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C/ORNL97-0465

CRADA Final Report
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MICROWAVE NITRIDATION OF SINTERED REACTION BONDED SILICON PARTS FOR NATURAL GAS FUELED DIESEL ENGINES

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Research sponsored by the U.S. Department of Energy, Assistant Secretary for Energy Efficiency and Renewable Energy, Office of Transportation Technologies, as part of the Heavy Vehicle Propulsion System Materials Program, under contract DE-AC05-96OR22464 with Lockheed Martin Energy Research Corporation

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MICROWAVE NITRIDATION OF SINTERED REACTION BONDED SILICON PARTS FOR NATURAL GAS FUELED DIESEL ENGINES

INTRODUCTION

The major reason for the failure of the introduction of ceramics into many applications has been cost of components. This is most noticeable in the transportation vehicle engine industry where ceramics would provide lighter, more fuel-efficient and less polluting engines. Silicon nitride ceramics are the leading candidate materials for high temperature structural applications because of their combination of excellent strength, fracture toughness, wear resistance, thermal shock tolerance and high temperature properties. Development has traditionally been directed towards materials with superior strength, fracture toughness, wear behavior, and creep resistance with cost a secondary consideration. Consequently, traditional materials tend to be very expensive and are not competitive with metal parts on a replacement basis in many applications. Sintered reaction-bonded silicon nitride (SRBSN) is a cost-effective material that is receiving increased industrial interest for structural applications at temperatures <1200°C. Compared to traditionally processed SRBSN ceramics, microwave processing can result in improved temperature uniformity, reduction of the total reaction time, and reaction in a more controlled environment around the parts.

Development of SRBSN materials for structural applications was being done by ORNL and Eaton Corporation. The ORNL work was done under the Ceramic Technology for Advanced Heat Engines Project. The focus of that work involved up-scaling of the process to large batch sizes. Eaton Corporation was interested in up-scaling the SRBSN process using conventional heating practices.

This cooperative project was a joint development program between Eaton Corporation and Lockheed Martin Energy Research (LMER). Cooperative work was of benefit to both parties. ORNL was able to assess up-scale of the microwave nitridation process using a more intricate-shaped part designed for application in advanced diesel engines. Eaton Corporation gained access to microwave facilities and expertise for the nitridation of SRBSN materials. The broad objective of the CRADA established with Eaton Corporation and ORNL was to develop cost-effective silicon nitride ceramics compared to the current materials available.

RESULTS

The initial work involved nitriding Eaton "green" parts by microwave (MWF) and conventional graphite furnace (GF) methods used at ORNL. The first experiment in this activity was a nitridation of Eaton silicon parts using microwave heating. Prior to the microwave nitridation, the parts had binders removed by a 1°C/min heat to 500 °C in the microwave furnace. Figure 1 shows silicon parts, as placed in a silicon nitride crucible and surrounded by fiber board insulation in a 2.45 GHz microwave cavity. Parts were heated in N_2 4-vol. % H_2 gas to 600°C and then the supply gas was switched to N_2. The peak nitridation temperature was 1350° C. The heating cycle was 13 h. The parts appeared to nitride uniformly with an average weight gain of 62.7 %. The weight change for sample, 1350°C MWF, is shown in Figure 2. Figure 3 is a photograph of nitrided valve seats from this microwave nitridation. The second experiment in the second activity was a comparison scale-up nitridation of valve seats in a graphite element furnace. Figure 4 is a photograph of the set-up used for this nitridation test. Since one of the main difficulties of nitriding the green silicon valve seats is the handling of parts during loading, the air burn out of parts prior to nitridation was omitted. The parts were

heated at 1°C/min to 600° C in N_2 to remove volatile binders, followed by a normal nitridation cycle. Once again, the peak temperature for nitridation was 1350° C, with a total heating cycle of 13 h. Figure 2 shows an average weight gain of 62.9 % for sample group 1350°C GF. Figure 5 is a photograph of a few of the samples after nitridation showing a silicon carbide layer on some samples. The SiC layer was probably due to the interaction of the silicon in the samples with residual carbon resulting from the volatile binders in the crucible.

The next activity of this CRADA was a series nitridation-and-sintering experiments. These experiments were performed in a graphite furnace with vacuum capability, in order to remove carbon materials from the sample crucibles during binder volatilization. Figure 6 is a photograph of one of the crucibles used for nitridation and subsequent sintering. The photo shows nitrided and sintered samples on a "Crystar" SiC plate, which was supported by silicon nitride porous beads (3M Co.). In other experiments, samples were also covered by a layer of the porous beads for atmosphere control during sintering. Previous, in-house experiments have demonstrated that Si_3N_4 parts packed in Si_3N_4 powders during sintering steps had less weight losses. The concept explored here was to use beads, instead of powders. Powder packing can result in melted silicon parts during nitridation, however beads have been shown to be a cover material that does not trap too much of the exothermic heat of nitridation. In experiment 1, performed without a bead cover, the sample group, designated 1750°C-B in Figure 2, had an average weight change of 51.6 %. This lower weight gain, versus 62.9% for nitridation alone, is a combination of a nitridation weight gain plus a sintering weight loss, here a 11.3 % weight loss. Sample group 1750°C+B, which were covered with the porous beads had a weight gain of 56.5 %, showing the atmosphere protection of the bead cover. Figure 7 is a graph of the sintering behavior of the two groups of samples. The 1750°C-B samples had average densities of 94.5 % (based on a 3.4 g/cm^3 theoretical density) and the 1750°C+B group had average densities of 93.0 %. It is believed the 1750°C+B group had the lower densities because the weight losses are associated with silica volatilization and resulted in materials with higher theoretical densities. This would give an apparent lower density to the parts covered by the beads. Since the densification at 1750° C was lower than desired, nitridation-sintering runs were made at 1775°C and 1800° C with and without bead cover. The nitridation weight gains for these runs are given in Figure 2, with +B and -B designating the packing arrangement as with or without bead cover, respectively . The data show that the bead cover prevents weight loss at the higher 1775 and 1800° C temperatures. Data in Figure 7 shows that the densification at 1775° C was higher for the -B group, however at 1800° C there was no difference observed in the densities for the two packing arrangements.

To evaluate the effect of the sintering temperatures and packing arrangements on the sample properties, simple load failure tests were performed on the samples. The round valve seats were placed on their outer rim in an Instron 4465 Materials Testing System. The samples were then compressed by the Instron until failure of the rings and the load at failure recorded. Figure 8 is a summary of the data obtained. The results for the three sets of samples processed in the vacuum graphite furnace at 1775 and 1800°C show that the bead cover was detrimental to strength. Only minor differences were seen in strengths of the samples processed without a bead cover at the two test temperatures.

Another activity performed for the Eaton CRADA was an exploration of the use of elevated pressure nitrogen for nitridation and sintering of silicon preforms. Work has been done by other research groups on gas pressure nitridation of silicon preforms, and extensive work has been done at ORNL on gas pressure sintering of Si_3N_4, so it seemed logical to test how a combination of gas pressure nitridation and sintering would benefit processing of the Eaton silicon valve seats. In this experiment the samples containing

binder were placed on a SiC plate in graphite crucible. The samples were heated to 600°C in vacuum for binder removal and then heated to 1350°C in 0.7 MPa (100 psig) N_2 gas pressure for nitridation. The pressure was removed and the samples then heated to 1775°C for 30 min. The pressure was then raised to 0.7 MPa (100 psig) and the samples heated to 1850° C for sintering. The total heating cycle minus cool down was 8.3 h. Figures 2, 7, and 8 show data for weight gain, densities, and load to failure for these 1850°C gas pressure sintered samples. The data show that the weight loss was similar to the samples processed at 1800° C, the density of 99 % T. D. was higher than all other sample groups, and the average strength of 158 kg (347 lb) was significantly higher than any other group of samples. Gas pressure nitridation and sintering appears to have a potential for rapid processing of valve seats with improved strength.

The last activity of this project was gelcasting of silicon materials provided by Eaton. A basic flow sheet for the gelcasting process is shown in Figure 9. Two batches of silicon powders which consisted of Eaton proprietary formulations were shipped to ORNL. Work was performed to test the compatibility of the silicon materials with four different gelcast monomer systems. Two of the gelcast systems were shown to give satisfactory green bodies with both types of silicon materials provided by Eaton. However, it was found that materials could not be milled overnight with the gelcast reagents due to auto-catalysis of the monomer system and premature gelling of the silicon materials as shown in Figure 10. Consequently, testing was done to assess the effect of Si type and gel system on the gelling time as shown in Figure 11. As-received Globe Si was used as a standard for comparison purposes. The effect of gel system on gel time is shown in Figure 12. To compensate for premature gelling, a gel inhibitor was introduced into the slurries which improved the inhibition to gelation. Experiments determined that the Eaton silicon materials could be cast within the first 6 hours of the milling process.

Figure 13 shows typical shapes of the test green bodies cast with the two types of Eaton silicon powders using two gelcast monomer systems. The molds do not represent Eaton parts, but rather generic parts for testing purposes. Cast samples were shipped to Eaton for examination. A written procedure for gelcast forming of Eaton powders was prepared and sent to Eaton.

CONCLUSIONS

The following conclusions can be made from the work performed under the CRADA:

(1) Demonstrated that the binder burnout step can be incorporated into the SRBSN processing in the microwave furnace.

(2) Scale-up of the microwave nitridation process using Eaton Corporation parts showed that the nitridation weight gains were essentially identical to those obtained by conventional heating.

(3) Combined nitridation and sintering processes using silicon nitride beads as packing powders results in degradation of the mechanical properties.

(4) Gelcasting of silicon nitride materials using Eaton Si mixtures was demonstrated.

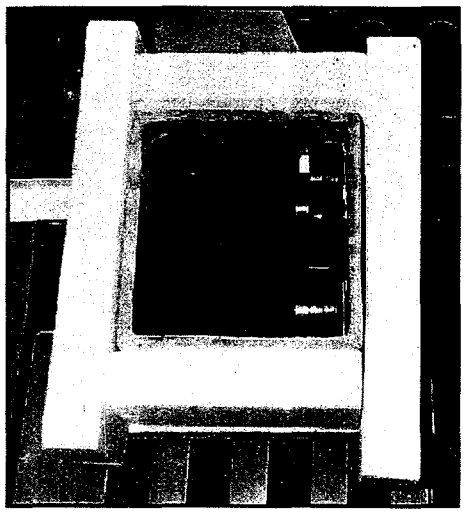

Figure 1. Set-up for the nitridation of Eaton silicon valve seat parts.

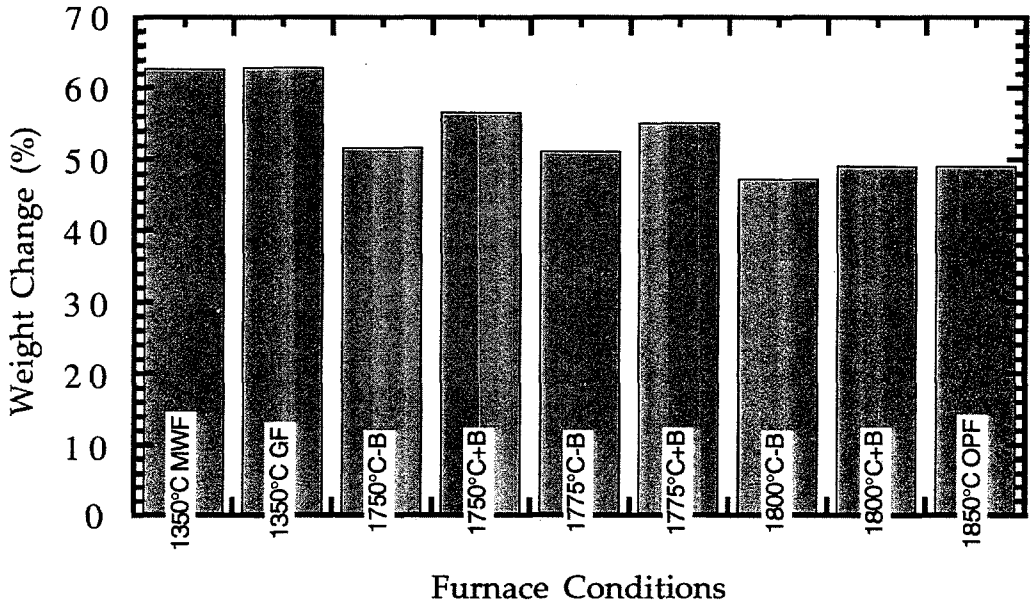

Figure 2. Weight change for silicon valve seats processed by different furnace conditions.

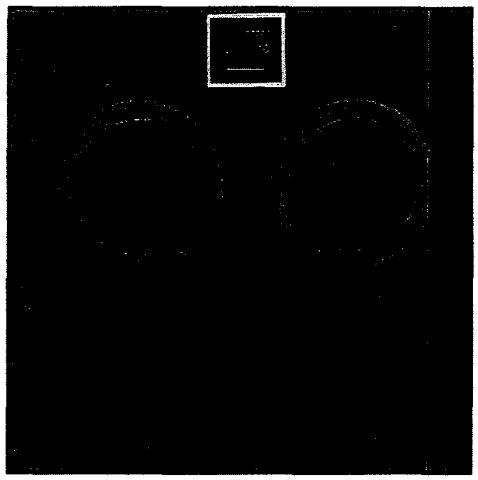

Figure 3. Photograph of several of the microwave nitrided valve seats.

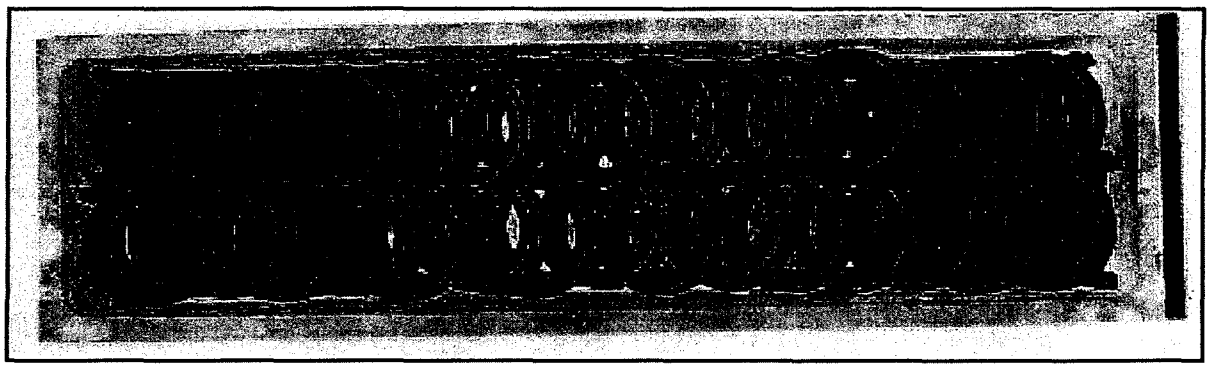

Figure 4. Photograph of the graphite crucible and silicon valve seats prior to nitridation.

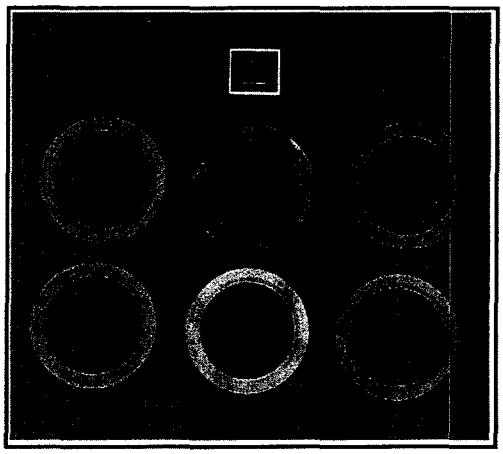

Figure 5. Photograph of valve seats after nitridation in a graphite furnace.

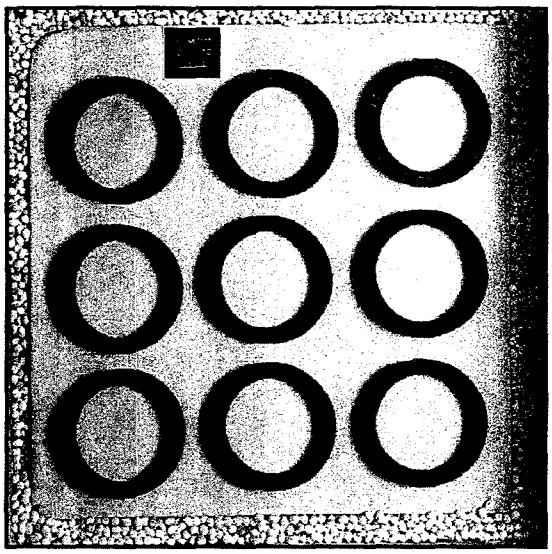

Figure 6. Photograph of nitrided valve seats in a graphite crucible used for one step nitridation and sintering runs (without silicon nitride bead cover).

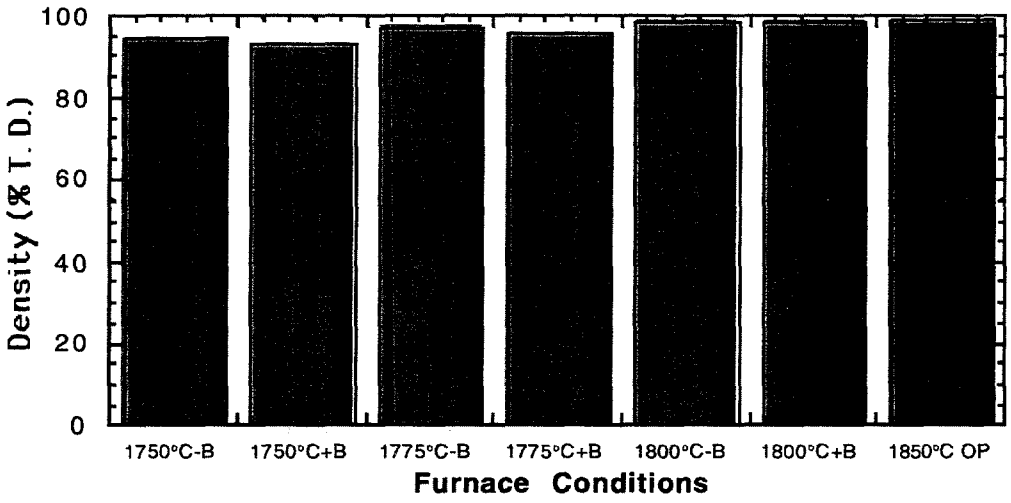

Figure 7. Densities for silicon valve seats processed by different furnace conditions.

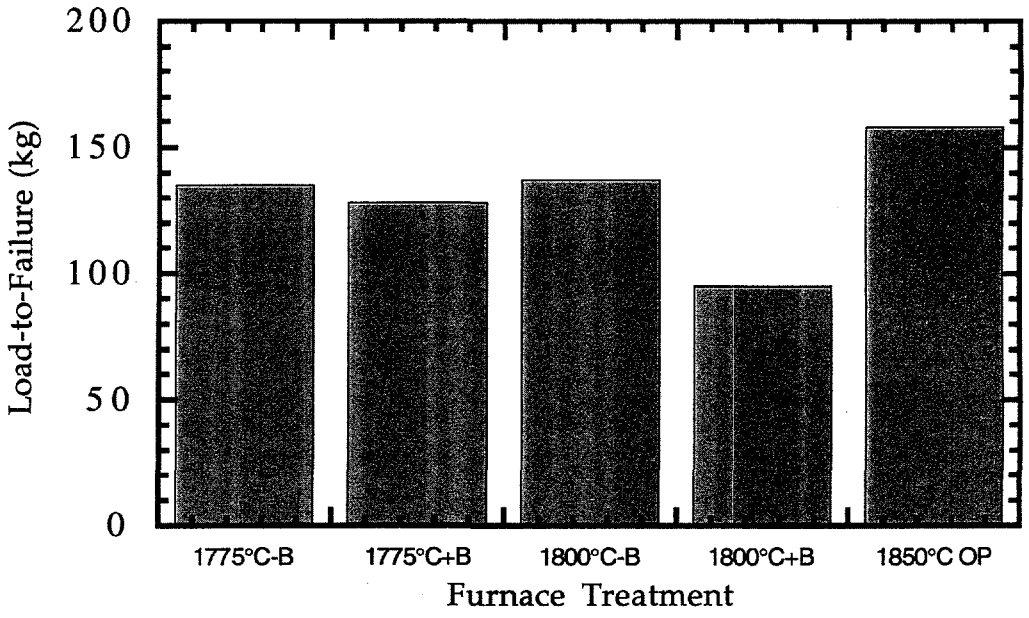

Figure 8. Load to failure data for compression test of valve seats processed by different furnace conditions.

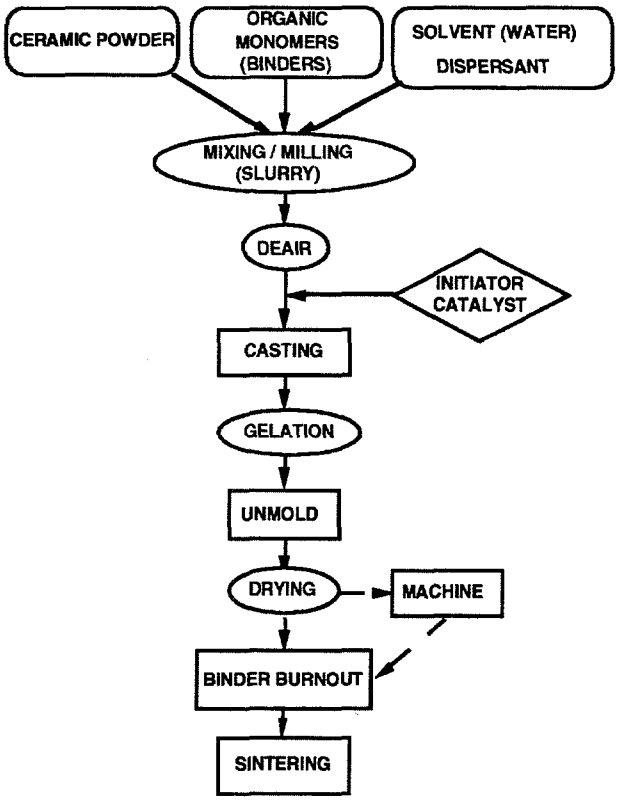

Figure 9. Basic flowchart for the gelcasting process.

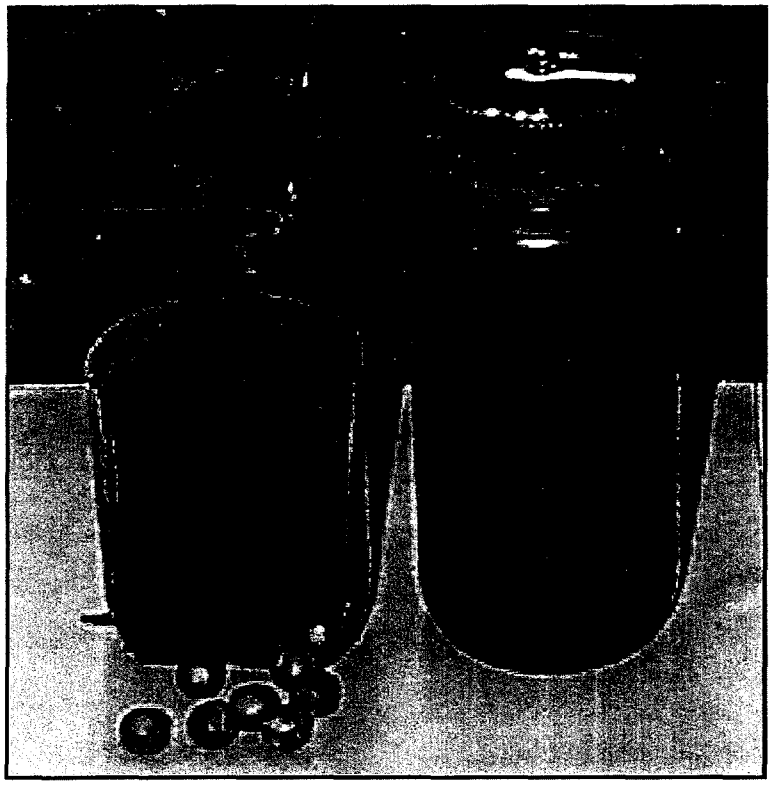

Figure 10. Initial gelcast trials showed premature gelation of silicon and monomer(s) occurred during milling operations. Partial mill jar (left) shows gelled Si slurry and loose milling media.

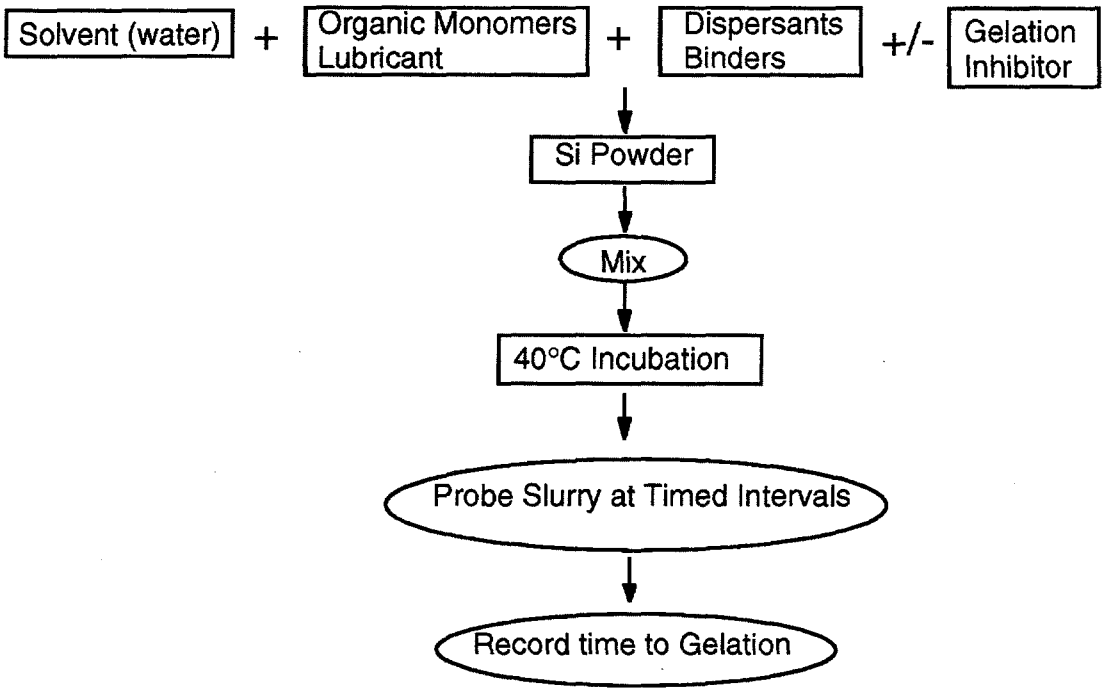

Figure 11. Process steps in evaluation of monomer and Si type on gel initiation with Eaton Si.

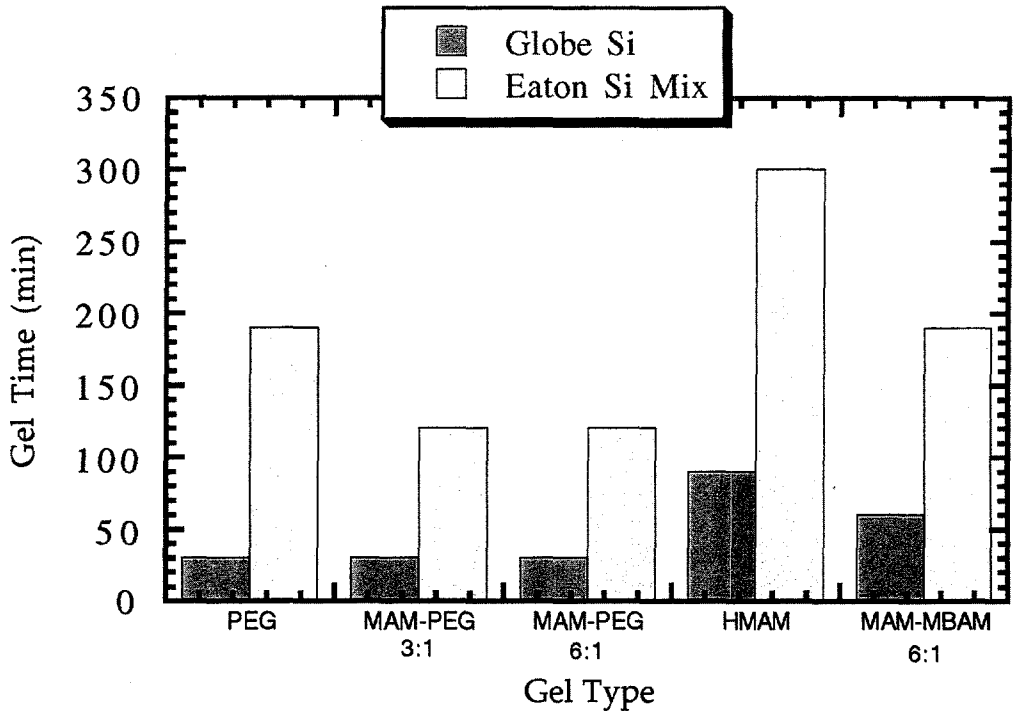

Figure 12. Gel initiation time varied for different Si powders and monomers. As-received Globe Si was the most reactive material tested.

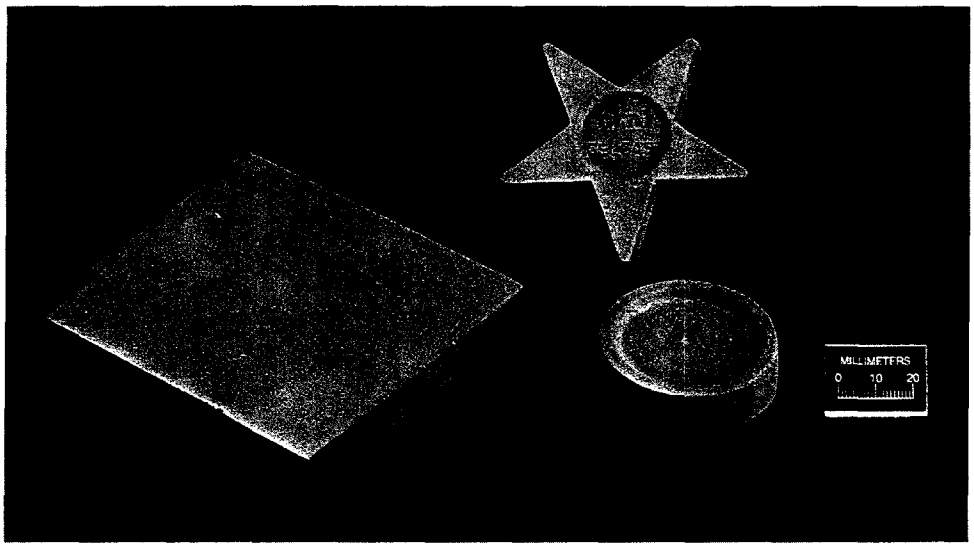

Figure 13. Silicon green preforms of Eaton Powders formed using gelcast techniques.

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