SAND99-0237C

Processing and Characterizing Alumina / Aluminum Composites with Tailored Microstructures Formed by Reactive Metal Penetration

Erica Corral*, University of Texas at El Paso, El Paso, TX, Bill Fahrenholtz, University of New Mexico, Albuquerque, NM, Ron Loehman, Kevin Ewsuk, and Don Ellerby, Sandia National Laboratories, Albuquerque, NM

Materials Processing (1846)

August 4, 1998

In industry, the need to maximize energy efficiency depends on the availability of suitable advanced materials. Ceramic composites are exemplary materials for many advanced engineering applications because they exhibit good thermal stability, oxidation resistance and enhanced toughness. Presently, ceramic composite fabrication processes are costly, often requiring high temperatures and pressures to achieve reasonable densities. Our research is focused on developing a processing technique, that will allow production of alumina/aluminum composites using relatively low temperatures and without the application of an external force, thus reducing the processing costs. Our composites were formed using Reactive Metal Penetration (RMP), which is a process involving the reaction of molten Al with a dense ceramic preform. The result is a near net shape ceramic/metal composite with interpenetrating phases. The volume fraction of metal in the composites was varied by doping an aluminosilicate ceramic preform with silica. For this study we fabricated composites using pure mullite and mullite doped with 23 and 42 weight percent silica, yielding 18, 25, and 30 volume percent metal in the composites, respectively.

Optical and Scanning Electron Microscopy were used to characterize the homogeneity and scale of the microstructure. The scale of the microstructure varied with preform composition, the reaction temperature and with secondary heat treatments. Four-point bend testing was used to evaluate the influence of microstructure on strength and reliability. During these studies a gradient in the microstructure was observed, which we further characterized using microhardness testing. Alumina/aluminum composites formed by RMP show higher toughness then monolithic alumina and have the potential for improved reliability when compared to monolithic ceramics.

Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under contract DE-AC04-94AL85000.

DISCLAIMER

I. INTRODUCTION

In industry the need to maximize energy efficiency depends on the availability of suitable materials. Ceramic composites are exemplary materials for energy applications because of their high stiffness-to-weight ratio, excellent high temperature stability, good oxidation resistance, and enhanced toughness. Additionally, their electrical and thermal properties can be varied through control of their composition and microstructure. Various *in situ* forming techniques have been used to fabricate ceramic-metal composites with high volume fractions of ceramic, including the directed metal oxidation process, chemical vapor infiltration and the reaction bonded aluminum oxide process. Presently, enhancement in properties versus the cost of these fabrication processes are not significant enough to make composite materials competitive with other more traditional materials[1]. Our research is focused on a processing technique that will allow low cost production of composites with improved reliability. Composite synthesis by reactive metal penetration (RMP) has been proven very effective in the formation of alumina/aluminum composites. RMP results in near-net-shape ceramic and metal-matrix composites with control of both composition and microstructure. Near-net-shape fabrication eliminates the need to machine or diamond grind parts after processing, significantly reducing the costs and also reducing the amount of waste from these finishing operations.

This work is based on the discovery of R.E. Loehman of Sandia National Laboratories and A.P. Tomsia of Pask Research and Engineering that when molten aluminum is placed in contact with a dense mullite preform it penetrates the ceramic and converts it to a composite with interpenetrating phases. In order for RMP to take place two requirements must be met. First, the Gibbs energy for reaction must be negative and second, the molten metal must wet the ceramic (i.e. the contact angle $\theta < 90°$). For the reaction between aluminum and mullite the $\Delta G_r(1200K) = -1014$ kJ and $\Delta G_r(1600K) = -828$ kJ and has a wetting angle less than $90°$[2]. The composites we studied were based on the following reaction between mullite and aluminum,

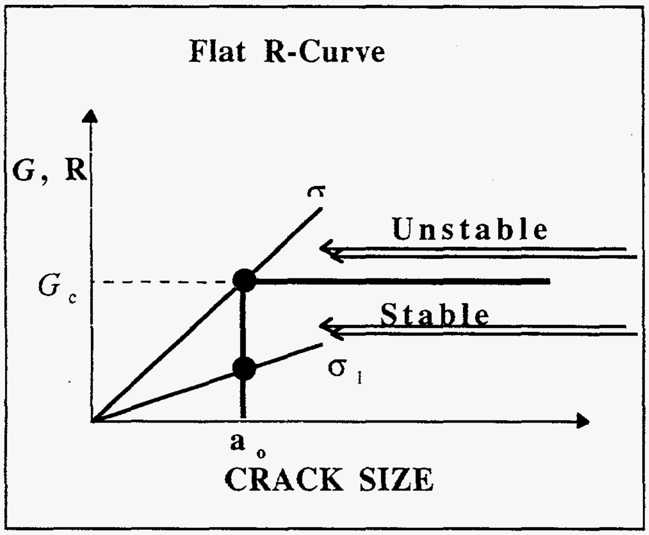
$$3Al_6SiO_{13} + (8+x)Al \rightarrow 13Al_2O_3 + (6-y)Si + (x)Al + ySi \uparrow$$

In this reaction molten aluminum reacts with and reduces the mullite to form alumina and elemental Si. The Si then diffuses out of the preform into the aluminum bath and is replaced by aluminum. The ability to draw out the silicon after the reaction allows the toughness and hardness of the composites to be tailored. Composites can also be formed to near-net-shape with excess aluminum and by adjusting the porosity of the ceramic preform to accommodate the increased volume of Al present in the composite after reaction[3].

The composites we are studying show resistance curve or R-curve behavior[4]. R-curve behavior occurs when a materials toughness increases with increasing crack length. For the materials we are studying the reason for this behavior is the formation of bridging metal ligaments. They apply a force across the crack face reducing the stress intensity at the crack tip and increasing the toughness of the material. The toughness continues to increase until the metal ligaments holding the faces together begin to fail behind the crack tip. At this point a steady state bridging length is formed, which represents the plateau of the R-curve. The existence of an R-curve for these materials allows for the possibility to design a more flaw tolerant composite with enhanced reliability.

Figure 1. shows the difference between a flat R-curve and a rising R-curve. The plots are of the materials resistance in terms of strain energy release rate, or fracture toughness and driving force for crack propagation, both having the same units, versus the crack extension. Figure 1a. shows a flat R-curve for a typical ceramic. Stable crack growth occurs at a given stress = σ_1 where the materials resistance to crack growth is constant with crack growth and as the crack grows the materials resistance remains higher than the driving force for crack growth. Unstable crack growth occurs at σ_2 because the driving force for crack growth is greater or equal to the materials resistance to crack growth. The driving force increases with crack length growth but the materials resistance remains constant resulting in fracture. Figure 1b. shows a rising R-curve typical of one of our composites. At σ_1 the driving force for crack growth is less than the resistance to crack growth of the matrix. Stable crack growth occurs at stress = σ_2, and σ_3 because the change in the driving force for crack growth is still less than the change in the materials resistance with crack growth. When the stress reaches σ_4 the

driving force equals the materials resistance and the crack grows unstably until failure. Flaws less than a_c result in stable crack growth and therefore R-curve materials are expected to be more flaw tolerant and more reliable.



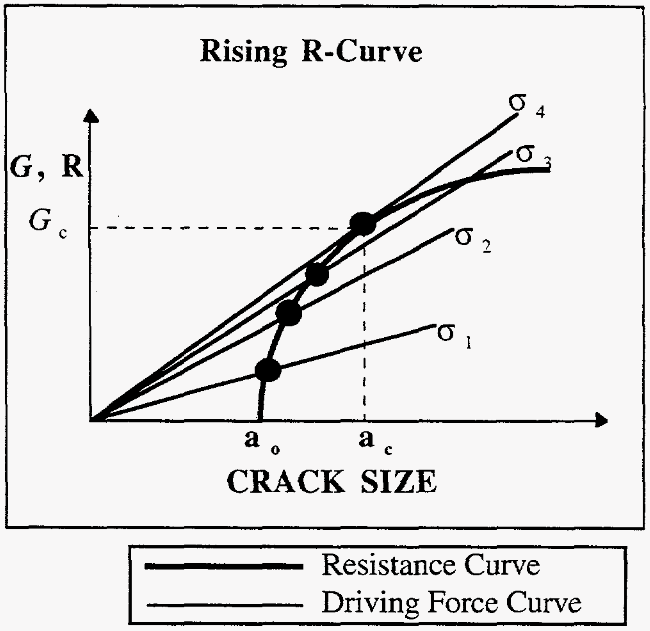


Figure 1a. This graph shows a flat R-curve for a typical ceramic.

Figure 1b. This graph shows a rising R-curve typical one of our composites.

Weibull statistics are an indication of a materials reliability, based on a number of strength measurements[5]. The analysis is conducted based on the fact that all materials will fail due to flaws and based on the size distribution of these inherent flaws your reliability will increase or decrease. A distribution of strengths have a distribution of flaw sizes. A narrow distribution is desired resulting in a more reliable material failing over a smaller range of flaws. The Weibull modulus is the slope of a linear regression fit to the data of a plot of ln ln (1/Possibility of Survival) versus ln (strength). The steeper the slope the more reliable the material which relates back to the narrow range of strength values. R-curve materials are expected to have a narrow distribution of strengths and flaws which would result in a higher Weibull modulus and increased reliability.

II. EXPERIMENTS

A. Preform Processing

In order to increase the metal content in the composites, mullite powder was doped with silica. In order to dope the material the mullite powder was suspended in an aqueous slurry and a colloidal silica slurry was then added. The final slurry was mixed then dried and crushed into powder. Powders of mullite and mullite doped with 23 and 42 weight percent Silica were pressed in a uniaxial press at 5000 psi. The pellets were then cold isostatically pressed at 25 Kpsi. The mullite pellets were fired in a air at 1690°C for two hours. The doped pellets were fired in air at 1550°C for two hours. All preforms attained a final density of greater than 98% theoretical.

B. Composite Synthesis

Ceramic preforms were reacted with an 1100 aluminum alloy in flowing UHP argon in a resistance heated alumina tube furnace. The pure mullite was reacted at 1100°C for 48 hours and again for an additional 24 hours with new Al. The pure mullite system yields 18% metal composites. The 23 and 42 weight percent preforms were reacted at 1100°C for 24 hours and again for another 48 hours with new Al. This system yields 25 and 30% metal composites, respectively. The second run with new Al draws out more residual Si from the composite. For the remainder of this work composites which undergo this second heat treatment will be referred to as low Si composites and those that do not will be referred to as high Si composites. Heat treatments were also conducted on reacted samples at 1500°C for 24 hours to coarsen the microstructure.

C. Microstructural & Image Analysis

Microstructure of the reacted composites were studied using optical and scanning electron microscopy (SEM). SEM techniques consisted of etching out the aluminum phase with dilute HCl or using a low operating voltage of 10 keV to slightly charge the continuous alumina phase. In the images taken, the metal appears black and the alumina phase gray. Image analysis techniques were used to study volume fraction of the metal phase, and metal ligament sizes. Volume fraction measurements were made using IPLab Spectrum which is a quantitative stereology computer program. Images taken at 700x on the SEM were analyzed by identifying the phase of interest based upon contrast differences between the phases. The low voltage SEM technique results in a sharp contrast between the phases. The program counts the number of pixels of a particular phase and the total number of pixels in the image and calculates an area fraction, which is estimated to be the same as the volume fraction. A minimum of three images were used to verify volume fraction for a given composite. Ligament size measurements were made using the Mean Linear Intercept method using the three circle grid test[6]. The three target circle was used to count the number of grain intersections, N, on a minimum of three SEM 700x images. The volume fraction of the desired phase was calculated using IPLab Spectrum and multiplied by the normalization of the target circles total circumference, L_T, according to the following equation,

$$L = V_v L_T / N$$

We then assumed a three dimensional spherical geometry for the grains. The spacial grain diameter equation multiplies a geometrical constant, 1.5, by the mean linear intercept value to obtain final ligament size measurements. The spacial grain diameter equation is shown below,

$$D = 1.5 L$$

D. Mechanical Testing Measurements

Vickers microhardness measurements were made on cross-sections and on top and bottom pieces of the composites using a 10 kg load. The cross-section measurements were taken every 0.5 mm beginning near the aluminum source moving across the sample toward the opposite side from the source. The top and bottom measurements were taken at random. Figure 2 shows a sketch of the composite. In this work, top and bottom are parallel to the reaction direction, with the cross-section perpendicular to the reaction direction.

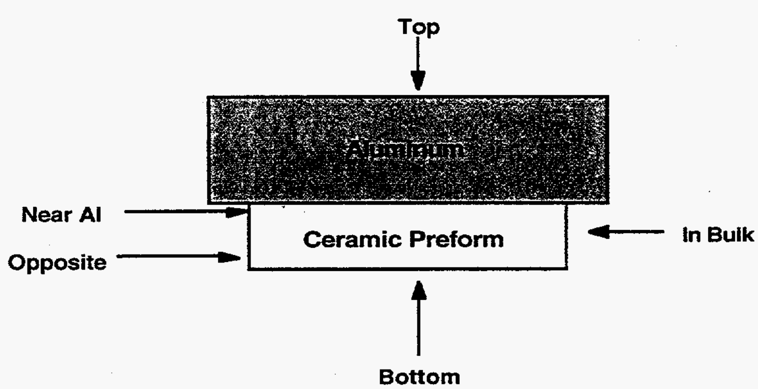


Figure 2. The sketch shows one of our composites before reaction and the terminology we have assigned it after reaction for reference.

Strength testing was conducted using a Material Testing System on a minimum of 30 samples for pure mullite, and 18, 25, and 30% metal composites. A four-point bend test was used on rectangular bar samples 3 x 4 mm, with an inner and outer span of 10 mm and 20 mm respectively. These samples were polished to a 1μm finish and the edges were beveled to eliminate any stress concentrations at the edges. From these measurements Weibull statistics were calculated by plotting the ln ln (1 / Possibility of Survival) versus ln (Strength) in which the slope is equal to the Weibull modulus. In order to determine the probability of survival the samples were ordered in ascending strength and assigned a number with the weakest being number one. The probability of survival is calculated according to the following equation, where i is the designated number and n is the total number of samples,

$$Ps = 1 - (i - 0.5 / n)$$

RESULTS & DISCUSSION

A. Microstructure & Image Analysis

Composite composition varies with preform composition resulting in 18, 25, and 30% volume fraction metal composites (Figure 3). Elevated temperature heat treatments after initial RMP reactions coarsen composite microstructures. The metal ligaments are more localized and not as continuous (Figure 4). Characterization of the microstructure revealed the presence of a microstructural gradient (Figure 5). This gradient shows very aligned flow lines of aluminum that grow in size as the distance from the source increases. Opposite the Al source, the flow lines disappear and the metal is more irregularly shaped but still continuous. Images were also taken of the top and bottom of the composite to further illustrate the gradient (Figure 6). To explain these images we assumed that the composite was composed of a ceramic matrix and continuous metal fibers. From these images it appears that the aluminum has penetrated the ceramic and begins to grow in the form of very small and aligned fibers with a small increase in diameter. Up until approximately 1 mm in depth into the composite the small fiber gradient is observed and then the fibers continue to grow down to the bottom with a largely increasing diameter.

Image analysis techniques were used to verify the increase in metal volume fraction and metal ligament size observed in the microstructural gradient. Volume fraction measurements taken of cross-sections for the 18 and 25% metal composites verify an increase in volume fraction of metal as the distance from the Al source increases, 15 - 18% and 23 - 35%, respectively. They also show that, at a 1 mm depth, the largest increase in volume fraction occurs by as much as 2% for the 18% metal composite and 8% for the 25% metal composite (Figure 7). In addition, metal ligament size measurements verified an increase in ligament size as the distance from the Al source increased. These measurements also showed the greatest increase in size at the 1 mm depth (Figure 8).

The presence of this gradient is still an unknown part of the RMP mechanism. One reason for this could be that at the top surface, where the metal is in contact with the ceramic, a planar, two-dimensional reaction takes place on the surface in the shape of small cross-sectional fibers. Then there seems to be a rate controlling step that controls the reaction up until about 1 mm into the composite. Once that critical distance is reached the reaction becomes more three-dimensional throughout the remainder of the ceramic.

B. Mechanical Properties

The results of microhardness testing on the microstructural gradient for the 18, 25, and 30% metal composites show a decrease in hardness as the distance from the source increases. Near the Al source there is less metal, resulting in a higher hardness value. As the metal ligament size and volume fraction increase, the hardness of the material decreases. An overall evaluation of hardness values for the three composites show that the 18% metal composites yield the highest hardness values. The 25 and 30% metal composites show an increase in hardness with increase in silicon content, this is a measure of the effectiveness of the heat treatments in removing the residual Si (Figure 9). The results from microhardness measurements done on the top and bottom of the composites verify the microstructural evaluation made from the images taken. The top section of the composites consistently yielded higher hardness values when compared to the bottom section for all three composite compositions, which reinforces the image analysis data that shows a low metal content on the top versus the bottom (Figure 10).

The highest strength material was the 25% metal, low silicon composite with a strength of 360 MPa. That was followed by the 18% metal, low silicon with 340 MPa and 30% metal, low silicon with 270 MPa. The coarsened composites had the lowest strengths, possibly due to the metal phase no longer being continuous. The coarsened composites were always the lowest in strength and comparable, in strength to pure mullite of 204 MPa (Figure 11). When comparing the composites of high and low silicon content with the same metal volume fraction, the higher the silicon content the lower the strength for all three compositions (Table 1). This reduction in strength is most probably due to a decrease in toughness with increasing Si content.

Strength testing was conducted to calculate the Weibull modulus of pure mullite and the 18, 25, and 30% metal composites. The Weibull modulus of the pure mullite was measured to compare the composites to a typical ceramic.

Table 2. shows the Weibull modulus values for the materials tested. The Weibull modulus values for the composites were relatively low indicating low reliability for the composites. If the R-curve was influencing the reliability we would expect the composite moduli to be higher than that of mullite. Such low Weibull values tend to indicate that the R-curve is not influencing the reliability of the materials. It appears the inherent flaws which form during composite processing are too large to be influenced by the R-curve.

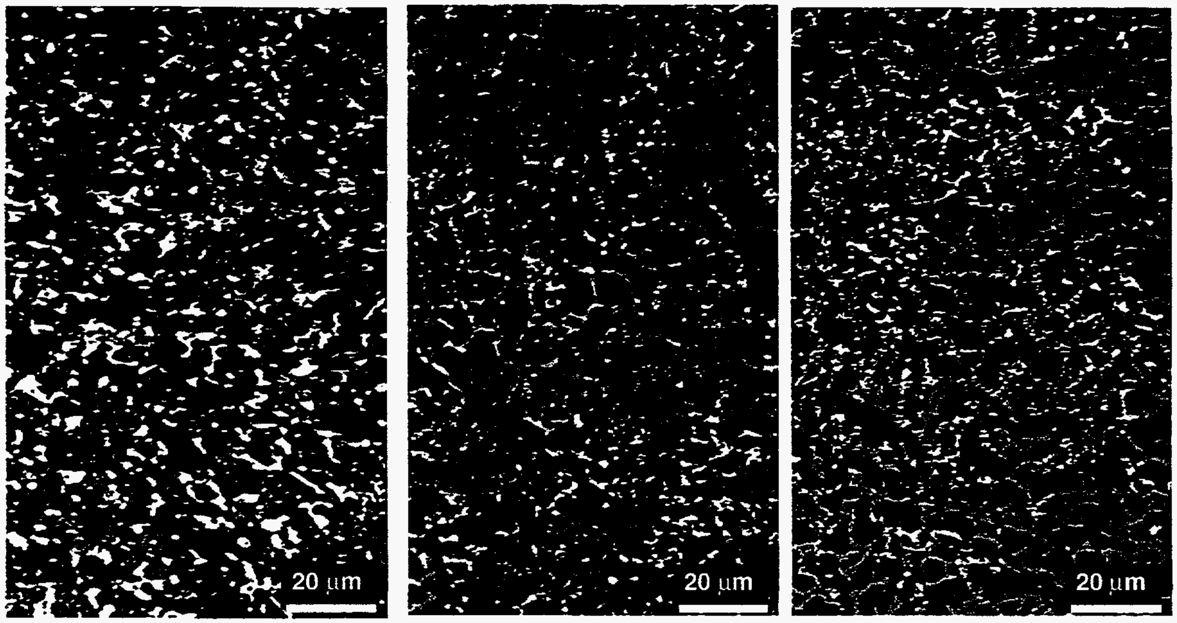
Table 2. Weibull modulus for ceramic and composites.

Volume Fraction Metal	Weibull Modulus
Pure Mullite	**6**
18%	**8**
25%	**6**
30%	**6**

CONCLUSIONS & RECOMMENDATIONS

Composite synthesis by RMP can successfully fabricate alumina/aluminum composites to a near-net-shape. Aluminun reacts and reduces the mullite to form alumina and aluminum with elemental silicon. The composition of the composites can be tailored by doping the pure mullite preforms with 23, and 42 weight percent silica resulting in 18 volume percent composite from the reaction with pure mullite and , 25, and 30% metal volume fraction composites from the reaction between the doped preforms. The size of the metal ligaments can be controlled by secondary, elevated temperature heat treatments, and residual Si can be drawn out by a secondary heat treatment with a new piece of aluminum. Microstructural analysis reveals that metal volume fraction and ligament size increase and microhardness decreases with increasing distance from the Al source with the composite. The presence of the microstructural gradient gives rise to the question of what in the reaction mechanism is causing its formation. Further evaluation of the gradient through image analysis and microhardness methods verify that there is a 1 mm critical distance for the rate controlling step to produce the gradient. From strength testing we were able to conclude that, due to the low Weibull modulus values, the R-curve in RMP composites has no influence on reliability. Coarsening heat treatments decrease composite strength.

Future work should focus on understanding the controlling mechanism that creates the microstructural gradient, and on coming up with an activation energy for coarsening alumina/aluminum composites formed by RMP. Experiments varying the reaction time could help determine when the gradient is produced, or if it is an inherent step in the reaction process. Other experiments varying the initial reaction temperature also may be of some help in understanding why the microstructure coarsens at the elevated temperature secondary heat treatments.

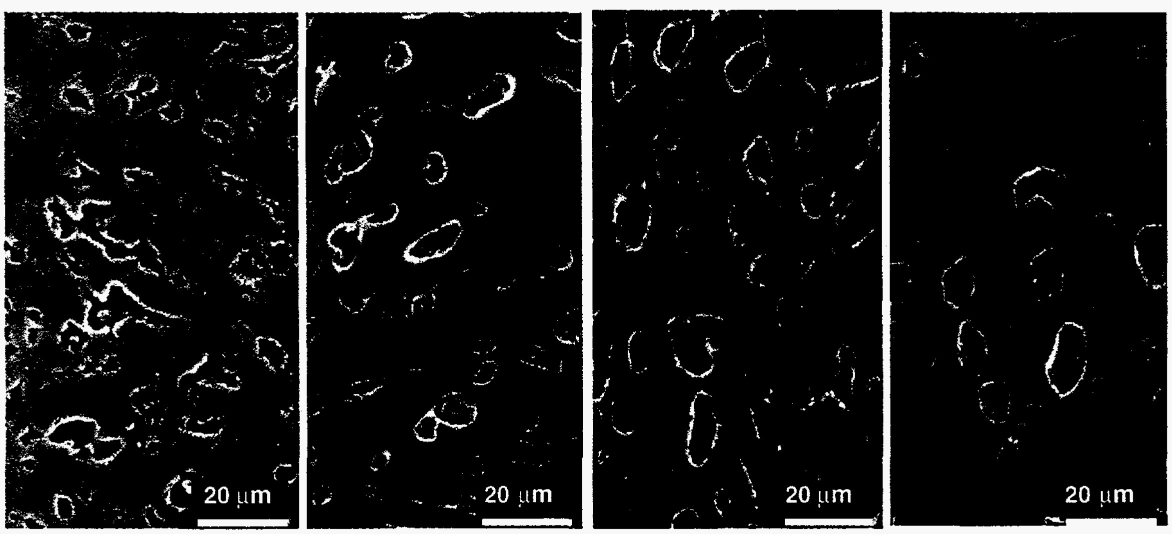


Pure Mullite
1100°C 48 hrs

25% Metal
1100°C 24 hrs

42% Metal
1100°C 24 hrs

Figure 3.
In these optical micrographs the lighter phase is the metal and the dark phase is the ceramic. The images show that metal increases in size and volume fraction as the amount of silica in the preform increases.



1100°C 48 hrs
3 µm

1425°C 24 hrs
6 µm

1500°C 24 hrs
7 µm

1650°C 24 hrs
8 µm

Figure 4.
For these SEM images the metal has been etched out using HCl and appears as porosity in the images. They show how the metal ligament size increases with increasing heat treatment time and temperature, from 3µm to 8µm..

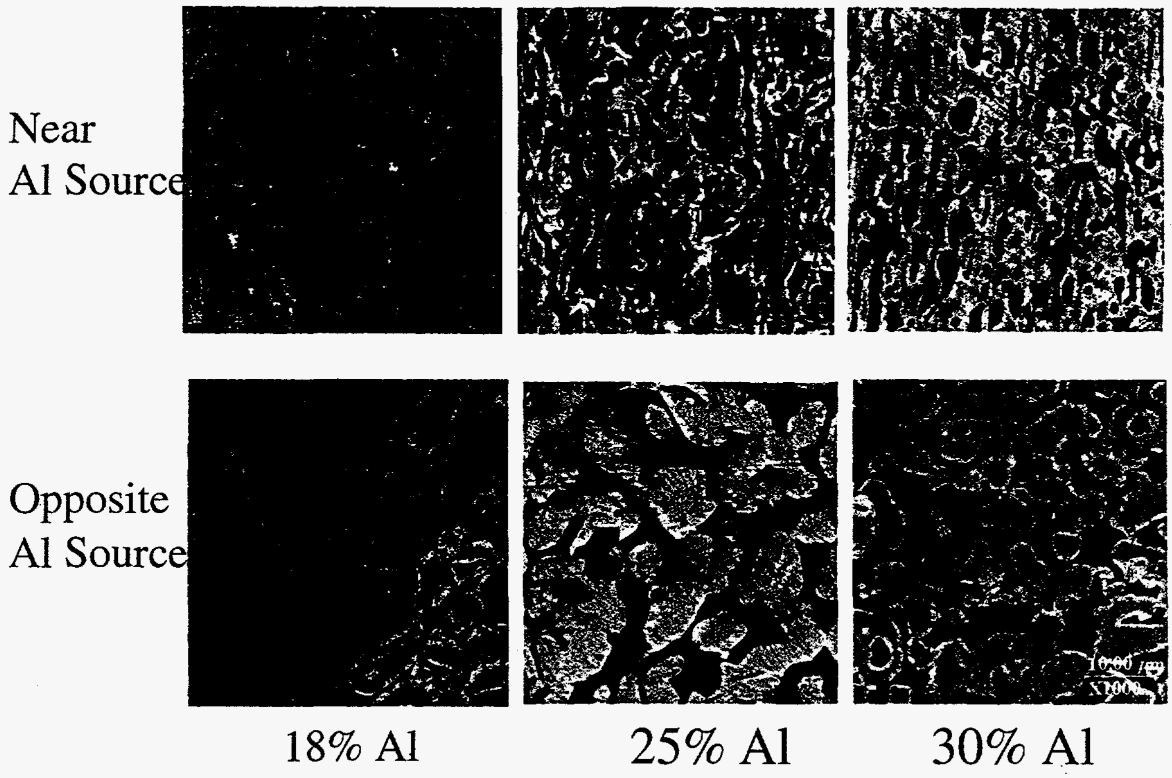


Figure 5.
The microstructural gradient begins at the Al source as small aluminum flow lines that increase in size and volume fraction as the distance from the source increases. In these images the black phase is metal and the gray phase is the ceramic.

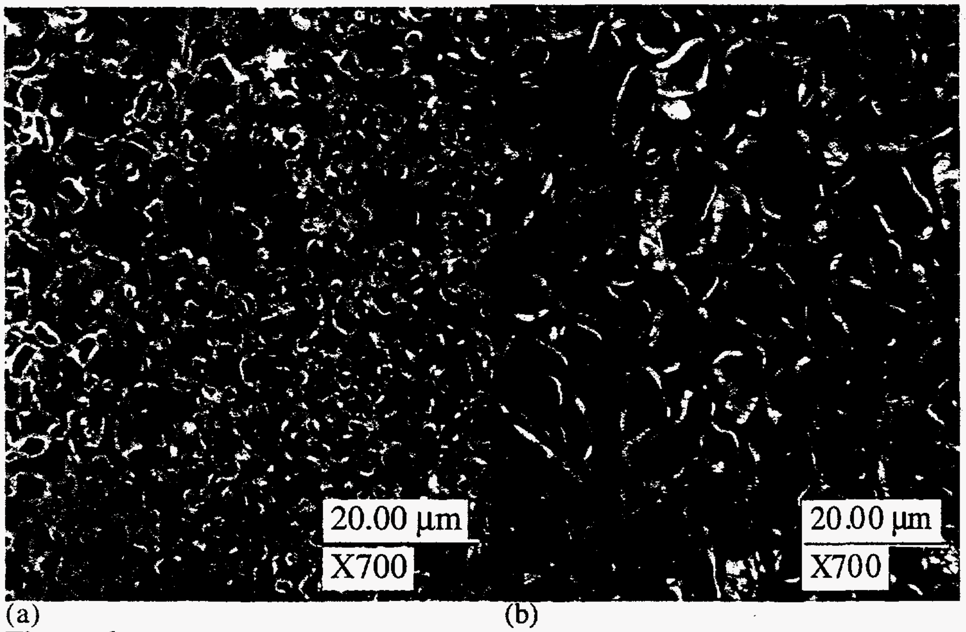


Figure 6.
The SEM micrographs show a 25% metal composite from the (a) top and (b) bottom. The top has a metal volume fraction of 21% and the bottom has a metal volume fraction of 32%.

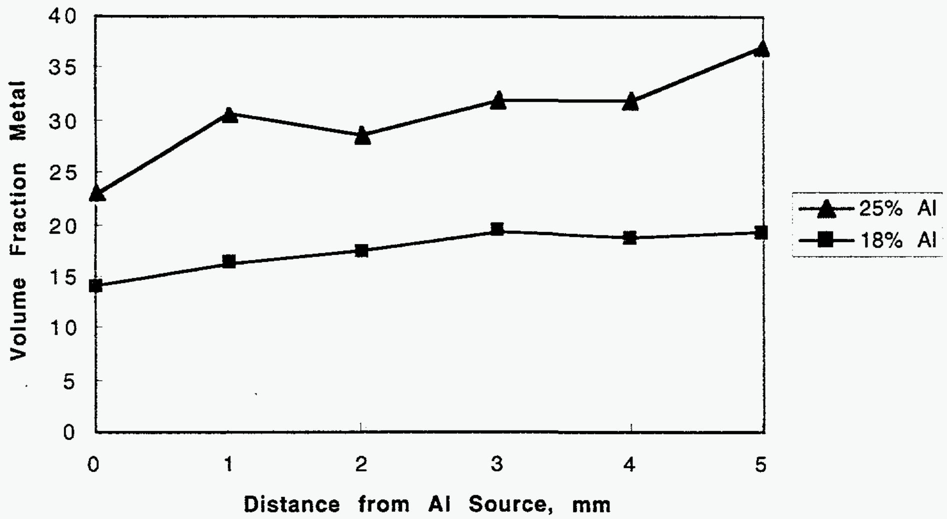


Figure 7.
The volume fraction of metal versus depth for the 18 and 25% metal composites show an increase in volume fraction as the depth increases from the Al source.

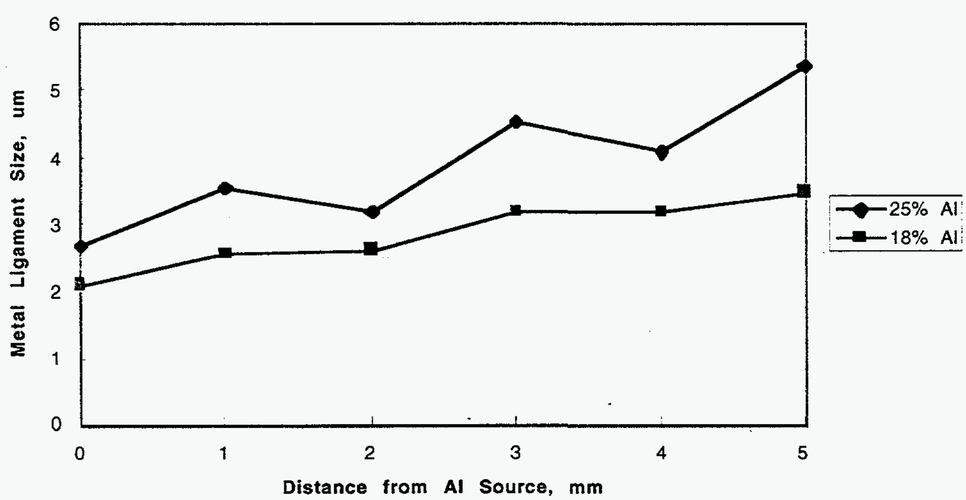


Figure 8.
The metal ligament size versus depth for the 18 and 25% metal composites show an increase in ligament size as the depth increases from the Al source.

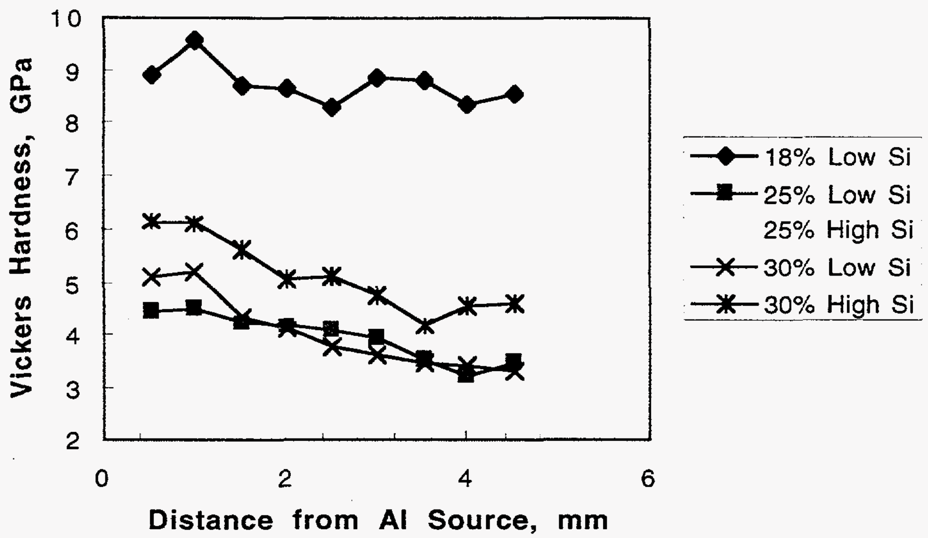


Figure 9.
Microhardness for different composite compositions decreases as the distance from the Al source increases.

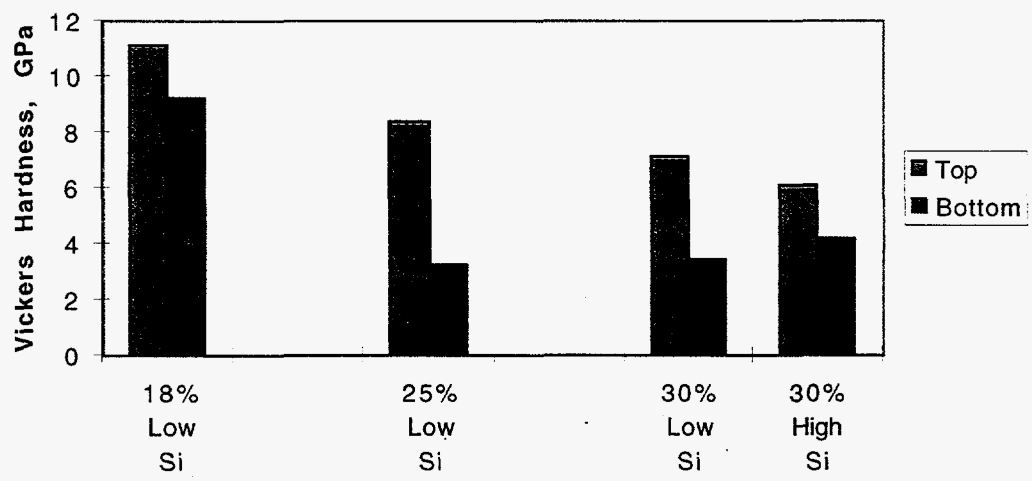


Figure 10.
Microhardness for the top versus bottom show that the top yields much higher hardness values than the bottom indicating higher ceramic content at the top.

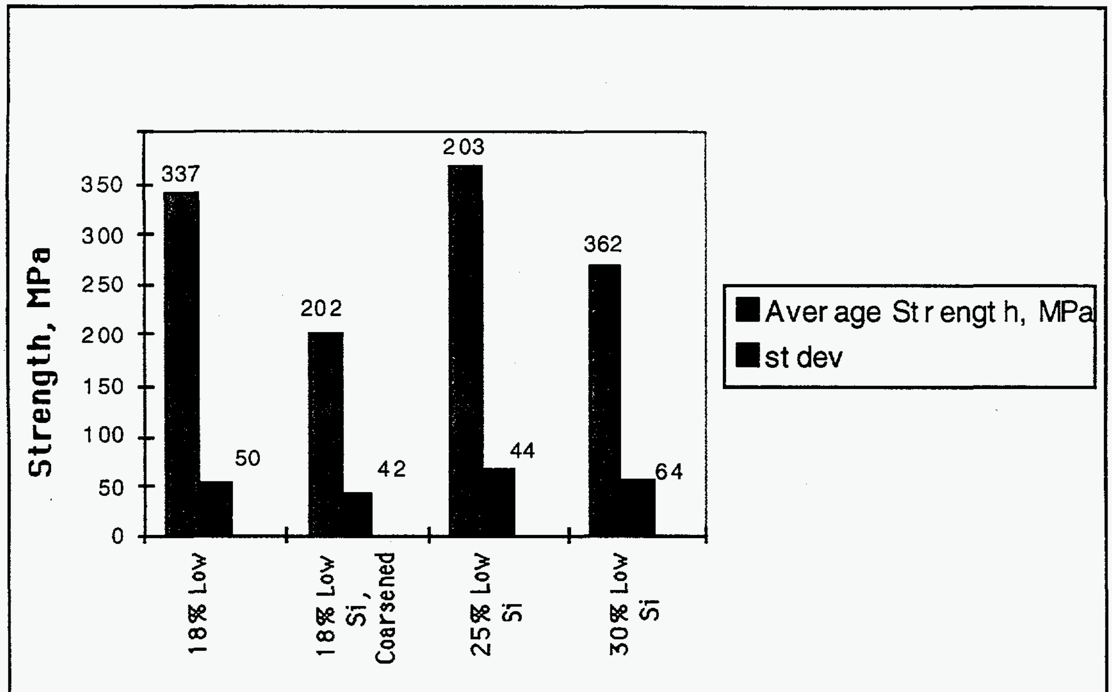


Figure 11.
The highest strength material was the 25% low Si composite with a strength of 362 MPa. That was followed by the 18% Low Si composite with 270 MPa. The coarsened composite had the lowest strength.

Table 1.
When comparing the overall strengths of all composite and pure mullite the highest strengths went to the 25%, low Si composite. For all composite compositions the coarsened composites resulted in the weakest strengths. Also, as the Si content increases the strength of the composites decrease.

	Average Strength, MPa	STDEV
Pure Mullite	204	44
18% Low Si	337	50
18% High Si	246	44
18% Low Si Coarsened	202	42
25% Low Si	362	65
25% Mid Si	310	57
25% High Si	271	33
25% Low Si Coarsened	250	73
30% Low Si	267	54
30% Mid Si	246	30
30% High Si	175	7

REFERENCES

[1] K.G. Ewsuk, S.J. Glass, R.E. Loehman, A.P. Tomsi and W.G. Fahrenholtz, "Microstructure Properties of Al_2O_3 - Al(Si) and Al_2O_3 - Al(Si) - Si Composites Formed by *In Situ* Reaction of Al with Aluminosilicate Ceramics," J. Metallurgical and Materials Transactions, 27 [A], pp. 2122-2129 (1996).

[2] K.G. Ewsuk, R.E. Loehman, and W.G. Fhrenholtz, "Sandia National Laboratory: Quarterly Report," unpublished work, 1998.

[3] R.E. Loehman, K.G. Ewsuk and A. P. Tomsi, "Synthesis of Al_2O_3 - Al Composites by Reactive Metal Penetration," J. Am. Ceram. Soc., 79 [1], pp. 27-32, (1996).

[4] T.L. Anderson: *Fracture Mechanics: Fundamentals and Applications*, CRC Press, Boca Raton, FL, 1995, pp. 46-48.

[5] J.B. Wachtman: *Mechanical Properties of Ceramics*, Hohm Wiley and Sons, Inc., New York, NY, 1996, pp. 92-115.

[6] G.F. Vander Voort: *Metallography: Principles and Practice*, McGraw - Hill Book Company, New York, NY, 1984, pp. 435-465.