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CHEMICAL REACTION IN A HOT-PRESSED Al_2O_3-GLASS COMPOSITE

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ABSTRACT

A study of the effect of hot pressing variables upon a chemical reaction within a two-phase system was undertaken. The reaction between alumina and sodium disilicate glass to form nephelite ($Na_2O \cdot Al_2O_3 \cdot 2SiO_2$) was investigated. This reaction was studied using X-ray diffraction, electron microprobe, and petrographic techniques. The nephelite was found to nucleate at the surface of the alumina and grow into the glass matrix.

I. INTRODUCTION

In recent years considerable work has been directed toward the properties of two-phase systems and the effect of the dispersed phases upon the mechanical properties of composites. Physical aspects, such as volume fraction, particle geometry, and thermal expansion have been studied in an effort to enhance the mechanical properties. Little work has been done, however, on improving these mechanical properties by chemical techniques such as interfacial bonding or chemical reactions.

Several studies have shown that some physical properties, such as compressive strength, can be enhanced by hot pressing during a chemical reaction.[1-5] Chaklader and McKenzie[6] showed about a six-fold increase in the compressive strength of a fireclay when hot pressed during the dehydroxylization reaction with 20,000 psi as compared to 5000 psi.

Chemical reactions can occur during the normal process of hot pressing and can, in fact, occur at lower temperatures as a result of the applied pressure. Carruthers and Wheat[7] found mullite formation at 650°C in a china clay hot pressed during the dehydroxylization reaction with 30,000 psi applied.

In order to better understand hot pressing of composite systems and to control properties of the resultant product, a detailed knowledge of any reactions occurring during the process must be known. Alumina (Al_2O_3)-sodium disilicate ($Na_2O \cdot 2SiO_2$) glass was chosen as a system for investigation. In this system the phases react at high temperatures to form nephelite ($Na_2O \cdot Al_2O_3 \cdot 2SiO_2$).

Fulrath[8] has investigated the internal stresses in a glass-ceramic composite using powdered alumina and sodium disilicate glass. At hot-pressing temperatures of 850°C and higher it was found that a second phase, nephelite, was formed. The nephelite formation was found to directly influence the internal stress and was proposed as a possible mechanism of stress transfer.

Pask[9] studied the sintering of alumina-sodium disilicate compositions. The formation of bridges between the alumina particles which stiffened the structure was observed. This stiffening was attributed to the formation of nephelite on the surface of the alumina which helped to hold the alumina particles together. These bridges would collapse at the carnegieite-alumina eutectic temperature of 1475°C. It was postulated that hot pressing would break the bonds in these bridges and yield nearly theoretically dense bodies.

Sodium disilicate crystals and their nucleation and growth from the glass were studied by Scott and Pask[10] using a high temperature microscope. Only heterogeneous nucleation, nucleation on container walls at high temperatures and surface nucleation at low temperatures, was found. The high temperature nucleation occurred between 450°C and the melting point of crystalline sodium disilicate at 874°C. The maximum rate was found to occur at approximately 600°C. When the glass was exposed to air at temperatures of from 25 to 375°C and then heated to about 800°C, surface nucleation occurred. Both the alpha and beta forms of sodium disilicate were observed as crystallization products. Growth occurred between 600 and 870°C for both forms. The maximum growth rates

were observed at 800°C.

II. EXPERIMENTAL PROCEDURE

A. Glass

The sodium disilicate glass used in this investigation was made in the laboratory from silica flour and reagent grade sodium carbonate. The materials were dry mixed and then melted and refined in platinum crucibles at 1300°C in an electric furnace. Automatic rotation of the crucible on an inclined plane was used to increase the fining action. The glass was cast and then crushed and dry ground to -325 mesh in an alumina-lined ball mill with alumina pebbles. The density of the glass was 2.57 gm/cc.

B. Alumina

Commercial sapphire boules were used as the source of alumina. The boules were thermally shocked into coarse size fractions by heating to 1000°C and then quenching into cold water. The resulting particles measured a few millimeters in diameter. This procedure also eliminated any possibility of contamination of the alumina by iron from a crusher. Final reduction was performed by using an alumina-lined ball mill with alumina pebbles. The ground particles were separated into several size fractions and then introduced into a commercial d-c plasma jet in order to spheroidize the particles. The spherical alumina that was obtained was X-rayed and found to be almost entirely α-Al_2O_3. A slight trace of γ-Al_2O_3 was found.

C. Hot Pressing

The glass and alumina spheres were weighed into the proper volume fractions, thoroughly mixed with isopropyl alcohol, and dried. The use of isopropyl alcohol instead of water prevented the attack of both the glass and the alumina by water. The measured densities of 3.97 and 2.57 for the alumina and sodium disilicate glass, respectively, were used in calculating the required volume fractions.

The hot-pressing arrangement is shown in Fig. 1. The mixed powders were loaded into a tungsten carbide die body and graphite plungers were inserted. The extreme fluidity of the glass at the hot-pressing temperatures made a tungsten carbide die body necessary. After loading, the die body was positioned in the vacuum chamber. A Pt-Pt, 10% Rh thermocouple was inserted in the die body and the system was evacuated to less than a micron pressure.

Resistance heating was used with a 115 mil molybdenum heating coil. Rates of cooling from the maximum temperature were controlled by the furnace's free cooling rate. A linear differential transformer attached to the bellows was used as a measure of the compaction of the sample in the die. Hot pressing of the composite samples was done at temperatures greater than 750°C in order to obtain the nephelite phase while preventing crystallization of either the alpha or beta sodium disilicate. Preliminary investigations showed that the nephelite first appeared at 750°C while under the minimum pressure used.

The hot-pressed samples were sectioned and mounted in a clear casting resin. All samples were polished with a set of silicon carbide

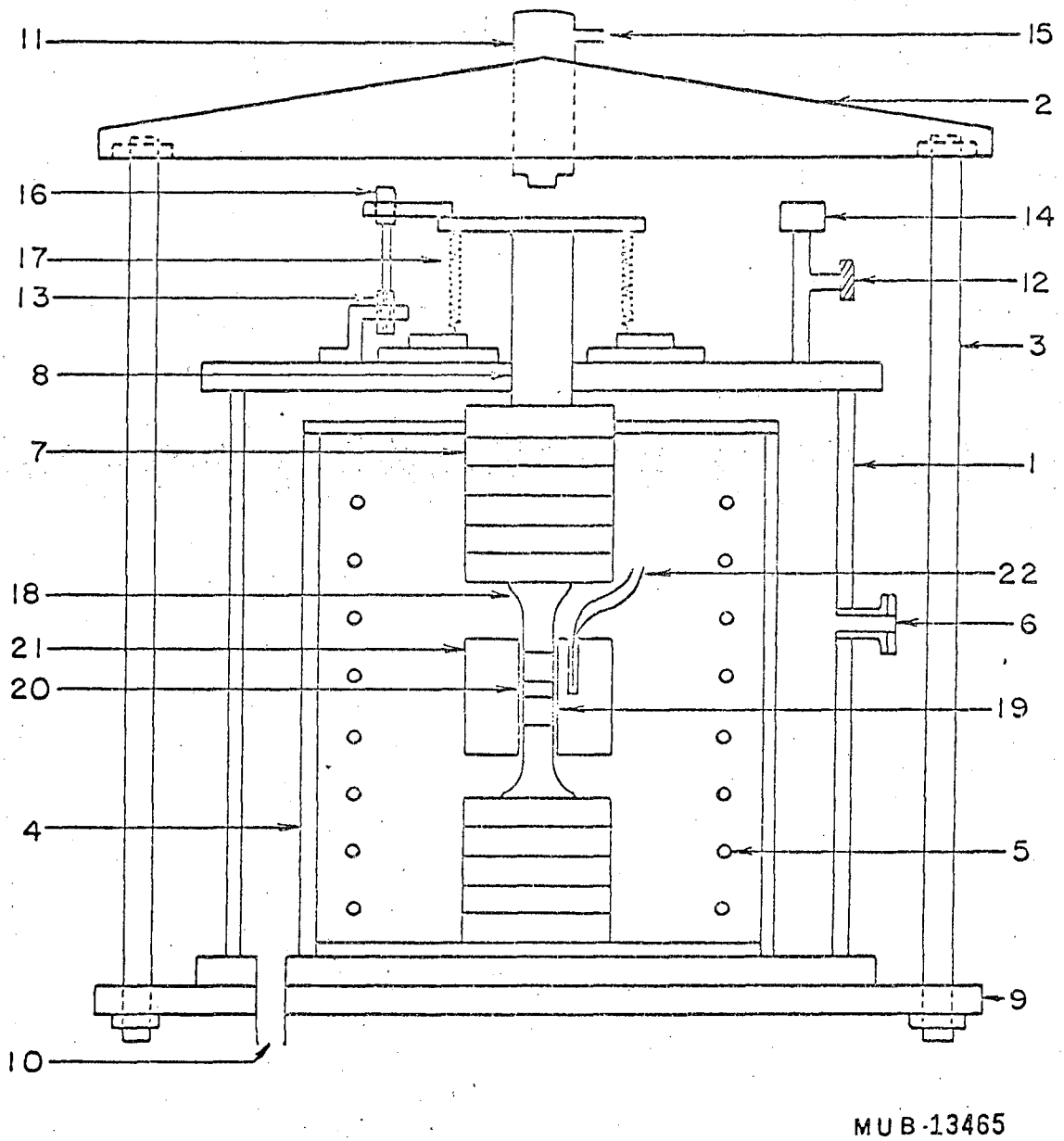

Fig. 1 Schematic diagram of hot press.

KEY

1. Vacuum cover
2. Top yoke
3. Load bearing column
4. Radiation shield
5. Mo heating coil
6. Sight window
7. Insulating spacers
8. Plunger
9. Bottom support plate
10. Vacuum port
11. Hydraulic ram
12. Air inlet
13. Linear variable differential transformer
14. Vacuum gauge
15. Pressure inlet
16. Micrometer head
17. Bellows
18. Graphite plunger
19. Graphite plug
20. Sample
21. Tungsten carbide die body
22. Thermocouple

papers (240, 400, and 600 grit) and then finished on a series of diamont paste laps (6, 2, and 1/2 micron diamond). Carbon was vapor deposited on the finished samples to provide a conductive surface suitable for electron microprobe analysis.

D. Electron Microprobe

A Materials Analysis Company electron probe was used for the simultaneous analysis of aluminum and silicon. The characteristic radiation emitted by the elements in the specimen was resolved by properly positioned potassium acid phthalate (KAP) crystals and the intensities were measured with proportional detectors. A motor-driven gear mechanism moved the sample in a step-wise fashion relative to the electron beam. Integrated counts were taken at various intervals along the radius of an alumina sphere and into the glass sufficient to give a smooth curve of concentration as a function of distance. The beam diameter was 1μ and the depth of penetration was a maximum of 3μ. These values are small compared with the ∿70μ Al_2O_3 particle size. In order to minimize the instability of the alkali glass as a result of the electron beam heating, short counting times (10 sec.), a low sample current (0.02μA), a low voltage (15 KV), and a relatively heavy carbon coating were used.

All data obtained from the proportional counters were corrected for background, absorption, counter dead time and non-linearity, fluorescence, and atomic number. In this case the counter dead time, fluorescence, and atomic number corrections are ngligible and the background can be accounted for by a simple subtraction. The absorption, however, requires

more careful consideration. Corrections were made for several compositions ranging from pure glass to pure alumina for both aluminum and silicon radiation. Detailed procedure and mass absorption coefficients were taken from Smith.[11] The electron microprobe was equipped to take photomicrographs of the sample and to take photographs of the X-ray image of every element as displayed on an oscilloscope.

III. RESULTS AND DISCUSSION

A. X-Ray

Samples of 40 $^{v}/_{o}$ alumina spheres and 60 $^{v}/_{o}$ glass were pressed at 800°C and 2000 psi for various holding times. These samples were then X-rayed to determine the extent of nephelite formation. A sample spinner was used in order to insure that the X-ray beam covered a representative portion of the sample face. Peak areas for both alumina ($2\theta = 25.5°$, Cu K_α) and nephelite ($2\theta = 23.1°$, Cu K_α) were used to estimate nephelite concentration. Care was taken to avoid samples that showed any crystallization of either form of sodium disilicate. The peak area was then plotted as a function of holding time as seen in Fig. 2. The curve rose sharply and leveled off at a maximum nephelite content indicating that the reaction of the alumina with the glass is rapid. This reaction rate for the overall reaction, however, is no indication of the rate controlling step in the reaction.

A second set of samples was hot pressed under the same conditions, except that a particle size of -400 mesh was used rather than -270+325 mesh in the previous set. Peak area measurements were made in the same manner. The resulting curve had the same shape as the previous one, but

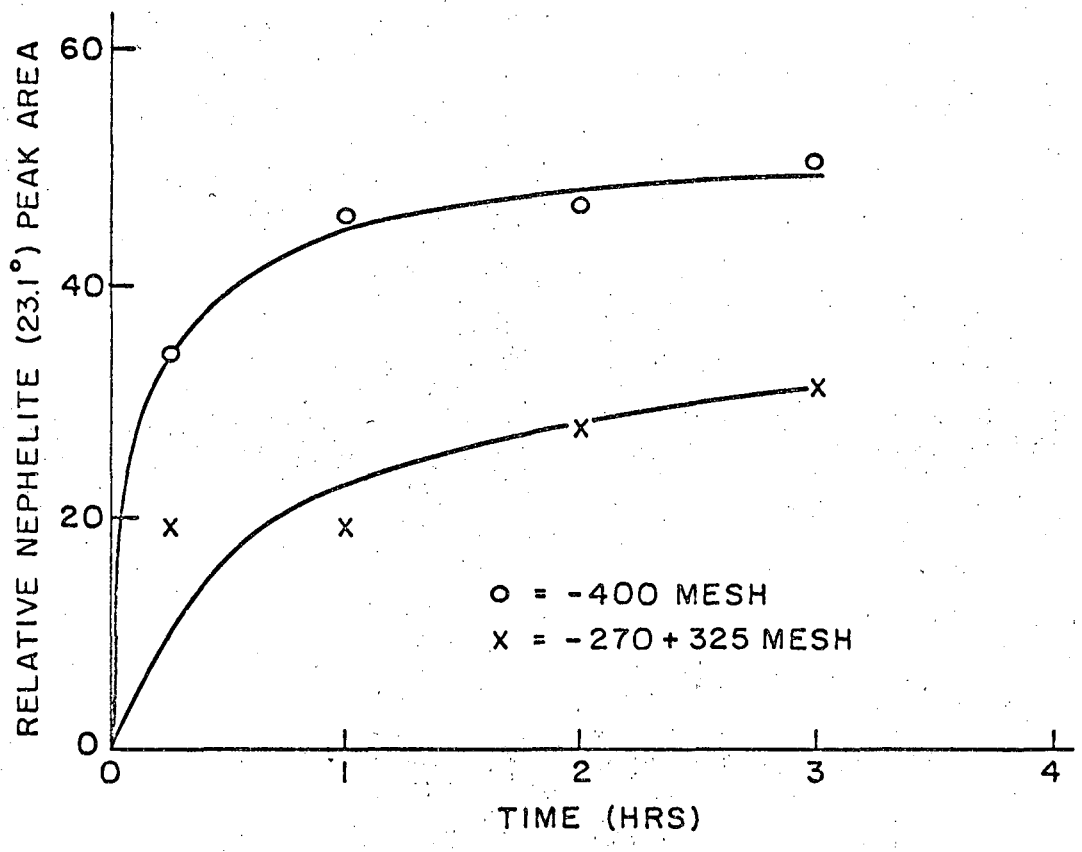

Fig. 2 Effect of holding time and particle size upon nephelite formation (800°C and 2000 psi)

MUB 13017

in the -400 mesh samples about twice as much nephelite was formed at each corresponding holding time, indicating that surface area plays an important part in the alumina-glass reaction.

B. Photomicrograph

The formation of nephelite can be seen when the composite is viewed with transmitted light. A 40 $^{v}/_{o}$ alumina sample was cut and a thin section was made. When viewed under transmitted light, laths and feathers of nephelite were seen in the vicinity of the alumina spheres. Another portion of the same sample was powdered. A refractive index of between 1.52 and 1.55 for discreet particles of nephelite was measured using calibrated immersion oils. The particles showed the pleochroism that is characteristic of nephelite, changing from yellow to green under crossed Nicols. A representative photomicrograph showing the nephelite particles can be seen in Fig. 3. The nephelite grows radially from the sphere into the glass.

Microprobe data showed the alumina concentrations in the matrix for this sample to vary from 12.0 to 19.5 $^{wt}/_{o}$ Al_2O_3. The Al and Si profiles for one of these samples can be seen in Fig. 4. With this level of Al_2O_3 in the glass matrix the primary phase upon crystallization at the temperatures used in this work would be nephelite.[12,13] This can be seen in Figs. 5 and 6. There was no indication of any step in the curve at the alumina-glass surface, implying that the nephelite is not formed as a shell around the alumina spheres. The alumina spheres serve as nucleation sites for the nephelite crystallization and the crystals grow into the glass phase. Occasional nephelite crystals will

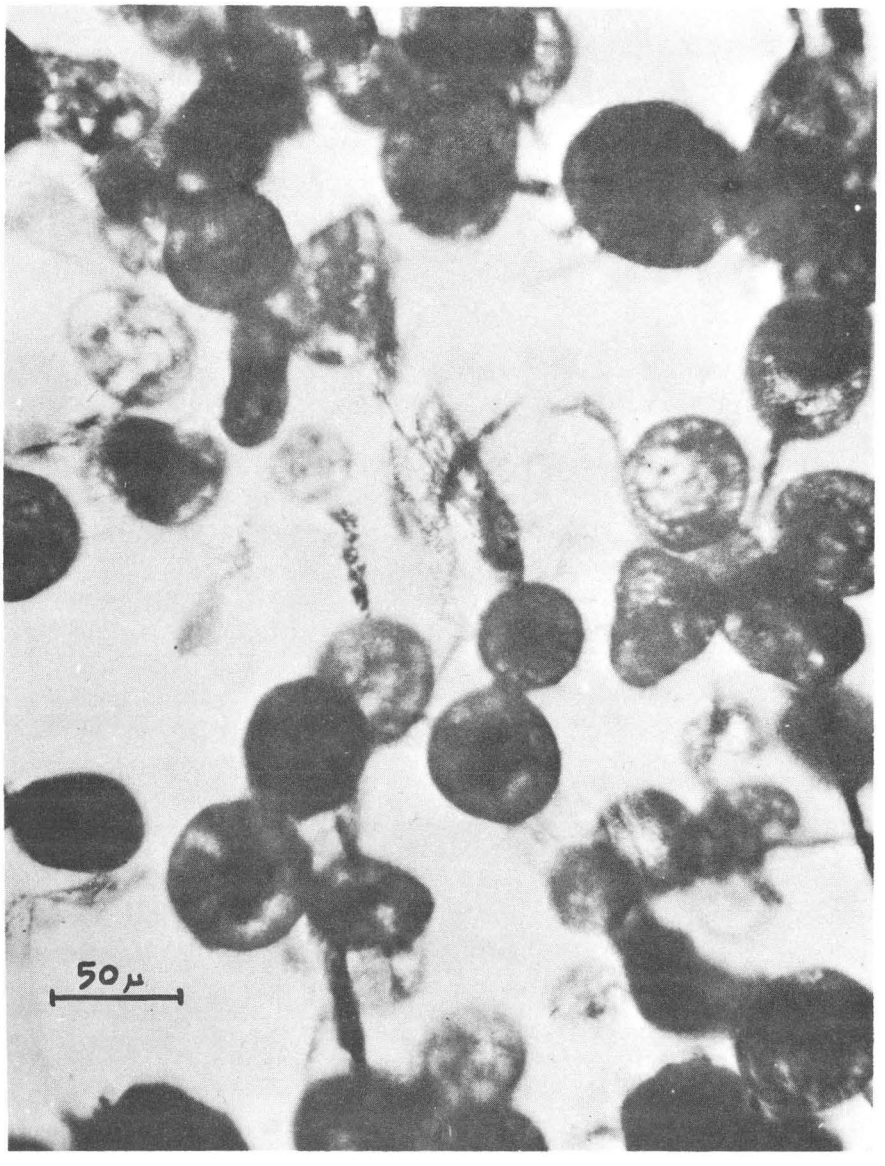

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Fig. 3. Photomicrograph of thin section of 40v/o spheres composite (800°C and 2000 psi).

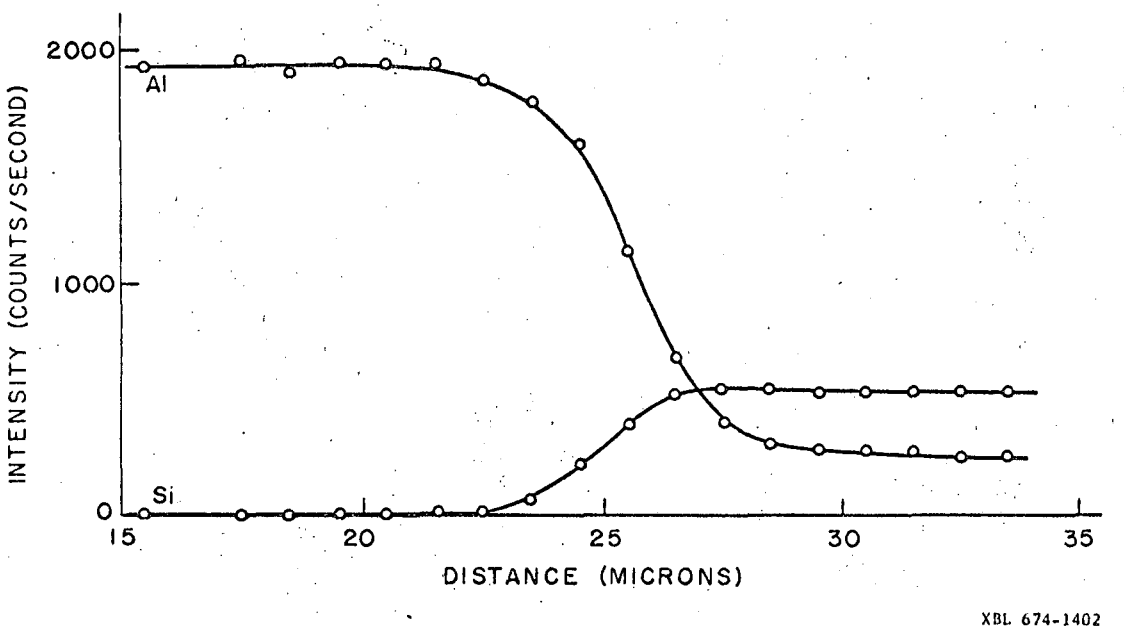

Fig. 4 Electron microprobe profile of 40 v/o spheres composite (800°C and 2000 psi).

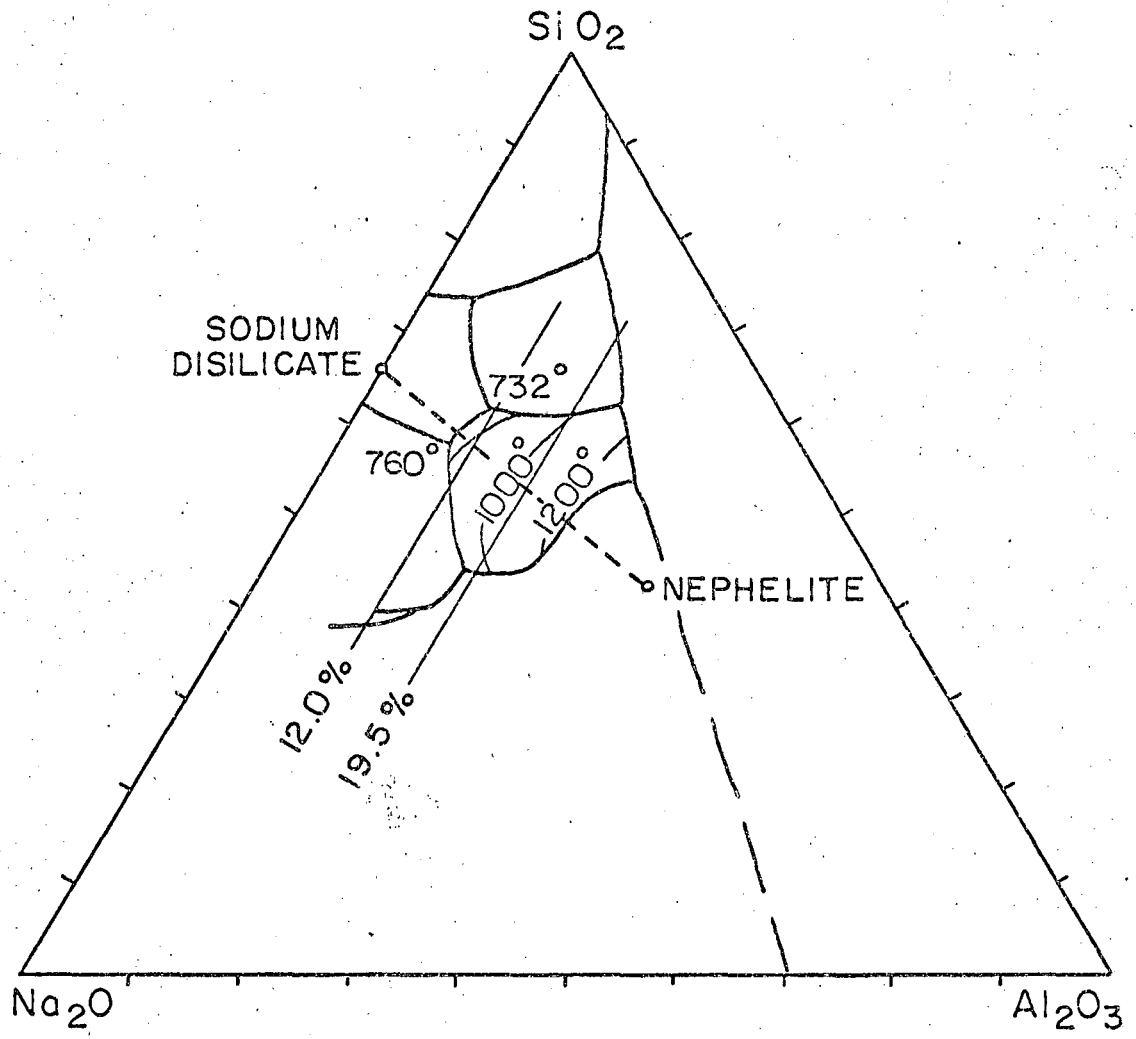

Fig. 5 Portion of Na_2O-Al_2O_3-SiO_2 system under study.[12,13]

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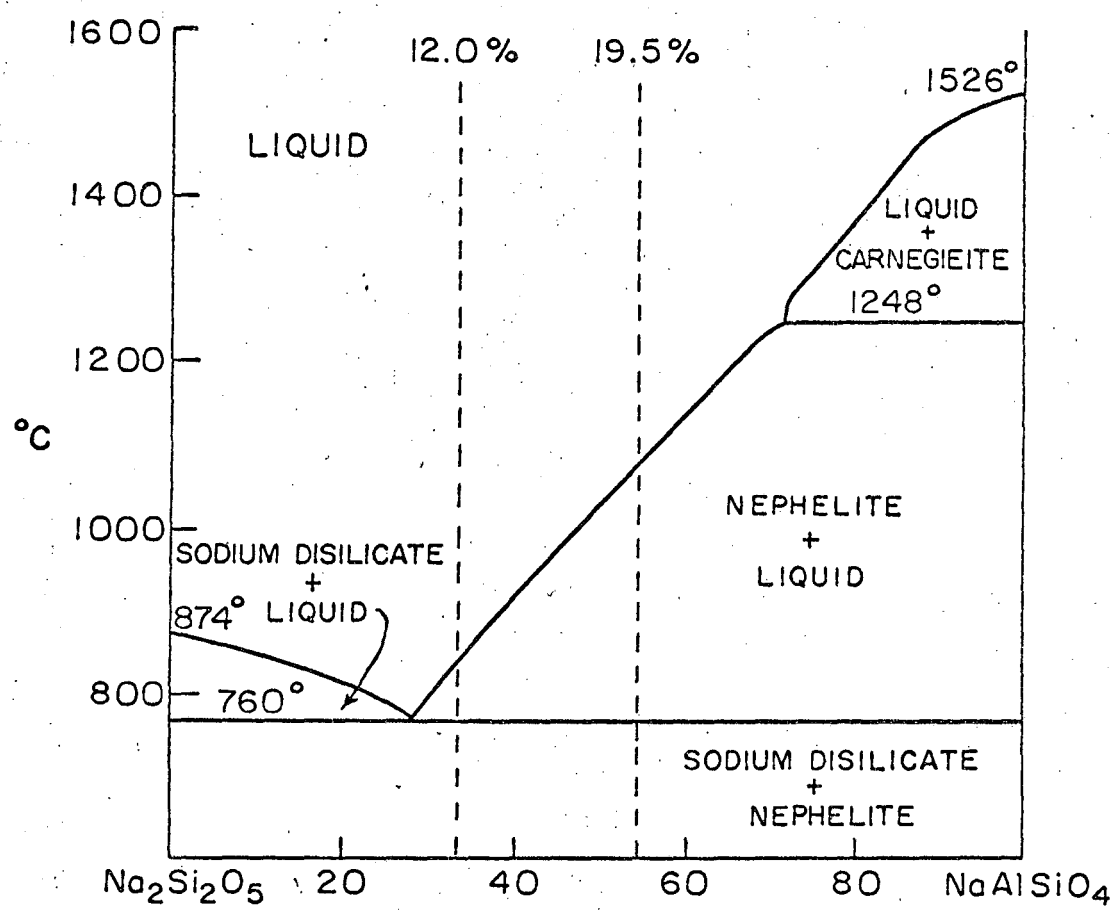

Fig. 6 Portion of Al_2O_3-$Na_2Si_2O_5$ system under study.

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be seen isolated in the matrix, but these are believed to be a result of the sectioning process.

C. Electron Microprobe

Samples made with 10 $^{v}/_{o}$ alumina spheres were X-rayed to attempt to verify the formation of the nephelite phase. None of these samples showed any trace of the main nephelite peak. Samples pressed under the same conditions, but with 40 $^{v}/_{o}$ alumina spheres, did show a marked nephelite peak. Photographs of the X-ray image generated by aluminum as displayed on the oscilloscope were taken of both 10 $^{v}/_{o}$ and 40 $^{v}/_{o}$ samples pressed at 850°C and 2000 psi for 10 minutes. These are shown in Figs. 7 and 8. The aluminum content in the matrix increases with an increase in the volume fraction of alumina in the composite due to the increased surface area.

Composites of 10 $^{v}/_{o}$ alumina spheres formed at from zero to 3000 psi, applied pressure between 775°C and 900°C, and from holding times of 10 minutes to 4 hours were probed. Probing was done from the center of a sphere outward into the glass and silicon and aluminum concentrations were measured at selected points. The values obtained for aluminum concentrations were corrected, converted to Al_2O_3 concentrations, and plotted as a function of distance from the center of the sphere. The concentration values formed smooth profiles in every case, indicating again the lack of nephelite formation under these conditions.

Since all other parameters--pressure, temperature, particle size, and holding time--were the same for both the 40 $^{v}/_{o}$ and the 10 $^{v}/_{o}$ samples, the factor responsible for the presence of the nephelite must

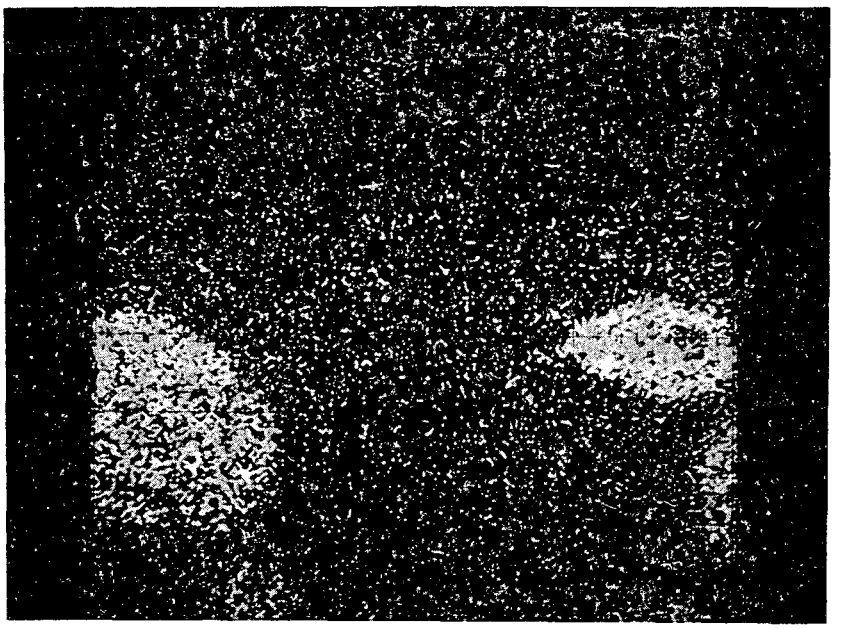

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Fig. 7 Oscilloscope photograph of 10 v/o spheres composite (Al radiation ~350X, 850°C, 2000 psi, 10 min.).

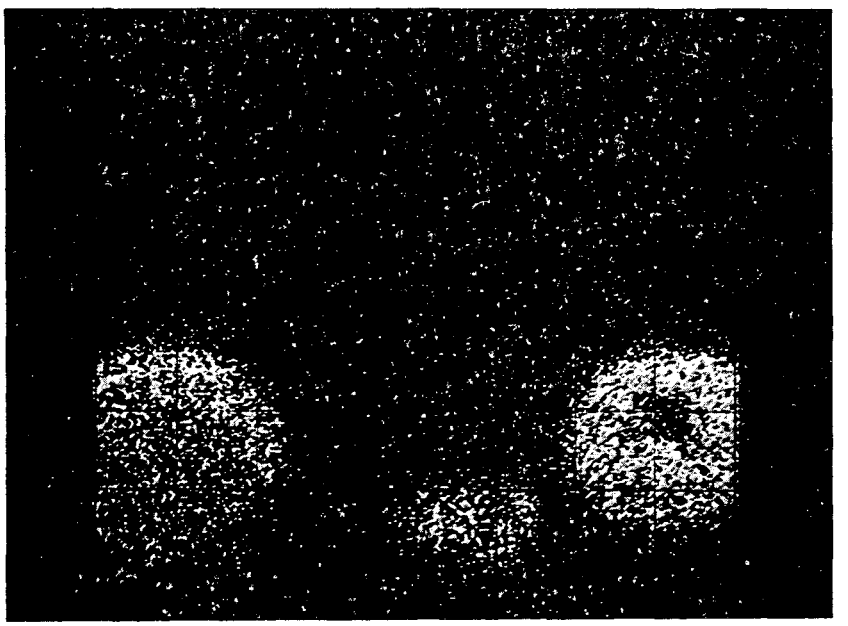

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Fig. 8 Oscilloscope photograph of 40 v/o spheres composite (Al radiation ~350X, 850°C, 2000 psi, 10 min.).

be the level of alumina in the glass matrix. Thus the reaction between the alumina and the glass is dependent upon the migration of alumina into the glass. Once a certain alumina level is reached, the reaction can proceed and the nephelite is formed in the glass and not as a shell around the alumina sphere.

IV. SUMMARY

Chemical reactions can occur in a two-phase composite during normal hot-pressing processes. The reaction between alumina and sodium disilicat glass to form nephelite was found to occur at hot-pressing temperatures of 750°C and higher. The nephelite was found to nucleate at the surface of the alumina sphere and grow into the glass phase.

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BIBLIOGRAPHY

1. A. C. D. Chaklader and M. N. Shetty, "Ceramic-Metal Composites by Reactive Hot Pressing," Trans. Met. Soc. AIME, 233 [7] 1440-43 (1965).

2. A. C. D. Chaklader and V. T. Baker, "Reactive Hot Pressing: Fabrication and Densification of Non-Stabilized ZrO_2," Bull. Am. Ceram. Soc., 44 [3] 258-59 (1965).

3. P. E. D. Morgan and E. Scala, "The Formation of Fully Dense Oxides by Pressure Calsintering of Hydroxides," Department of Materials Science and Engineering, Cornell University, Ithaca, New York.

4. A. C. D. Chaklader, "Reactive Hot Pressing: A New Ceramic Process," Nature, 206 [April 24] 392-93 (1965).

5. T. G. Carruthers and T. A. Wheat, "Hot Pressing of Kaolin and Mixtures of Silica and Aluminum Oxide," Meeting on Fabrication Science, Brighton, England (October 1964).

6. A. C. D. Chaklader and L. G. McKenzie, "Reactive Hot Pressing of Clays," Bull. Am. Ceram. Soc., 43 [12] 892-93 (1964).

7. T. G. Carruthers and T. A. Wheat, "Hot Pressing of Kaolin and of Mixtures of Alumina and Silica," Proc. Roy. Soc., #3, Fabrication Science, September 1965.

8. R. M. Fulrath, "Internal Stresses in Model Ceramic Systems," J. Am. Ceram. Soc., 42 [9] 423-29 (1959).

9. Joseph A. Pask, "Effect of Interfacial Reactions on the Densification of Crystal-Glass Systems," Transactions of the VIIth International Ceramic Congress, London, 1960, 1961. Brit. Cer. Soc., Federation House, Stoke-on-Trent, pp. 481-91.

10. William D. Scott and Joseph A. Pask, "Nucleation and Growth of Sodium Disilicate Crystals in Sodium Disilicate Glass," J. Am. Ceram. Soc., 44 [4] 181-87 (1961).

11. J. V. Smith, "X-ray Emission Microanalysis of Rock-Forming Minerals, I. Experimental Techniques," J. Geol., 73 [6] 830-64 (1965).

12. J. F. Schairer and N. L. Bowen, "The System Na_2O-Al_2O_3-SiO_2," Am. J. Sci., 254, 129-95 (1956).

13. J. F. Schairer and N. L. Bowen, "Melting Relations in the Systems Na_2O-Al_2O_3-SiO_2 and K_2O-Al_2O_3-SiO_2," Am. J. Sci., 245 (4) 193-204 (1947).

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