CONTAINERLESS LIQUID-PHASE PROCESSING OF CERAMIC MATERIALS

FINAL REPORT

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by

Dr. J.K.Richard Weber, Principal Investigator
Dr. Paul C. Nordine, Co-Investigator

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Containerless Research, Inc.
910 University Place
Evanston, IL 60201

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Richard Weber and Paul Nordine
Containerless Research, Inc., Evanston, IL 60201, USA

Background:

The present project builds on the results of research supported under a previous NASA grant to investigate containerless liquid-phase processing of molten ceramic materials. The research used an aero-acoustic levitator in combination with cw CO_2 laser beam heating [1,2] to achieve containerless melting, superheating, undercooling, and solidification of poorly-conducting solids and liquids. Experiments were performed on aluminum oxide, binary aluminum oxide-silicon dioxide materials, and oxide superconductors, the results and their interpretation are presented in detail in the referenced publications [1-9].

Accomplishments in the research were to:

1. Investigate liquid-phase processing, undercooling, and solidification of aluminum oxide, alumino-silicate, and YBaCuO melts *vs* the ambient (pO_2) and thermal history.

2. Conduct CO_2 laser melting experiments in reduced gravity aboard the KC-135 in collaboration with scientists from École Polytechnique Université de Montréal.

3. Develop a new method, laser hearth melting, for synthesis of bulk, high purity ceramic oxide materials from powders.

4. Characterize processed materials using SEM, X-ray diffraction analysis, and optical microscopy.

5. Perform collaborative research with other NRA-supported investigators at Jet Propulsion Laboratory, University of Missouri-Rolla, University of Wisconsin-Madison, and Vanderbilt University.

6. Publish and present results.

Experimental Methods:

Containerless melting experiments were performed with *ca.* 0.3 cm. diameter spherical specimens of oxides which were made by laser hearth melting [9]. Specimens were levitated in an aero-acoustic levitator [1,2]. The levitation force is primarily aerodynamic and is stabilized by the smaller acoustic forces to obtain precise control of the position of levitated solid and liquid samples. Laser beam heating and melting become possible to allow liquid phase processing and property measurement experiments under containerless conditions at very high temperatures.

A schematic plan view layout of the instruments used to observe the levitated specimen is presented in Figure 1. The levitator provides wide optical access to the specimen making it possible to integrate a variety of non-contact diagnostic instruments.

Results:

Selected results from th research are presented below. Full reports of the methods and results of this research can be found in the literature [1-10].

The ambient oxygen fugacity (or pressure) was shown to have a large effect on the properties and solidification behavior of oxide melts. Figure 2 presents measurements of the degree of undercooling for molten aluminum oxide as a function of the ambient oxygen fugacity and cooling rate. Figure 3 presents the oxygen fugacity dependence of the absorption coefficient for molten aluminum oxide.

Aluminum oxide is a highly stoichiometric material for which any composition changes in response to changes in the ambient oxygen fugacity are exceedingly small. Nevertheless, it can be seen in these results that the small composition changes that do occur have a profound influence on the measured properties and phenomena. Other systems in which a large effect of the ambient oxygen fugacity have been found include the formation of amorphous (glass) materials upon cooling of melts for materials with (i) the yttrium-aluminum garnet (YAG) composition and (ii) the mullite ($Al_6Si_2O_{13}$) composition [10].

Pask [11] predicted that aluminum oxide-silicon dioxide melts should exhibit liquid-liquid phase separation under non-equilibrium undercooled conditions. However observation of this phenomena must contend with the fact that cooler regions of the liquid become transparent, and it is the development of transparent regions that is taken to indicate phase separation. Since rapid cooling or large temperature gradients are needed to access the undercooled state, ambiguities occur. We observed that regions of different optical brightness formed in the liquid for rapidly cooled melts. The distribution of these regions was not related to the known temperature gradients that also occurred. Upon further cooling, the samples crystallized to form solids of different composition, which could occur whether or not liquid phase separation was present. The results suggest that liquid-liquid phase separation occurred, but further work is required to prove that the observation has no other interpretation. It may be necessary to perform undercooling experiments under more quiescent levitation conditions, e.g., in low gravity, to fully investigate this phenomenon.

The residual Cr^{3+} content of aluminum oxide was investigated in collaboration with Dr. A. Biswas (Jet Propulsion Laboratory) by performing LIF studies after containerless melt purification. It was demonstrated that containerless processing decreased the Cr^{3+} content by several orders of magnitude from the already small amount of a few ppm. Final Cr^{3+} contents of the samples were as small as 10^{12} atoms/cm^{-3}. Figure 4 shows the Cr^{3+} concentration in processed specimens as a function of the processing conditions.

Additional liquid-phase processing experiments were performed on (i) glass formation in the calcium oxide-gallium oxide system with Professor Delbert Day and Dr. Chandra Ray from the University of Missouri-Rolla; (ii) levitation melting of basalt materials with Professor Reid Cooper and Mr. John Fanselow from the University of Wisconsin-Madison; and (iii) levitation melting of YBaCuO superconductors with Professor William Hofmeister and Mr. James Olive from Vanderbilt University.

Need for Microgravity:

Containerless ground-based research capabilities will ultimately be insufficient to fully investigate the research hypothesis. Microgravity conditions will be required to achieve sufficient mechanical quiescence and thermal and chemical homogeneity while also obtaining the control of melt chemistry and purity provided in containerless experimental conditions. For example, in microgravity, chemical transport rates can be made sufficiently small, after isothermal equilibration with the ambient gas, that negligible composition changes during subsequent processing steps. Rapid stirring of the melts resulting in rapid composition changes is unavoidable on earth, due to natural convection, the forces required in levitation, and the Marangoni and the buoyant forces that result from property gradients in the liquid specimens.

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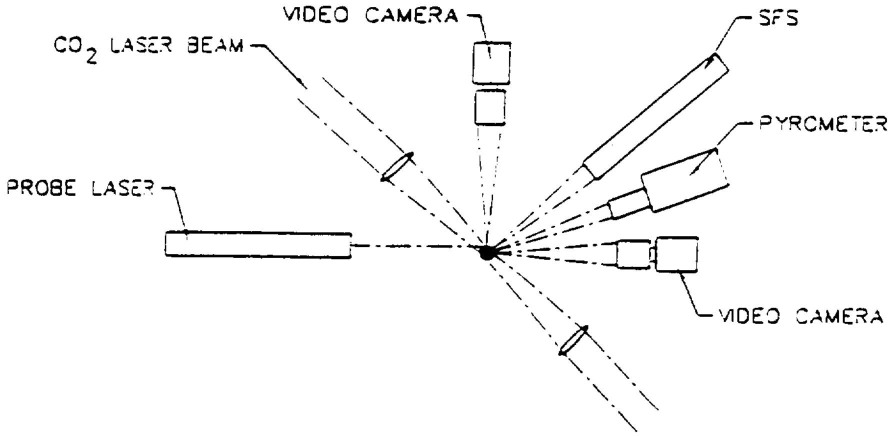
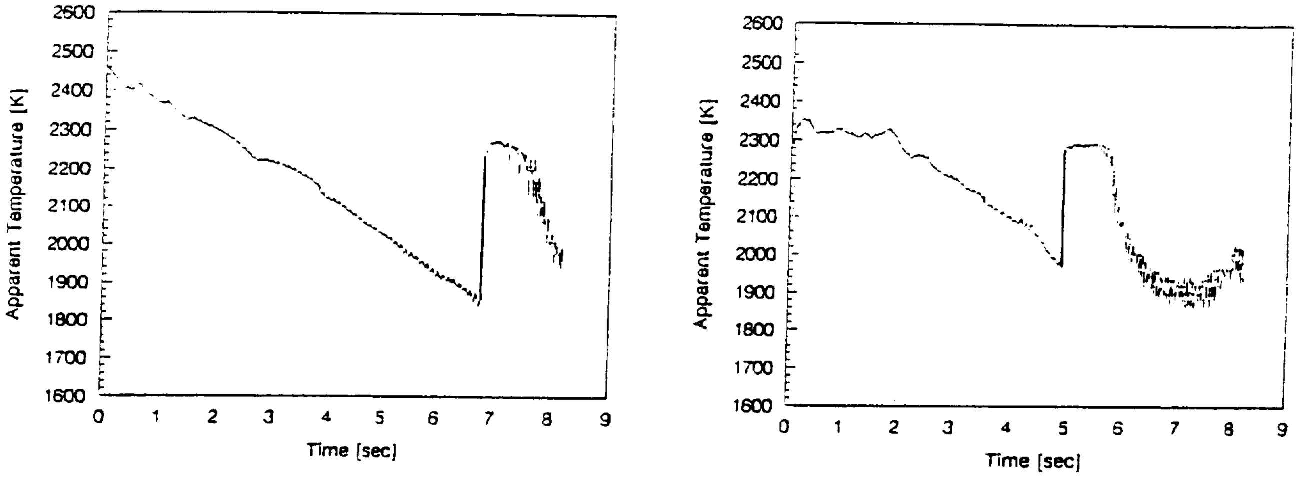


Figure 1. Schematic layout of the aero-acoustic levitator and associated instruments.



a

b

Figure 2. Cooling curves showing undercooling and recalescence of liquid aluminum oxide formed from sapphire. (a) Slow cooling in argon, and (b) slow cooling in oxygen by programmed reduction of laser intensity. From ref. 5.

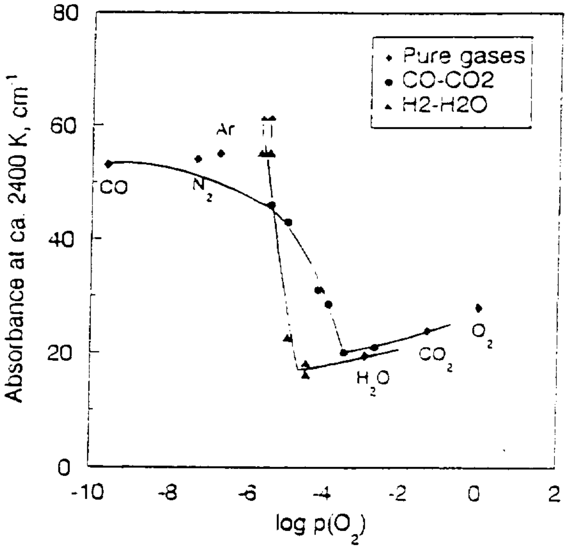


Figure 3. Spectral absorption coefficient at $\lambda = 0.633$ μm of molten aluminum oxide at approximately 2400 K *vs* ambient oxygen pressure. From ref. 8.

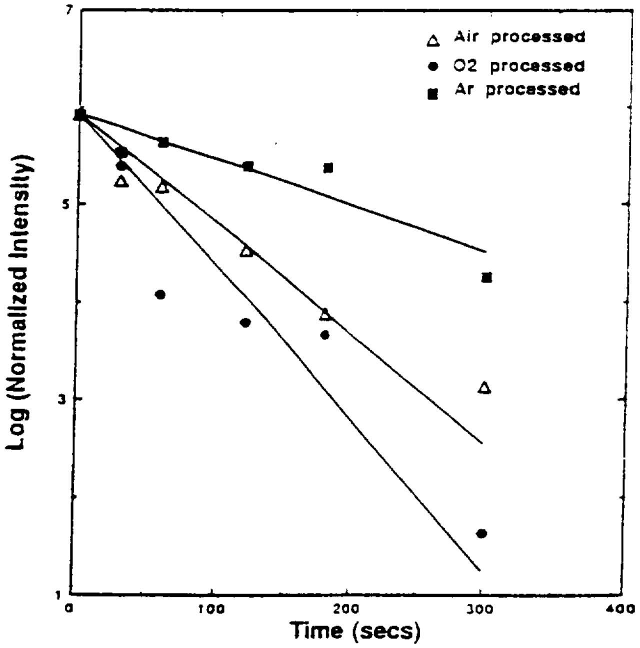


Figure 4. Logarithm of normalized LIF intensity *vs* time for molten sapphire specimens processed in argon, air and oxygen. The lines represent least squares fits to the data obtained by constraining the intercept. From ref. 6.

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