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CRADA Final Report
for
CRADA Number ORNL92-0125

MICROWAVE PROCESSING OF SILICON CARBIDE

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Dow Chemical Company

Prepared by the
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managed by
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ABSTRACT

A Cooperative Research and Development Agreement (CRADA) between Lockheed Martin Energy Systems, Inc. (LMES) and Dow Chemical Company was initiated on May 3, 1993. (Lockheed Martin Energy Research, Inc. (LMER) replaced LMES). The completion date for the Agreement was December 1996. The purpose of this project is to develop microwave processing techniques to produce superior silicon carbide. Sintered silicon carbide is an attractive material for use in high-stress, high-temperature, high-wear, or highly corrosive applications. However, use in these applications has been hampered by a lack of consistency in strength, density, and other physical properties. It is proposed that the enhanced sintering that has been achieved using microwaves in oxide and halide systems be applied to the sintering of these materials to produce a more highly controlled density and microstructure. This will, in turn, increase the strength and Weibull modulus of the sintered body.

The use of microwave energy to anneal for a moderate temperature (1400- 1600°C) anneal in a high vacuum ($<10^{-4}$ Torr) results in an improvement in the sintered density and density distribution. These changes in turn result in improved properties of the sintered compacts. Further, scale up of the process has resulted in the routine production of 3 kg components in excess of 4 cm in thickness.

OBJECTIVES

The overall objective of this project is to identify and scope out ways that microwave heating can positively impact the fabrication of silicon carbide components. Silicon carbide has been a difficult material to sinter traditionally. One of the reasons for this is oxide contamination on the surfaces of grains. Dow Chemical, has discovered an annealing technique which can 'clean' the surface of individual grains prior to high temperature firing. This technique involves mixing additives into the powder which under thermal treatment react with surface contaminants to form gaseous species which are carried away. Dow has learned that this technique is quite successful in promoting densification during final high temperature firing. They however discovered a significant limitation when scaling this technique to thick cross sections required for some commercial products. The technique is a thermally activated process requiring temperatures in the 1400°C to 1600°C range. At these temperatures significant grain coarsening is likely for prolonged exposures. Microwave annealing of thick cross sections is thought to be a remedy to this.

Attainment Of Objectives

SiC compacts were successfully annealed in the microwave furnace. Insulation techniques were developed which controlled the thermal gradient in the samples. Microwave annealing was shown to result in higher and more uniform densities of thick components than could be achieved with conventional annealing technology. A scale up of the technology developed was also successful. Routine processing of 100 gram cylinders was scaled and routinely demonstrated up to a size of 3 kg.

Sponsor Benefits

DOE has been a long time sponsor of microwave processing work. Prior to work in ceramics, the fusion energy program invested heavily in high power microwave energy development for heating plasmas. ORNL has been a leader in the development of this technology. This development is inherently high risk in that industry does not have the proper equipment to conduct research in this area. This CRADA is a good opportunity to transfer this technology to industry.

This CRADA is a good fit to our core competencies here at ORNL. We have the strongest and most diverse technical ceramics program in the country. Our people have the necessary skills in materials and microwave engineering to perform the research. We have a unique combination of furnacing capability giving us the required resources to perform this CRADA in house.

Dow Chemical is a materials company that has made a substantial investment in advanced ceramics. We have every reason to expect that Dow will view this technology as an important part of their technical ceramics portfolio. One patent application has resulted from this work to date.

TECHNICAL DISCUSSION

Dow pressed and burned out 70 cylinders of high quality, sinterable silicon carbide of approximately 100 grams. Half of these were annealed conventionally. The other half were annealed in the microwave. The conditions were to anneal in a 10^{-4} torr vacuum for 0.5, 2, and 8 hours and at temperatures of 1400, 1500, and 1600°C. The microwave anneals were conducted in a diffusion pump vacuum with a 2.45 GHz microwave source. Figure 1 shows the insulation technique which was developed for these experiments. The conventional anneals were performed in a graphite furnace and a roughing pump vacuum. Annealing was followed by a conventional sintering schedule:

5°C/minute to 2100°C in Argon
Soak 30 minutes at 2100°C
Furnace cool

The immersion densities were determined for the bulk samples (cylinders). The samples were then sliced as shown in figure 2. The results of the density measurements on the machined slices are broken down into conventional and microwave annealed samples, and displayed in figure 3. The densities of the slices were all very close to the bulk sample densities.

The microwave annealed samples are all of a higher density than the conventional anneal. Another significant observation is that in both the microwave anneal and conventional anneal cases, the 1600°C temperature shows a higher sintered density after the two hour anneal than after the 8 hour anneal. Both the 1400°C and 1500°C temperatures, the 8 hour anneal yields the higher densities. It appears that anneals for short times at 1600°C is about equivalent to 8 hour anneals at 1400°C or 1500°C, whether the anneals are done in a microwave or conventionally.

To further understand the effect of the microwave field all slices were further machined into a row of seven cubes. Each cube from the slice weighed approximately 0.5 grams. Density determinations significantly better than 1% (.03 g/cc) was desired. An immersion technique using an apparatus developed at NIST was used which utilized a five place

balance, remote sample articulation, and a 25.5 μm diameter nichrome wire suspending the weighing basket which was oxidized to yield a minimum wetting angle with the water bath. One data set for 1600°C, 2 hour anneals is shown in figure 4.

The results demonstrate that the microwave anneals are clearly superior in reducing the density gradients after sintering. General patterns are observed for both the microwave anneals and the conventional anneals: as anneal time increases at 1400 or 1500°C, the density increases and the gradient decreases, but at 1600°C an 8 hour anneal resulted in a decrease in overall density compared to the 2 hour anneal. These observations indicate that the general phenomena occurring for both microwave anneals and conventional anneals are similar. In a previous study [1], this was concluded to be an effect of temperature and pressure enabling the reduction of SiO_2 at the surfaces of the SiC powder, which at higher temperatures (e.g. 1300° or above) resulted in a coarsening of the microstructure and reducing driving force for densification. The absolute results for this study are also consistent with those of the previous study: at 1400°C and approximately 2 hours, the density varied from 3.13 g/cc at the edge to 3.07 g/cc at the middle in the previous study, and in this one from 3.10 g/cc at the edge to 3.06 g/cc at the middle.

A very interesting observation of the microwave annealed samples for 8 hours at 1500° and 1600°C was the drop in density at the surface of the components. Observation of samples of this type revealed a reaction layer which is discolored. The samples have a pale skin which for the longest times and highest temperatures would peal from the samples. Figure 5 is a microscopic comparison of the surface versus the interior of a sintered cylinder. Increased porosity is clearly observed here. Coating the samples with a graphite paint eliminated this problem. One possible explanation for this phenomena is that in the conventional furnace a large mass of graphite is at the annealing temperature during processing. This can prevent stray contaminants such as oxygen from building in the furnace. Due to the heating nature of microwaves the sample is the largest mass of material at temperature. Contaminants such as oxygen which are not quickly pumped from the insulation casket are available to react with the sample cylinders.

Following these experiments a scale up effort was conducted to demonstrate that microwave processing has general utility for commercial processing of SiC. A series of 500 gram cylinders were annealed conventionally and in the microwave. Figure 6 shows a photograph of three SiC cylinders, originally 10 cm diameter by 4 cm thick. The left most cylinder is as pressed green, the center cylinder has been microwave annealed, and the right cylinder has been microwave annealed and sintered. Attempts to process these cylinders in the same manner as the smaller ones was unsuccessful. The increased size of the sample resulted in excessive thermal gradients and cracking. Figure 7 is a photo of the insulation casket which was used to microwave anneal the cylinders. In order to control the thermal gradient generated in the cylinder a suscepting paint was used on the boron nitride container to partially absorb microwave energy and radiate thermal energy toward the SiC cylinder. A comparison was made of a cylinder annealed in this arrangement and one annealed conventionally. These samples were annealed at 1500°C for 1 hr. The samples were then fired to 2150 °C. The other details of the firing are as described above. Each sample was sliced into approximately 90 bend bars and tested for density, strength, toughness, and Young's Modulus. Table 1 shows the comparative differences between the microwave and conventionally annealed samples. In all cases the differences appear to be statistically insignificant. Figures 9 and 10 show contour plots of the density of the two samples. While there are some differences in the details of the contours there really is not enough difference in the data to be of note. While there was insufficient time in the project, it is expected that the microwave annelaing conditions could be optimized to yield a more uniform ceramic body.

A further attempt at scale up involved 3 kg plates. Figure 10 shows the plate along with the other two cylinder sizes used during this investigation. A similar insulating scheme was successfully used as in the 500 g cylinder experiments.

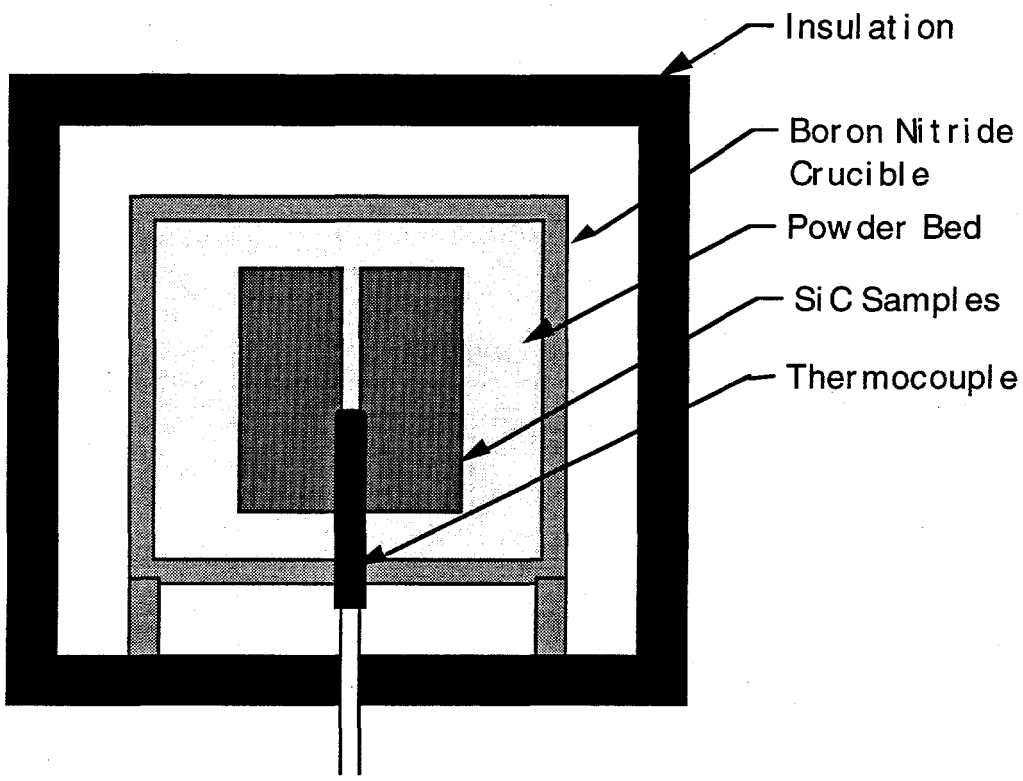


Figure 1: Crucible arrangement for microwave sintering of silicon carbide

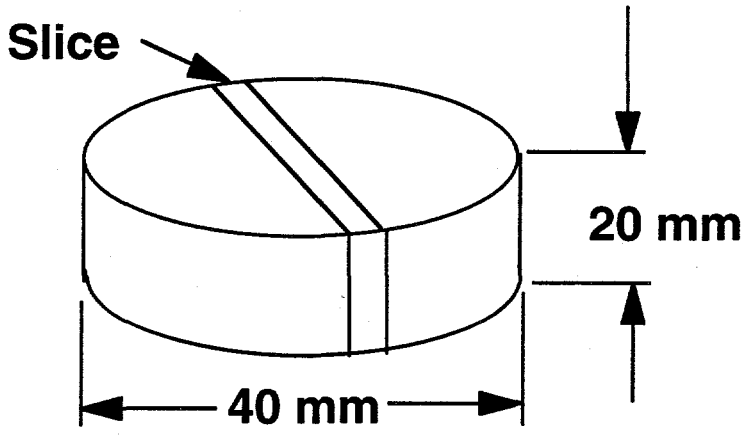


Figure 2: Schematic of cylindrical sample with a diametrical slice cut from it. Dimensions are approximate.

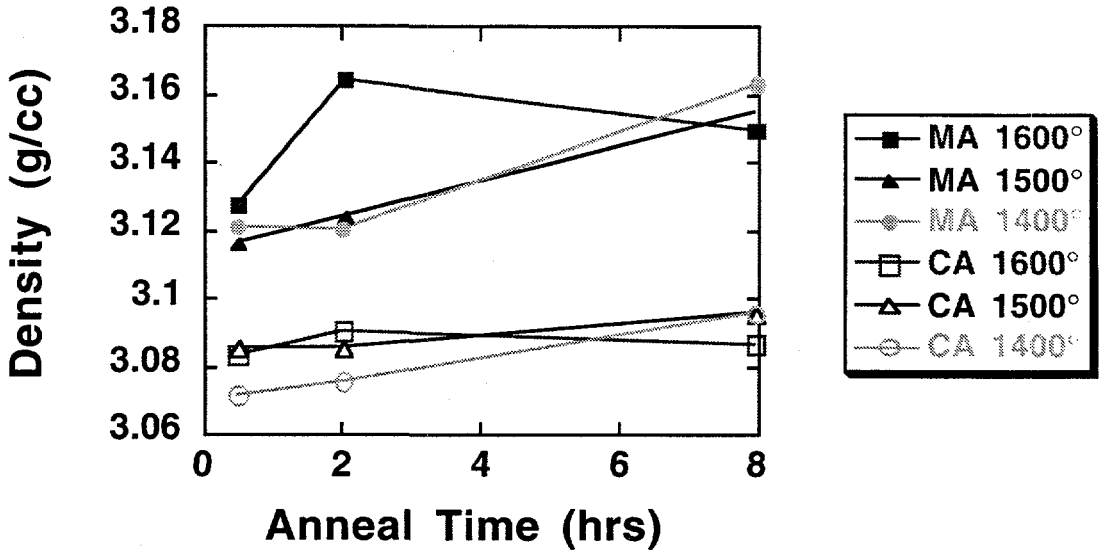


Figure 3: Sintered densities of microwave and conventional anneals. Samples are slice immersion densities. Open symbols are conventional anneals. Closed symbols are microwave anneals.

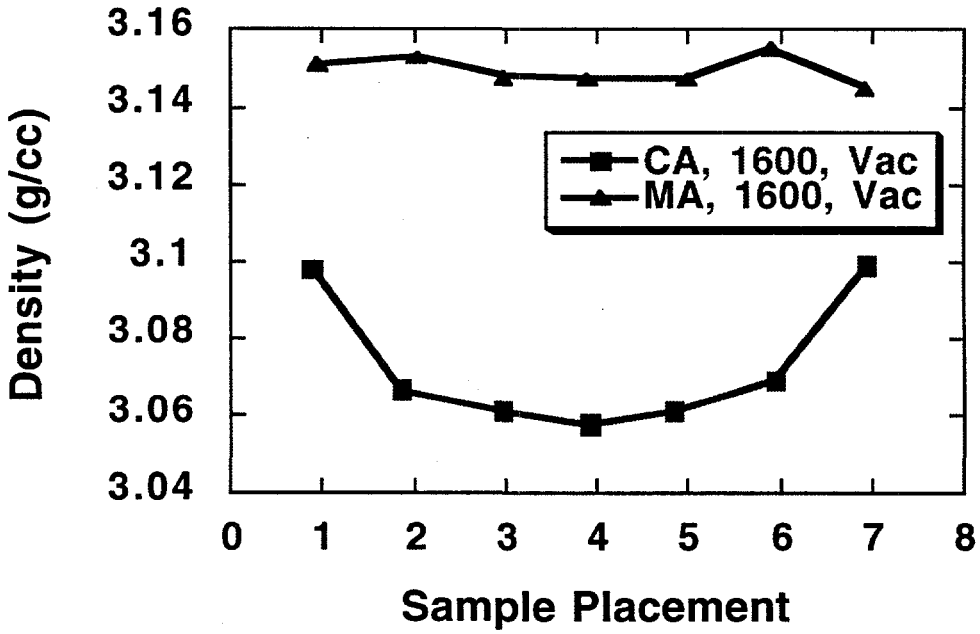
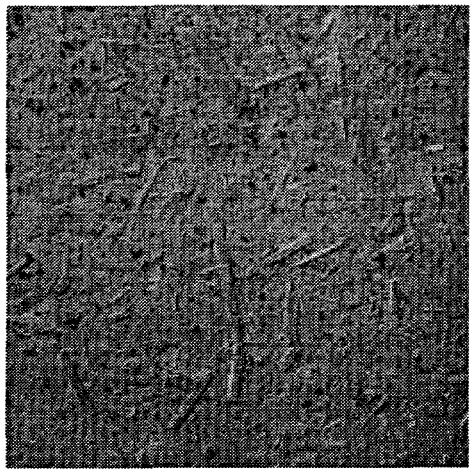
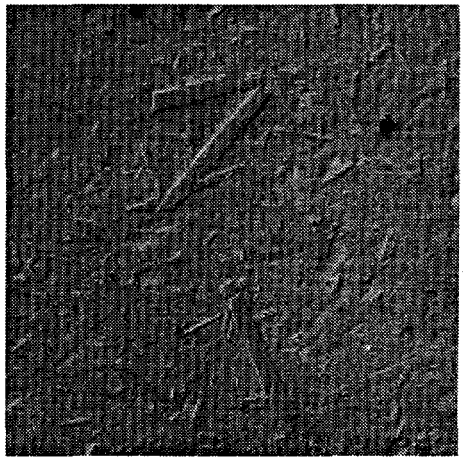


Figure 4: Sintered density results for 2 hour anneals.



Reaction Zone At The Sample Edge



Sample Interior

Figure 5: Comparison of edge and center microstructures of a sintered cylinder

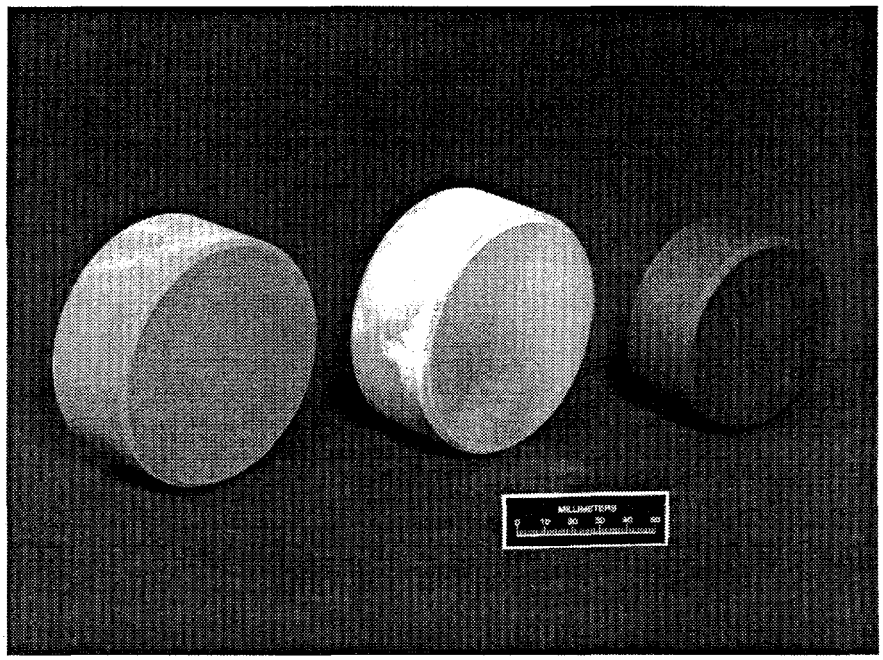


Figure 6: Green, annealed, and sintered SiC cylinders 10 cm diameter

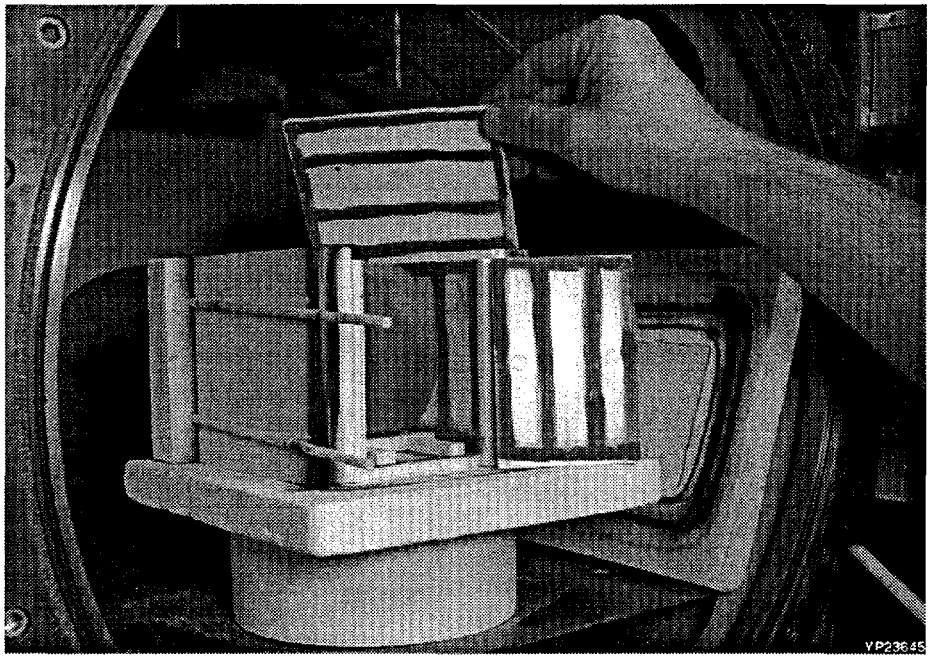


Figure 7: SiC insulation set up for scale up experiments

Table 1: Comparison data between microwave and conventionally annealed 500 g cylinders

	Microwave Annealed		Conventional Annealed	
	Mean	Std Dev	Mean	Std Dev
Strength (MPa)	450	79	452	94
Young's Modulus	396	24	382	29.4
Toughness (MPa √m)	3.5	0.4	3.5	0.2

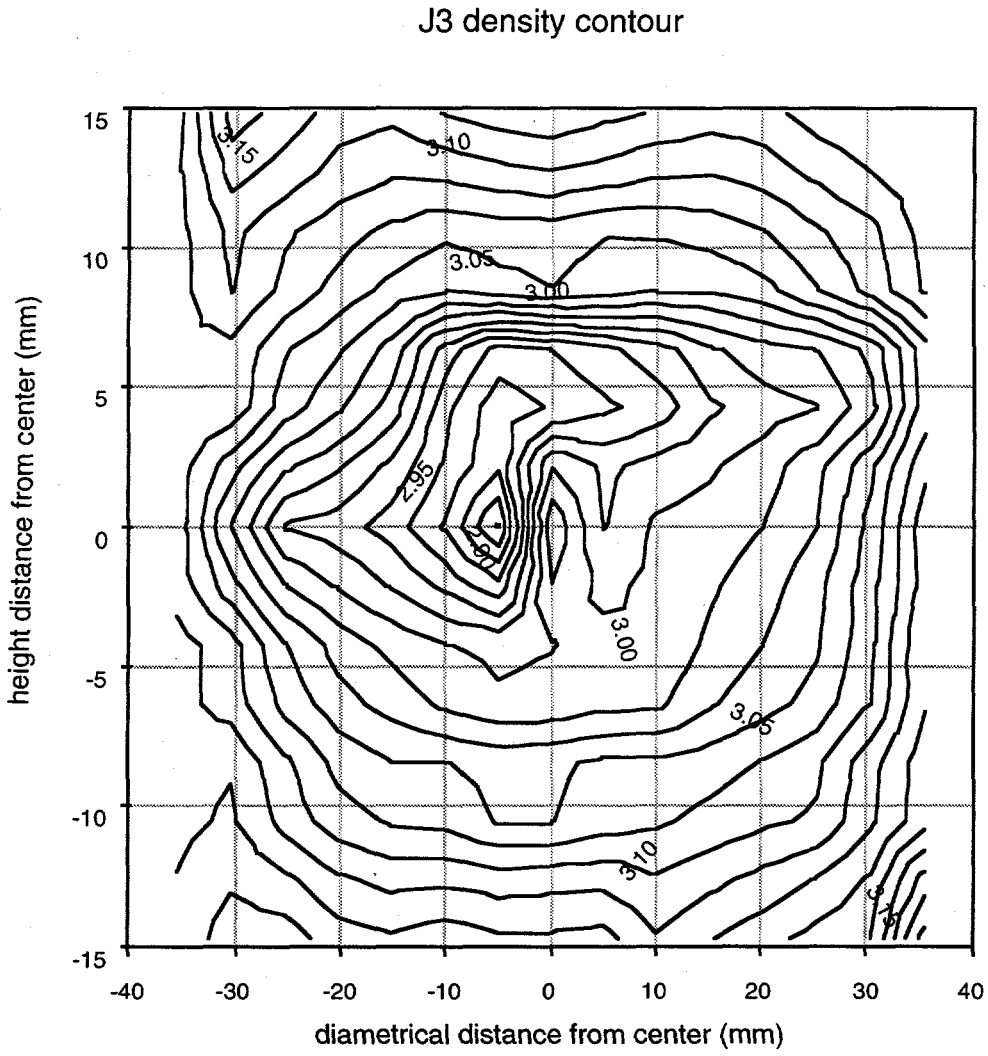


Figure 8: Density contour of a 500 g microwave annealed cylinder

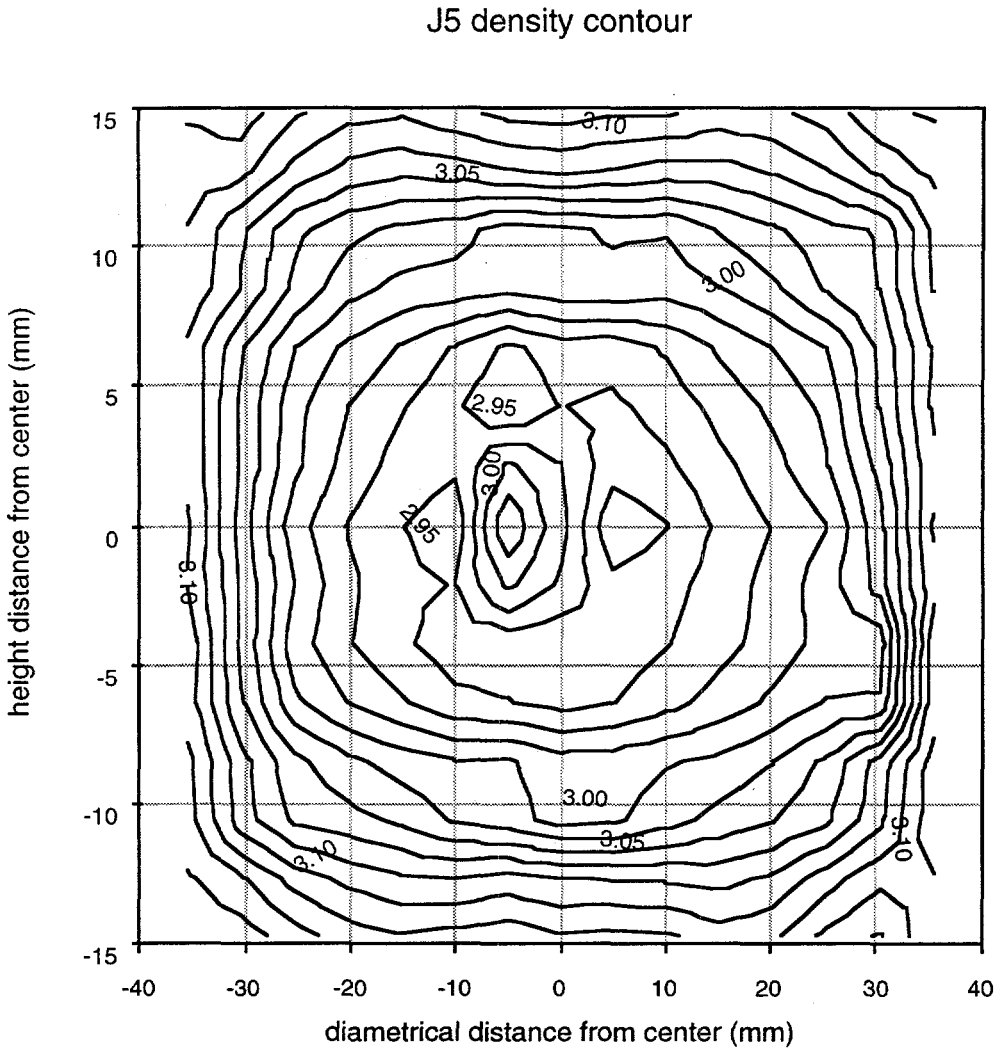


Figure 9: Density contour of a 500 g conventionally annealed cylinder

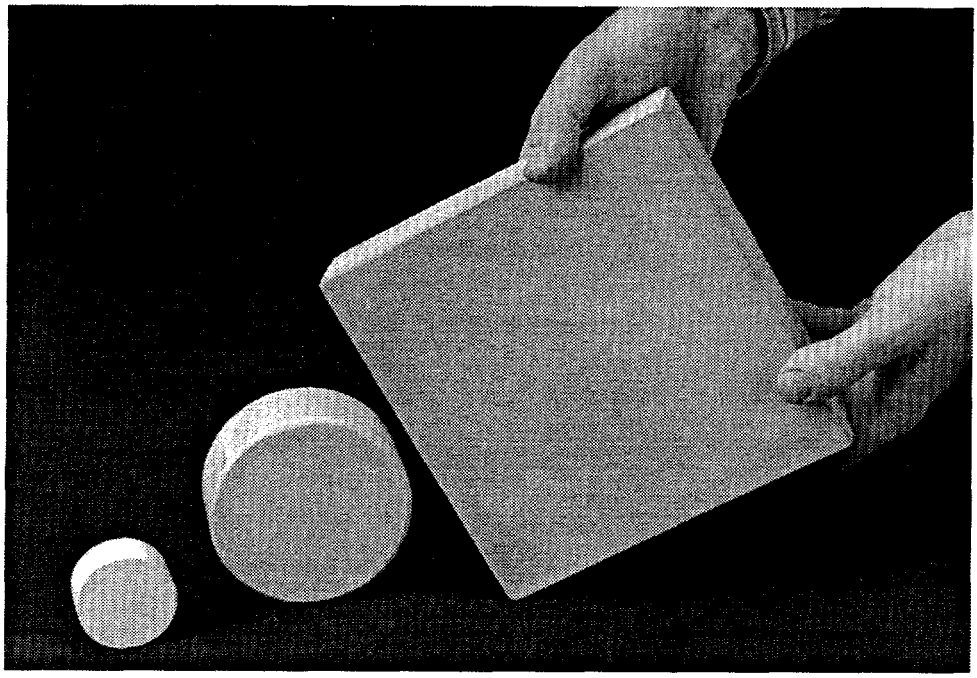


Figure 10: Scale up was successful from 100 grams to 3 kg parts

INVENTIONS

One invention disclosure was filed as a result of this CRADA. A patent application is being filed.

PLANS FOR FUTURE COLLABORATION

There are no immediate plans for future collaboration. Follow on work is being pursued in the area of ceramic armor.

CONCLUSIONS

The CRADA between LMER and Dow Chemical has been successfully completed. SiC compacts were successfully annealed in the microwave furnace. Insulation techniques were developed which controlled the thermal gradient in the samples. Microwave annealing was shown to result in higher and more uniform densities than could be achieved with conventional annealing technology. A scale up of the technology developed was also successful. Routine processing of 100 gram cylinders was scaled and routinely demonstrated up to a size of 3 kg.

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1. E. A. Ness and W. Rafaniello, "Origin of Density Gradients in Sintered Beta Silicon Carbide Parts", J. Am. Ceram. Soc., Vol 77[11], 2879-84 (1994).

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