NASA Contractor Report 179629

Zirconia Toughened, SiC Whisker Reinforced Alumina Composites Small Business Innovation Research

Phase I—Report
December 1985—October 1986

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(NASA-CR-179629) ZIRCONIA TOUGHENED SiC WHISKER REINFORCED ALUMINA COMPOSITES SMALL BUSINESS INNOVATION RESEARCH Final Report, Dec. 1985 - Oct. 1986 (Materials and Electrochemical Research Corp.) 46 p
N90-10294
Unclas
G3/27 0237144

October 1987

Prepared for
Lewis Research Center
Under Contract NAS3-24872

Date for general release October 1989

National Aeronautics and
Space Administration

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I PHASE 1 - OBJECTIVE

The main objective of the Phase I project was to establish the technical feasibility of producing superior tertiary ceramic composites, which utilizes two toughening materials, zirconia for transformation and microcrack toughening and SiC whiskers for crack deflection toughening. In a controlled microstructure alumina matrix. The controlled microstructure of the matrix is produced by controlling the nucleation frequency of alumina gel with seeds (submicron α-alumina). Further objectives were to establish the superiority of these composites with respect to fracture toughness over the best monolithic alumina, zirconia toughened alumina, and SiC whisker reinforced alumina and to establish the advantage of the sol-gel process over conventional processes.

II SCOPE

This report documents (1) the procedure and results for producing the composite gel, (2) the results of a study of the phase transformations of the zirconia particles and alumina matrix (3) the microstructure of the calcined composites, (4) SEM of hot pressed and fractured surface of the composites. Finally, a mathematical model is presented to describe the potential toughening behavior of the tertiary composite.

III INTRODUCTION

In recent years there has been a tremendous amount of research performed to develop engineered ceramic composites. Two ceramic composites that are currently the focus of extensive investigation are:

1. SiC-whisker Reinforced Alumina SWA) and;
2. Zirconia/Hafnia Toughened Alumina (ZTA)

The objective of this project has been to investigate and utilize two new concepts for producing a superior composite to either SiC-whisker reinforced alumina (SWA) or zirconia toughened alumina (ZTA). These two concepts are listed below.

1. Fabrication of a tertiary composite which utilizes both SiC-whiskers and zirconia/hafnia to toughen alumina.

2. Production of this composite via a sol-gel route, in which ultrafine α-alumina seeding is used to control the microstructure of the composites.

The concepts of producing a tertiary composite utilizing both SiC-whiskers and zirconia to toughen alumina and producing this composite via a sol-gel route which utilizes seed to produce a homogeneous tertiary composite with fine grained microstructure are new. Excellent uniformity of composite constituents can be achieved with sol-gel because problems of segregation during processing that are encountered during conventional processing techniques are avoided. However, the concept of using sol-gel has been discarded by most of the ceramic community because of poor results in earlier investigations. The problems experienced are high porosity [1] and runaway grain growth during processing of sol-gel derived alumina to its α-phase [2]. However, it has been demonstrated that grain growth can be inhibited by both seeding with α-alumina and impeding with zirconia particles [3-4]. We feel that the problem of runaway grain growth can, therefore, be overcome with these two inhibiting mechanisms while utilizing the obvious advantages of homogeneity and ease of densification obtained with the sol-gel process.

Sol-gels are colloidal suspensions halfway between molecular size particles and micro (nano) size particles which is, at the molecular building block level, the ideal stage for producing ceramic compositions with controlled properties. Sol-gel technology is a powerful synthesis technique used to produce reactive inorganic precursors for solid state reaction which can provide the control necessary to vary properties and achieve improved behavior in the solid composite. Microstructure can be tailored with the aid of sol-gel technology to produce specific engineered structural properties. Sol-gel technology opens new vistas for ceramic and composite materials preparation.

The emerging innovations in sol-gel processing and microstructural control permit the exploration of toughened ceramics utilizing fine particles which transform martensitically, as well as fibers (whiskers) and/or other possible second phase morphologies. Clearly, there is an opportunity, utilizing sol-gel technology, to develop advanced transformation toughened, whisker reinforced, ceramic composites which can result in international superiority in the same area of fabrication and implementation of engineered structural ceramic composites. Materials and Electrochemical Research (MER) Corporation and its commercial international partner KeraMont Research Corporation are vigorously pursuing the development of such composites for government and commercial utilization.

The conventional processes for production of composite ceramics have been mixed powder/fiber techniques. One method has been to mix the dry composite constituents in either a ball-mill or attrition mill; then remove the product and consolidate by hot-pressing or by cold pressing and sintering. Another very popular method has been to create a slurry by mixing the composite constituents in a liquid usually containing a dispersant and/or binders with a high shear mixer and/or with an ultrasonic mixer, filter the slurry with a filter-press; dry the cake; and then consolidate the dried cake by hot-pressing or by cold-pressing and sintering. Both of these techniques suffer from (1) segregation and incomplete mixing of composite constituents during possessing and, (2) large agglomerated particles of the secondary phase reinforcement.

Investigators have studied at least two other process for the production of ZTA in hopes of producing a more homogeneous composite than is possible with conventional processing techniques. One method is co-precipitation of zirconium and aluminum salts from aqueous solution followed by calcination in oxidizing environment [5]. The other method is simultaneous flame deposition of zirconia and alumina [6]. Both of these processes are new and have not been investigated in sufficient detail to determine their success. However, neither of these methods are compatible with the addition of whiskers for the production of a tertiary composite.

The sol-gel approach for the production of alumina sintered bodies has been investigated with both aluminum alkoxide and alumina monohydrate precursors [7, 8]. However, the measured mechanical properties of the sintered parts were poor and attributed to voids in the matrix created by the high shrinkage of the gel.

The technique of seeding an alumina sol-gel with α-alumina particles has been shown to provide the grain growth control and rapid densification necessary to produce a high quality alumina monolith that was lacking in earlier attempts using sol-gel. Kumagai and Messing have studied the effects of seeding Boehmite sol-gels with ultra-fine particles of α-alumina [3, 4]. They report enhanced densification, controlled grain growth and lower transformation temperatures for seeded sol-gels as opposed to unseeded sol-gels. The α-alumina seed particles act as nuclei for the transformation of theta to alpha alumina and result in an increase in the transformation kinetics and lowering of the transformation temperature by as much as 170 C. By increasing the seed concentration (i.e. nucleation frequency), a submicrometer aggregate-free microstructure develops, rather than the vermicular microstructure that usually characterizes the alumina transformation. Kuagai and Messing have shown that the number concentration of seeds rather than the weight or volume concentration is the governing factor in transformation kinetics. Also they have given an optimum seed concentration of 5 x 10^{13} seeds per c.c. based upon enhanced densification. Such a large number concentration requires that the diameter of the seed particles be well into the submicron range. We have used this phenomena to control the microstructure of Phase I proposed composites.

Milewski has published a paper that gives guidelines for the efficient use of whiskers in the reinforcement of ceramics [9]. He emphasizes that the aspect ratio of the fibers should be kept low (10-20) in order to obtain a high green density. He has determined that fibers with aspect ratios from 100 to 1,000, such as wool, will tangle readily; those with aspect ratios from 50 to 100 will bundle and clump; and those with aspect ratios from 10 to 30 flow and behave like powder. Aspect ratios of the fibers must be kept low (10-30) in order to avoid agglomerates when producing a fiber reinforced composite. We were limited in Phase I work, in regard to the type and aspect ratio of SiC, to those available commercially. However, Tateho Chemicals agreed to supply us with narrow distribution aspect ratio SiC for evaluation. This is one of the subjects proposed for Phase II. We believe, from the work and results of Phase I, that controlling the aspect ratio of SiC will have significant effect on the properties of the composites.

It has long been known that zirconia, when present as a dispersed phase, can toughen alumina. However, there is much debate about the exact mechanisms by which this is accomplished. Researchers have established that there are two distinct mechanisms by which zirconia toughens alumina. One is by stress induced martensitic phase transformation from the metastable phase (tetragonal) to the stable phase (monoclinic) that occurs in a zirconia particle in the strain field of a propagating crack tip. This phase transformation relieves stress. It is not clear whether the stress is relieved because energy is absorbed by activation energy of the phase transformation (nucleation barrier) or if it is the cancellation of tensional forces in a propagating crack tip by compressional forces exerted because of the dilation that occurs during the t-m phase change. The other mechanism by which zirconia can toughen alumina is by stress nucleated microcracking of the alumina matrix by monoclinic particles that have already been transformed from the tetragonal phase. This relieves stress by delocalizing the stress through local strain. Both mechanisms are important. In the words of Heuer, Claussen and Ruhle: "Both tetragonal (t) and monoclinic (m) ZrO_2 particles in ZrO_2-toughened alumina can give rise to toughening, in the stress field of a propagating crack, the t-ZrO_2 particles can undergo the stress induced t-m transformation and the residual stress around the already transformed m-ZrO_2 particles can cause microcracking." The toughening increments via these distinct mechanisms are comparable, and it appears that optimally fabricated ZrO_2-toughened Al_2O_3 should contain a mixture of t and m-ZrO_2 [10].

The metastability of t-ZrO_2 particles in ZTA and hence the degree of toughening via the stress induced t to m ZrO_2 phase transformation is a strong function of the microstructure of the composite. A nucleation barrier (a function of particle size, particle shape and matrix constraint) inhibits the transformation of a zirconia particle to its stable phase below the normal transformation temperature [11]. Zirconia particle size is a key parameter affecting the height of the nucleation barrier. There exists a critical minimum particle diameter (~50nm) below which the stress induced phase transformation can not take place [12]. Also, there exists a critical maximum particle size diameter above which the particle will spontaneously transform to the stable phase (m) upon cooling to room temperature (0.6 μm) [13]]. Clearly the diameter of the zirconia particles must be between these two limits if transformation toughening is to be achieved. Larger particles transform more easily in a stress field than do smaller particles. However, the temperature at which the reverse transformation, m to t, takes place is a measure of the maximum temperature at which transformation toughening can occur [14, 15]; and this temperature decreases with increasing particle size. Smaller zirconia particles give transformation toughening at higher temperatures than larger particles. The α-alumina seeding in our system is expected to play a role in controlling the size of zirconia particles by heterogeneous nucleation.

The use of whiskers or short fibers for reinforcement in composites has been under investigation for some time. Originally, fibers were used to reinforce glasses and metals [16]. As of late, whisker reinforcement of ceramic matrices has come into prominence. There is a large number combinations of whiskers and matrices that could be created. Wei and Beecher have stated some ground rules for compatibility of whiskers and matrix in whisker reinforced composites [17]. They state, "In order for a particular whisker and matrix to combine to form a successful composite, three areas must be considered; (1) the difference between the coefficient of thermal expansion of the fiber and that of the matrix, (2) elastic module of the matrix and fiber, and (3) chemical compatibility between the fiber and matrix at the processing temperature." Lately, use of strong single crystal SiC-whiskers to reinforce alumina has been under intensive investigation. It has been determined that both fracture toughness and fractured strength of this composite (SWA) can be at least double of that of monolithic alumina [17].

Toughening by whisker reinforcement involves several toughening mechanisms. However, the primary toughening mechanism in SWA, has been shown to be crack deflection [18, 19]. Faber and Evans have used a fracture mechanics approach to model the crack deflection mechanism for rod like whiskers. Whisker pullout has been shown to be another important toughening mechanism [20].

The whisker pullout mechanism has been modelled in a paper produced by Beecher, Tiegs, Ogle, and Warwick [19]. However, the model has severe deficiencies which makes a quantitative prediction of toughening with this model impossible. In this model whiskers are treated as solid rods that are aligned perpendicular to the tensile stress field. There is no attempt made to account for orientations of whiskers other than that. Also, a work of pullout is calculated that does not take into account the variable area of whisker matrix contact during pull-out.

We have modified the models of toughening and expanded them to include the interaction between toughening mechanisms. The results and implications of the modified model are presented in this report together with the experimental results of mechanical testing of the binary and tertiary composites prepared under this program.

IV. EXPERIMENTAL INVESTIGATIONS AND RESULTS

The purpose of the Phase I investigation was to demonstrate the technical feasibility of producing a high fracture toughness ceramic composite by utilizing both ZrO_2 toughening and SiC whisker reinforcement together with alumina gel which utilizes an α-alumina seeding technique for producing superior alumina matrix composites. To establish the feasibility for producing these two toughening inducing materials in toughened alumina composites, we proposed to carry-out the following activities utilizing statistically designed experiments.

1. Prepared alumina gel
2. Produce alumina particles from alumina gel
3. Add alumina particles and whiskers to Zirconia
4. Produce dried zirconia coated alumina-whisker composite powder
5. Hot press composite powder
6. Evaluate toughness and MOR of composites

1. Preparation Alumina Gel

Statistically designed experiments were conducted to investigate the feasibility of producing the alumina gel from aluminum chloride hexahydrate, ACH. The effect of calcination temperature (200-600°C), time (20-30 minutes), gas composition (nitrogen vs steam) during calcination, and pretreatment of the calcined products (water vs alkaline solution) were investigated.

The results of these experiments were not encouraging. The products produced at low temperature (<400°C) were high in chloride and dissolved rather than gelling in acid solution. The products produced at high temperature (>400) did not disperse well (they produced what is known as white wash instead of well dispersed gel). We, therefore, elected to use alumina monohydrate as the starting material for producing alumina gel instead of the ACH precursors.

Vista Chemicals produces dispersible alumina monohydrate products (catapal A, B, and D) on a commercial scale. These products have low cost and are highly dispersible,. Their dispersibility and gelling kinetics are well established (1). Since the objective of the proposed effort is to prove the additivity of toughening mechanisms rather than to develop new alumina gel precursors, it seems that producing alumina gel from ACH is much more involved than we had initially anticipated. Therefore, we elected to use Vista Chemical (Catapal B) as the starting material for producing the alumina gels.

Highly dispersed alumina monohydrate (>98% dispersibility) was prepared by dispersing Catapal B in dilute acidic solution (hydrochloric acid was used at 70°C). THe gel was obtained by increasing the acid concentration to 1.6 mmoles of H^+ per gram of alumina. An excellent homogeneous gel was obtained under these conditions. The measured viscosities of the gel exceeded 9500 centipoise. Such high viscosities insured that segregation of dispersed whiskers or α-alumina seed particles would be far too slow to cause heterogeneities that weaken the composites.

2. Production of Homogeneous Mixture of Composite Gel

We combined the proposed activities 2 and 3, into one major activity with the purpose of producing a homogeneous mixture of dispersed SiC whisker, zirconia precursor, and alumina gel. Four sets of statistically designed experimental studies were performed to establish the main effects and interactions of the process variables, listed in Table 1, upon the final properties of the composites. In the first set of statistically designed experiments, we investigated the effect of $ZroO_2$ content (using ZrOC solution as precursor), SiC content, SiC type (F-H and M-8) and seeding factor. The total number of fully factorial design experiments (2^4) is 16 experiments and sixteen composite gels were prepared. In the second set of experiments we fixed the seeding factor (i.e. we used 3% α-alumina seeds in all experiments) since from the results of the first test we were able to ascertain the effect of SiC (Tokai and Tateho whiskers). A fully factorial statistical test (2^3) of 8 experiments was conducted and 8 composite gels were prepared. The zirconia content and seeding factors were the independent variables for the third statistical test and 4 gels without SiC whiskers were prepared. In the fourth test, the SiC content (F-H SiC whiskers), and seeding factors were investigated without zirconia and another 4 composite gels were produced. The third and fourth tests were conducted to establish the increment of fracture toughness due to combining the two toughening mechanisms by comparing test results 3 and 4 with data obtained in statistical test 1 and 2.

TABLE 1

PROCESS INDEPENDENT VARIABLES FOR $ZrO_2/SiC/Al_2O_3$ COMPOSITE

Process Variables	+ve Level	-ve Level
α-Seeding	3% seed	Unseeded
ZrO_2 Content	15%	5%
ZrO_2 Precursor	ZrOC soln.(1)	ZrO_2 powder
Al_2O_3 Source	Sol-gel	Al_2O_3 powder
SiC Content	30%	15%
SiC Type(2)	M-8, F-H	Tokai, Tateho

(1) Zirconium Oxychloride Solution

(2) M-8 and F-H are equivalent SiC to ARCO Chemical SiC Whiskers (obtained from J. Milewski).

In total, 32 composite gels were generated for these statistically designed experiments. In addition, four composites were also prepared by mixing powders of alumina and ZrO_2 with dispersed SiC whiskers in solution to establish the advantage or disadvantage of the gel matrix approach.

In all experiments the SiC whiskers (the properties of the whiskers used are given Table 2) were cleaned by leaching in 50% HCl solutions, and thoroughly rinsed. The whiskers were dispersed in water by adjusting at pH 6 followed by ultrasonic dispersion. In the composites prepared from alumina monohydrate a 20 wt% alumina sol was prepared at 70°C by adjusting the pH to 3.7 using nitric acid. The sol was allowed to fully disperse. The dispersed SiC whiskers were then added to the sol. Next, the zirconia oxychloride solution was mixed in, which caused immediate gelling of the matrix. The gel was mixed with a top stirrer to homogenize the mixture.

The procedure utilized in this project to produce the composite gel is depicted in Figure 1. It is clear from Table 2 that we did not have ideal SiC whiskers, however, these were the only whiskers available to us at the time this project began. F-H and M-8 whiskers, were more particulate SiC than clean whiskers. The Tateho and Tokai whiskers on the other hand were clean whiskers, but they have a very high aspect ratio and too small a diameter for what is considered ideal. As mentioned before, we have arranged with Tateho to supply us with a very narrow aspect ratio distribution with appropriate diameter.

TABLE 2
PROPERTIES OF SiC WHISKERS

Manufacturer	Type	Aspect Ratio (L/D)	Diameter (µm)	Crystal Phase
Los Alamos	F-H	120^M	0.5	cubic
Los Alamos	M-8	75^M	0.7	cubic
NIAC*	SCW-1S Tateho	20-200	0.05 0.15	β
Mitsubishi	Tokai	50-200	0.1 0.5	β

* NIAC, Nissho Iwai American Corporation

M Aspect Ratio Determined by Milewski Method

A typical photomicrograph of the gel produced containing the ZrO_2. SiC whisker, α-alumina seed in alumina gel is shown in Figure 2. It is clear that the whiskers and α-aluminum seeds are well dispersed with no agglomeration or clumping gel matrix (which is translucent at this state).

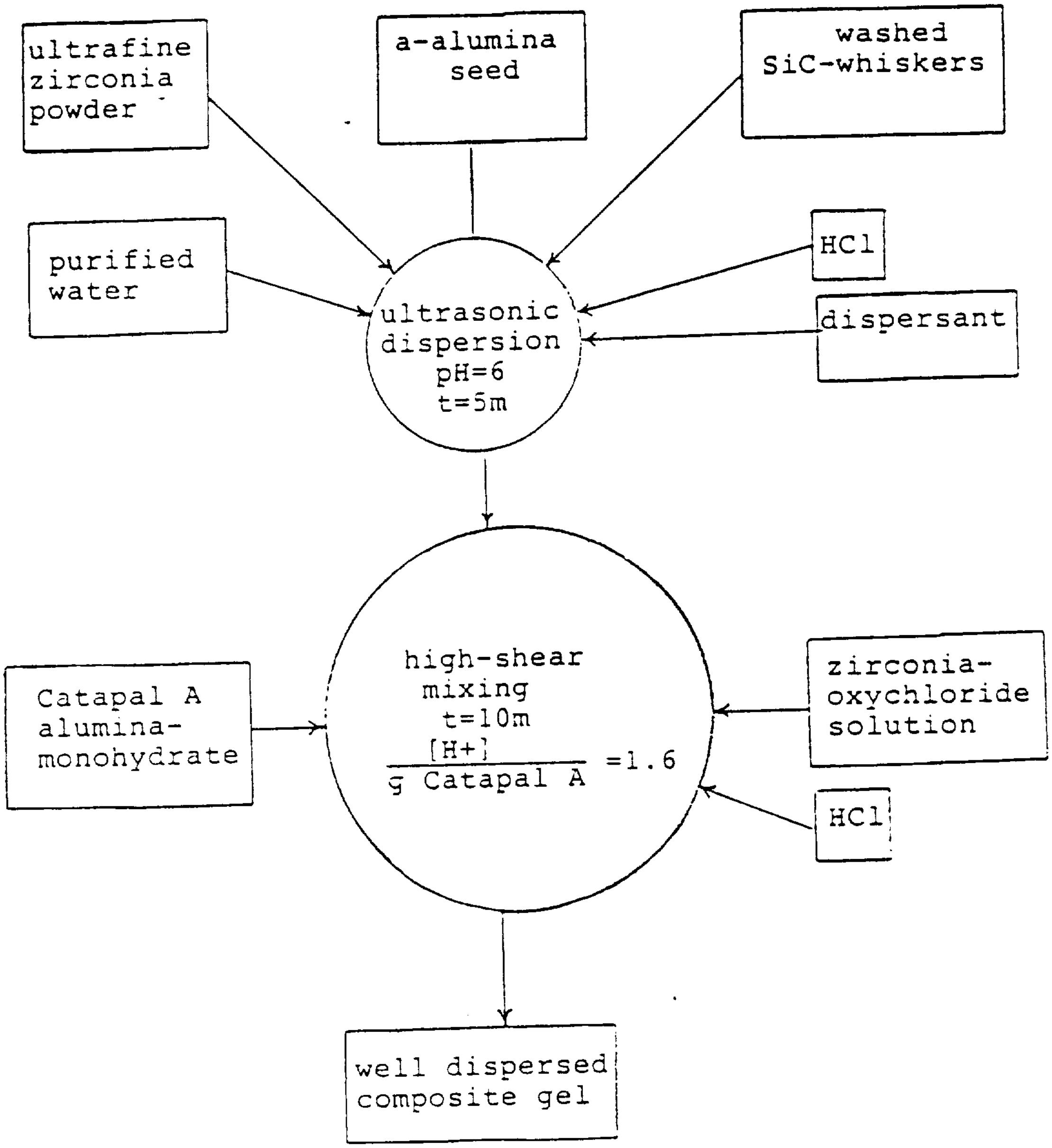

FIGURE 1
SOL-GEL COMPOSITE PREPARATION

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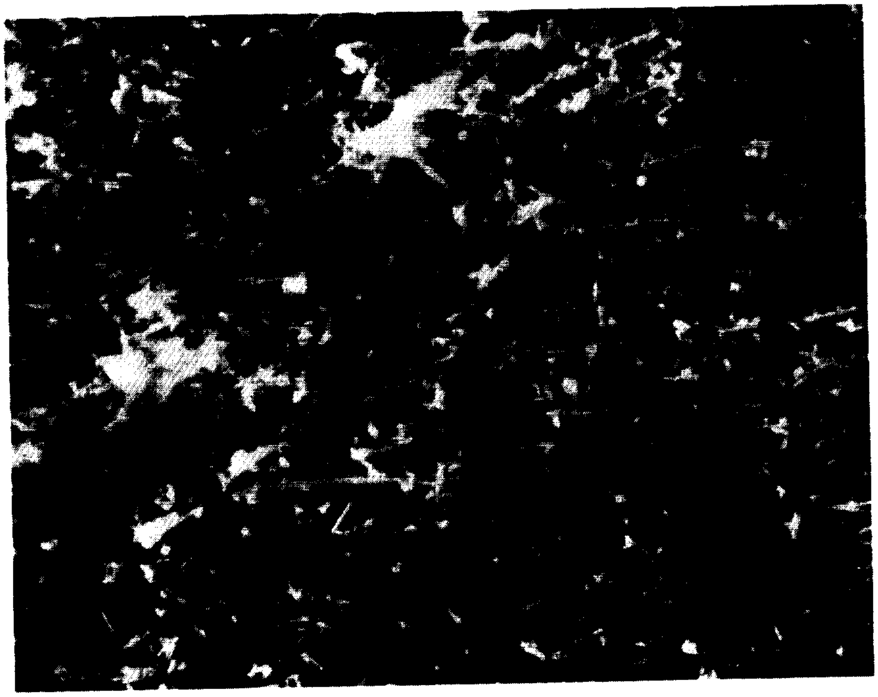

Figure 2. Photomicrograph of 15% ZrO_2, 15% SiC, 3% α-Alumina Seed Alumina Composite Gel

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3. Produce Dried Zirconia/SiC Whisker/Alumina Composite Powders

The 32 composite gels and the four slurries of mixed ZrO_2, Al_2O_3 powders and SiC whiskers were dried at 125°C. The dried gels were ball milled, calcined at 800°C for one hour to drive off all the chlorides and finally calcined at 1200°C for two hours to transform the ZrO_2 to the tetragonal phase and the alumina matrix to α-alumina.

The procedure for producing the dried composite gel is summarized in Figure 3.

We studied in detail the transformation of alumina and zirconia as a function of α-alumina seed, SiC whisker and temperature. For this study four composites gel compositions, Table 3, were prepared and calcined at 400°C, 600°C, 800°C, 1000°C and 1200°C for 1 hour. Samples were taken after each temperature interval for x-ray analysis. The dominant peak intensity (2Θ=35.2°) of α-alumina was plotted for each composite. Figure 4 for composites A and B and Figure 5 for C and D.

The effect of seeding composite gels with α-alumina can be seen by examining figures 4 and 5. The $O \rightarrow \alpha$ transition of the alumina matrix was enhanced by seeding with α-alumina in both composites with and without SiC-whiskers, as was expected. It appears that the $O \rightarrow \alpha$ phase transformation is somewhat inhibited by the presence of SiC whiskers. This implies that α-seeding is even more essential in the tertiary composite system than it is in the binary composite system from the point of view of ensuring controlled transformation of the alumina matrix.

Figures 6a and 6b demonstrate the effects of α-seeding upon zirconia particle growth. The composite that contains seed, (A) appears to have "grown" larger particles of zirconia. The larger particle growth can be attributed to smaller grain size of the α-alumina matrix, (diffusion occurs mainly along grain boundaries and a finer grain structure implies a higher grain boundary surface area).

The effect of seeding with α-alumina upon zirconia particle growth in the binary composites can be seen by comparing figures 6a and 6b. The seeded sample grew larger zirconia particles than the unseeded sample in identical calcination conditions. The evidence of increased particle growth is the presence of the monoclinic phase of zirconia. (Zirconia particles that exceed 0.6 μ-m in diameter transform spontaneously from tetragonal to monoclinic upon cooling to room temperature). The enhanced particle growth can be attributed to a finer alumina grain structure in the seeded sample. Diffusion of zirconia proceeds along the alumina grain boundaries. A finer alumina grain structure implies a higher grain boundary surface area and therefore a higher rate of zirconia diffusion. The particle size of the zirconia attained in the seeded sample was superior, with respect to toughening capacity, which was reflected in the fracture toughness measurements. Enhanced particle growth was not observed in the seeded composite that contained SiC-whiskers as

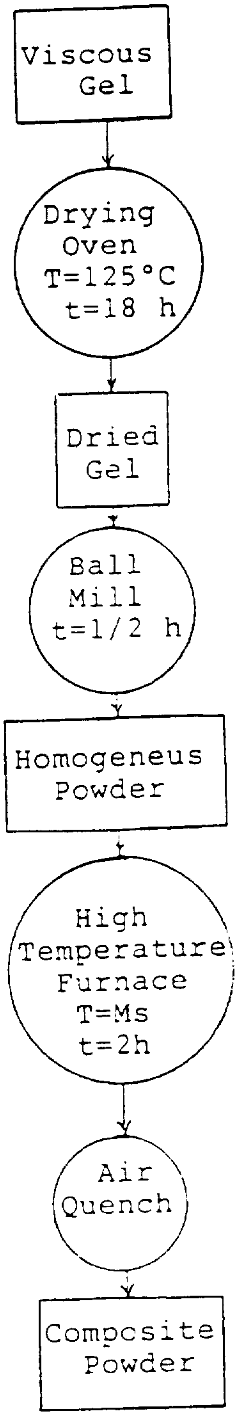

FIGURE 3

DRYING, GRINDING, AND CALCINATION OF GEL

TABLE 3. COMPOSITION OF COMPOSITES USED FOR TRANSFORMATION EXPERIMENTS

	A	B	C	D
%SiC	0	0	30	30
%ZrO_2	15	15	15	15
% -Seed	0	0	3	0

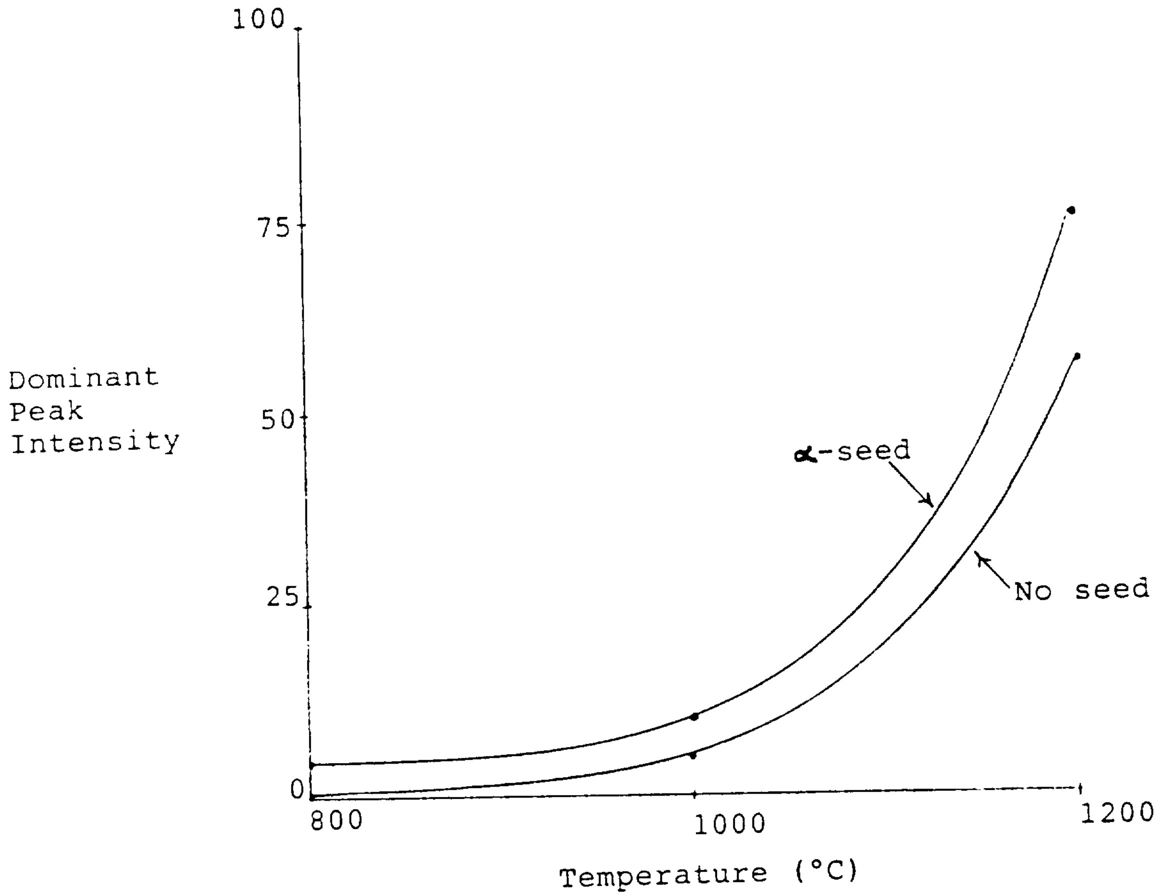

FIGURE 4

EFFECT OF α-SEEDING UPON θ-α ALUMINA TRANSFORMATION FOR BINARY ALUMINA-ZIRCONIA COMPOSITES

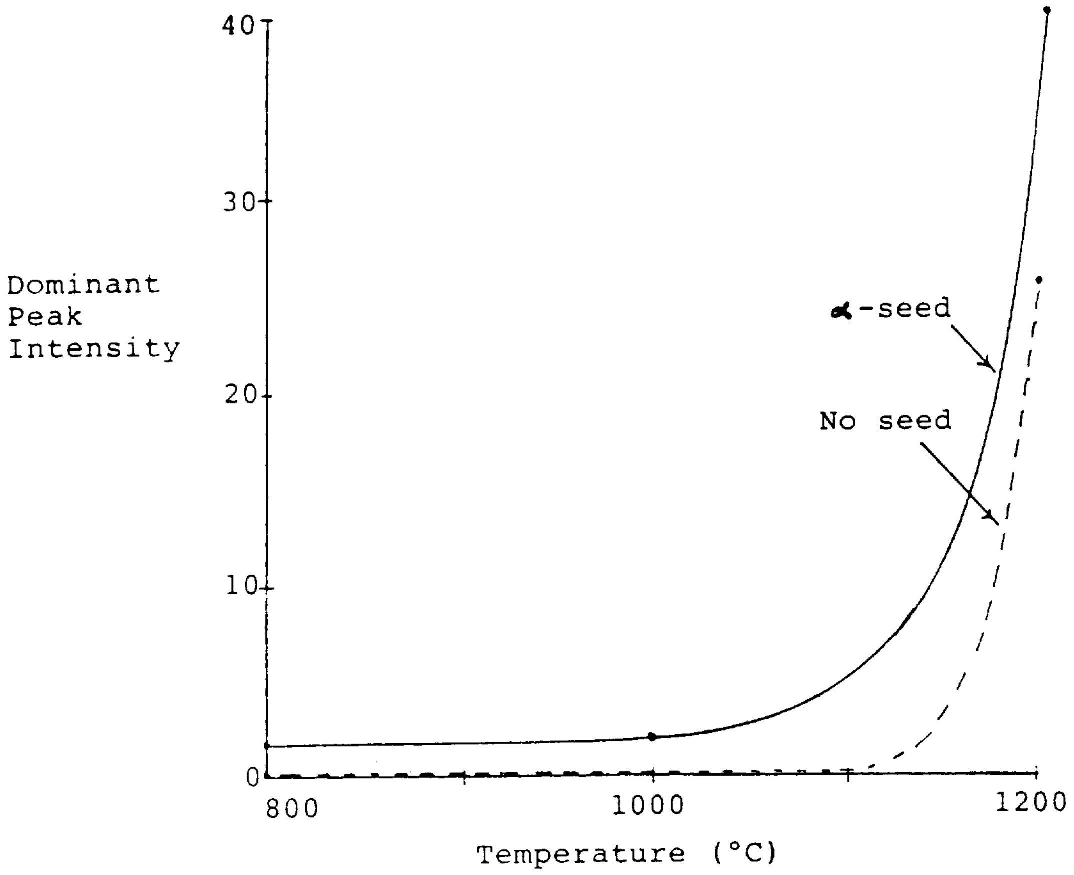

FIGURE 5.

Effect of α-Seeding upon θ→α Alumina Transformation for Tertiary Alumina-Zirconia-Silicon Carbide System

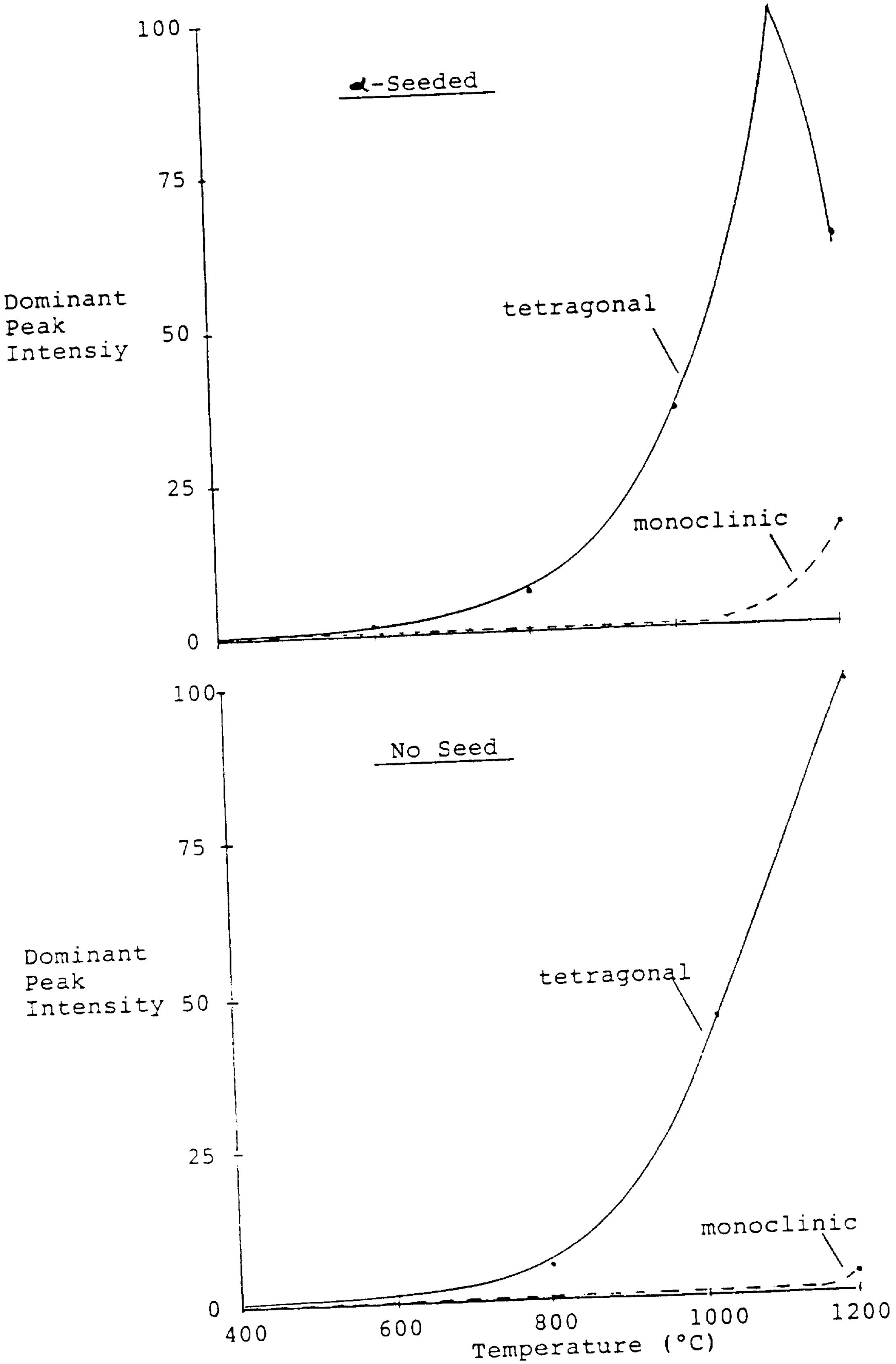

Figure6a & b. Effect of α-Seeding upon Zirconia Particle Growth and Transformations for Binary Alumina-Zirconia System compared to the unseeded. This might be due to SiC whiskers pinning alumina grain boundaries and impeding the diffusion of zirconia.

The effect of α-seeding was not only to control the alumina grain structure and transformation temperature, but also to enhance the growth of zirconia particles to the optimum size. The transformation temperature of ZrO_2 to the tetragonal form at about 1000°C which indicates that the ZrO_2 grain size in the tertiary composite is still acceptable. This implies that α-alumina seed is enhancing the generation of optimum ZrO_2 particles which should reflect on enhanced toughening effect of the binary composite. Indeed from the critical fracture toughness data (to be reported in a later section of this report) α-seed had significant effect on enhancing the toughening of the binary composite. This is unexpected since the general opinion and the reported data show that Al_2O_3-ZrO_2 binary composites produced from sol-gel produces low strength and low toughness composites. Accordingly, the effect of α-seeding is not only central to the alumina transformation but also to the ZrO_2 particle size and transformation. This is essential and a novel finding.

An interesting result was obtained by examining the SEM of the composite powders. In Figure 7, SEM's of calcined composite powder produced from gel, are shown. It can be seen that even on the micron scale, for the composite powder produced from the gel, the SiC whiskers are homogeneously distributed and embedded into the matrix. The non-uniform particle size distribution of this powder is due to the ball milling action of the dry gel. This, besides the fact that we did not have acceptable whiskers which was a major detrimental fact in consolidating our composites. In Phase II, we are proposing to investigate spin spray drying techniques to produce uniform size distribution of the composites without the detrimental effect of grinding. Photomicrographs of the (1200°C calcined) composite powder produced from gel calcined at 1200°C with and without seeds, are shown in Figure 8a and 8b, respectively. They demonstrate that seeds act as nucleation sites to produce fine-grained powder compared to unseeded system.

In summary, the following was observed, (1) well dispersed, fine microstructure, composite powder was obtained from the proposed concept, (2) the 800°C calcination of the composite gel produced powder with very low chloride levels (<30 ppm), without transformation of the zirconia (indicating that ZrO_2 particles are submicron in size), and alumina did not transform to the α-phase, (3) the 1200°C calcination, caused the transformation of the ZrO_2 and alumina to the desired crystalline phases (the seeded samples had fine microstructure), (4) the α-seeding was found to have significant effect on the transformation of ZrO_2 in binary composites while its effect was nullified by the SiC whisker in the tertiary composition, and (5) the seeding had significant effect on alumina transformation in both composite systems.

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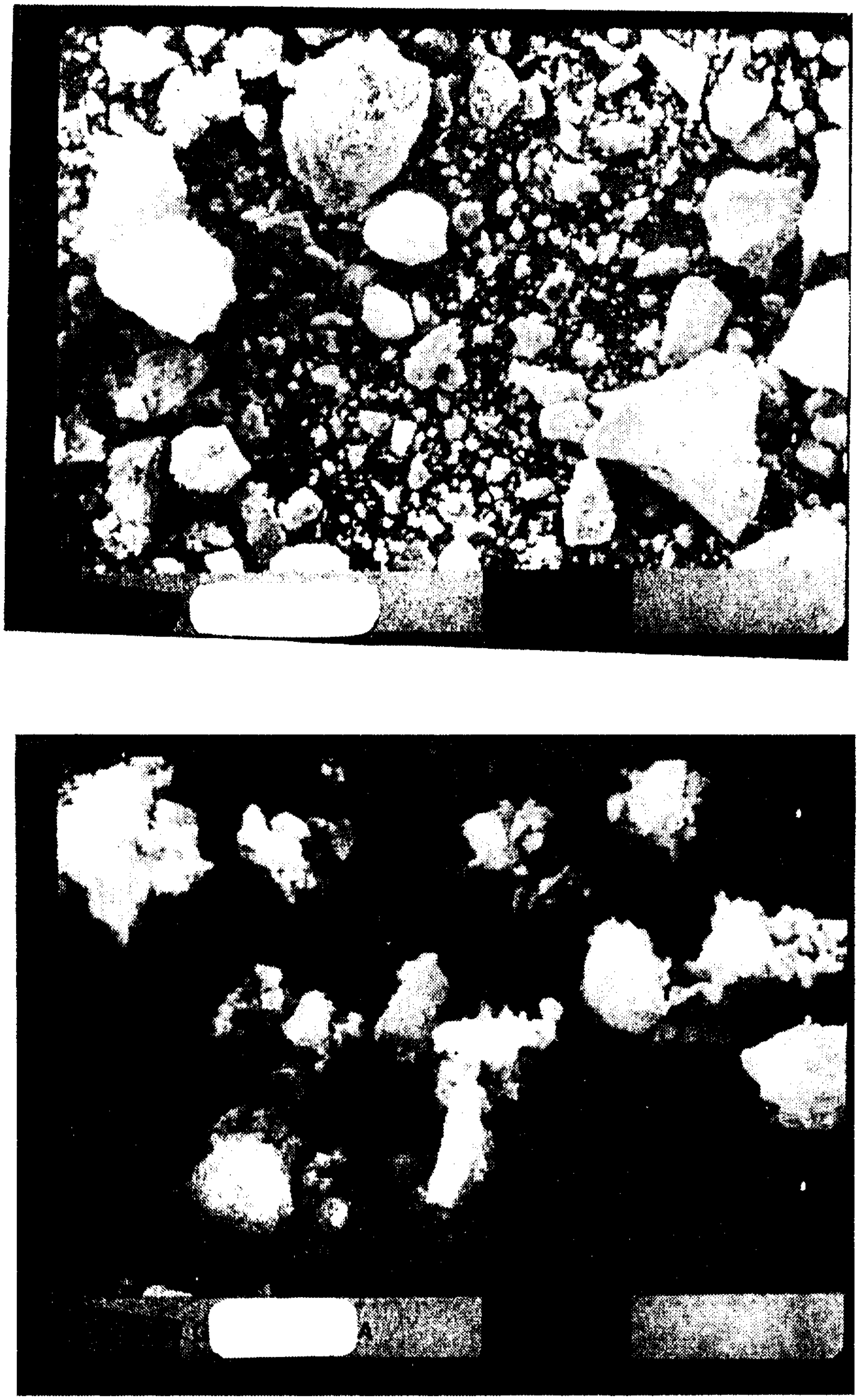

Figure 7. SEM Micrograph of 5% ZrO_2 /15% Sic/3% Seed 1200°C Calcined Composite

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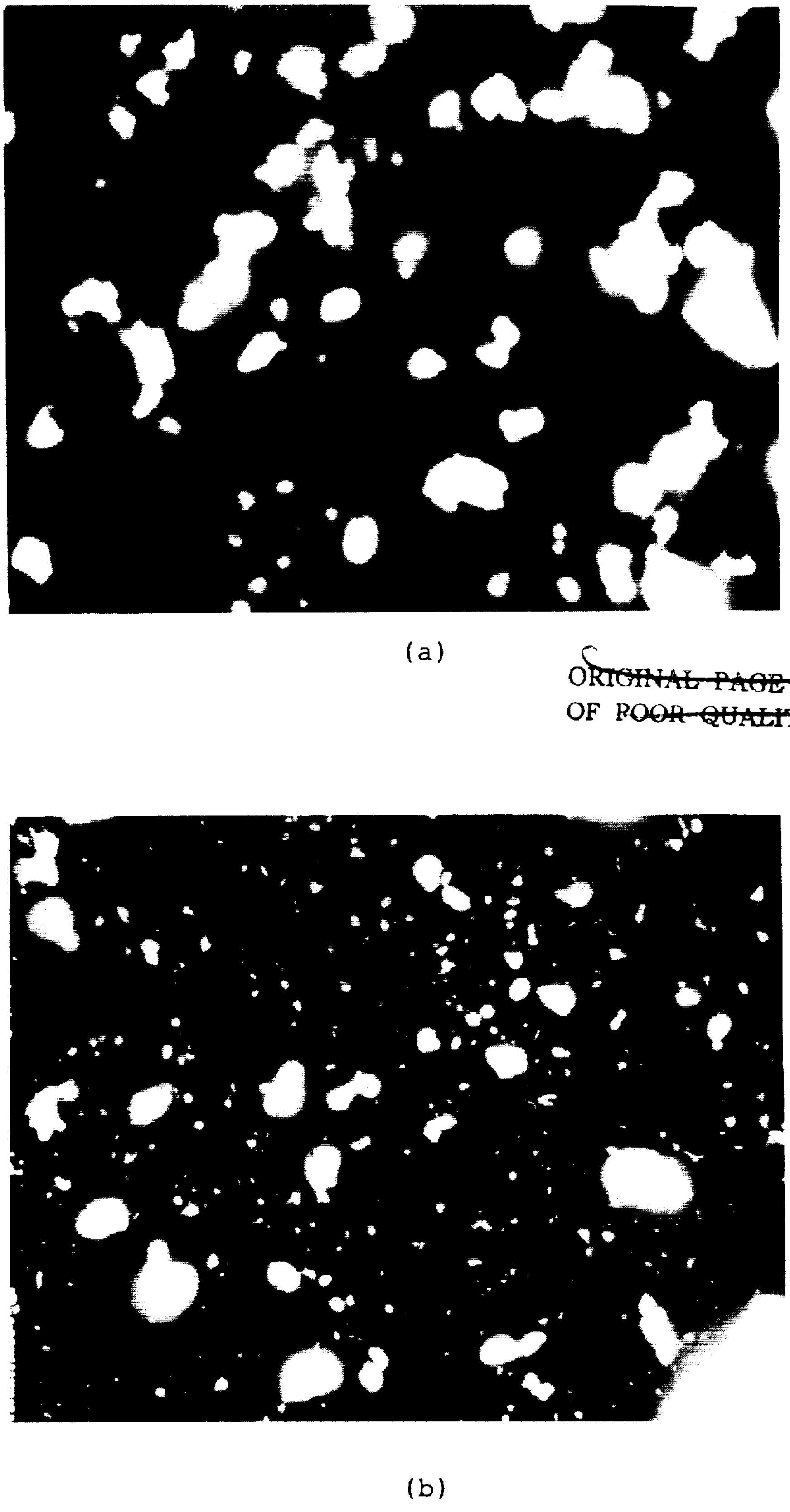

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Figure 8 Photomicrograph of 5 wt% ZrO_2/15 wt% SiC/Calcined Composite Powder, (a) Unseeded and (b) Seeded.

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4. Hot Press Composite Powder and Evaluation of Mechanical Properties

Composite powders using M-8, F-H and Tokai whisker were hot-pressed into a special configuration required for the mechanical testing at Lawrence-Livermore Laboratories (LLL).

Composite powder samples were hot pressed in the range of 5,000 to 10,000 psi at temperatures between 1375°C to 1475°C for about 40 minutes in multi-cavity graphite dies. The hot pressed parts were cut to size (1/2" diameter rods, and 3/4" length) and surface machined. Densities of the hot pressed composites were measured by the standard technique and a summary of results is given in Table 4. Except for the binary composite (which reached full theoretical density) all composites had low density ranging from as low as 71% to as high as 88% of theoretical density. The pressing temperature was not high enough to produce the liquid phase during sintering of these composite powders. In addition, the poor powder particle size distribution, as mentioned before, attributed to the ball milling of the composites, in combination with low sintering temperature most likely resulted in the low densities. It is interesting to note, however, that similar densities were obtained for composites with similar composition. For example, composites number K-5, K-1-19, K-1-13, and K-1-19 (Table 4) with 5% ZrO_2, and 15% SiC have densities of 85, 88, 85, and 85% respectively. This implies that the properties of these composites can be statistically analyzed using the technique of comparing means of matched samples.

It is interesting to note that the only samples that fully densified were the binary composites (Al_2O_3-ZrO_2) with α-alumina seed.

Four composite samples (using Tateho SiC whiskers) were also hot pressed, but at higher temperature. These composite powder samples were hot pressed at 4000 psi at 1670°C to 1690°C for 7 to 10 minutes. The temperature in this case was sufficiently high to possibly cause liquid phase sintering (Al_2O_3-ZrO_2 forms a eutectic with liquidus temperature of 1710°C). However, the time at pressure were relatively short, in our opinion, to allow for full densification; even though relatively high hot pressed densities over (90% of theoretical) were obtained for composite powders with low SiC whiskers contents (15 wt % SiC). The hot pressed samples were surface ground and sliced into 12 mm wide bars to serve as test samples for the mechanical testing.

5. Fracture Toughness Test Results

Hot pressed 1/2" diameter samples for composites listed in Table 4 were precision diamond machined to create a V-shaped CHEVRON slot. The specimen configuration is shown schematically in Figure 9. The machined samples were tested at room temperature for fracture toughness at LLL using a Teratek Fractometer. The Fractometer applies a controlled pressure inside the diamond-sawed slot. The pressure causes a crack to originate at the

TABLE 4. DENSITIES OF COMPOSITES HOT PRESSED AT

5000 TO 10,000 PSI AND 1375-1475°C

Composite	Composition			Type	Density	g/cc	%
#	%ZrO$_2$	%SiC	%Seed	SiC	Actual	Theoretical	Densification
1	5	15	0	F-H	3.07	3.93	78
2	5	30	0	F-H	3.02	3.84	79
3	15	15	0	F-H	3.46	4.03	86
4	15	30	0	F-H	2.84	3.94	72
5	5	15	4	F-H	3.35	3.03	85
6	5	30	4	F-H	2.91	3.84	76
7	15	15	4	F-H	3.3	4.03	82
8	15	30	4	F-H	2.79	3.94	71
9	5	15	0	M-8	3.44	3.93	88
10	5	30	0	M-8	3.03	3.84	79
11	15	15	0	M-8	3.16	4.23	78
12	15	30	0	M-8	3.31	3.94	84
13	5	15	4	M-8	3.33	3.93	85
14	5	30	4	M-8	3.04	3.84	79
15	15	15	4	M-8	3.32	4.03	78
16	15	30	4	M-8	2.95	3.94	75
17	5	15	4	Tokai	3.36	3.93	85
18	5	30	4	Tokai	2.93	3.84	76
19	15	15	4	Tokai	3.51	4.03	82
20	15	30	4	Tokai	3.07	3.94	78
25	5	0	0	-	3.1	4.03	77
26	5	0	4	-	4.06	4.03	100
27	15	0	0	-	3.63	4.15	87
28	15	0	4	-	4.21	4.15	100
29	15	15	-	F-H	3.22	4.07	80
30	15	15	-	M-8	3.11	4.03	77

* Mixed Powder

print of the "V"-shaped slot. The crack advances slowly and requires an ever-increasing load until the critical crack stress intensity is reached. The peak load to advance the crack through the critical location is linearly related to the specimen's fracture toughness. This test technique was used for the majority of composites studied under this contract, for convenience and quick evaluation of the processed composites. The objective here was simply to determine comparative K_{IC} values by a quick and simple technique. The accuracy of this technique and complete comparative analysis of this technique to different mechanical test techniques is beyond the scope of this study.

Composites, using Tateho SiC whiskers, were tested using the four-point, bend test.

The calculated critical fracture toughness from those test results for both series of composites are summarized in Table 5.

a. Statistical Analysis of KIC Data for Composites Using F-H and M-8 SiC Whiskers

Statistical analysis results of the data for composites made with F-H and M-8 SiC whiskers using the mean match samples technique is summarized in Table 6. From these results it is clear tht there is no statistical difference in fracture toughness of composites having F-H or M-8. Accordingly, K_{IC} data for composites using F-H and M-8 can be averaged. The results of the statistical analysis of the average K_{IC}'s (shown in Table 7) indicate that α-alumina seeding has a statistically significant effect, with 95% confidence, on increasing the fracture toughness of the tertiary composites. The mean increase in K_{IC} is 0.31 MPam$^{1/2}$ per wt% increase in α-alumina seed. Increased ZrO_2 content was also found, using the same statistical analysis technique, to have significant effect on increasing the fracture toughness of the composites. The mean increase in K_{IC} is 0.18 MPam$^{1/2}$ per 10 wt% increase in ZrO_2 content. It was also found that SiC whisker content has a substantially significant effect on composite fracture toughness, however, the effect is toughness by an average of 1.33 MPam$^{1/2}$. This surprising result can be attributed to the lower densities obtained with composites containing higher SiC whisker content. The hot pressing conditions were not changed to take into account the anticipated problem in processing composites with high SiC content.

Comparing the K_{IC} for mixed powder tertiary composites #29 and #30 with corresponding composites #3 and #11, produced from our sol-gel approach, respectively, it is clear that the sol-gel approach results in composites with enhanced fracture toughness. This is more apparent when comparing the K_{IC} of the tertiary composites produced by sol-gel with α-seed. It is clear that the sol-gel with seed approach results in tougher composites than mixed powder approach.

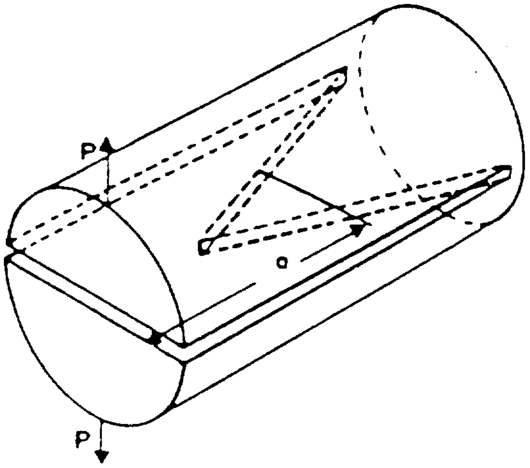


FIGURE 9. TERRATEK SPECIMEN CONFIGURATION FOR FRACTURE TOUGHNESS MEASUREMENT

P = 0.5 inches

a = 0.266 inches

TABLE 5. CRITICAL FRACTURE TOUGHNESS FOR COMPOSITES K_{ic}

Composite	Composition			Type/		%
#	%ZrO_2	%SiC	%Seed	SiC	K_{ic} $MPam^{1/2}$	Densification
1	5	15	0	F-H	4.46	78
2	5	30	0	F-H	3.20	79
3	15	15	0	F-H	5.60	86
4	15	30	0	F-H	2.70	72
5	5	14	4	F-H	6.63	85
6	5	30	4	F-H	3.80	76
7	15	15	4	F-H	5.40	82
8	15	30	4	F-H	3.43	71
9	5	15	0	M-8	5.37	88
10	5	30	0	M-8	3.79	79
11	15	15	0	M-8	4.49	78
12	15	30	0	M-8	4.49	84
13	5	15	4	M-8	3.44	85
14	5	30	4	M-8	3.85	79
15	15	15	4	M-8	5.37	78
16	15	30	4	M-8	4.62	75
17	5	15	4	Tokai	6.28	85
18	5	30	4	Tokai	5.06	76
19	15	15	4	Tokai	6.59	82
20	15	30	4	Tokai	4.52	78
21	5	15	4	Tateho	9.40	94
22	5	30	4	Tateho	9.87	92
23	15	15	4	Tateho	9.33	92
24	15	30	4	Tateho	10.06	90
25	5	0	0	-	3.17	77
26	5	0	4	-	7.09	100
27	15	0	0	-	5.54	87
28	15	0	4	-	6.07	100
29	15	15	-	F-H	5.03	80
30	15	15	-	M-8	4.10	77

TABLE 6. COMPARING FRACTURE TOUGHNESS MEAN OF MATCH SAMPLES USING F-H AND M-8 SiC WHISKERS

Composition, wt%			Fraction Toughness ($MPam^{1/2}$)			
SiC	ZrO_2	α-Seed	F-H	M-8	d_i	d_i^2
15	5	None	4.46	5.37	-.91	.83
30	5	None	3.20	3.79	-.59	.35
15	15	None	5.60	4.49	1.11	1.12
30	15	None	2.70	4.49	-1.79	3.20
15	5	3%	6.63	3.44	3.19	10.176
30	15	3%	3.86	3.85	0.01	0.00
15	15	3%	5.40	5.37	0.03	0.00
30	15	3%	3.43	4.62	-1.19	1.42
					0.14	17.293

$\bar{d} = -.0175$

$s_d = 1.6000$

$t_{test} = 0.0309 < t_{critical} = 2.306$

TABLE 7. STATISTICAL ANALYSIS OF THE EFFECT OF Γ-SEED USING F-H AND M-8

Composition		Fraction Toughness			
SiC	ZrO_2	Unseeded	Seeded	d_i	d_{i2}
15	5	4.915	5.035	-.12	-.014
30	5	3.495	3.855	-.36	.13
15	15	5.045	4.49	-.34	.12
30	15	3.595	4.49	-.43	.18

$d = -.31$

$s_d = 0.13$

$t_{test} = 4.66 > t_{critical} = 3.18$

b. Statistical Analysis of K_{IC} Data for Composites Containing <(F-H and M-8) vs Tokai Whisker> With α-Alumina Seed

The fracture toughness comparison of composites made of Tokai SiC whiskers and those made from F-H and M-8 is depicted in Figure 10. Statistical analysis indicates that the type of SiC whiskers is statistically significant with Tokai whiskers resulting in an average of 1.02 $MPam^{1/2}$ increase in toughening over those with the F-H and M-8 SiC whisker. ZrO_2 content seems to have not statistical effect on K_{IC} while again SiC whisker content has a negative effect on K_{IC} by an average amount of 1.44 $MPam^{1/2}$ for the 15 wt % increase in the SiC whisker content. This again can be explained by the low temperature pressing of these composites. In summary, it appears that tougher composites were obtained using Tokai whiskers compared to the F-H and M-8 whiskers.

c. Analysis of K_{IC} Data for Composite Containing Tokai SiC Whisker vs Tateho SiC Whisker, α-Alumina Seed

The four composites powders made with Tateho SiC whiskers were hot pressed at high temperature, low pressure and shorter time than the composites made with Tokai SiC whiskers, as mentioned previously. Accordingly, it was difficult to ascertain whether the effect was due to the whisker or the hot pressing conditions. We are positive that both factors are significant.

Accordingly, we were not able to statistically analyze the K_{IC} data. However, by comparison of the data, depicted in Figure 11, it is possible to conclude that: (1) the Tateho SiC and/or the hot pressing conditions had substantial effect on the fracture toughness of the composites. This could be due to the increase in density of the hot pressed parts, (2) ZrO_2 content does not seem to have a significant effect on K_{IC}; and (3) SiC content seems to have a negative effect using the Tokai SiC whiskers and a positive effect on toughness using the Tateho whiskers. This again can be explained by the effect of increased whisker content on decreasing the density which seems to be an overriding factor. Even though K_{IC} increased with increasing Tateho SiC whisker content, we would expect a much higher increase than obtained because the effect of increased SiC content on density also played a role here.

SEM of the fracture surfaces of composites containing Tokai and Tateho SiC whisker are shown in Figure 12. It is clear that composites with Tateho SiC whiskers were denser with less than composites with Tokai whiskers. It is interesting to note that no SiC whiskers where visible in the Tateho composite while they are visible in the Tokai composites. Neither composites show any evidence that the whisker pull-out mechanism is operative. Therefore, toughening has to be through ZrO_2 transformation and microcracking and SiC whisker crack deflection mechanisms.

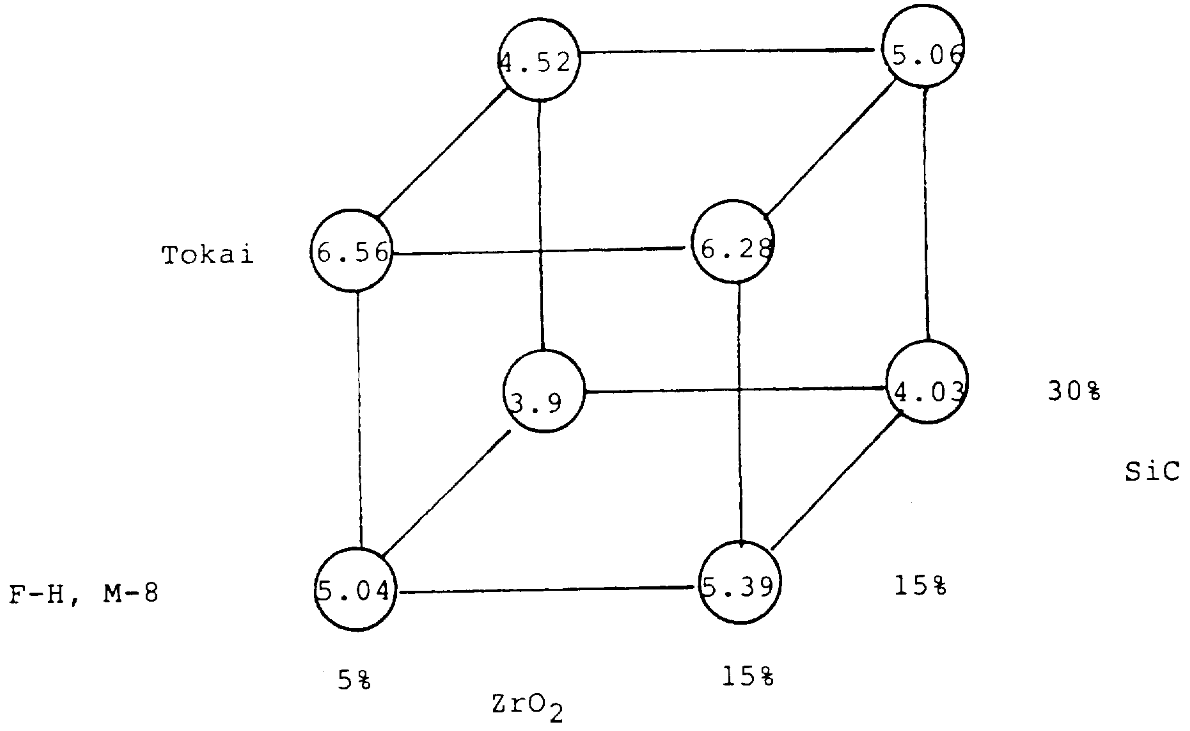


FIGURE 10 FRACTURE TOUGHNESS RESULTS - FACTORIAL DESIGN DIAGRAM FOR TERTIARY COMPOSITE

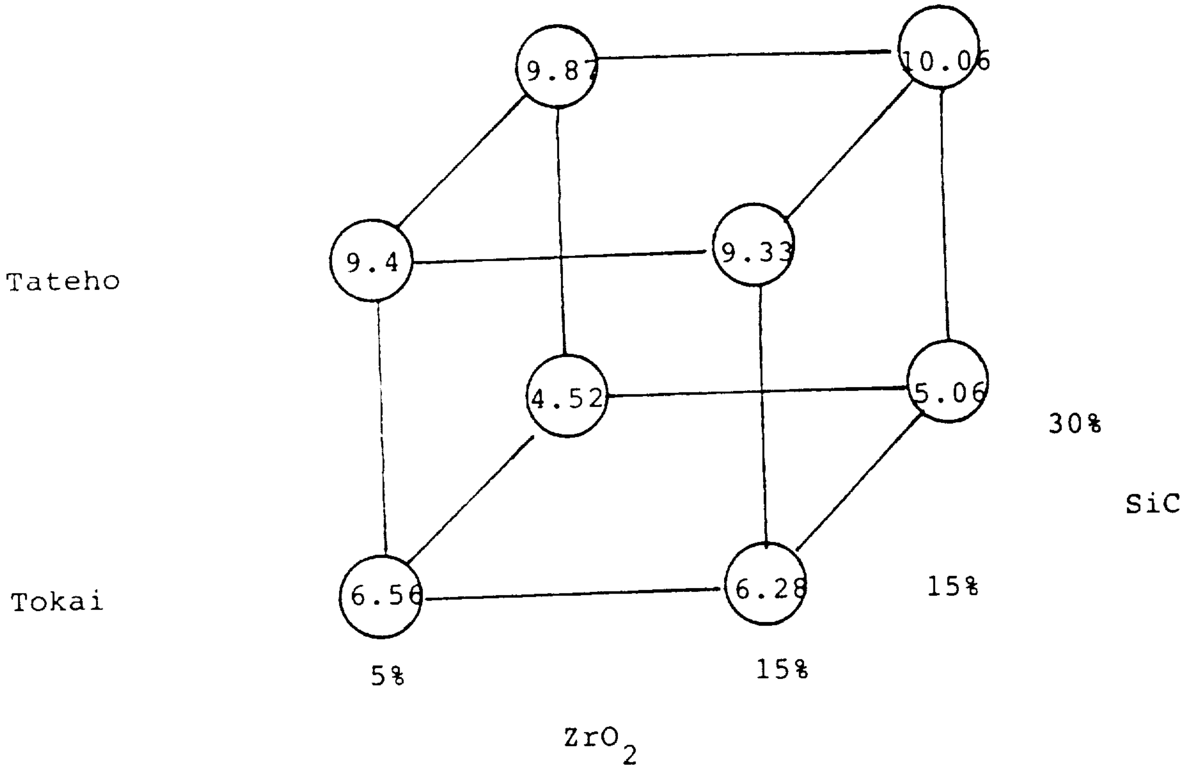
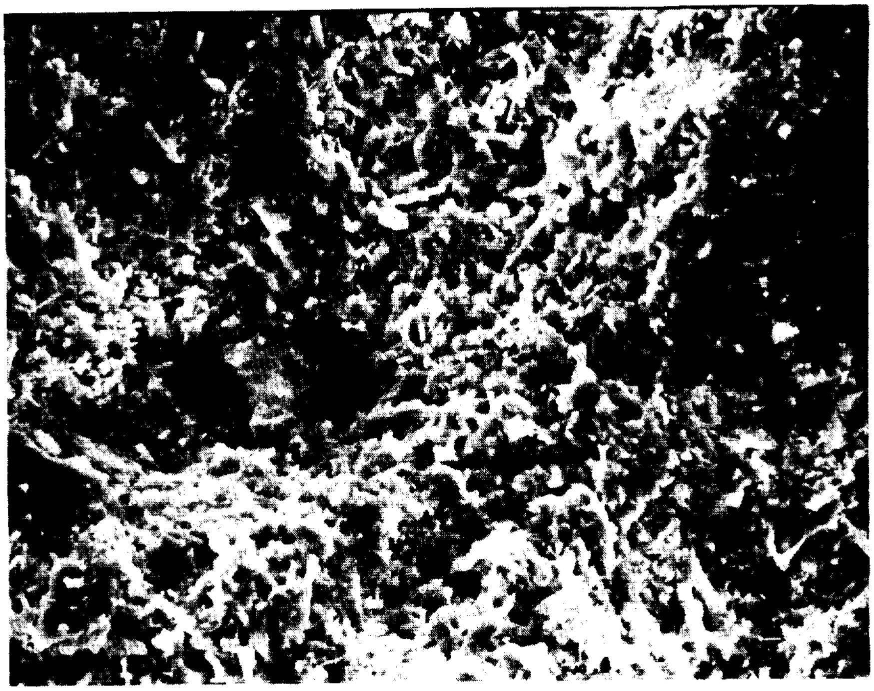


FIGURE 11. COMPARISON OF FRACTURE TOUGHNESS RESULTS OF COMPOSITES MADE WITH TOKAI AND TATEHO WHISKERS



(a)

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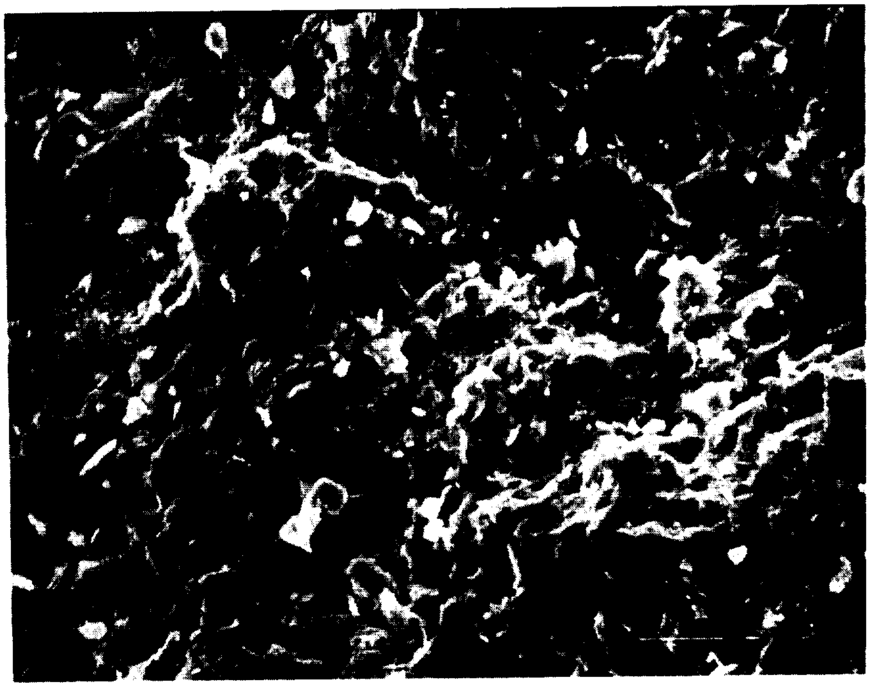

(b)

FIGURE 12 SEM OF FRACTURED SURFACE OF 15% ZrO_2 - 15% SiC TERTIARY COMPOSITE (a) TOKAI WHISKER, (b) TATEHO WHISKERS. 1000X MAGNIFICATION

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d. The Fracture Toughness of Binary (Al_2O_3-ZrO_2) Composites

The K_{IC}'s for the four binary (Al_2O_3-ZrO_2) composites produced from sol-gel with and without α-alumina seed are shown in Figure 14. It is clear that the α-alumina seed had a significant effect on the fracture toughness and also on the sintering of these binary composites (compare SEM of fractured surface in Figure 15a and b). It is interesting to note the fine particulate (presumable ZrO_2) in the completely fused (presumable alumina matrix) in Figure 15b. The fracture toughness of 7 $MPam^{1/2}$ for 5% ZrO_2 with α-alumina seed is considered excellent for binary ZrO_2 composite.

6. Fracture Toughness Model and Data Analysis

We have examined the toughness mechanism in SWA and ZTA and have predicted how they would interact in a tertiary system. The toughening mechanisms in SWA are crack deflection and whisker pull-out. Each toughening mechanism will be first described separately, then a prediction of how they will interact in a tertiary system is proposed.

(a) Whisker Pull-out Mechanism

The schematic of the whisker pull-out mechanism is shown in Figure 16.

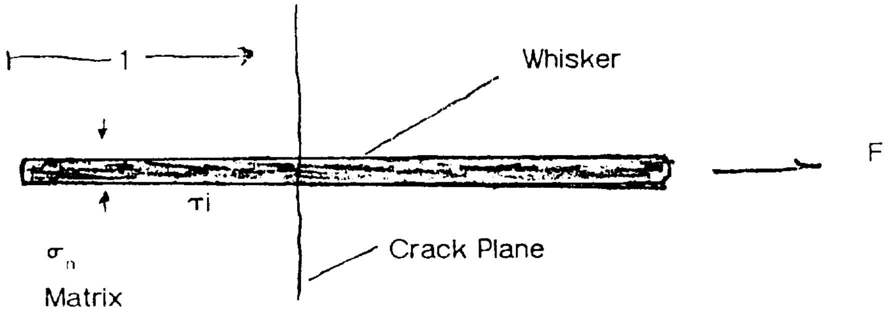


Figure 15

The force exerted on the whisker by the matrix in the axial direction is given by

$F = A_i\tau_i = (2\pi rl)\tau_i$ (1)

τ_i = interfacial shear stress

A_i = interfacial contact area between matrix and fiber

The interfacial shear stress is given by

$\tau_i = \mu\,\sigma_n$ (2)

μ = coefficient of friction

σ_n = compressional stress due CTE mismatch of the fiber and the matrix when cooling from sintering temp.

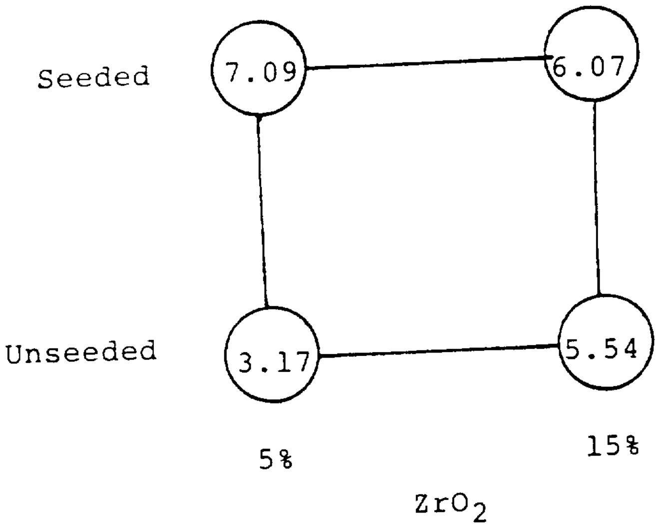
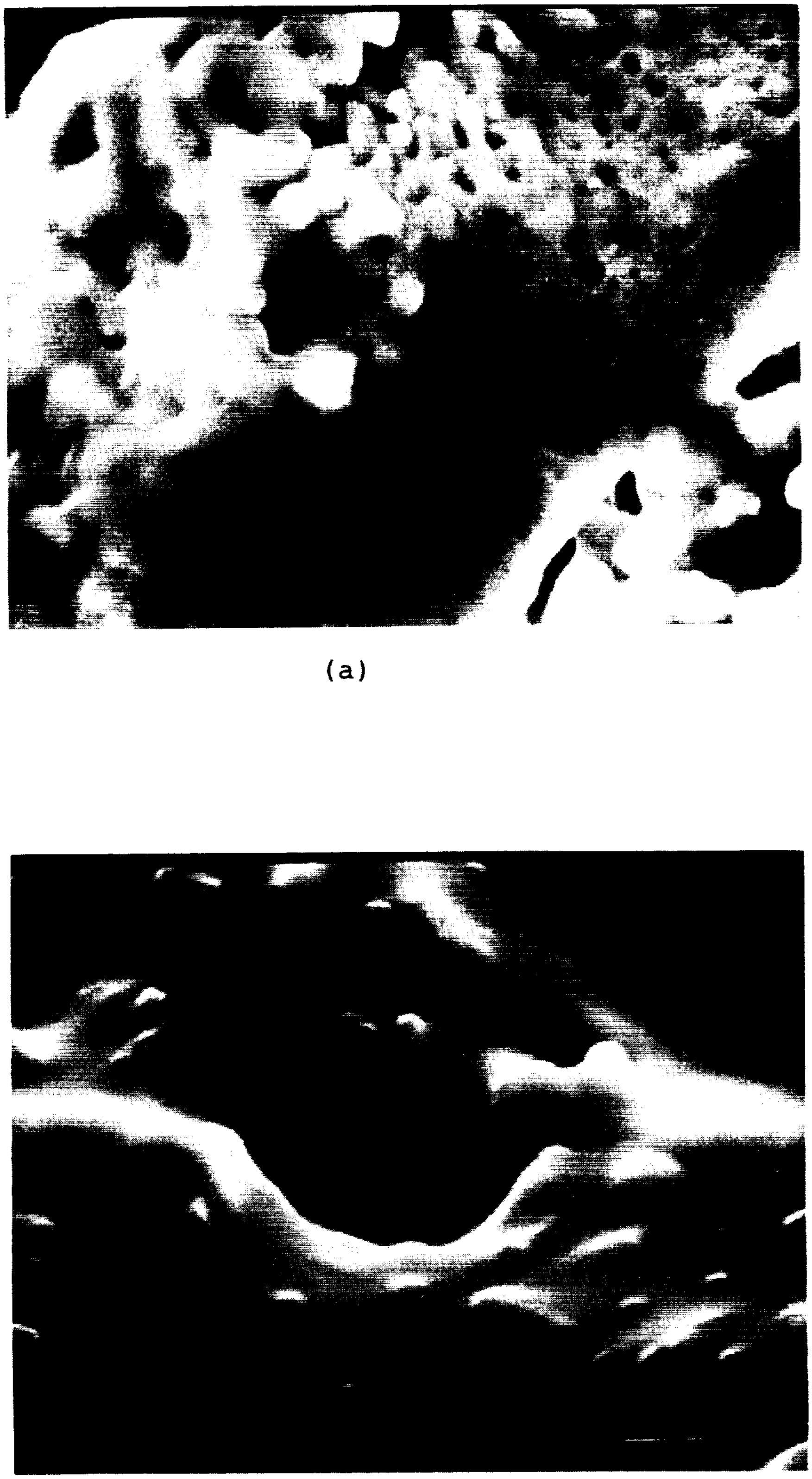


FIGURE 14. FRACTURE TOUGHNESS RESULTS - FACTORIAL DESIGN DIAGRAM FOR BINARY SYSTEM



(a)

(b)

FIGURE 15. SEM OF FRACTURE SURFACE OF BINARY (5% ZrO_2) COMPOSITE (a) WITHOUT (b) WITH Seed. 5000X MAGNIFICATION

The tensile stress generated during whisker pull-out is given by

$\sigma_w = F/A_w = F/\pi r^2 = 2\pi/\tau_i/r$ (3)

A_w = cross section area of whisker

The compressional stress is evaluated using Selsing's Equation $_w$here:

$\sigma_n = (\alpha_w - \alpha_m)\ T/\{[1+\nu_m)/2E_m]+[(1-2\nu_m)/E_w]\}$ (4)

ν_m = Poisson's Ratio of the Matrix

α_m and α_f are the CTE's of the matrix and fiber respectively. E_m and E_f are Young's modulus of the matrix and fiber respectively. If the tensional stress in the whisker exceeds the fracture stress of the whisker, the whisker will break. The tensional stress, as seen in equation (3), is a function of the length of the whisker that is imbedded in the matrix, the radius of the whisker and the compressional stress. A critical ratio of length of whisker embedded to whisker diameter can be determined from equation (2) and (3).

$$L/D = \frac{\sigma_{wf}}{4\sigma_n \mu} \qquad (5)$$

σ_{wf} = fracture tensile stress of whisker

If this ratio exceeds the critical value the whisker will break/ Toughening can be achieved with whiskers that are intercepted by a crack plane so that the length of whisker embedded divided by the whisker radius exceed this ratio. Betcher, Tiegs, Ogle, and Warwick reported that this critical aspect ratio is expected to increase with temperature because the normal compressional stress due to CTE mismatch will decrease with increasing temperature.

A qualitative understanding of the parameters that govern the toughening imparted by whisker pull-out is obtained by calculating the work of pull-out of a single whisker aligned perpendicular to the tensile stress field that is intercepted by a crack at a distance less than the critical length from the whisker end 1. This work of pull-out can be evaluated from the following integral.

$W = \int F\,dl = r1^2\pi\tau_i = \int_{\ell}^{\ell_f} \pi r \tau_i\,(l^2 - l_f^2)$ (6)

The toughening increment is equal to the sum of all the individual works of whisker pull-out. Whisker volume fraction and aspect ratio are the only factors that the manufacturer has control over the affect the work of pull-out. Therefore, it makes sense to think that the higher the volume fraction of whisker the greater the toughening increment. Also, aspect ratio should be optimized to work of pull-out. The optimum ratio is expected to be slightly greater than two times the critical aspect ratio.

(b) Crack Deflection Mechanism

The primary toughening mechanism is SWA has been shown to be crack deflection (2). Faber and Evans have used a fracture mechanics approach to model the crack deflection mechanism for rod like whiskers (3,4). Where the rod like whiskers in the near field of a propagating crack perturb the crack front causing a reduction in stress intensity. When a crack front approaches a whisker it will characteristically tilt out of the plane of advance at an angle theta.

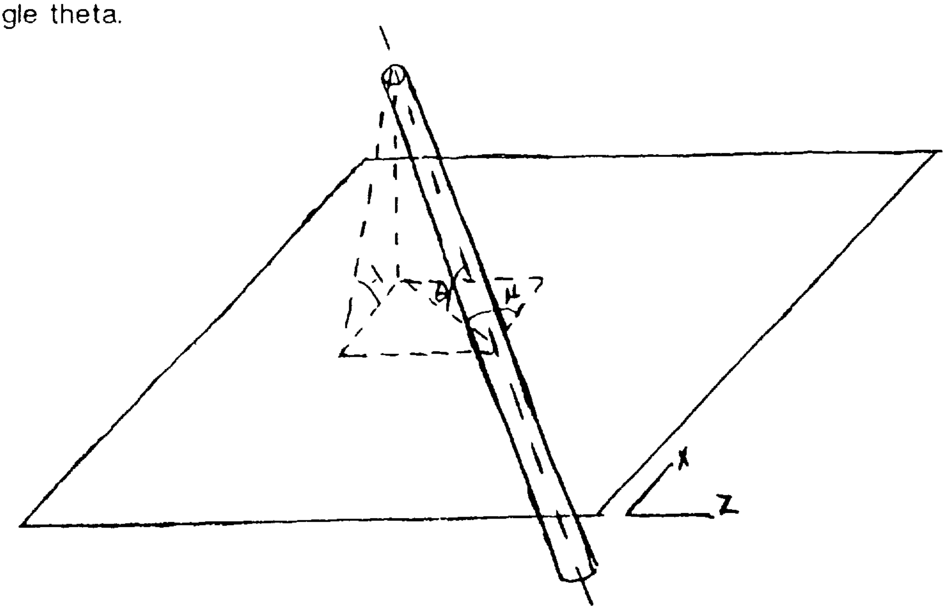


Figure 16. Crack Tilt Mechanism

The tilted crack has Mode I (opening) and Mode II (sliding) contributions. Subsequent crack advance can result in crack front twist caused by interaction with an adjacent whisker.

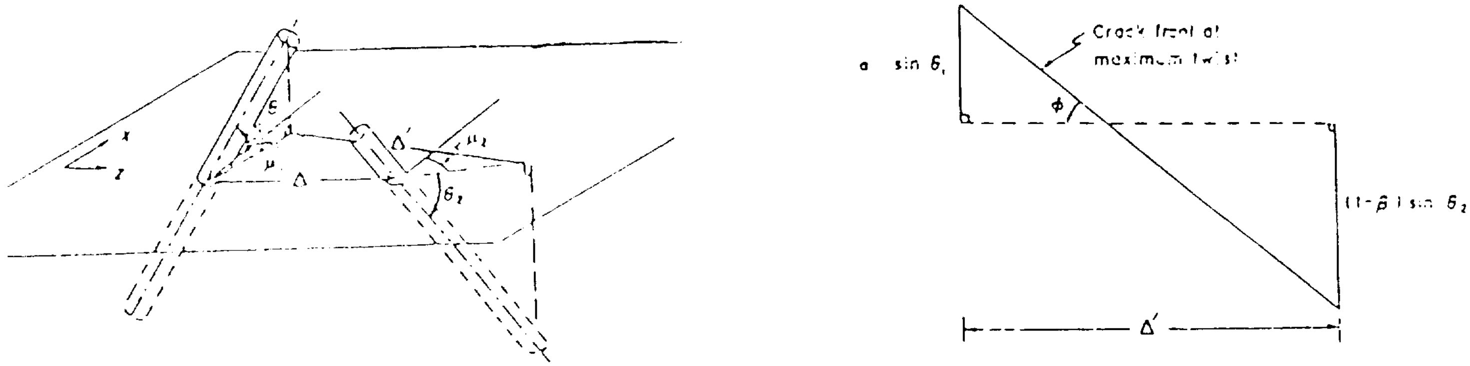


Figure 17. Crack Twist Mechanism

The crack twist mechanism incorporates Mode I and Mode III (tearing) contributions. The increase in fracture toughness imparted by the crack deflection perturbation is evaluated from the local stress intensity factors k_1, k_2, and k_3 as a function of deflection trajectory.

Crack advance is then assumed governed by the strain energy release rate G, pertinent to each segment of the crack front along its deflected trajectory.

$$EG = k_1^2(1 - \nu^2) + k_2^2(1 - \nu^2) - k_3^2(1 + \nu) \qquad (7)$$

E = Young's Modulus of the Matrix
ν = Poisson's ratio of Matrix
k_1 = Mode I Stress Intensity Factor
k_2 = $_M$ode II Stress Intensity Factor
k_3 = Mode III Stress Intensity Factor

The average G, <G>, across the crack front is then considered to represent the net crack driving force. A comparison of <G> with the corresponding G^m for the undeflected crack gives the predicted toughening increment G. The predicted toughening is evaluated for the crack tilting and crack twist mechanisms separately and then multiplied to give the total toughening increment due to the crack deflection perturbation. The local stress intensity factors for the crack tilt mechanism is represented as follows:

$$k^t_1 = K_{11}(\Theta)K_1 \qquad (8)$$
$$k^t_1 = K_{21}(\Theta)K_1$$

where K_1 is the critical stress intensity factor of the matrix and K_{11} (0) and K_{21} (0) are angular functions associated with tilted cracks. Correspondingly, the stress intensity factors applicable to the crack twist mechanism can be expressed as

$$k^t_1 = K_{11}(\Theta)k^t_1 + K_{12}(\Theta)k^t_2 \qquad (9)$$
$$k^t_1 = K_{31}(\Theta)k^t_1 + K_{32}(\Theta)k^t_2$$

where K_{ij} (Θ) are angular functions associated with crack twist and k^t_1 and k^t_2 are the local stress intensity factors for the crack tilt mechanism. The increment of toughening due to both the crack tilt and crack twist of whisker mechanisms were evaluated assuming a random distribution of rods for various rod volume fractions and aspect ratios. The increment of toughening is predicted to increase rapidly until a whisker volume fraction; $v_w = 0.1$. Then the toughening increment is predicted to increase slowly to $v_w = 0.2$ after which no further toughening occurs. The toughening increment increases asymptotically with whisker aspect ratio to about 4, $v_w > 0.2$. Little increase in toughness increment is predicted for aspect ratios greater than 12. It is interesting to note that the magnitude of each stress intensity factor in equations (7) and (8) is directly proportional to that of the unperturbed matrix.

C. Transformation and Microcrack Toughening

Cracking in ZTA occurs mainly in the matrix. Kosmac, Swain and Claussen (5) demonstrated that the critical stress intensity factor of the matrix in ZTA may be considered to be the sum of three factors, i.e.,

$$K_I = K_0 + \Delta K^m + \Delta K^T \qquad (10)$$

K = Critical Stress Intensity Factor of Matrix

where ΔK^m and ΔK^T are functions of the particle sizes and volume fractions of the monoclinic and tetragonal phases respectively. They report that roughly equal volume fractions of the t and m phases and a total zirconia volume fraction of 15% gives the greatest toughening.

D. Interaction of Toughening Mechanisms

The toughening increments due to the crack deflection mechanism and the transformation and microcracking mechanisms are expected to be multiplicative in a tertiary composite which utilizes both SiC-whiskers and zirconia to toughen alumina. The reason why can be seen by looking at equations (8) and (9) which were derived by Faber and Evans and were used to determine the local stress intensity factors and hence the degree of toughening for the crack tilt and crack twist mechanisms.

Equation (8) is seen to be the product of two separate functions. The first function $K_{ij}(\theta)$ is a function of whisker-matrix residual stresses, whisker aspect ratio and whisker volume fraction only. The second function, K_I which is the stress intensity factor for the matrix shown in equation (10) is the sum of the K_0 of the alumina matrix and ΔK^m and ΔK^t_g the increments due to microcrack and transformation toughening, respectively in ZTA. Therefore, if the matrix of ZTA was considered to be the matrix material for the crack deflection mechanism; one might expect the local stress intensity factors to be described as follows by substituting equation (10) into equation (8)

$$k^t = K_{11}(\theta)[K_0 + \Delta K^t + \Delta K^m] \qquad (11)$$

$$k^t = K_{21}(\theta)[K_0 + \Delta K^t + \Delta K^m]$$

This representation indicates that the stress intensity factors of the whisker reinforced composite determined by the crack tilt mechanism is directly proportional to the increase of stress intensity factor of the matrix due to microcrack and transformation mechanism. Correspondingly the stress intensity factors for the crack twist mechanism shown in equations (9) are products of the stress intensity factors for the crack tilt mechanism and functions of whisker orientation, aspect ratio and volume fraction. Therefore, the stress intensity factors for the crack twist mechanism are also seen to be directly proportional to the stress intensity factor of the matrix. The above representation indicates that the increments of toughening due to the crack deflection mechanism and that due to microcrack and transformation mechanisms would be multiplicative. This suggests that a tremendous increase in toughness could be achieved by producing a tertiary composite utilizing both SiC-whiskers and zirconia to toughen alumina.

The incorporation of zirconia into SWA is not expected to influence the increment of toughening due whisker pull-out to a high degree. The difference is the CTE's of SiC and ZrO_2 is not as great as that of SiC and Al_2O_3, therefore, the interfacial shear stress would not be expected to be as high. However, if a whisker is adjacent to a t-zirconia particle that transforms the dilation that occurs would create a large compressional force upon the whisker creating a large interfacial shear. Whisker pull-out is expected to account for about the same degree of toughening in the tertiary composite as is observed in ZTA.

Accordingly, we expect at least from the theoretical point of view that the toughening increments from the crack deflection mechanism and the transformation and microcracking mechanism should be multiplicative. Also, an additional increment of toughening will be realized from the whisker pull-out mechanism.

7. Comparison of Model with K_{IC} Data

The interaction of the crack deflection mechanism due to SiC whiskers, with the transformation and microcrack mechanisms, due to zirconia particle, has been described in equation (12), where $K(\Theta,\Theta)$ is predicted by Faber and Evans to have a value of approximately 3.5 for the whiskers aspect ratios and volume fraction that we used in our study. However, actual values of $K(\Theta,\Theta)$ are substantially less. Actual values can be determined from

$$K(\Theta,\Theta) = K_{IC}/K_o \qquad K_o = K_{IC} \text{ of Monolithic Alumina} \quad (12)$$

The value of $(\Delta^T K^T + \Delta K^m)$ is the difference between the K_{IC} of ZTA and monolithic alumina. Therefore, expected values of K_{IC} for the tertiary composite (SiC-ZrO_2-Al_2O_3) can be predicted from known values of K_{ic} for SWA, ZTA and monolithic alumina. These values along with the calculated values for the tertiary composites using Tateho whiskers, where we used four point bending techniques, are given in Table 8, together with adjusted data from ORNL (to correspond to the same composition of our work). The calculated data is done using the K_{ic} values of ZTA from both mixed powder and gel.

It is clear from the results presented in Table 8 that (1) our proposed sol-gel approach resulted in superior fracture toughness composites than the mixed powder approach of ORNL, (2) ORNL data is lower than the calculated data using K_{ic} for gel ZTA, (3) the K_{ic} we obtained for our tertiary composites are generally higher than the values calculated using the K_{ic} for ZTA derived from powder, but lower than the K_{ic}'s calculated using the K_{ic}'s for ZTA derived from gel. Conclusions (2) and (3) implies that the calculated values represent the maximum expected K_{ic} value for each approach. Accordingly mixed powder approach has the maximum potentials of producing composites with up to 11.4 MPam$^{1/2}$ while the sol-gel approach has the potential of up to 15.45 MPam$^{1/2}$.

TABLE 8. COMPARISON OF ACTUAL K_{IC}'s WITH CALCULATED VALUES

Composite Composition		K_{IC} this work	K_{IC} Calculated for gel	K_{IC} Adjusted ORNL	K_{IC} Calculated for Mixed Powder
ZrO_2	SiC				
5	15	9.4	12.99	7.6	7.88
5	30	9.87	15.45	8.0	9.37
15	15	9.33	11.13	8.6	9.63
15	30	10.06	13.22	9.2	11.44

K_{IC} for ZTA, Monolithic Al_2O_3 and SWA are:

Monolithic Al_2O_3 = 3.9 $MPam^{\frac{1}{2}}$
ZTA (5%) powder = 4.3 $MPam^{\frac{1}{2}}$
* gel = 7.09 $MPam^{\frac{1}{2}}$
ZTA (15%) powder = 5.25 $MPam^{\frac{1}{2}}$
* gel = 6.07 $MPam^{\frac{1}{2}}$
SWA (15%) = 7.15 $MPam^{\frac{1}{2}}$
SWA (30%) = 8.5 $MPam^{\frac{1}{2}}$

* K_{IC} measured using TerraTek technique, all others measured using single edge notch beam four point bending techniques.

V. CONCLUSIONS

1. Sol-gel approach has demonstrated the potential of producing tertiary composites with superior fracture toughness.

2. α-alumina seeds have a significant effect on the alumina and zirconia phase transformation, sintering behavior and consequently on the fracture toughness.

3. α-alumina seed/gel approach produced superior toughened binary composites even with very low ZrO_2 content.

4. SiC type an consolidation condition are significant in producing superior toughness composites.

5. A maximum K_{ic} for tertiary composites can reasonably be estimated by a model we developed. According to this model, our approach has the potential of producing composites with K_{ic} of 15 $MPam^{1/2}$.

6. A tertiary composite was produced with K_{ic} of 10 $MPam^{1/2}$, which is superior to any published data for a similar system.

VI. POTENTIAL APPLICATION

The potential in ceramic composites for superior engineering materials is attracting much attention worldwide. With the proper combination of ingredients, ceramic-ceramic composites hold promise for tough materials without sacrifice in the advantage that ceramics have over metals, and polymers. High performance ceramic composites have a wide range of potential applications such as, cutting tools, wear parts, military and aerospace applications and hear engine parts. Such application can materialize and new market opportunity can occur only if an economically formulated composite powder, a low cost method of consolidation, and high mechanical and thermal stability performance is achieved. The developed binary and tertiary composite under this program offers the potentials for producing will engineered ceramic powder with the right ceramic properties from simple low cost process steps. This could lead to low cost consolidation techniques. The major cost factor will be the SiC whisker. However, several companies are active in the U.S. to produce whisker at <$50/lb compared to existing prices of $125 to $250/lb. Accordingly, it is conceivable that by the end of this program we could produce engineered ceramic composite powder on a commercial basis for under $20/lb. At this projected cost, a potentially large market could develop.

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Report Documentation Page

1. Report No.
NASA CR-179629

2. Government Accession No.

3. Recipient's Catalog No.

4. Title and Subtitle
Zirconia Toughened, SiC Whisker Reinforced Alumina Composites
Small Business Innovation Research
Phase 1 – Report
December 1985 – October 1986

5. Report Date
October 1987

6. Performing Organization Code

7. Author(s)
R.O. Loutfy, K.L. Stuffle, J.C. Withers, and C.T. Lee

8. Performing Organization Report No.
None

10. Work Unit No.
324-01-00

9. Performing Organization Name and Address
Materials & Electrochemical Research (MER) Corporation
4233 South Fremont Avenue
Tucson, Arizona 85714

11. Contract or Grant No.
NAS3-24872

13. Type of Report and Period Covered
Contractor Report
Final

12. Sponsoring Agency Name and Address
National Aeronautics and Space Administration
Washington, D.C. 20546

14. Sponsoring Agency Code

15. Supplementary Notes
Project Manager, Sunil Dutta, Materials Division, NASA Lewis Research Center.

16. Abstract

The overall objective of this Small Business Innovation Research Phase 1 project was to develop a ceramic composite with superior fracture toughness and high strength, based on combining two toughening inducing materials: zirconia for transformation toughening and SiC whiskers for reinforcement, in a controlled microstructure alumina matrix. The controlled microstructure of the matrix is obtained by controlling the nucleation frequency of the alumina gel with seeds (submicron α-alumina). The results obtained in this study demonstrated the technical feasibility of producing superior binary composites (Al_2O_2-ZrO_2) and tertiary composites (Al_2O_3-ZrO_2-SiC). Thirty-two composites according to statistically designed experiments were prepared, consolidated, and fracture toughness tested. Statistical analysis of the results demonstrated that: (1) SiC type was the key statistically significant factor for increased toughness (2) sol-gel processing with a-alumina seed had a statistically significant effect on increasing toughness of the binary (Al_2O_2-ZrO_2) and tertiary composite (Al_2O_3-ZrO_2-SiC) compared to the corresponding mixed powder processing, (3) ZrO_2 content within the range investigated had a minor effect. Binary composites (Al_2O_3-ZrO_2) with an average critical fracture toughness of 6.6MPam$^{1/2}$, were obtained. Tertiary composites with critical fracture toughness in the range of 9.3 to 10.1 MPam$^{1/2}$, were obtained. These results indicate that these composites are superior to zirconia toughened alumina, and SiC whisker reinforced alumina ceramic composites produced by conventional techniques with similar composition from published data. A mathematical model was also developed to describe the critical fracture toughness for the tertiary composites which indicates that the toughening increments due to the SiC and ZrO_2 are expected to be multiplicative.

17. Key Words (Suggested by Author(s))
Ceramics; Toughening; SiC-whisker; Zirconia; Alumina;
Sol-gel; Hot pressing

Date for general release October 1989.
Subject Category 27

19. Security Classif. (of this report)	20. Security Classif. (of this page)	21. No of pages	22. Price*
Unclassified	Unclassified	48	A03

National Aeronautics and
Space Administration

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Cleveland, Ohio 44135

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