

# GAS-PHASE SOLID FREEFORM FABRICATION OF SiC CERMETS USING SALDVI

James E. Crocker, Leon L. Shaw, and Harris L. Marcus  
Institute of Materials Science, Department of Metallurgy and Materials Engineering  
University of Connecticut, Storrs, CT 06268

## Abstract

Selective Area Laser Deposition Vapor Infiltration (SALDVI) is an experimental solid freeform fabrication (SFF) technique aimed at the direct fabrication of ceramic and ceramic/metal structures and composites. SALDVI uses a layer-by-layer approach in which powders are infiltrated with solid material deposited from gas precursors by chemical vapor deposition (CVD) using laser heating. Experiments have been performed with CO<sub>2</sub> and Nd:YAG lasers using the silicon carbide forming gas precursor Si(CH<sub>3</sub>)<sub>4</sub> and Cu, Mo, and Ni metal powders. The microstructure of the resulting SiC/metal cermets was investigated in relation to the processing history. In some cases, the formation of intermetallic silicide phases was observed.

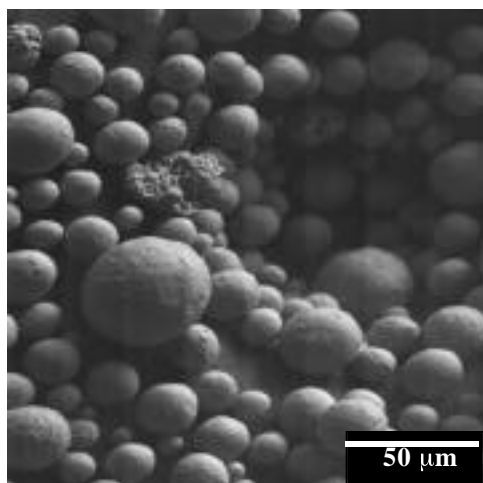
## Introduction

SALDVI is a layer-by-layer approach to SFF in which porous layers of loose powders are densified by depositing solid material from gas precursors into the pore spaces using laser chemical vapor infiltration (CVI)<sup>1</sup>. Because the CVI process can deposit a variety of desirable materials in pure form, SALDVI is capable of building ceramic and composite net shapes and shapes with functionally graded compositions such as embedded devices<sup>2</sup> in a single machine. SALDVI using ceramic powders and the SiC-forming gas Si(CH<sub>3</sub>)<sub>4</sub> has been previously investigated<sup>3</sup>. The laser induced processing temperature distribution, gas precursor pressure, laser scanning speed, and the particle size of the starting powder were found to affect the infiltration and densification rates of the bulk SALDVI shapes. The nanocrystalline nature of the solid material deposited from the Si(CH<sub>3</sub>)<sub>4</sub> gas precursor by laser CVD on solid ceramic substrates has also been well characterized on the micro and atomic scales<sup>4</sup>. In all of this previous work, the ceramic substrate remains chemically compatible with the vapor deposited SiC throughout the range of processing temperatures experienced during fabrication. In this study, the fabrication of SALDVI cermets using Cu, Ni, and Mo metal powders and Si(CH<sub>3</sub>)<sub>4</sub> gas is explored. The affinity of these metals for forming a range of intermetallic compounds with free Si combined with their lower melting temperatures, more so for the Cu and Ni than the Mo, makes their chemical stability with the vapor deposited SiC uncertain. In the following, the processing temperature and time at temperature are varied to examine the effect on the extent of reaction between the starting powders and the vapor infiltrated matrix. Scanning Electron Microscopy (SEM) with Energy Dispersive X-ray Spectroscopy (EDS) is used to probe the local elemental compositions at each processing condition. X-ray diffraction is used to detect the formation of intermetallic phases in the bulk samples.

## Experiment

The SALDVI workstation consists of a vacuum chamber, a powder delivery system, a 50 watt continuous wave CO<sub>2</sub> (10.6 μm wavelength) or a 150 watt continuous wave Nd:YAG (1.06

$\mu\text{m}$  wavelength) laser beam, an xy table with scanning mirrors, and an optical pyrometer temperature probe. All components are computer controlled. In these experiments the surface temperature measured by the optical pyrometer was used in a feedback loop to adjust the laser output power as necessary to maintain a constant surface temperature, termed the target temperature, throughout the experiment. The laser beam spot size was nominally 1 mm in diameter and Gaussian in shape. The  $\text{Si}(\text{CH}_3)_4$  gas pressure was 10 Torr. The sample geometry consisted of a single line one beam diameter in width, 20 mm in length, and three layers in height at 120  $\mu\text{m}$  per layer. The Cu, Ni, and Mo powders range in size from a few microns up to 50  $\mu\text{m}$ , are mostly spherical, and pack to an initial powder bed density of about 55 percent. Figure 1 illustrates the size distribution and morphology of the as-received Mo powder. As it was impossible to heat the pure Cu powder to the desired target temperature with either laser, 10 weight percent Si powder was added to improve laser absorption. The Ni and Mo powders were processed in the pure, as-received state. Samples were fabricated at target temperatures of 1000, 1100, and 1200°C, and at laser scanning speeds of 1.25, 2.5, and 5.0  $\mu\text{m}/\text{s}$ . Considering the laser



spot size of 1 mm, these scanning speeds result in laser dwell times or average heating times of 800, 400, and 200 s, respectively. Polished cross-sections of each condition were examined in the SEM and the local chemical composition of the Si and Cu, Ni, or Mo was probed with EDS. No attempt was made to quantify the carbon in the sample with this method. Selected samples were also analyzed with X-ray diffraction. Finally, the mechanical behavior of the three cermets was compared in four-point bending.

Figure 1. Molybdenum powder particles before SALDVI processing.

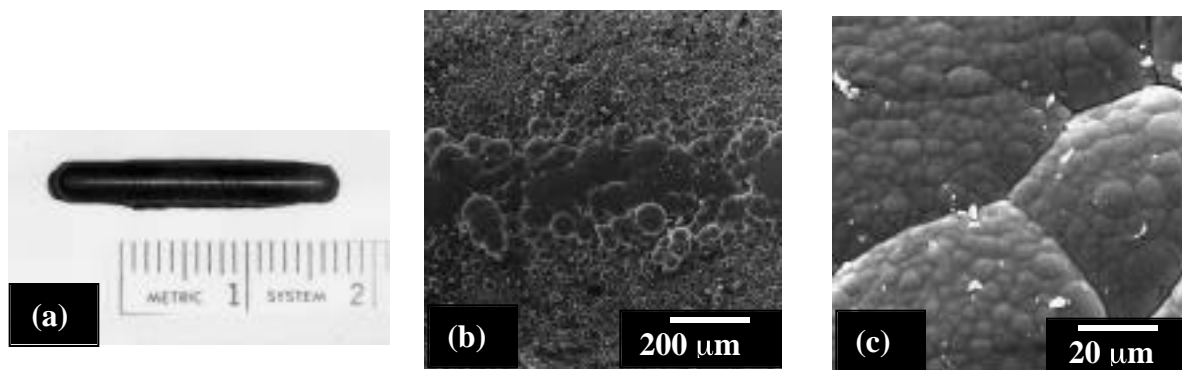


Figure 2. Optical (a) and SEM photos (b) and (c) of centerline region of Mo powder vapor infiltrated with SiC at 1000 C target temperature and 400 s average heating time.

## Results

Figure 2a shows a typical as-fabricated single line, three layer, 20 mm long SALDVI sample. The centerline of the scan, where the intensity of the laser beam is highest, consists of a region of dense vapor infiltrated powder. The density decreases to that of the initial powder at the sample edges, which can be easily removed by fine grinding. SEM photos of the dense centerline region are shown in Figure 2b and 2c for Mo powder processed at a target temperature of 1000 C and average heating time of 400 s. The dense region is about 400  $\mu\text{m}$  wide and shows the nodular surface appearance common to vapor deposited surfaces.

### A. Cu and 10 wt. % Si powder

SEM images of the SiC vapor infiltrated Cu-10 wt. % Si powder are presented in Figure 3 (a-c) for a target temperature of 1000 C and for average heating times of 200, 400, and 800 s, respectively. Figure 4 shows the result for a target temperature of 1200 C and an average heating time of 200 s. The original Cu particles are clearly distinguishable from the surrounding vapor deposited SiC matrix. However, in all cases, EDS measurements of the Cu and Si indicate that the composition within the particles are uniform and are equivalent to that obtained for a  $\text{Cu}_5\text{Si}$  standard (8.8 wt. % Si). Small amounts of Cu, up to 5 wt. %, were also measured in the SiC matrix within a few microns of the particle surface. The observed compositions showed little dependence on target temperature and heating time. The presence of particle pull-outs in the cross-sections is an indication of the high stresses that exist across the interface between the particles and the matrix due to the thermal expansion mismatch between Cu, SiC, and their reaction products.

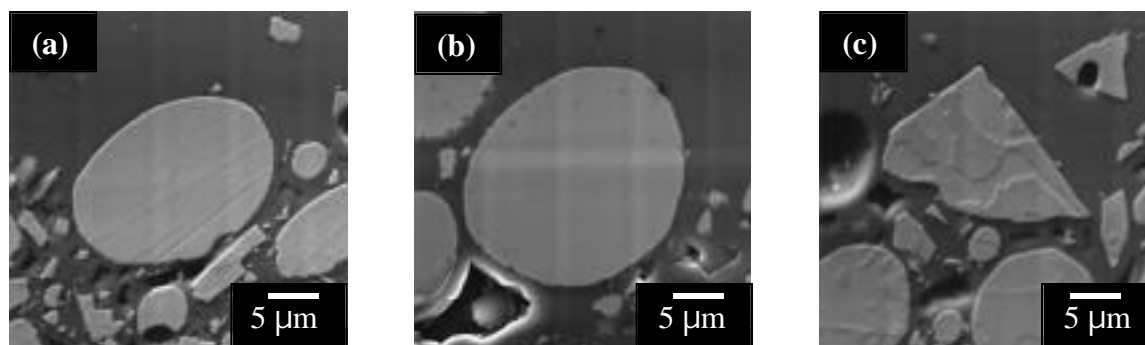


Figure 3. SEM photos of Cu-10 wt. % Si powder infiltrated with vapor deposited SiC at 1000 C target temperature for (a) 200 s, (b) 400 s, and (b) 800 s average heating times.

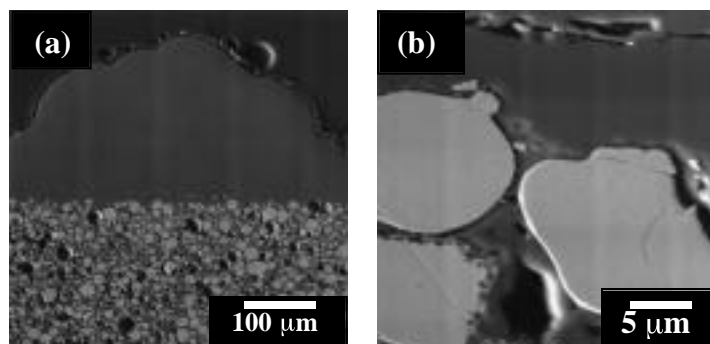


Figure 4. SEM photo of Cu-10 wt. % Si powder infiltrated with vapor deposited SiC at 1200 C target

temperature for 200 s average heating time.

## B. Ni powder

Figure 5a shows a SEM image of a cross section through the centerline region of a SALDVI sample of Ni powder and vapor infiltrated SiC at a target temperature of 1000 C and 800 s average heating time. Evidence of severe reaction between the Ni particles and the vapor deposited SiC matrix is apparent. The SEM image in Figure 5b shows the reaction zone associated with one of the Ni particles near the surface of the sample. EDS measurements of the Ni and Si compositions in the center of these particles indicate a uniform composition corresponding to  $\text{Ni}_2\text{Si}$  (19.7 wt. % Si). The gray zone surrounding the particle measures a higher Si content, up to 30 wt. %. In the SiC matrix just adjacent to this gray zone, up to 5 wt. % Ni is detected. Again, similar to the Cu cermet, in Figure 5a there is evidence that some of the reacted particles have debonded from the surrounding matrix.

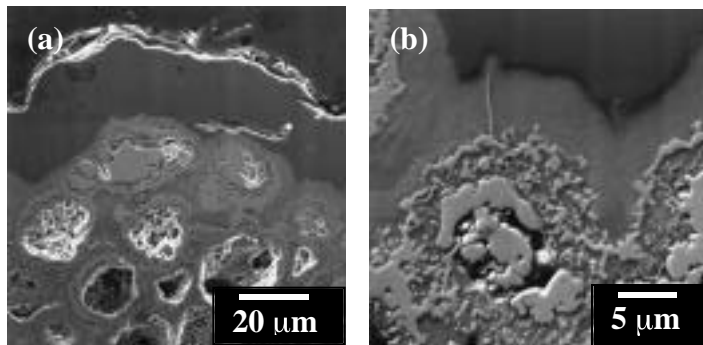


Figure 5. SEM photos of Ni powder infiltrated with vapor deposited SiC at 1000 C target temperature for 800 s average heating time.

The effect of the processing target temperature is illustrated in Figure 6. Figure 6a shows a Ni particle from a sample processed at a target temperature of 1000 C for a heating time of 200 s. EDS probes detected no Si at the center of the particle, up to 5 wt. % Si at the edge of the particle, 20 wt. % Si in the zone surrounding the particle, and a few wt. % Ni in the SiC matrix adjacent to the reaction zone. Figure 6b shows a more pronounced reaction zone from a sample processed at a target temperature of 1200 C for an average heating time of 200 s. The Ni and Si composition in the particle measured by EDS is uniform and richer in Si than that of the  $\text{Ni}_2\text{Si}$  phase. The Si content in the regions surrounding the particles is greater than 30 wt. %.

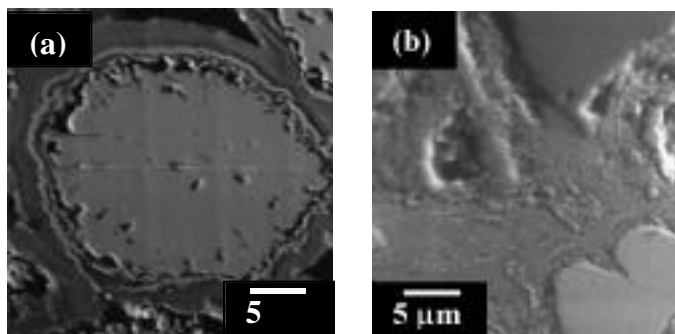


Figure 6. SEM photos of Ni powder infiltrated with vapor deposited SiC for 200 s average heating time and (a) 1000 C and (b) 1200 C target temperature.

### C. Mo powder

The Mo powder showed no reaction with the vapor-deposited SiC at a target temperature of 1000 C for the three heating times examined here. No Si was measured by EDS within the Mo powder particles, nor any Mo into the SiC matrix. Figure 7a shows the structure of a Mo/SiC cermet processed at a target temperature of 1000 C and a heating time of 400 s. The lack of pullouts in the cross-section indicates that the Mo particles are well bonded to the SiC matrix. This is not unexpected as Mo and SiC exhibit similar thermal expansion behavior. The solid density, including powder and vapor deposited SiC, is about 95 % in this region. Figure 7b shows the fracture surface across two adjacent layers of a 3 layer Mo/SiC sample. It is apparent that the fracture path goes around, rather than through, the Mo particles. Also, there is continuous vapor deposited material across the layers.

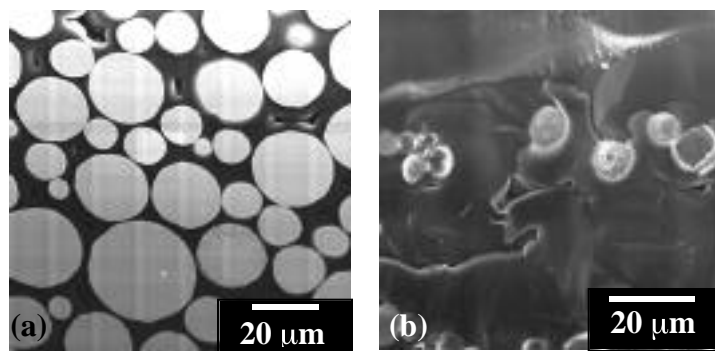


Figure 7. SEM images of Mo powder infiltrated with vapor deposited SiC at 1000 C target temperature and 400 s average heating time (a) cross-section and (b) fracture surface.

### D. Mechanical Behavior

SALDVI cermet samples processed at 1000 C target temperature and 400 s heating time were mechanically tested in four point bending. Only one sample of the Ni cermet was sufficiently sound for the test. Three samples each of the Mo and Cu-10 wt. % Si cermets were tested. The failure loads for each are compared in Figure 8. The failure loads for the Mo/SiC cermet correspond to a beam strength of about 50 MPa.

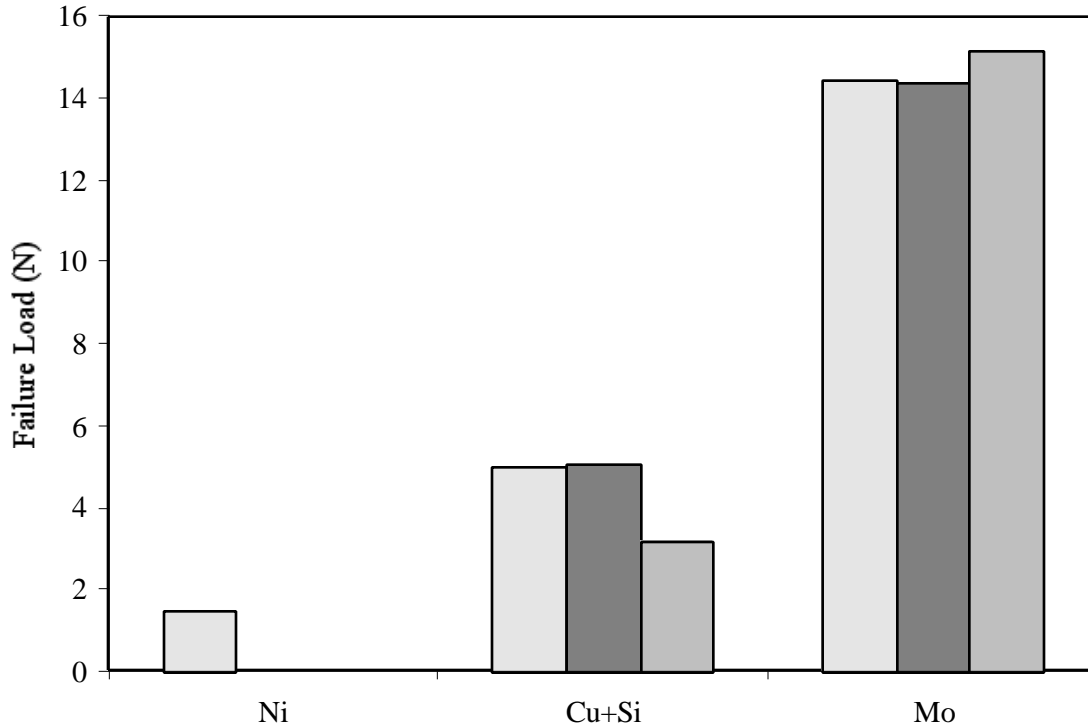


Figure 8. Failure loads in 4-point bending for SALDVI samples of Ni, Cu-10 wt.% Si, and Mo powders processed at 1000 C target temperature and 400 s heating time.

### Discussion

The microstructures of the three SALDVI cermets reveal varying degrees of reactions between the metal powders and the vapor deposited SiC matrix. Both the Cu and Ni powders react with vapor deposited SiC during the SALDVI process at all of the processing temperatures and heating times examined here. For the Cu-10 wt. % Si powder, particles at least 20  $\mu\text{m}$  in diameter reach a uniform composition indicative of a Cu silicide phase even at the shortest heating time of 200 s and lowest processing temperature of 1000 C. Further evidence of Cu silicide formation was observed in preliminary x-ray diffraction measurements at 1000 and 1200 C target temperatures. These results indicate that Si is a fast diffuser in Cu. The observed reactions between Cu and Si are not due only to the presence of the elemental Si in the initial powder mixture however. Similar EDS measurements for a SALDVI cermet fabricated using an initial powder of Cu-50 vol. % SiC also detected Si within the Cu particles, so at least some of the diffusing Si comes from the vapor deposited material.

In the Ni case, the extent of the reactions progressed more notably with increasing processing temperature and heating durations. At a target temperature of 1000 C and 200 s heating time, Si diffuses only a few microns into the Ni particle (Figure 6a). Increasing the heating time by a factor of four results in a fully reacted particle up to 20 wt. % Si in the center (Figure 5b). Increasing the processing temperature to 1200 C for a 200 s heating time increased the Si composition measured at the center of the particles higher than 20 wt. % (Figure 6b). The particles sampled here were located in similar regions of each sample, where the temperature and

time at temperature are highest. Because the Gaussian beam shape results in a distribution of temperatures and heating times, certainly other regions in each sample will show varying degrees of reaction. Though the carbon content was not quantified in this study, the reaction between Ni and SiC likely results in free carbon, as Ni does not form a carbide. A diffusion study between Ni and SiC at 1000 C and 1150 C found a reaction zone consisting of alternating layers of Ni<sub>2</sub>Si and Ni<sub>2</sub>Si with carbon, consistent with the Ni-Si compositions reported here<sup>5</sup>. The reaction path from pure SiC to pure Ni at 1150 C in their study suggests that diffusion can occur entirely in the solid state, even though some of the binary Ni-Si silicide phases are liquid below this temperature. It is not clear if carbon plays a similar stabilizing role in the Cu-Si-C system.

For the Mo/SiC cermet, no Mo-Si interdiffusion was detected by EDS for the 1000 C target temperature. This is not surprising as the melting temperature of Mo is 2610 C, so diffusion would be expected to occur slowly at 1000 C. The Mo/SiC cermet shows the highest bending strength of the three cermets. This behavior is attributed to the close thermal expansion match between the two materials resulting in few particle debonds compared to the Cu and Ni cases.

### **Conclusions**

The fabrication of SiC cermets by SALDVI using Cu, Ni, and Mo powders was investigated. The Cu and Ni powders reacted with the vapor deposited SiC at the normal SALDVI processing temperatures and scan speeds to form microstructures with various interesting compositional features, including the formation of intermetallic phases. No such reactions were observed for the Mo/SiC cermet, although only the lowest processing temperature of 1000 C was currently investigated. The highest bend strength of 50 MPa was measured for the Mo/SiC cermet.

### **Acknowledgement**

The authors acknowledge the support for this research by the Office of Naval Research (grant #N00014-95-1-0978).

### **References**

1. B.R. Birmingham and H.L. Marcus, "Silicon Carbide Shapes by Selective Area Laser Deposition Vapor Infiltration," Proceedings of the Solid Freeform Fabrication Symposium, The University of Texas at Austin, 1994, pp. 348-355.
2. J.E. Crocker, S. Harrison, L. Sun, L.L. Shaw, and H.L. Marcus, "Using SALDVI and SALD with Multi-Material Structures," *JOM*, **50**, 21-23, December, 1998.
3. J.E. Crocker, L. Sun, H. Ansquer, L.L. Shaw, and H.L. Marcus, "Processing and Characterization of SALDVI Ceramic Structures," Proceedings of the Solid Freeform Fabrication Symposium, The University of Texas at Austin, 1999, pp. 495-501.
4. J.E. Crocker, S.L. Harrison, L. Sun, L.L. Shaw, and H.L. Marcus, "Localized CVD and the Ultrafine Grain Structure," Proceedings of TMS Ultrafine Grained Materials Symposium, Nashville, TN, March, 2000.

5. M.R. Jackson, R.L. Mehan, A.M. Davis, and E.L. Hall, "Solid State SiC/Ni Alloy Reaction," *Met. Trans. A*, vol. 14A, March, 1983, pp. 355-364.