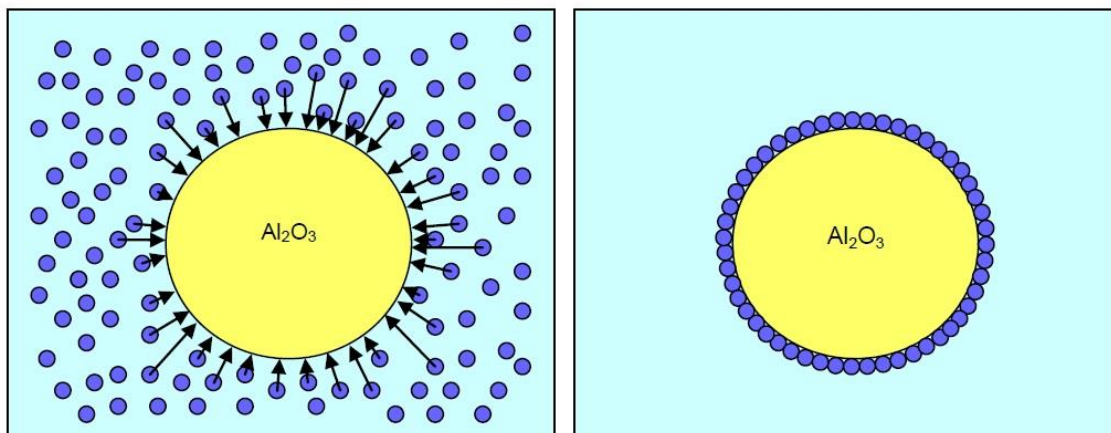


Figure 10. At an ideal pH of 3.0-4.5, negatively charged colloidal silica particles are attracted to the positively charged surface of alumina. The colloidal silica particles coat the alumina making it negatively charged. Once agglomerated, pH is then increased to 7.0 to 10 to create a uniform negative charge thus imparting long-term stability on the new composite particles (illustration not to scale).⁴

A 10v/o alumina suspension was created using deionized water. The pH was adjusted using 6M nitric acid until stabilization was obtained around a pH of 6 in order to achieve a positive surface charge. 50nm colloidal silica (Ludox ®, TM-50, W. R. Grace & Co., Cambridge, MA) was added as a 50w/o suspension at a pH of 8.9. Enough colloidal silica was added to fully coat the alumina particles. Uncoated and coated alumina particles can be seen in Figure 11.

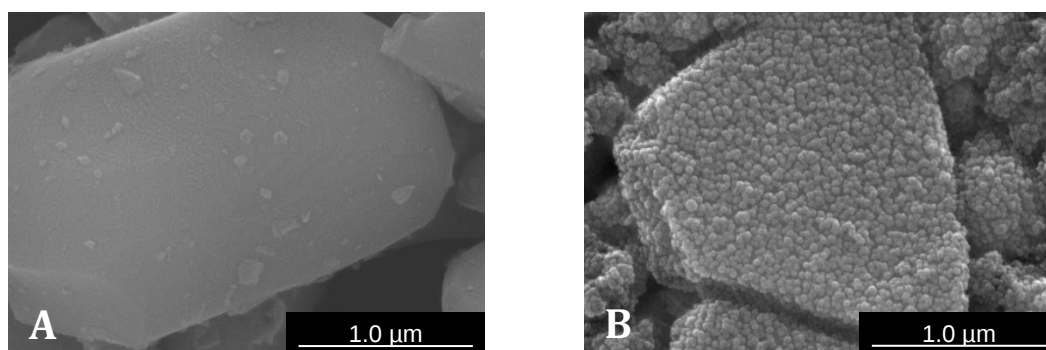


Figure 11. Uncoated alumina (A) and alumina coated with silica (B) demonstrating that the heterocoagulation process was successful.

The final alumina-coated silica suspension was then centrifuged for 30 minutes, rinsed, and centrifuged again to eliminate excess silica. Another 10v/o alumina suspension was created and left uncoated. This uncoated alumina suspension was then mixed with the coated suspension at ratios of 1:4 and 1:2 to produce 25% coated and 50% coated suspensions respectively. These different levels silica were desired in order to obtain different levels of liquid upon firing.

3. Slip Casting

60 pellets of each composition having a 1.27cm diameter were slip cast using a Lexan die on a gypsum mold. After slip casting, all pellets were dried in a drying oven at 110°C overnight to ensure the removal of all moisture.

4. Doping via Salt Solution Infiltration

Slip cast samples were doped using CaCl_2 to achieve molar ratios of $\text{CaO}:0.37\text{SiO}_2$ and $\text{CaO}:5\text{SiO}_2$. Saturated solutions of $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ and $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ were prepared according to the batches in Table I. Using the molecular weight of calcium as 40.08g/mole the percent calcium in each solution was calculated.

Table I. Calcium chloride solution compositions.

	$\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$	$\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$
MW (g/mole)	147.02	219.07
DI water (g)	90	500
Ca in solution	16.91%	5.57%

$\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ was utilized to obtain the 1:0.37 ratio and $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ was used to obtain the 1:5 ratio. The salt additions were infiltrated into the samples using a drop-wise method.

5. Chemistry Verification

Samples were fired to 1000°C to eliminate chlorine prior to analysis and then crushed. Chemistry verification was completed using inductively coupled plasma-emission spectroscopy (ICP-ES, ACME Analytical Laboratories LTD., Vancouver, BC Canada). The initial ICP results indicated that the desired ratios of CaO to SiO₂ were not successfully achieved, so new samples were made and the doping process was performed again with more precision. The results of the second ICP analysis are presented in Table II verifying the dopant chemistries. Full chemical analyses are presented in the Appendix.

Table II. ICP-ES results confirming the correct ratios of CaO to SiO₂.

	Liquid Level	wt% SiO₂ (moles)	wt % CaO (moles)	Molar Ratio (CaO:SiO₂)
Invert	Low	1.46 (0.024)	3.93 (0.070)	1.0:0.37
	High	2.44 (0.041)	6.54 (0.117)	1.0:0.37
Normal	Low	2.72 (0.045)	0.52 (0.009)	1.0:5.23
	High	4.42 (0.074)	0.83 (0.015)	1.0:5.33

C. SINTERING

A molybdenum disilicide bottom loading furnace was used for the purpose of this experiment. Samples were initially fired to 1400°C, 1600°C, and 1700°C using a ramp rate of 10K per minute with a one hour dwell time. The 1400°C samples were later re-fired to 1500°C and 1550°C after density measurements were completed.

D. SAMPLE CHARACTERIZATION

1. Density Measurements

Bulk density measurements were executed based on an immersion method and the ASTM C-20 standard modified for small specimen sizes.¹⁹ A minimum of four specimens from each composition were used in the density analysis.

True density was also measured in order to normalize the measured bulk density against the maximum possible density. Pellets were crushed to eliminate internal porosity and the powder density was measured using a helium pycnometer (AccuPyc 1330, Micromeritics, Norcross, GA).

2. Microstructure

Microstructural analysis was performed via SEM on polished samples (FEI Quanta 200f Environmental Scanning Electron Microscope (ESEM), FEI, Delmont, PA). Samples were ground using metal reinforced diamond grinding discs. 30 μ m, 10 μ m, and 6 μ m discs were used for preliminary grinding followed by 6 μ m and 1 μ m diamond paste on cloth wheels for final polishing. Samples were sputter coated with Au-Pd prior to imaging.

IV. RESULTS AND DISCUSSION

A. CHEMSITRY

Reaction paths and sample compositions after firing can be seen below in the CaO-Al₂O₃-SiO₂ ternary phase diagram in Figure 12.

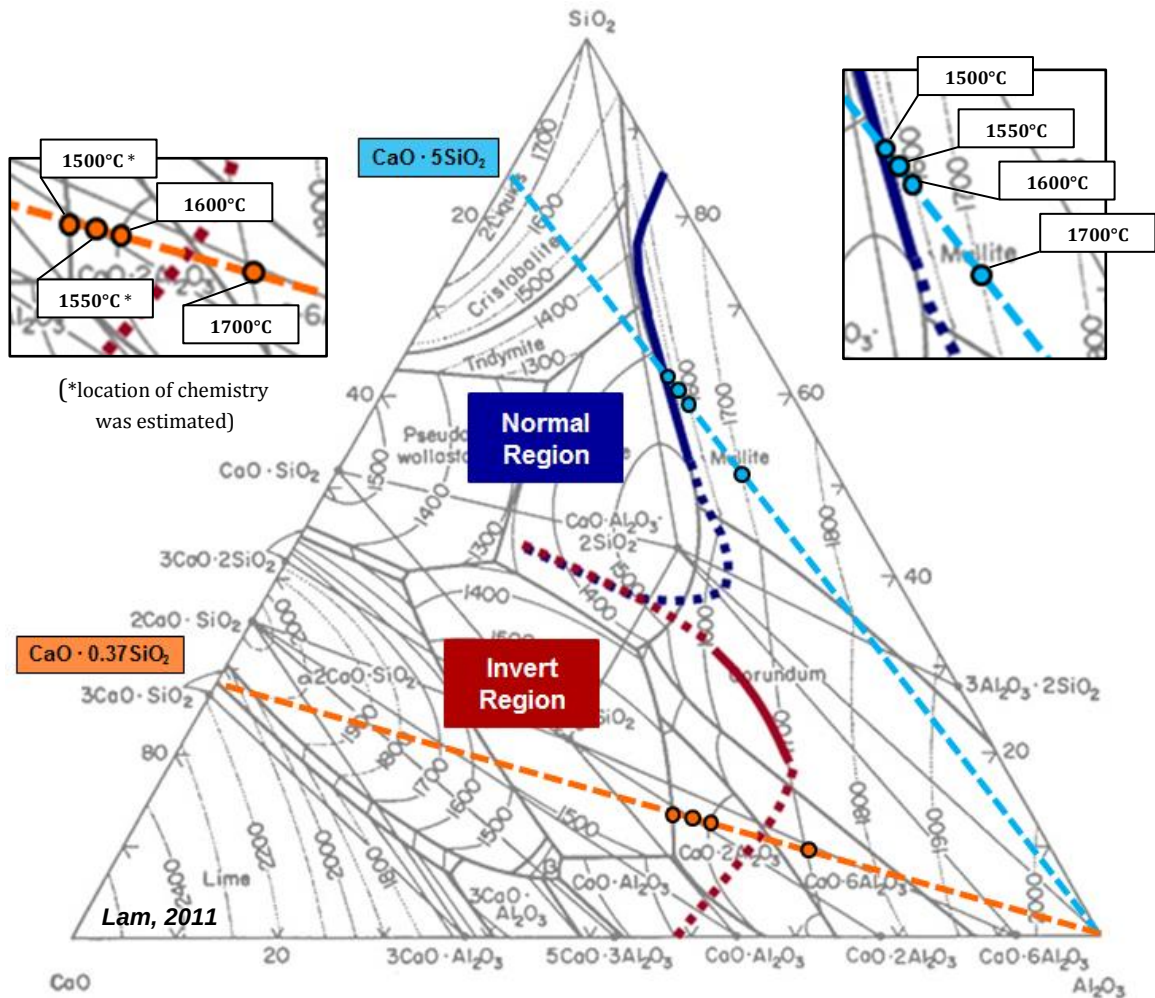


Figure 12. Reaction paths are indicated by dashed lines to form invert and normal glasses for the additive ratios of CaO:0.37SiO₂ and CaO:5SiO₂. Sample compositions after firing are seen on the appropriate reaction path indicated by circles.

Based on the isotherms on the $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$ phase diagram (Figure 13) the percent alumina that dissolved into the glass phase during firing was estimated and plotted in Figure 13.

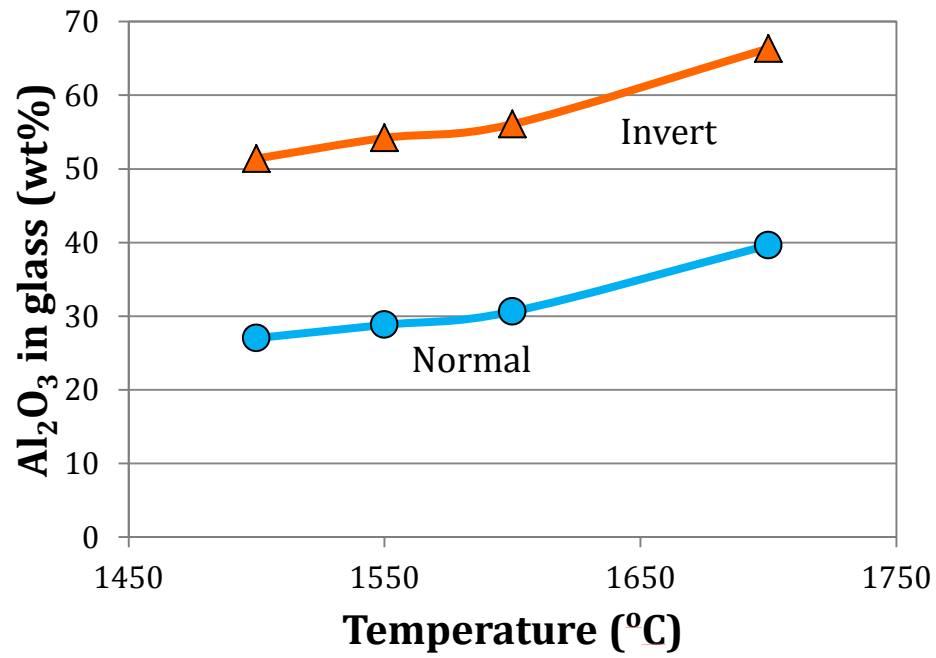


Figure 13. Percent alumina dissolved into the glass as a function of temperature.

The amount of alumina dissolved in invert glasses is much higher than that of normal glasses. The alumina difference is due to the location of the glass formation boundary indicated in Figure 12.

B. DENSITY MEASUREMENTS

Initially, samples were fired to 1400°C, 1600°C, and 1700°C based on previous work by Lam,¹ however the 1400°C were later re-fired to 1500°C and 1550°C in order to better observe the densification behavior between 1400°C and 1600°C. The completion of the additional firing temperatures was essential when comparing the invert and normal glass containing samples.

It was found that samples containing a low viscosity liquid experienced maximum densification at a lower temperature than samples containing a high viscosity liquid. Average measured density and standard deviation values, at varying firing temperatures, for samples containing invert and normal glass are shown in Table III.

Table III. Average measured densities via immersion.

Temperature (°C)	Apparent Bulk Density (g/cm ³) (standard deviation)			
	Invert, low liquid level	Invert, high liquid level	Normal, low liquid level	Normal, high liquid level
1400	2.340 (0.0263)	2.408 (0.0265)	2.428 (0.0326)	2.647 (0.0269)
1500	2.917 (0.0308)	3.195 (0.0595)	2.598 (0.0257)	2.867 (0.0217)
1550	3.610 (0.0145)	3.553 (0.0135)	3.195 (0.0048)	3.415 (0.0359)
1600	3.751 (0.0068)	3.598 (0.0313)	3.543 (0.0354)	3.683 (0.0219)
1700	3.738 (0.0076)	3.534 (0.0163)	3.811 (0.0032)	3.761 (0.0090)

In Figure 14 it is shown that samples with low viscosity, invert glasses reached maximum densification around 1600°C while samples with high viscosity, normal glasses achieved maximum densification at 1700°C. (Error bars are not visible because the data points are too large to allow for the error bars to be seen).

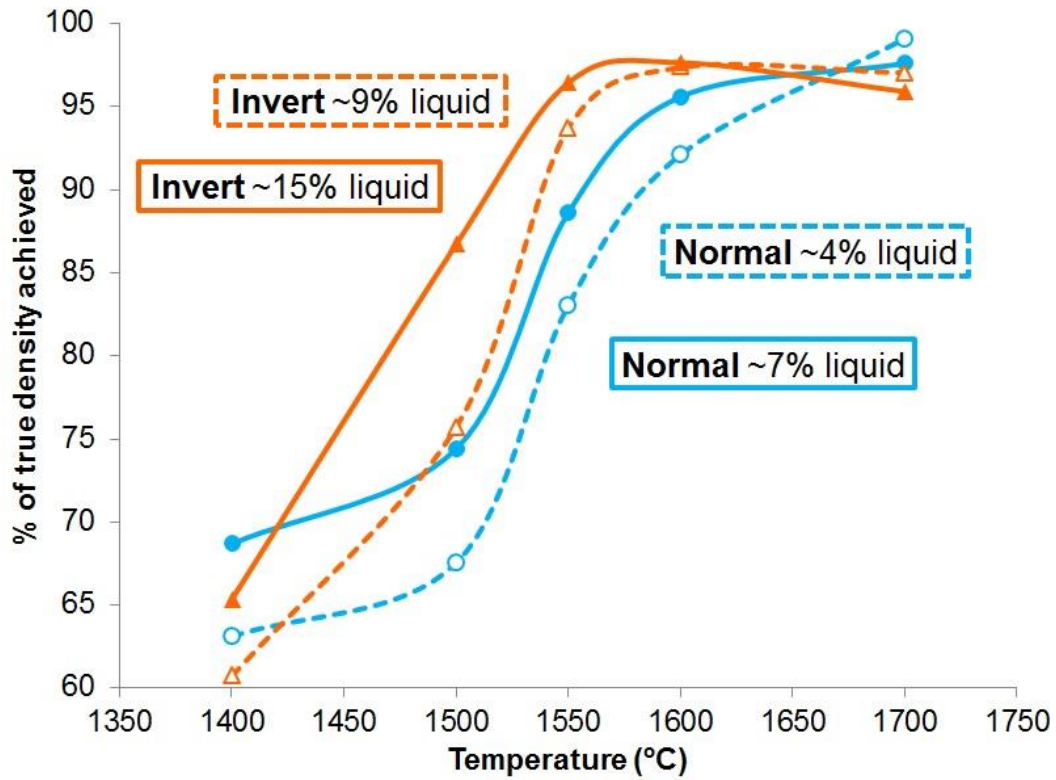


Figure 14. Densification with a liquid phase illustrating that low viscosity, invert glasses reach maximum density around 1600°C while high viscosity, normal glasses reach maximum density around 1700°C.

At 1500°C invert glasses are predicted to have at least two orders of magnitude lower viscosities than normal glasses.¹³ As previously discussed in the literature review, the controlling mechanism for densification in the second stage of liquid phase sintering is diffusion of the material through the liquid phase. Liquids having a lower viscosity allow for easier mass transport during densification, thus resulting in higher densification at lower temperatures.

The true density values for fully dense samples are presented in Table IV and compared to average measured densities in Figure 15.

Table IV. Average measured densities via immersion and true densities via helium-pycnometer.

	Invert, low liquid level (9%)	Invert, high liquid level (15%)	Normal, low liquid level (4%)	Normal, high liquid level (7%)
Measured Density (g/cm³)	3.751	3.598	3.811	3.761
True Density (g/cm³)	3.852	3.685	3.847	3.853
% Dense	97.38	97.65	99.07	97.61

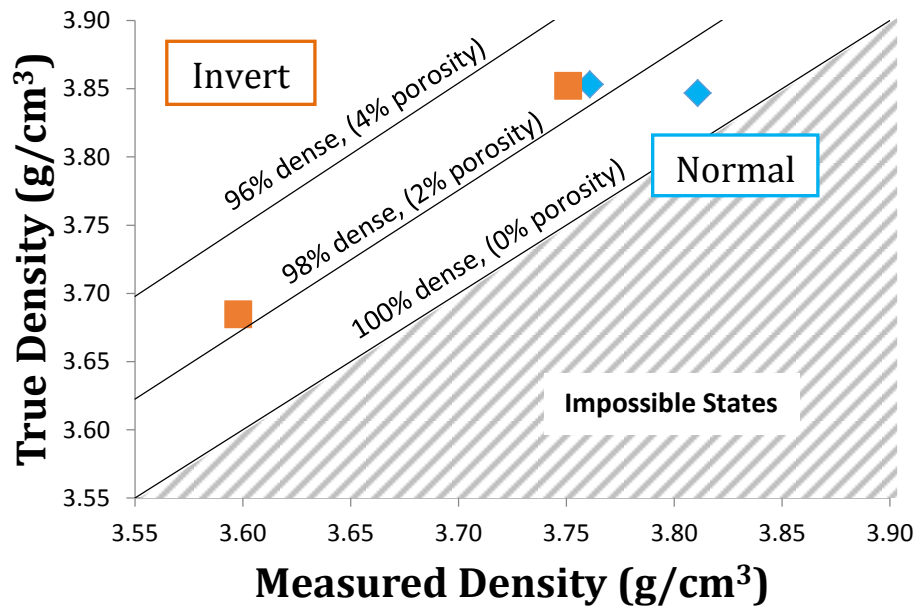


Figure 15. Plot of measured density versus true density.

It is illustrated in Figure 15 that at maximum density samples still contain some closed porosity. The microstructures support this observation.

C. MICROSTRUCTURE

Microstructures of samples containing normal and invert glasses are presented in Figures 16 and 17 respectively.

When comparing the samples containing a normal glass fired to 1550°C with low and high liquid level in Figure 16 it is clear that the overall density appears to be higher in the sample containing more liquid. A similar relationship is observed for the samples fired to 1600°C. These observations are supported by the plot presented in Figure 14. However, when approaching maximum density the images illustrate that the samples have become more similar in porosity. This indicates that the preliminary densification process may correlate with the amount of liquid in the system. Further work is necessary to evaluate the effect of the liquid quantity. The final density, however, does not appear to be influenced by the liquid level present. It can also be seen that the maximum density for normal samples is achieved at 1700°C.

Microstructures of samples containing an invert glass can be seen in Figure 17. At a temperature of 1550°C a relationship between liquid level and densification is observed. Contrary to the results of the normal samples, at 1600°C the density appears to be independent of the liquid level. This behavior can be attributed to the fact that invert samples reach maximum density around 1600°C. It can also be hypothesized that for invert samples the early stages of densification are influenced by the amount of liquid, while the later stages appear to be unaffected.

When comparing the images for normal and invert samples it can be observed that at 1550°C the density of normal samples is substantially lower than that of invert samples. It is not until the normal samples reach 1600°C that their density is comparable to invert samples fired to 1550°C. This observation supports the idea that samples containing an invert glass will densify at a lower temperature. Additionally, sintering samples at smaller temperature increments will better illustrate the densification behavior between the already tested sintering temperatures.

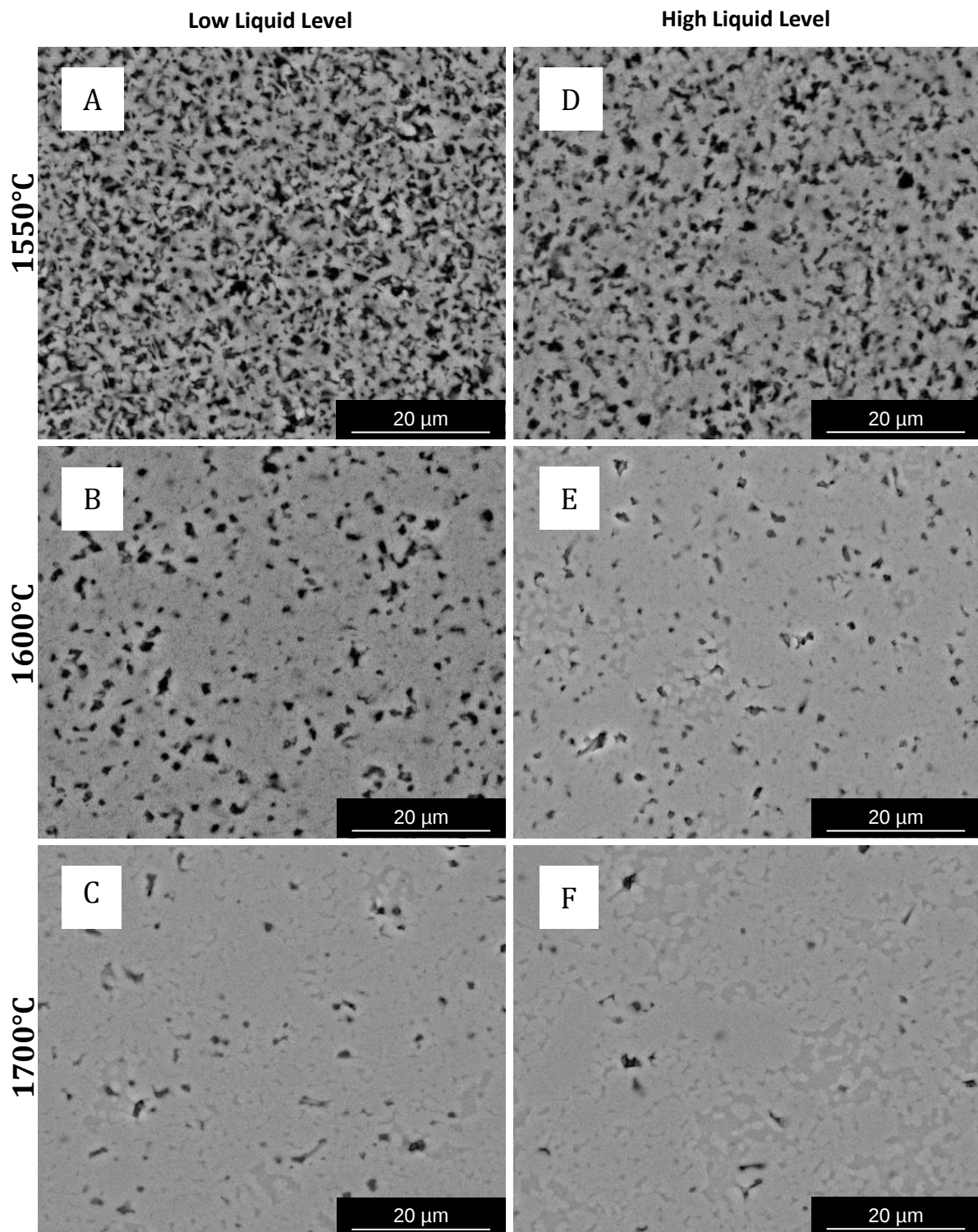


Figure 16. Backscattered electron micrographs of samples containing a normal glass and fired to 1550°C (A and D), 1600°C (B and E), and 1700°C (C and F).

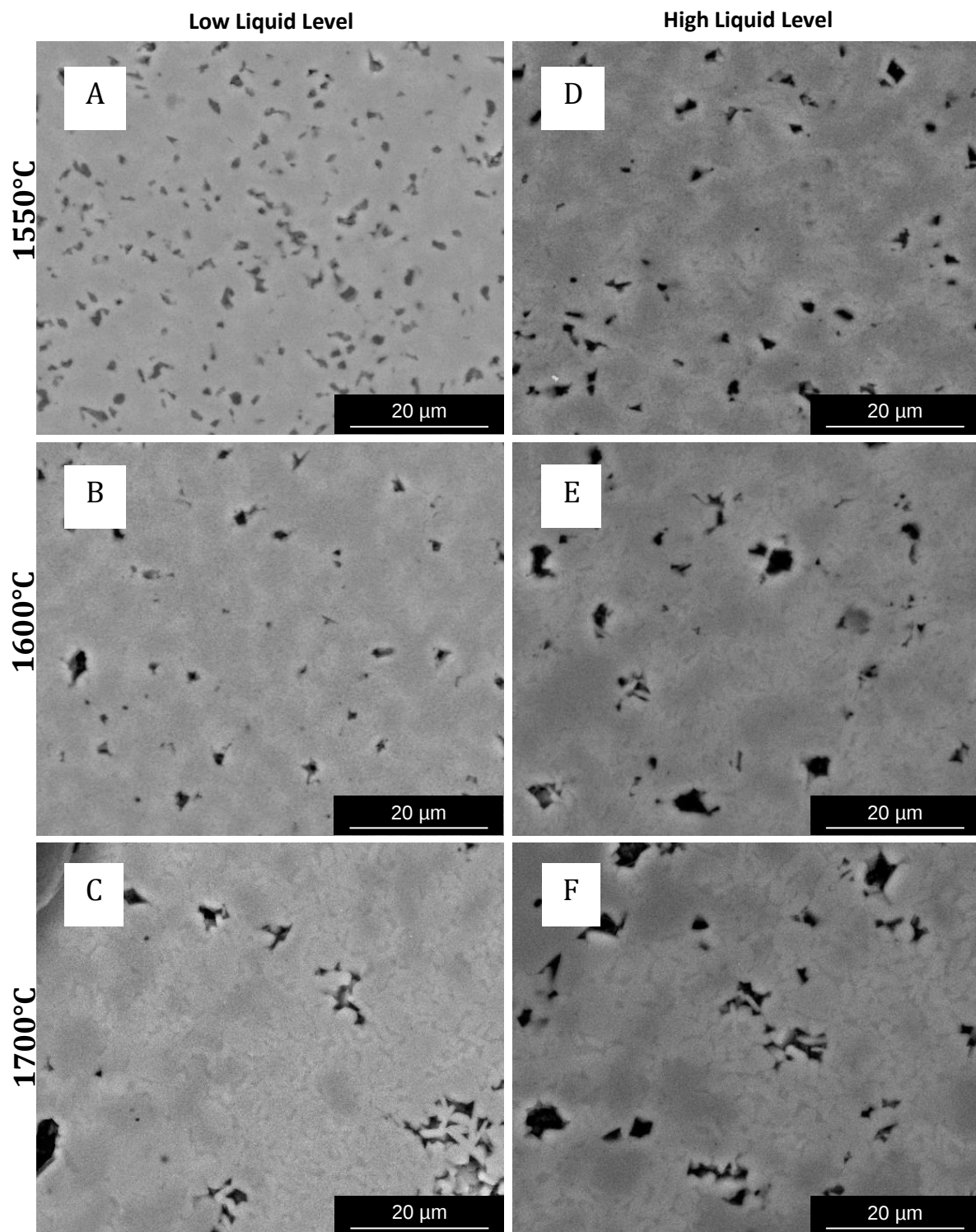


Figure 17. Backscattered electron micrographs of samples containing an invert glass and fired to 1550°C (A and D), 1600°C (B and E), and 1700°C (C and F).

The overall uniformity of the microstructures illustrates that the heterocoagulation process was a successful means of introducing glass into the alumina system because it prevented the formation of large glassy regions.

V. EVIDENCE OF DE-SINTERING WITH INVERT GLASSES

An unexpected phenomenon called de-sintering occurred in the low viscosity liquid samples. De-sintering is proposed to occur when the rate of grain growth exceeds the rate of densification. This can be best seen in Figure 17 when comparing images E and F. These images show that the samples appear to be increasing in porosity as grain growth increases. De-sintering results in a decrease in overall density as temperature increases beyond the temperature at which maximum density was achieved. Figure 14 supports this argument as it shows that the density of low viscosity liquid samples noticeably decreased above 1600°C. A t-test between two means was completed on the density at 1600°C and 1700°C to determine if there was any statistical significance between the two. The resulting p-value proved that there was a statistical significance.

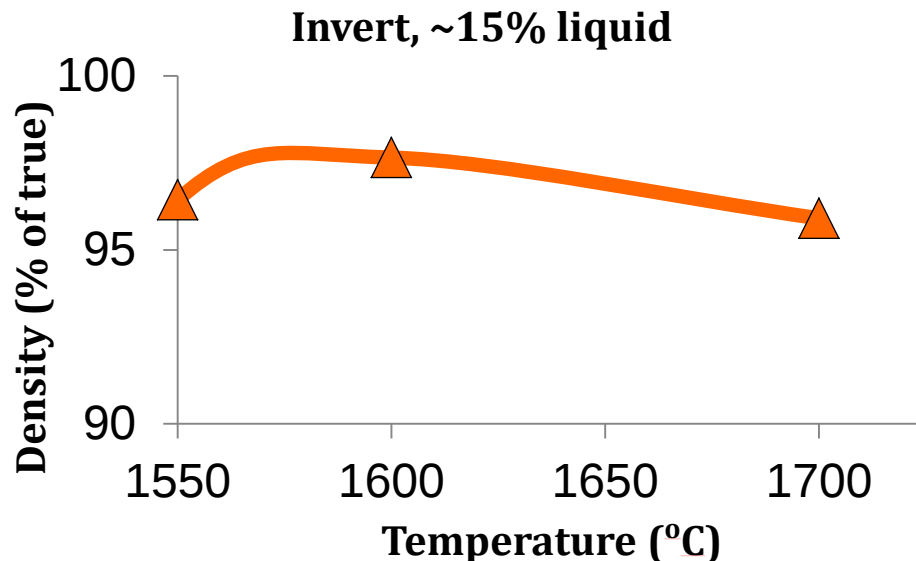


Figure 18. Evidence of de-sintering for invert glasses.

VI. CONCLUSIONS

The hypothesis appears to be correct: samples containing a low viscosity liquid densified at 1600°C while samples containing a high viscosity liquid densified at 1700°C. This proves that the densification temperature is dependent on the viscosity of the grain boundary liquid. As viscosity increases, the densification temperature appears to increase.

VII. FUTURE WORK

Future work for this study is proposed to evaluate that the densification temperature appears to be independent of the liquid level. This can be done by creating an invert glass with approximately 5% liquid and a normal glass with approximately 10% liquid. The temperature at which these samples reach full densification will either prove or disprove the assumption stated above. A schematic illustrating the proposed future work can be seen in Figure 19.

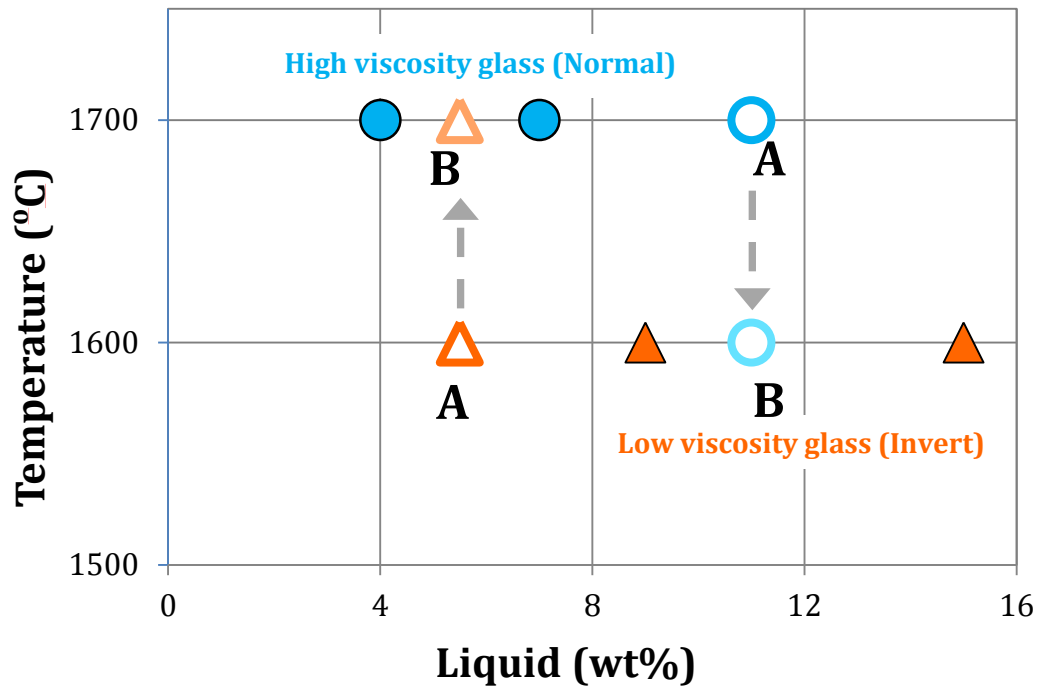


Figure 19. Proposed future work to confirm hypothesis by bracketing low and high viscosity liquid levels (open symbols on plot). Case A means the hypothesis was correct. Case B means the hypothesis was incorrect.

If the viscosity of the liquid phase dictates the densification temperature rather than the amount of liquid, then a low liquid invert glass will reach full densification at 1600°C (open triangle A) and a high liquid normal glass will reach full densification at 1700°C (open circle A). If the amount of liquid dictates the densification temperature rather than the viscosity of the liquid phase, then a low liquid invert glass will reach full densification at 1700°C (open triangle B) and a high liquid normal glass will reach full densification at 1600°C (open circle B).

IIX. REFERENCES

1. T. Lam, "*Glass Formation Boundary Approach to the Sintering of Alumina*," Ph.D. Thesis, Alfred University, Alfred, NY, 2010.
2. K.J. DeCarlo, T.F. Lam, and W.M. Carty, "*Dissolution of Alumina in Silicate Glasses and the Glass Formation Boundary*," *Ceram. Trans.*, **209**, 61-9 (2010).
3. N.P. Padture and H.M. Chan, "*Improved Flaw Tolerance in Alumina Containing 1 vol% Anorthite via Crystallization of the Intergranular Glass*," *J. Am. Ceram. Soc.*, **75** [7], 1870-5 (1992).
4. W.M. Carty, "*Controlled Distribution of Nano-scale Sintering Dopants*". US Patent US 8192679 B2, 2012.
5. T. Kimura, Y. Kaneko, and T. Yamaguchi, "*Consolidation of Alumina Zirconia Mixtures by a Colloidal Process*," *J. Amer. Cer. Soc.*, **74** [3], 625-626, (1991).
6. R.M. German, *Liquid Phase Sintering*; p. 65-151. Plenum Press, New York, 1985.
7. M.N. Rahaman, *Ceramic Processing and Sintering*; p. 620-668. Marcel Dekker, New York, 2003.
8. J.S. Reed, *Principles of Ceramics Processing, 2nd Edition*; p. 608-609. Wiley-Interscience, New York, 1995.
9. J.E. Shelby, *Introduction to Glass Science and Technology*, 2nd ed. Royal Society of Chemistry, 2005.

10. J. Otminski, "*Predicting Glass Formation from Melt Viscosity and Fragility*", B.S. Thesis, Alfred University, Alfred, NY, 2013.
11. R. de Levie, "*How to use Excel in Analytical Chemistry and in General Scientific Data Analysis*", pp. 311. Cambridge University Press, UK, 2001.
12. SciVision, SciGlass Version 6.5, Glass Property Information System, Lexington, MA, 2005.
13. T. Lam, Private communication.
14. M. Moesgaard and Y. Yue, "*Compositional Dependence of Fragility and Glass Forming Ability of Calcium Aluminosilicate Melts*," *J. Non-Cryst. Solids*, **355** [14-15], 867-873, (2009).
15. P. A. Marchlewski, A.R. Olszyna, K.J. Kurzydowski, B. Ralph, "*Grain Growth in High-Purity Alumina Ceramics Sintered from Mixtures of Particles of Different Sizes*," *Ceram. Int.*, **23**, 157-63, (1997).
16. A.R. Olszyna, P. Marchlewski, and K.J. Kurzydowski, "*Sintering of High Density, High-Purity Alumina Ceramics*," *Ceram. Int.*, **23**, 323-28, (1997).
17. K. McDevitt, "*The Effect of Impurities on Microstructure Evolution in Alumina*", B.S. Thesis, Alfred University, Alfred, NY, 2013.
18. B. Brydson, S. Chen, et. al., "*Microstructure and Chemistry of Intergranular Glassy Films in Liquid-Phase-Sintered Alumina*," *J. Amer. Cer. Soc.*, **81** [2], 369-79, (1998).

19. ASTM Standard C20-00, *“Standard Test Methods for Apparent Porosity, Water Absorption, Apparent Specific Gravity, and Bulk Density of Burned Refractory Brick and Shapes by Boiling Water”* ASTM International, West Conshohocken, PA, 2010.

IX. APPENDIX

Table V. Complete ICP-ES analysis results

		Ca:SiO ₂	1:5	1:5	3:1	3:1
		actual CaO:SiO ₂	1:5.33	1:5.23	2.68:1	2.69:1
		% alumina	0.946772	0.966421	0.905633	0.9439
Analyte	Unit	MDL				
SiO ₂	%	0.01	4.42	2.72	2.44	1.46
Al ₂ O ₃	%	0.01	94.45	95.84	86.66	91.53
Fe ₂ O ₃	%	0.04	<0.04	0.04	<0.04	<0.04
MgO	%	0.01	0.02	0.02	0.02	0.02
CaO	%	0.01	0.83	0.52	6.54	3.93
Na ₂ O	%	0.01	0.04	0.03	0.03	0.03
K ₂ O	%	0.01	<0.01	<0.01	<0.01	<0.01
TiO ₂	%	0.01	<0.01	<0.01	<0.01	<0.01
P ₂ O ₅	%	0.01	<0.01	<0.01	<0.01	<0.01
MnO	%	0.01	<0.01	<0.01	<0.01	<0.01
Cr ₂ O ₃	%	0.002	<0.002	<0.002	<0.002	<0.002
Ba	PPM	5	31	34	32	34
Ni	PPM	20	<20	<20	<20	<20
Sr	PPM	2	5	5	12	9
Zr	PPM	5	18	16	17	15
Y	PPM	3	<3	<3	<3	<3
Nb	PPM	5	<5	6	<5	<5
Sc	PPM	1	<1	<1	<1	<1
LOI	%	-5.1	0.2	0.8	4.3	3
Sum	%	0.01	99.97	99.99	99.99	99.97
TOT/C	%	0.02	<0.02	<0.02	<0.02	0.03
TOT/S	%	0.02	<0.02	<0.02	<0.02	<0.02

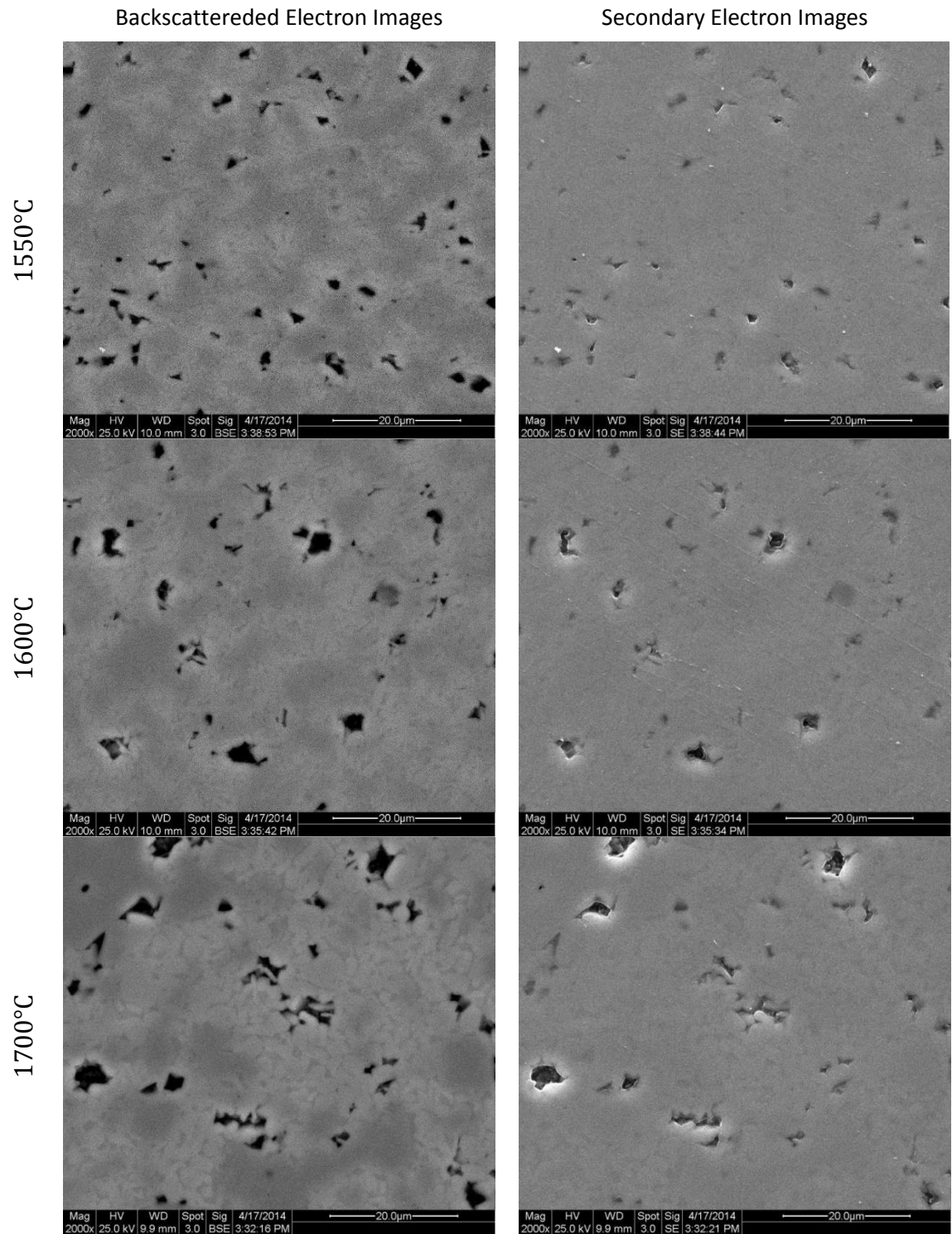


Figure 20. 15 % invert glass (size bar=20µm).

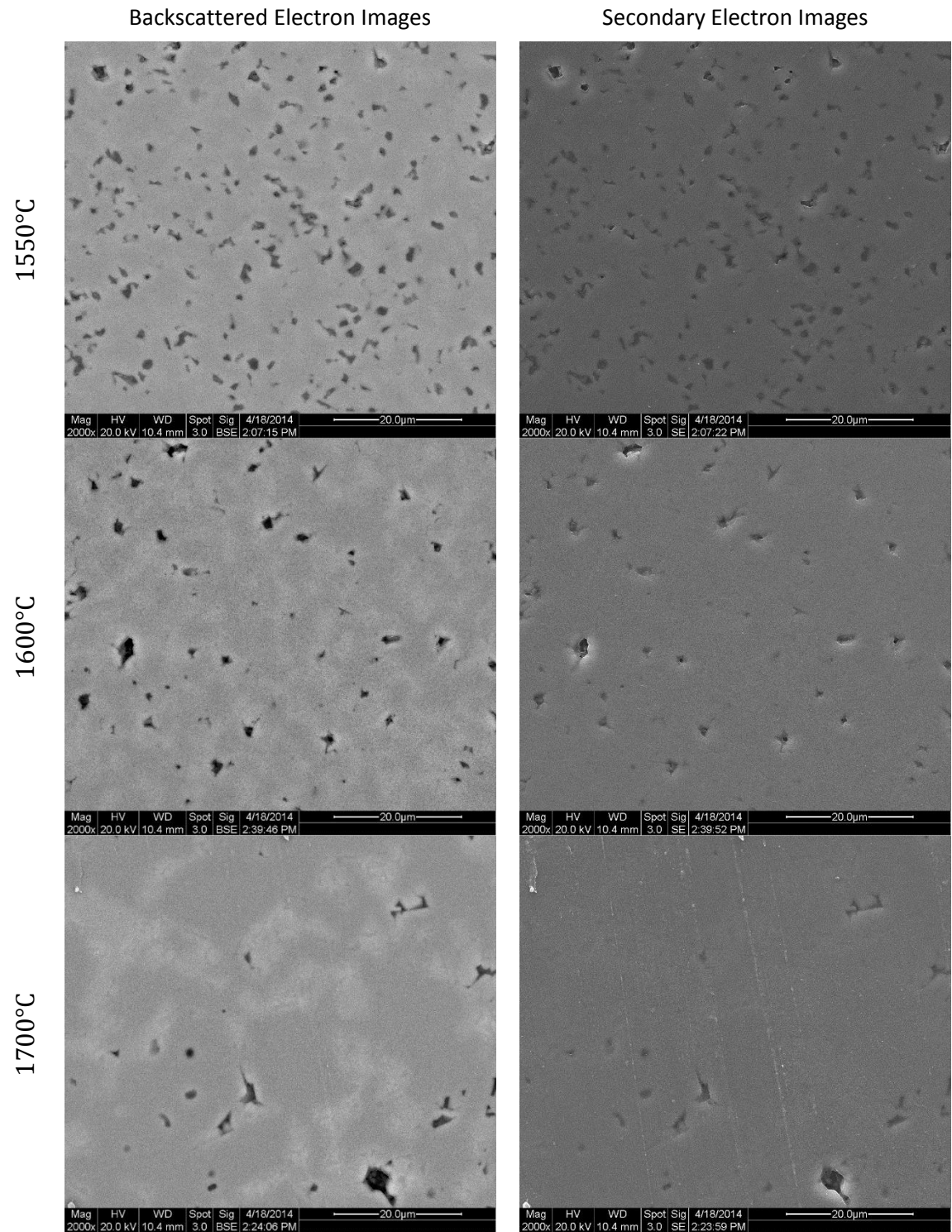


Figure 21. 9% invert glass (size bar=20μm).

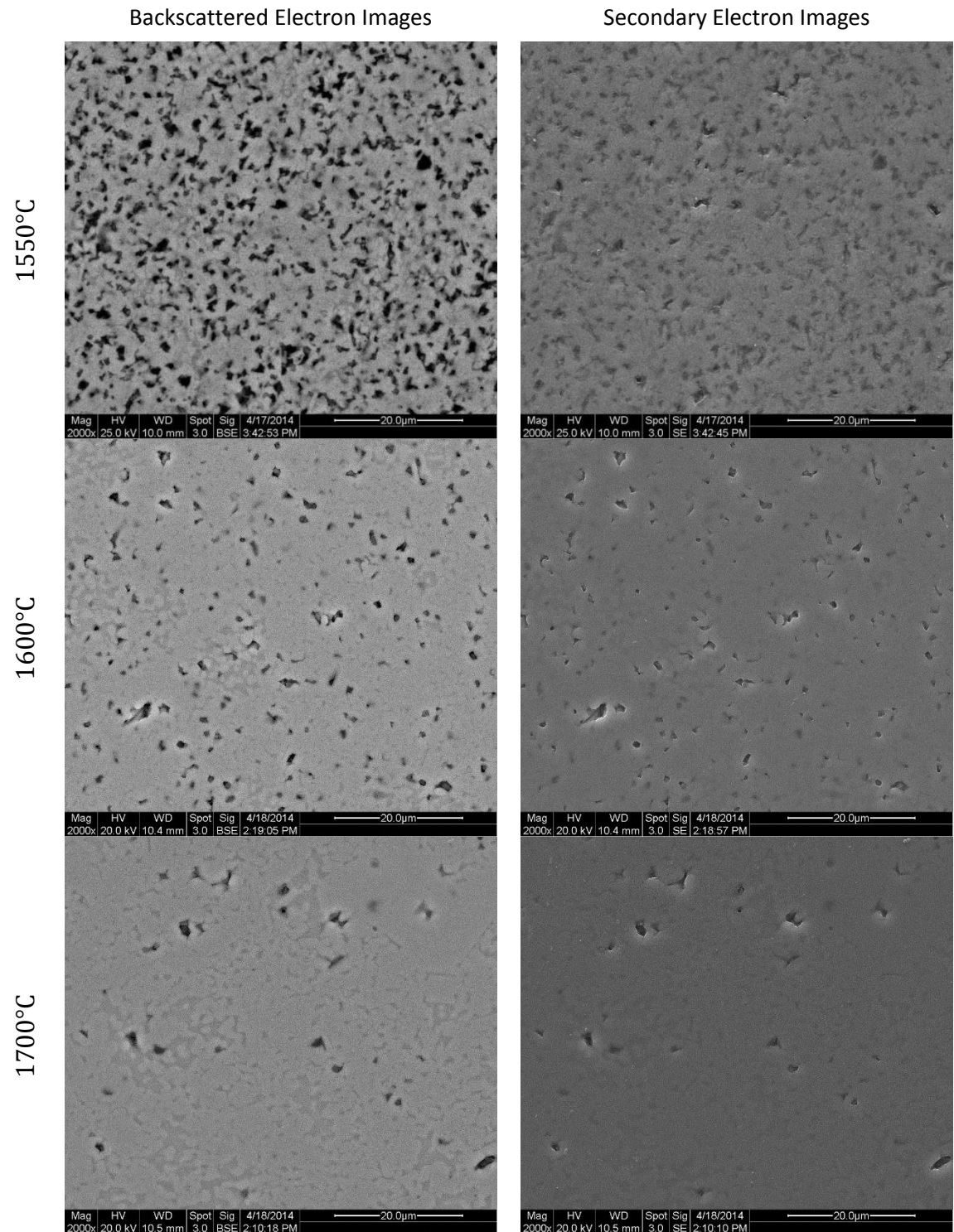


Figure 22. 7% normal glass (size bar=20µm).

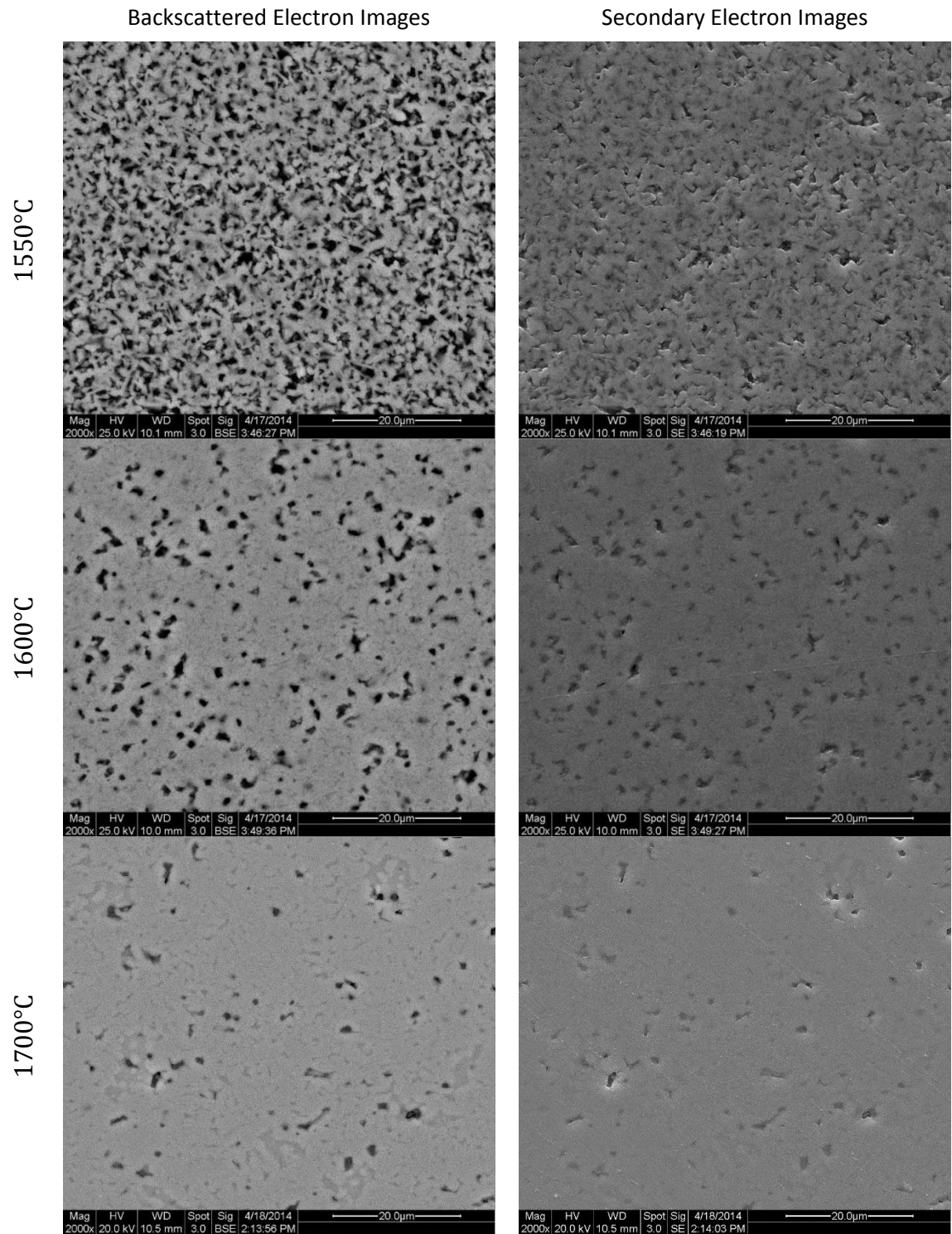


Figure 23. 4% normal glass (size bar=20µm).

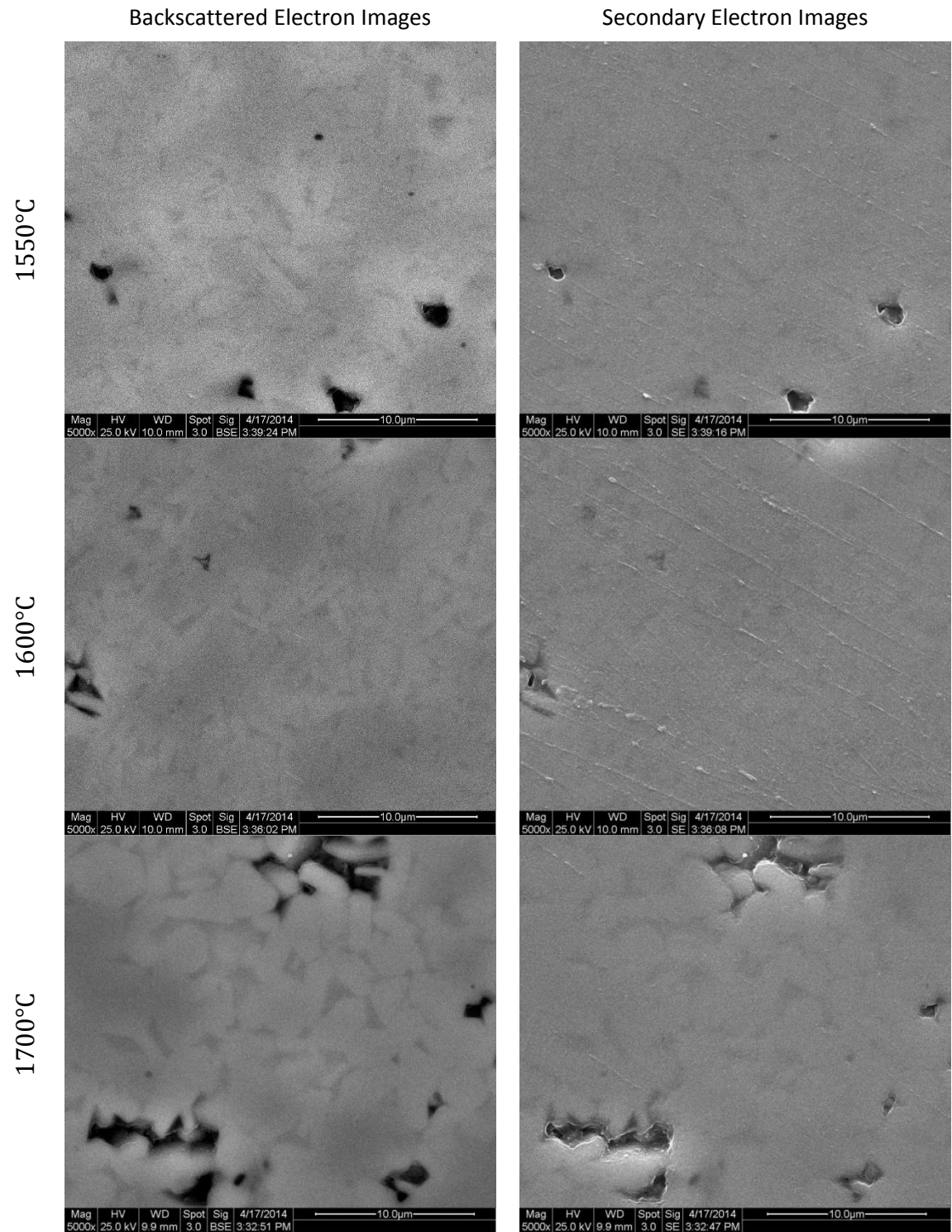


Figure 24. 15% invert glass (size bar=20µm).

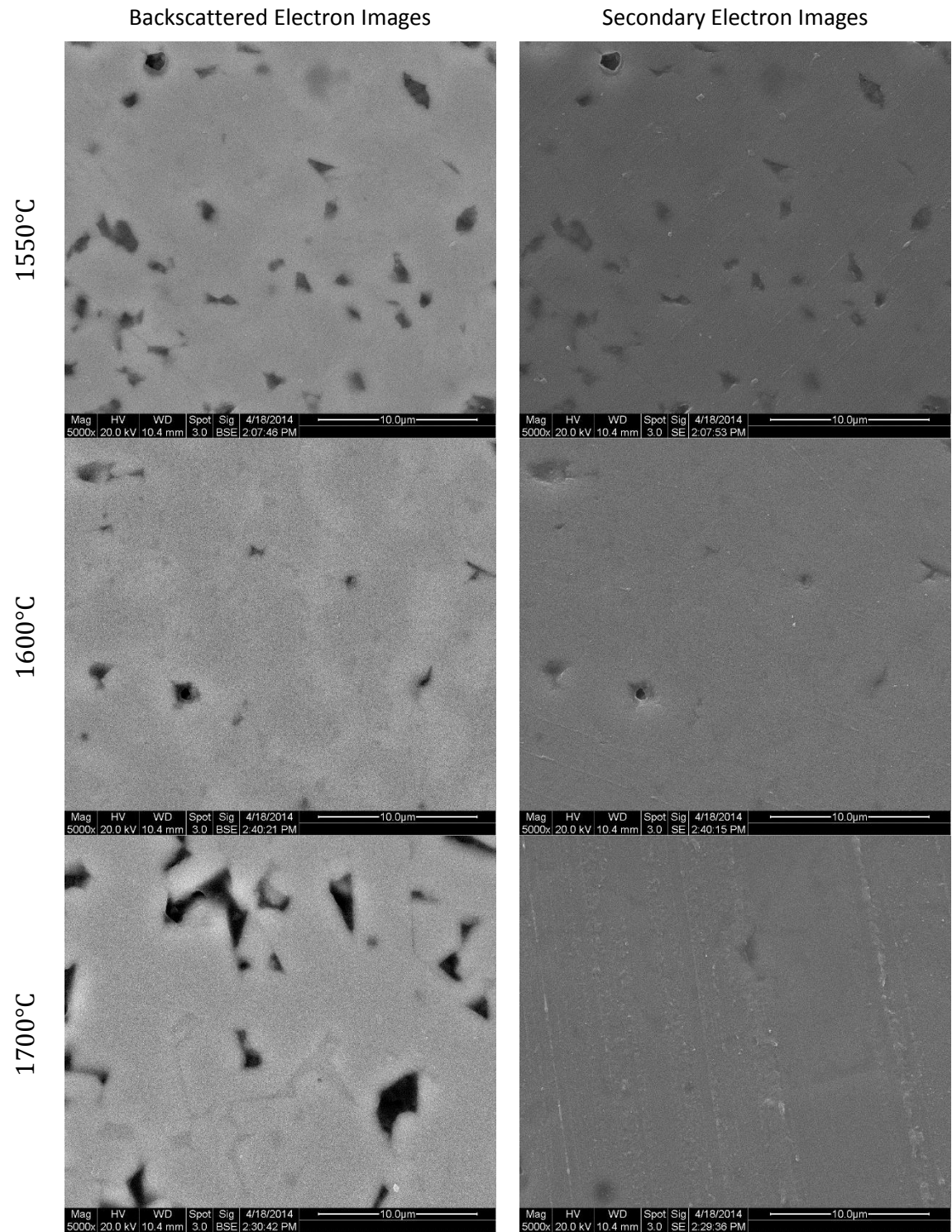


Figure 25. 9% invert glass (size bar=20µm).

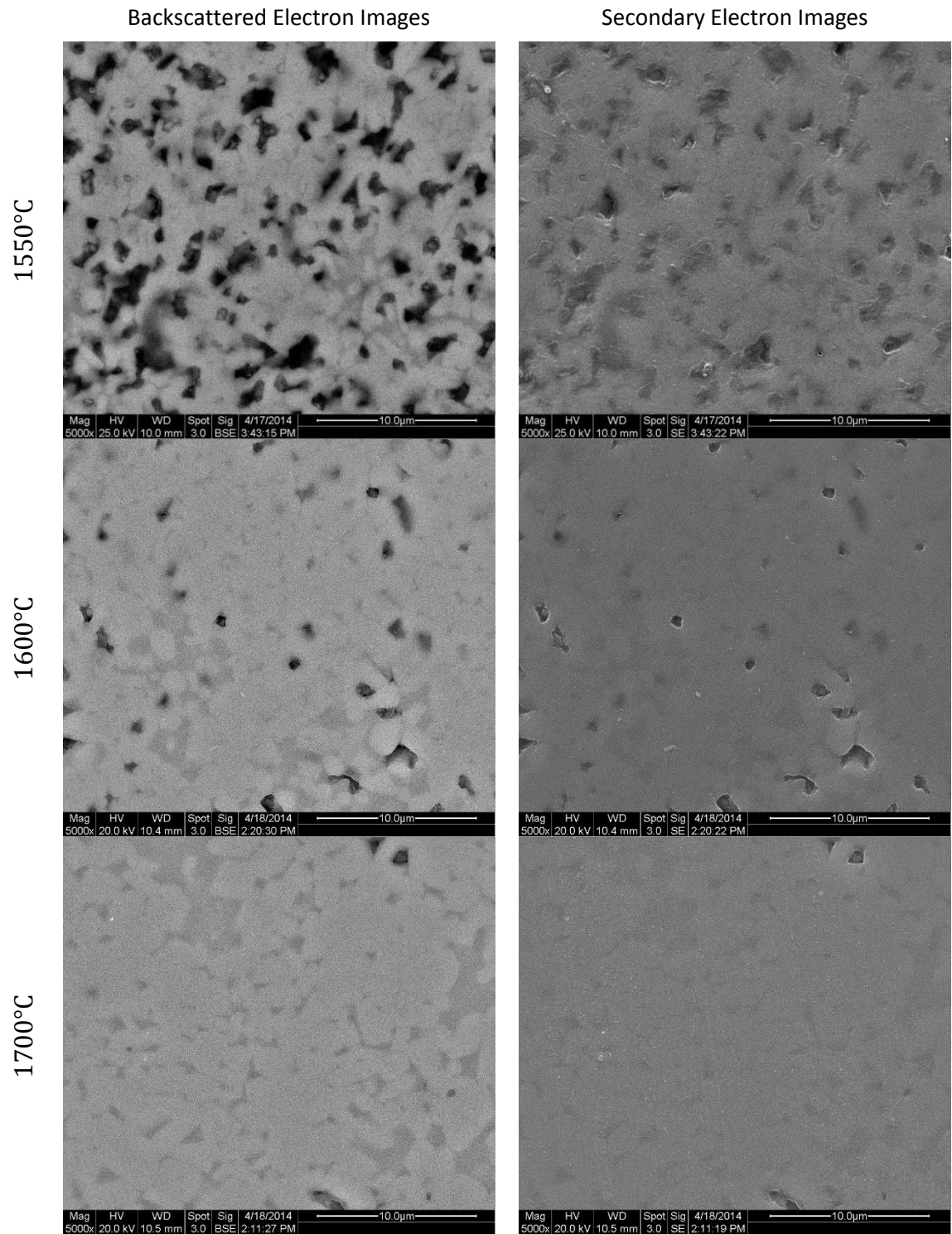


Figure 26. 7% normal glass (size bar=20µm).

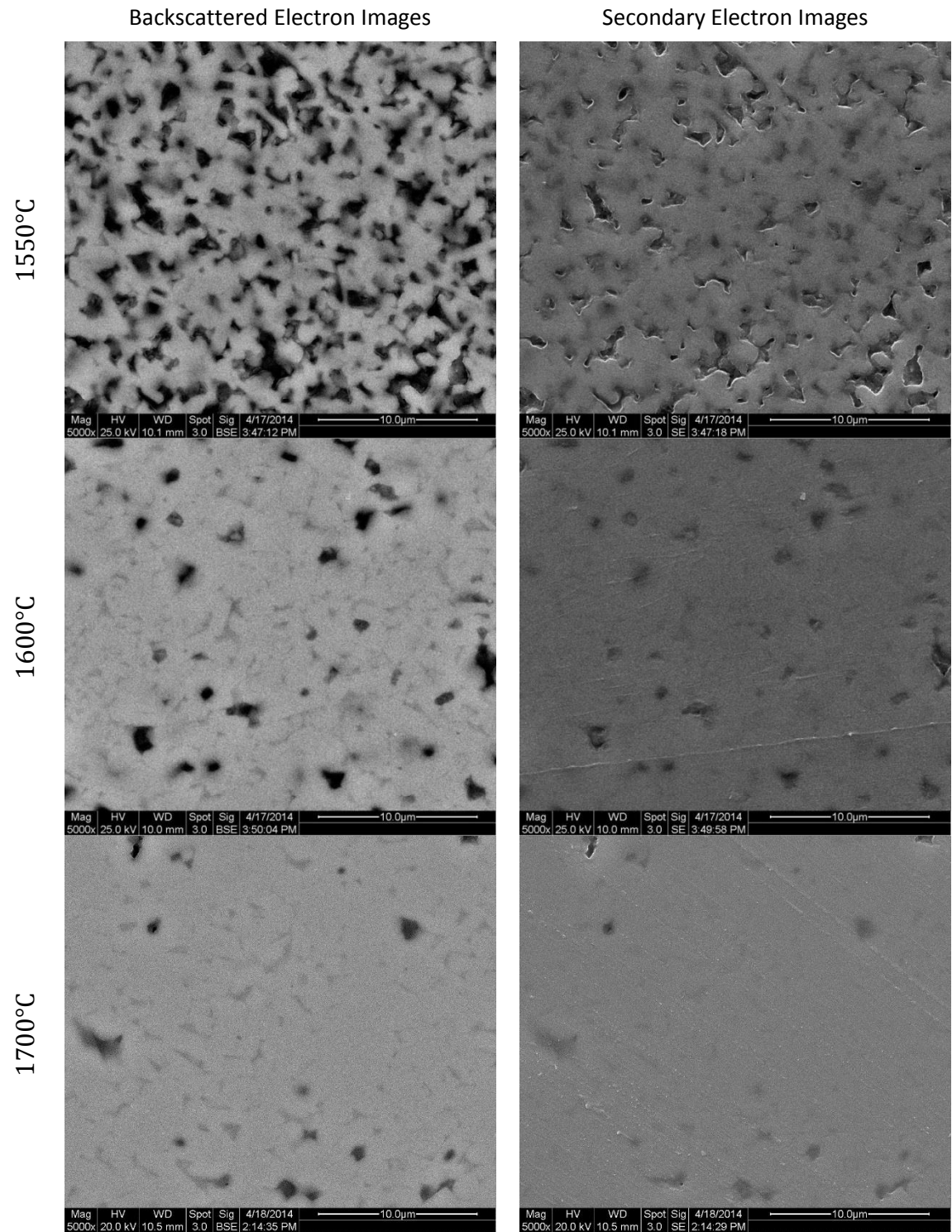


Figure 27. 4% normal glass (size bar=20µm).