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Niobium Oxide-Metal Based Seals for High Temperature Applications

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ABSTRACT

The present final report describes technical progress made in regards to evaluating niobium oxide/alumina as a high temperature seal material. Fabrication and characterization of specimens comprising niobium oxide and alumina composites of various compositions was performed. The goal was to identify regions where a glass formed. There were no experimental conditions where a glassy phase was unequivocally identified. However, the results led to the formation of an interesting class of fibrous composites which may have applications where high compliance and high toughness are needed. It is clear that vapor phase sintering is an active mass transport mechanism in Nb_2O_5-Al_2O_3 composites (Figure 1), and it may be possible to design porous materials by utilizing vapor phase sintering.

The compositions evaluated in the present work are 52, 60, 73, 82 and 95 mol. % Nb_2O_5 with the remainder Al_2O_3. These were chosen so that some eutectic composition was present during cooling, in an attempt to encourage glass formation. However, the presence of large, elongated crystals, both in the slow cool and the quench experiments indicates that the driving force for crystallization is very high.

Several joints were formed between high purity alumina with two compositions (60 and 82 mol. %) forming the joint. These were created by grinding and polishing alumina surfaces and stacking them end-to-end with the powdered Nb_2O_5-Al_2O_3 material in between. Joining was accomplished in air at temperatures between 1400ºC and 1450ºC. The joints failed during subsequent machining for strength bars, indicating low strength. It may be possible to use the compositions evaluated here as a joint material, but it seems unlikely that a glassy phase could be produced while joining.

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RESULTS OF WORK DURING THE REPORTING PERIOD

APPROACH

Proposed Concept and Specific Objectives. The concept proposed is to utilize a reaction between the native oxide in Nb and Al_2O_3 to create a wettable, thermodynamically stable compound that can be used to seal oxides to oxides or metals for high temperature application. Our preliminary results indicate that a liquid phase forms in Nb-Al_2O_3 powder compacts at elevated temperatures (~1400ºC) and remains amorphous during cooling. The phase diagram between Nb_2O_5, which is believed to be the native oxide of Nb in this case, and Al_2O_3 indicates the presence of a eutectic at approximately 1400ºC [3]. The next section includes a more detailed discussion of phase equilibria – a literature search revealed the presence of three, somewhat conflicting phase diagrams. Indications that the liquid phase which forms at elevated temperature is not crystalline include the lack of detection with x-ray diffraction, and the unique contrast in the SEM (Figure 2). Furthermore, it is clear in Figure 2b that this secondary phase wets alumina; note that the alumina grain size is the same in b) as in a) and that all the grains are coated with this phase. The work described in this proposal will focus on understanding the conditions that maximize the formation of this secondary phase. While the appropriate ternary diagram has not yet been developed, it is likely that the presence of a third constituent lowers the eutectic temperature, indicating that the system may be tailored to create a material with the desired sealing temperature.

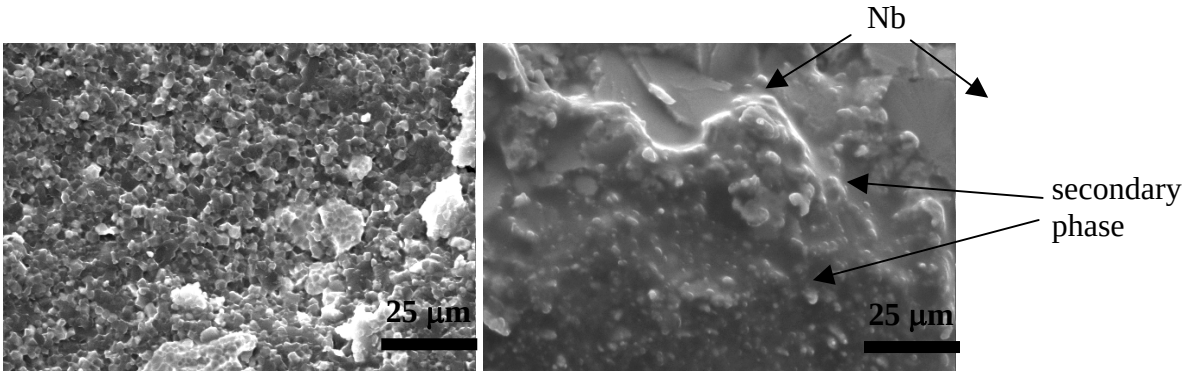


Figure 2. Scanning electron micrographs of the fracture surfaces of Nb-Al_2O_3 composites for a **a)** 20 % Nb composition, and **b)** 60 vol. % Nb composition. a) contains mostly Al_2O_3 grains, fractured intergranularly, but does not contain secondary phase. b) indicates that all of the alumina regions (lower two thirds of the micrograph) are covered with a secondary phase, believed to be amorphous. This secondary phase provides the low contrast appearance in the image. Its presence occurs only in Nb/Al_2O_3 compositions above about 60 vol. % Nb.

The following objectives serve to determine whether or not the proposed system is feasible for sealing high temperature gas separation membranes:

1. Establish the experimental conditions necessary to produce a glassy phase in Nb-Al_2O_3 compacts.

2. Explore compositions with regards to wetting and thermal stability.

3. Produce and mechanically test several porous/dense alumina joints.

THEORETICAL CONSIDERATIONS

The following three are the only known existing phase diagrams for Nb_2O_5-Al_2O_3 (Figure 3). It is noted that several discrepancies between the three diagrams exist, particularly at the high Nb_2O_5 composition range. Relatively little is known about equilibrium states in this system.

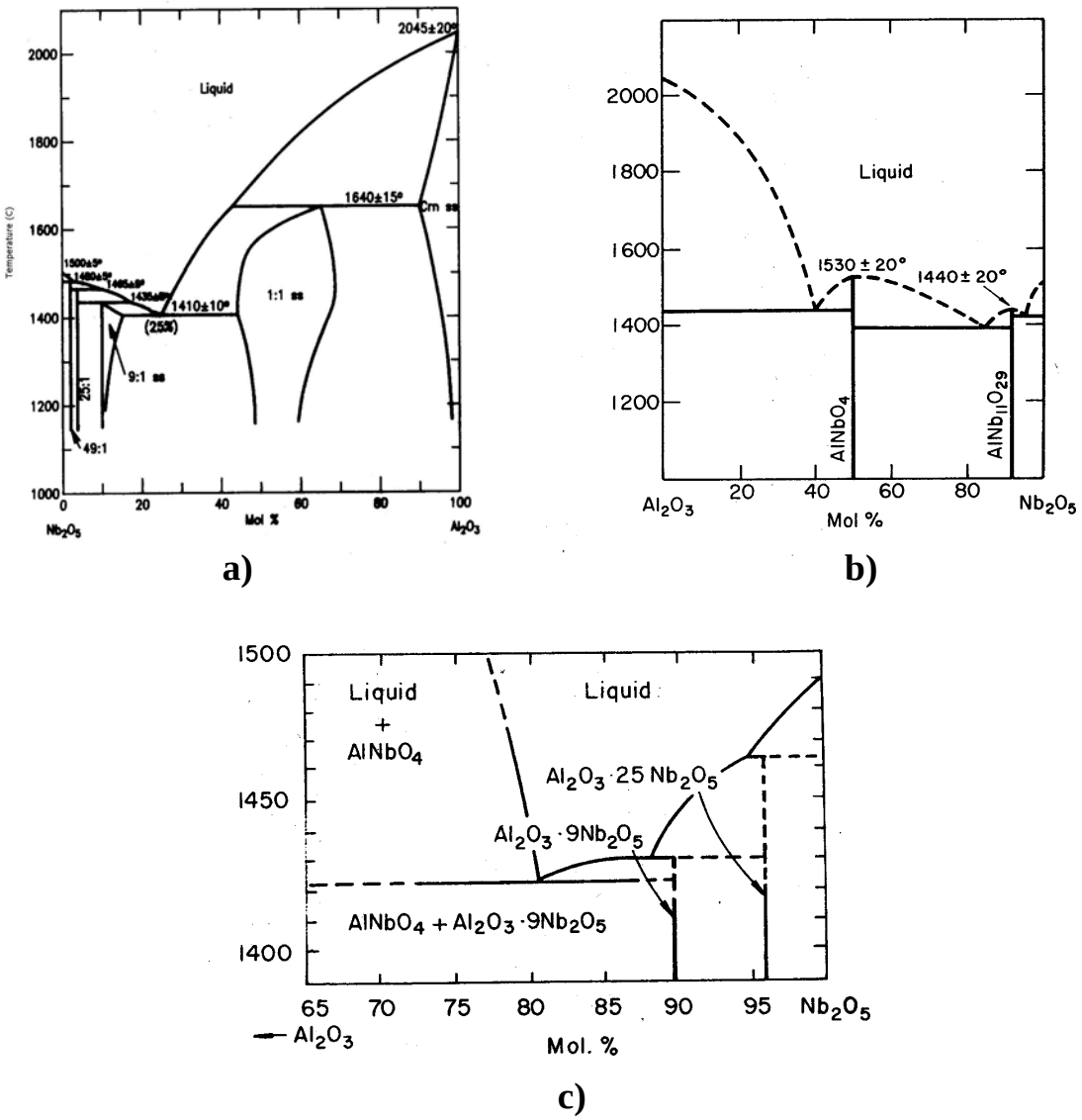


Figure 3. The three existing phase diagrams for Al_2O_3-Nb_2O_5 are in disagreement. **a)** from [3]; **b)** from [4]; **c)** from [5].

However, the three diagrams agree that a eutectic exists between Nb_2O_5 and Al_2O_3, and the wide variety of compositions studied in the present experiments is designed to encompass the eutectic composition.

It is noted that an application of the well-accepted Zachariasen's rules that establish the conditions which constitute what oxides are glass formers shows that Nb_2O_5 is a conditional glass former [6]. A conditional glass former implies that it can form a glass in the presence of another oxide. It is hypothesized that the secondary phase observed in the present study (Figure 2b) is a Nb_2O_5-based glass which formed due to the presence of Al_2O_3 during the melt. It is possible that another oxide, such as CaO, may also enable Nb_2O_5 to form a glass. While Nb_2O_5 has not previously been observed to form a glass as a bulk (i.e., from the melt), it has as a thin, semiconducting film [7].

The considerations discussed above suggest that compositions near the eutectic may form glass at relatively low temperatures.

The following phase diagram (Figure 4) illustrates the most relevant compositions examined to date. Various peak temperatures and cooling rates were used.

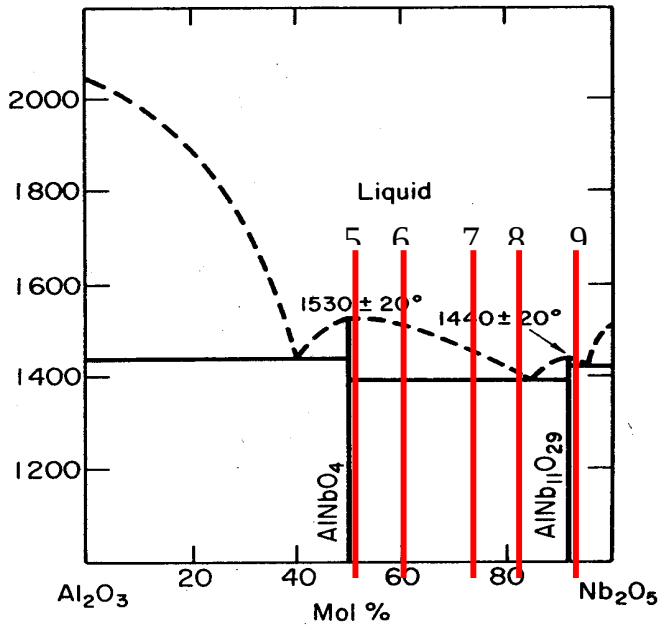


Figure 4. Phase diagram chosen for systematic compositional variations. Bold vertical lines indicate the compositions examined in most detail in the present study.

RESULTS AND DISCUSSION

Table 1 provides the compositions examined to date. The cold pressed and sintered specimens were prepared as follows. Powders of Nb_2O_5 and Al_2O_3 were mixed in appropriate ratios to achieve the desired mol % Nb_2O_5. The powders were ball-milled in a Nalgene bottle with Al_2O_3 mixing balls for 8 hours. The powders were then dried in a Pyrex dish at 70°C and then sieved through No. 100 mesh screen. The powders were then poured into a 1 inch diameter steel die and cold pressed at 6.9 MPa. After extraction, the pellets, about 0.5 inches in height, were placed into a high purity Al_2O_3 crucible in an air furnace with $MoSi_2$ elements. They were heated to either 1420ºC or in one case 1450ºC at 7ºC/min and held at temperature for 30 minutes, after which they were cooled at about 10ºC/min.

Many of the microstructures contained fibrous, elongated grains, as shown in Figure 5. While fracture tests were not performed, cracks that did form appeared to be impeded by these fibrous regions (Figure 1b).

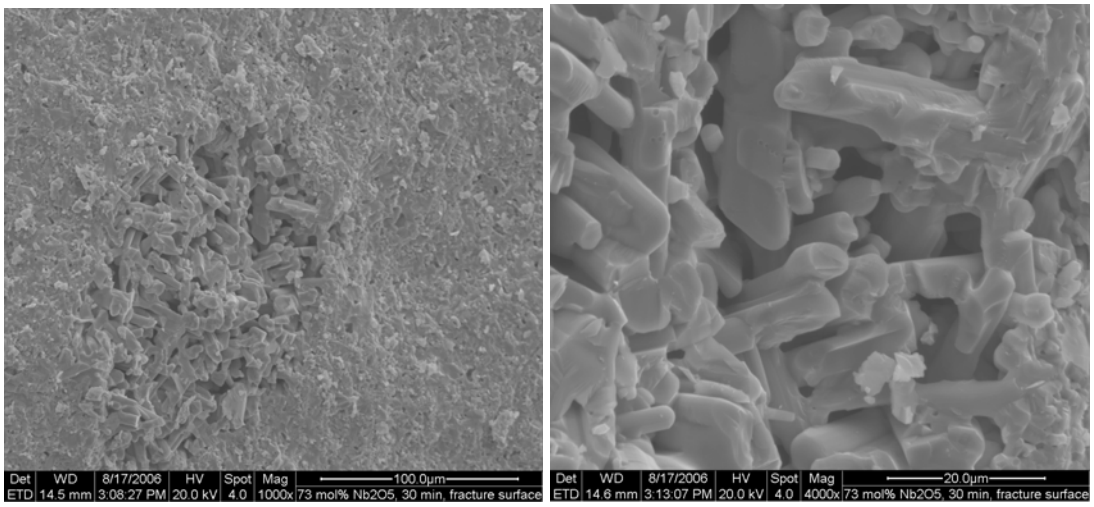


Figure 5. Microstructure of 73 mol. % Nb_2O_5 composition, showing elongated microstructure. **a)** Lower magnification. **b)** Higher magnification.

Table 1. Summary of experiments conducted.

Composition (mol % Nb_2O_5)[1]	Processing Route[2]	XRD[4]	Visual Inspection	SEM
60	HP	$AlNbO_4$ and $AlNb_{11}O_{29}$	dark gray to black; coarse grained	no glass
75 wt. % Nb	HP[3]	NC	sliver with gray particles (Nb); porous	NC
82	HP	$AlNbO_4$ and $AlNb_{11}O_{29}$	dark gray to black; coarse grained	no glass
	furnace heat treatment of above specimen	$AlNbO_4$ and $AlNb_{11}O_{29}$	melted; light green color with white crystals	no glass
90 wt. % Nb	HP[3]	NC	silver with gray particles (Nb); porous	NC
52	CS	$AlNbO_4$ and $AlNb_{11}O_{29}$	shape change indicating creep; white, rough and porous	no glass
60	CS	NC	surface melted, whitish gray	NC
73	CS	$AlNbO_4$ and $AlNb_{11}O_{29}$	melted; coarse elongated crystals; whitish gray	no glass
95	CS, 1450ºC	NC	melted; glaze; coarse, elongated crystals; whitish-gray	NC

[1] unless otherwise noted
[2] HP indicates vacuum hot pressed at 1300ºC.; CS indicates cold pressed and sintered at 1420ºC unless otherwise indicated
[3] indicates that these specimens were prepared by pre-oxidizing the Nb to form Nb_2O_5.
[4] NC indicates not completed yet.

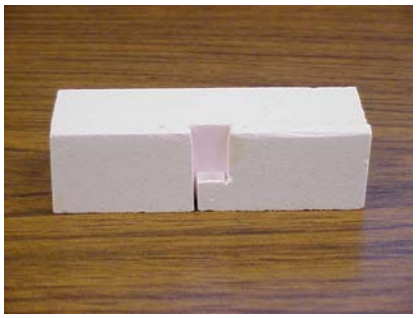
Two significant sets of experiments were conducted since the last reporting period. These are described next.

The tendency for glass formation was examined by conducting quench experiments in which 5 grams of the 82 mol. % Nb_2O_5 composition was heated in a Pt crucible to 1500ºC. This experiment was performed in collaboration with Professor James Shelby at Alfred University. Professor Shelby is an expert in this area and provided the materials, facilities and performed the experiments. The mixture was removed from the furnace (at 1500ºC) and immediately poured into water. Very large crystals

developed quickly. These results indicate the it will be very challenging if not impossible to form a glass with this composition. Other compositions were not attempted because it is believed that the 82 mol. % composition has the highest likely hood of forming a glass. More experiments were not performed because the Pt crucible develops a coating that is difficult to remove.

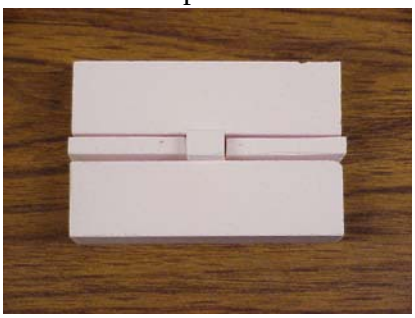
Despite the lack of glass forming ability for this composition, attempts were made to use it to join alumina. Because of recent work by Corning Inc., it is apparent that the thermal expansion coefficient between Nb_2O_5- Al_2O_3 compositions can be tailored to be near that of Al_2O_3, and thus it was felt worthwhile to attempt joint fabrication. Dense, high purity Al_2O_3 was obtained from CoorsTek Inc. It was cut into cubes approximately 1 cm on an edge. One face was then polished to 3 mm diamond past and cleaned with acetone and ethanol. One such cube was placed in a fixture comprising silicate based refractory, machined especially for the purpose of holding the specimens during bonding. A photograph of this split fixture is shown in Figure 6. The fixture parts were sprayed with BN spray to minimize contamination. Subsequently, a small amount (~1 g) of powder comprising the appropriate mol. % Nb_2O_5 was placed onto the polished and cleaned surface. A second Al_2O_3 cube was placed on top. Approximately 0.5 kg was placed on top, producing a pressure of about 0.1 MPa. Temperatures of 1420ºC and 1450ºC were used with a heating rate of 5ºC/min and a cooling rate of 100ºC/min. The lower temperature led to a lack of bonding as evidenced by separation of the parts during their removal from the fixture. The higher temperature led to a joint that appeared reasonably strong, but failed during subsequent cutting processes in an attempt to machine strength bars for 4 point bending. It may be that other compositions, or an increase in the applied pressure would increase the joint strength, but these have not yet been attempted.

Side View



a)

Top View



b)

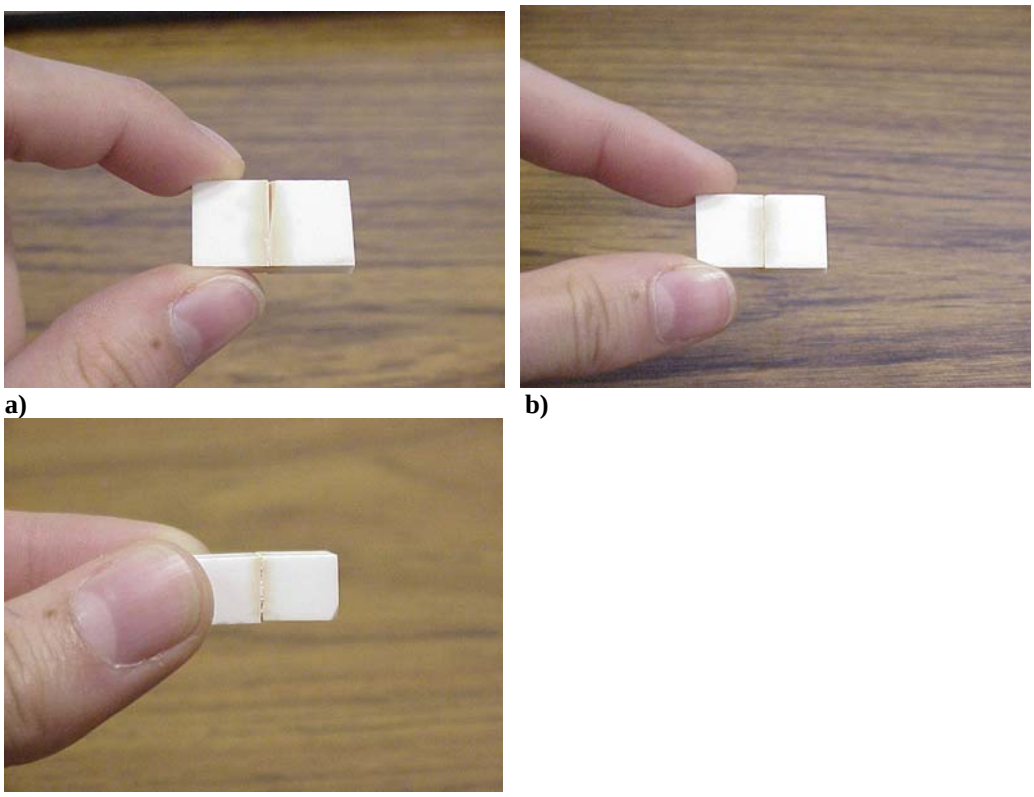
Figure 6. Side **a)** and top **b)** view of alumina brick that was used to hold the ceramic joints in place during processing.

The following table summarizes the results of these bonding experiments.

Table 2. Summary of the different joint experiments performed and their results.

mol% Nb_2O_3	*Holding Temp [deg. C]*	*Holding Time*	*Other Conditions*	*Results*
82	1450	6 h	Used porous alumina refractory brick. Light pressure applied	Unsuccessful; did not bond together. Some discoloration of the outside edges, orange cream in color.
82	1450	6 h	Used porous alumina refractory brick. No external pressure applied	Unsuccessful; did not bond together. Discoloration of the outside edges, orange cream in color.
82	1450	6 h	Used denser alumina from Coorstek. No external pressure applied.	Unsuccessful; did not bond together. Discoloration on the faces and outside edges. Orange cream in color.
82	1450	30 min	Used denser alumina from Coorstek. No external pressure applied.	Partially successful; bonded together but very weak. Broke easily by hand in the joint material area. Under the microscope sparse crystals, indicating a weak bond. Orange discoloration present.
82	1430	30 min	Used denser alumina from Coorstek. No external pressure applied.	Partially successful; bonded together and did not break by hand. Did break, though, when placed in clamp to be cut. Broke in the joint material area. Orange discoloration present.
52	1430	30 min	Used denser alumina from Coorstek. No external pressure applied.	Partially successful; bonded together and did not break by hand. Did break, though, when placed in clamp to be cut. Broke along the joint. Very crystalline, and had visible solids indicating too much powder and that it did not all melt.

Figure 7 shows several of the joints formed. It may be seen that joining was successful, but strengths are estimated at a few MPa.



a) **b)** **c)**

Figure 7. a) 82 mol. % Nb_2O_5, 30 min at 1450ºC; **b)** 82 mol. % Nb_2O_5 30 min at 1430ºC **c)** 52 mol. % Nb_2O_5, 30 min at 1450ºC.

Because of the lack of success of bonding dense alumina, the porous alumina received from James Shen at Arrhenius Laboratory in Sweden have not yet been joined, though it is likely that joint strengths would be enhanced due to infiltration of the joint material into the pores of the body.

CONCLUSIONS and FUTURE

Based on the quench experiments performed by James Shelby at Alfred University, it is unlikely that the present compositions examined will form a glass. However, those results do not preclude utilizing this material as a joining compound. With the correct conditions (composition, applied pressure and cooling rate during bonding) it may be that high strength bonds form.

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COST STATUS

Charges for faculty labor, student hourly wages, chemicals and other services totaled near $50,000 for the entire project.

SUMMARY OF SIGNIFICANT ACCOMPLISHMENTS

Quench experiments have shown that the presently studied systems do not form glasses easily and there may be no conditions under which glass would form.

Joints between alumina and alumina using Nb_2O_5-Al_2O_3 powders are relatively weak.

While this is an interesting material system based on the presence of vapor phase sintering and the varied microstructures, it seems unlikely that it can be used for joining alumina.