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This research focuses on the development and analysis of structural ceramics reinforced by fibers. The objective is to derive a light-weight composite that has superior durability, strength and fracture toughness, and energy absorption capability as a structural material. The investigation involves the use of theoretical techniques in predicting the composite mechanical performance based on the fiber and matrix properties, laboratory development of material processing and fiber dispersion, and experimental testing of the fibrous composites. The project examines several innovative techniques of fiber reinforcement for enhanced ceramic composite toughness.

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FIBER REINFORCED STRUCTURAL CERAMICS FOR CONSTRUCTION

~~Final~~ Technical Report

by
Victor C. Li (Principal Investigator)
and Christopher K.Y. Leung

Period: January 15, 1987 - December 25, 1987

U. S. ARMY RESEARCH OFFICE

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Introduction

This research project has the ultimate goal of developing a light-weight, durable, strong and impact resistant ceramic composite for use in certain advanced constructed facilities. While cost could be the limiting factor of how and where the developed material will be used, this investigation chooses to focus largely on technological advancements. A complementary project in the Program of Advanced Construction Technology focuses on the economic assessment of ceramics used for construction.

The investigation adopts a systematic approach. A model fiber/matrix material system is first identified, for the purpose of carrying out experimentation which will evaluate micromechanical parameters. This is performed in conjunction with micromechanical model studies which relate material micro-structures and micro-mechanisms to macroscopic composite properties. These investigations should result in (1) a better understanding of the effect of processing procedure on the micromechanical features and properties of the matrix, and the fiber/matrix interface; (2) a better understanding of the contribution of these micro-structures to composite behavior; (3) optimization methodology of material constituents, such as fiber aspect ratio and/or fiber surface treatment; (4) optimization methodology of processing conditions. The combined effect of these results is the systematic engineering of the internal structure of fiber reinforced ceramics to meet the ultimate project goal described in the previous paragraph.

For this project period, we have focused on the four major investigations described below. Much time has been devoted to processing the model glass matrix and to setting up the Omni-mixer and the MTP-press acquired for this project. These equipment are essential for specimen preparation. We expect major accomplishments in experimentation and data acquisition and analysis in the next project period.

Statement of Problem Studied

(1) Initial analysis of achievable mechanical properties for various reinforced and unreinforced ceramics to determine the class of ceramic materials with the highest potential for development into a construction material. Random short-fiber reinforced ceramics was selected.

(2) Selection of particular fiber and matrix for a model composite material which can be processed conveniently at a moderately low temperature. Experiments and analysis will be based on the model material.

(3) Survey of processing techniques to determine the best processing procedure for the model material.

(4) Preparation of specimens of the model composite and preliminary SEM investigations on fracture surface to understand microstructure and failure mechanisms of the composite.

Summary of Major Research Findings

(1) From the literature, mechanical properties of ceramics were obtained and are summarized in Table 1. It is obvious from the table that ceramics are very stiff materials (modulus about an order of magnitude higher than concrete) with high compressive strength (about two orders of magnitude higher than concrete). However, its flexural strength is only moderate and its toughness is relatively low. Hence, some means of toughening must be employed to improve the properties of ceramics. Currently known toughening mechanisms for ceramics are summarized in Table 2 (from Evans[1]). It can be concluded from the table that fiber reinforcement is the most efficient way to improve toughness. Moreover, it is a very general technique which can be applied to almost all kinds of ceramics, while techniques involving transformation toughening and micro-crack toughening can only be realized in some special ceramic material systems. Fiber-reinforced composites have been produced successfully employing some of the ceramic materials in Table 1 as matrix. Mechanical properties of such fiber-reinforced composites are tabulated in Table 3 and the improvement in toughness is clearly reflected from the values of K_{1C} and G_F.

Most current studies on ceramic composites have concentrated on continuous fiber composites, which exhibit very high toughness and flexural strength values, and whisker reinforced ceramics, which have high potential in elevated temperature applications. These materials have shown impressive performance but are very high in cost due to complicated processing procedure for continuous fiber composites and high cost of whiskers in whisker composites. Also, for continuous fiber composites, strength and toughness in the transverse direction are much lower than in the fiber direction and so full advantage of material property can be made only if the principal direction of tensile stress in the

structure is known beforehand. This is clearly not the case in structures such as pavements where loading is applied essentially as point loads rather randomly on the surface. Techniques like lamination may be used which translate into additional cost. In civil engineering applications, where the material is needed in bulk, cost will be an important consideration. Random short-fiber reinforced ceramics, which can be processed rather simply, may be a good compromise between performance and cost.

From Table 3, it can be observed that introduction of short fibers may lead to a slight decrease in flexural strength but a high increase in toughness. Since the flexural strength of ceramics is much higher (usually by 1 or 2 orders of magnitude) compared to traditional construction materials, the slight decrease may not be significant. However, the great increase in toughness is important in reducing catastrophic structural failure. Moreover, short fiber reinforced composites exhibit an increase in toughness as the crack grows (the R-curve behaviour) and it has been shown that this can lead to a higher reliability for the material[2] (Fig.1). From Table 2, currently achievable toughness values for both whisker and continuous fiber reinforced ceramic are given. The potential toughness value for random short fiber reinforced ceramics should lie somewhere between the values for these two groups. Through the development of a micromechanical model relating micro-properties with macro-behaviour and the study of processing-microstructure interaction, it may be possible to optimize the properties of short fiber composites so that toughness values close to those for continuous fiber reinforcements may be attained.

For reasons discussed above, we conclude that random short fiber reinforced ceramics have the highest potential to be developed into an advanced construction material. Thus, our studies will concentrate on this

kind of composite.

(2) To be able to optimize the properties of the composite material, the first step is to develop a micromechanical model that can relate macro-behaviour (e.g. strength, toughness) to micro-properties (e.g. fiber/matrix interfacial properties, thermal mismatch). Then, important microscopic parameters can be identified and optimized through processing control.

To develop the micro-mechanical model and to show that optimization can be achieved, we must be able to process various kinds of specimens for experiments to be carried out. However, most currently used engineering ceramics have to be processed at high temperatures under very complicated control which render it difficult as well as costly to carry out large scale experimentation. Hence, we decided to develop and verify our micromechanical model by using a model material system which has mechanical behaviour representative of most fiber-reinforced ceramics but can be easily processed. This model material may not be used in practice (due to its low strength and toughness as well as its low durability). However, with the help of this model material, we can understand the mechanics of fiber-reinforced materials and how their properties can be optimized. Then, we can apply this knowledge to optimize the properties of other practical material systems. The choice of matrix and fiber for the model system are discussed below.

The model matrix has to be brittle to be representative of ceramic behavior. For this purpose, glass is a good candidate and indeed, Lithium aluminosilicate (LAS) is a glass ceramic often used as matrix material for fiber reinforced ceramic composites. For our investigation, the matrix should also have a moderately low processing temperature as processing temperature of

composites is solely determined by that of the matrix. The low processing temperature enhances the ease of processing and enables better experimental control. Glasses of some compositions exhibit these required properties. Glasses have the further advantage that they densify by viscous flow rather than sintering (which is essentially a diffusion process) and hence it is much easier to produce a dense glass than a dense engineering ceramic. An extensive survey was carried out through the glass literature and two candidates were identified: a lead tin fluorophosphate glass[3] and a lead phosphate glass with various oxide additions[4]. Both glasses are not commercially available and have to be processed in our laboratory. Processing of the fluorophosphate glass involves the emission of fluorine which has to be carefully controlled for health reasons. Moreover, the fluorine may also react with the material in the furnace wall causing damage to the furnace. As a result, the lead phosphate glass has been chosen as the matrix material. This glass has a viscosity as low as about 10000 Poise at 300 °C. Thus, depending on applied pressure, this glass can be processed at 300-400 °C (compared with > 1000 °C for most ceramic systems). At such low temperatures, processing can be quite easily controlled.

Fibers can essentially be divided into three groups: inorganic fibers, metallic fibers and synthetic fibers. Synthetic fibers soften at temperatures below 500 °C and this is generally too low for practical ceramic composites. Metal fibers can also deteriorate at high temperatures through softening and reaction with the matrix though tough composites have been developed with some particular metal fibers in ceramic matrix (e.g. Nickel fiber in MgO[5]). We choose to use an inorganic fiber in our model composite since they are compatible with most ceramic systems even though some metal fibers can also be used in special cases. Most inorganic fibers are very expensive. Graphite and glass have the lowest cost. Glass fibers cannot be used here as it may react

with the matrix glass material. Graphite fiber starts to oxidize in air only above about 450 °C and thus can be used with the lead phosphate glass mentioned above even if we carry out the processing in air. Thus, graphite fiber becomes the best choice.

In summary, for the purpose of this experimental study and subsequent micro-mechanical analyses, it is found that a graphite/lead phosphate glass material system provides the most convenient model composite.

(3) There are many available processing techniques for fiber reinforced materials. For random short fiber reinforced composites, the two most common techniques are (i) injection or pouring of melted matrix with fiber, and (ii) mixing of matrix powder and fiber followed by pressing. In the first technique, the matrix is heated up to such a degree that it becomes fluid enough to flow freely. Then fiber is mixed in and the melt is either injected or poured into a mould. For the second technique, the fiber and matrix are first mixed up and then hot pressed to form the composite.

The injection technique is most suitable when a part of a complex shape (e.g. a helmet) is to be formed. However, it is usually difficult to determine and control the fiber distribution in the composite processed in this manner. There are two reasons for this. When the matrix becomes fluid, the fibers tend to float to the top or sink to the bottom depending on relative densities. Also, the injection or pouring procedure can affect fiber orientation. This will add to our micromechanical model an extra unknown which is hard to determine.

For simply shaped parts as required for most civil engineering applications, the mixing and pressing technique was adopted. In this case, if the fiber is well mixed with the matrix before putting everything into

the die, the fiber distribution in the final product is essentially random in 2-D (Note that they are not random in 3-D since fibers tend to lie perpendicular to the pressing direction). It is decided that a cylindrical die is to be used. The formed part is then cut to give prismatic specimens. The whole processing procedure is illustrated in Fig. 2.

To facilitate processing, two pieces of equipment, the OMNI-mixer and the MTP-14 press have been acquired and set up. The advantageous features of these equipment are summarized in Tables 4 and 5.

(4) To prepare specimens of the model composite, the first step is to process the phosphate glass which will be used as model matrix material. Glass processing essentially follows the procedures described in Ref. 4. After it is made, the glass is broken into fine powder so that fibers can be mixed in to make a composite.

As described before, the actual specimens for property measurements will be prepared by mixing of matrix and fiber followed by hot pressing. However, at this stage, for preliminary qualitative investigations, specimens are prepared simply by mixing a few bundles of graphite fiber into the glass matrix and then remelt the glass on a hot stainless steel plate. On cooling, a small piece of composite material is obtained. It is then loaded to failure and the fracture surface is observed under the Scanning Electron Microscope (SEM). This simple preliminary investigation does provide us with some useful information on microstructure features and failure mechanism of this kind of composite.

Figs. 3 and 4 are micrographs (taken with the Cambridge Instrument SEM purchased on the MIT PACT equipment budget) showing typical features that can be observed on the fracture surface around a fiber bundle. The first important observation is the clean surface on

the sides of protruding fibers (this is particularly clear in Fig.3, which is at a higher magnification). The absence of chemical products suggests that there is no chemical bonding between the matrix and the fiber and thus the major contribution to interfacial strength is due to friction and interlocking. This implies that the interfacial strength is sensitive to radial pressure on the fiber caused by mismatch of thermal expansion coefficient of matrix and fiber. An investigation of the dependence of interfacial strength on radial pressure will thus be important in the optimization of thermal mismatch (through varying expansion coefficient of the matrix by cooling it at different rates) and this will be one of the major investigations in the second year of this project.

In a micromechanical model being developed, the composite is modelled as one consisting of individual fibers completely surrounded by matrix. However, from Fig.4, it is quite obvious that if fibers stay as a whole bundle, matrix material may not be able to penetrate into the bundle. As a result, the inner fibers just slide against each other under low friction, offering little resistance to crack growth. Hence, impenetrable bundles are undesirable and should be either separated into single fibers or processed in such a way as to allow matrix penetration. By controlling the mixing operation, we may be able to break the bundles up (ideally into randomly distributed single fibers). Through varying the processing temperature and pressure, we can control the extent of matrix penetration into remaining bundles. Thus, to be able to compare experimental results with our model, we should make sure that the processing conditions will give us a composite with well embedded fibers in the matrix.

In Fig.3, protruding fibers on the fracture surface shows that fibers that are completely surrounded by matrix will not break right on the fracture surface.

This is evident of the fact that the crack does not cut through the fibers directly. Instead, there is some slipping along the fiber/matrix interface. For the case in Fig.3, slipping has not yet advanced to the end of the fiber to cause the full fiber length to be pulled out. The fiber probably ruptures at the weakest point within the most highly stressed region (which is the region near the fracture surface) and then undergo a small amount of pull-out. Whether a fiber will break or pull out is governed by the embedded length of the fiber as well as the interfacial strength. If the embedded length is small enough or if the interfacial strength is low enough, the whole fiber could be pulled out. In general, it is desirable to design the microstructure of the composite to ensure fiber pull-out rather than rupture. It has been recognized [6] that the pull-out mechanism absorbs more energy and results in a higher composite toughness.

Pictures of fracture surfaces, while being useful in understanding failure mechanisms, fail to provide information on the actual failure sequence in the composite. One of our planned further investigation is to load specimens directly under the SEM. This will provide even more direct information on the propagation of cracks in the material and especially on crack propagation across fibers.

In conclusion, SEM observations provide information on fracture mechanisms which act as a basis for micro-mechanical modelling and a check to the validity of modelling assumptions. With these observations, we can also monitor the effect of processing on microstructures. This kind of investigation will be important at all stages of the study.

Participating Scientific Personnel

1. Victor C. Li, Associate Professor of Civil Engineering, MIT. Principle Investigator on this project.

2. Christopher K.Y. Leung, Ph.D candidate, Dept. of Civil Engineering, MIT. Graduate research assistant on this project.

3. John Haggerty, Senior Research Scientist, Dept. of Material Science and Engineering, MIT. Consultant on this project.

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TABLE 1: - UNREINFORCED CERAMICS

MATERIAL	E (GPa)	σ_c (MPa)	σ_f (MPa)	K_{1C} (MPa $\sqrt{m}$)	G_f (KJ/m^2)
HIGH-PERFORMANCE CERAMICS					
ALUMINA (DENSE)	380	3000	300-400	3-5	0.023-0.066
SILICON CARBIDE	410	2000	200-500	3-4	0.02-0.039
SILICON NITRIDE	310	1200	300-850	4	0.05*
GLASS/GLASS CERAMICS					
SODA GLASS	74	1000	50	0.7	0.003
BOROSILICATE GLASS	65	1200	90	0.8	0.003
LITHIUM ALUMINOSILICATE	83		200	2	0.05*
CEMENTITIOUS MATERIALS					
CEMENT	20-30	50	7	0.2	0.1
CONCRETE	30-40	50	7	0.2	0.1
HIGH STRENGTH CEMENT (WITH 5-15% SILICA FUME)	34	100	12	<0.2	<0.1
DSP CEMENT	80	250		0.29*	0.001
WARM-PRESSED CEMENT	40	650	68 (σ_t)		
MDF CEMENT	50	200	150	3.29	0.2-0.4

NOTE:- σ_c: COMPRESSIVE STRENGTH
σ_f: FLEXURAL STRENGTH
σ_t: TENSILE STRENGTH

MDF : MACRO-DEFECT FREE
DSP : DENSIFIED SYSTEM WITH ULTRA-FINE PARTICLES

* K_{1C} OR G_F VALUES WITH (*) ARE ESTIMATED FROM THE OTHER VALUE THROUGH $EG = K^2$

TABLE 2 TOUGHENING MECHANISMS IN CERAMICS

Toughening Mechanism	Material	Maximum Toughness (MPa $\sqrt{m}$)	Comments
Fiber Reinforced (CONTINUOUS)	LAS/SiC	> 20	Steady-State
	Glass/C	> 20	-Cracking
	SiC/SiC	> 20	
Whisker Reinforced	Al_2O_3/SiC(0.2)	10	Amorphous
	Si_3N_4/SiC(0.2)	14	Interphase
Ductile	Al_2O_3/Al(0.2)	> 12	Steady-State
Dispersion	B_4C/Al(0.2)	> 14	-Cracking
	WC/Co(0.2)	20	
Transformation	PSZ	18	Non-linear
Toughened	TZP	16	
	ZTA	10	
Microcrack	ZTA	7	
Toughened	Si_3N_4/SiC	7	

TABLE 3 : REINFORCED CERAMICS

MATERIAL	FIBER	V_f (%)	WAY OF REINFOR-CEMENT	E (MPa)	σ_f (MPa)	K_{1C} (MPa $\sqrt{m}$)	G_F (KJ/m^2)	PROCESSING TEMP.
HIGH-PERFORMANCE CERAMICS								
ALUMINA	SiC	20	Random	424	800	8.7	0.18	
SILICON NITRIDE	GRAPHITE	30	Continuous	188	454	15.6	4.77	
GLASS/GLASS-CERAMICS								
PYREX (BOROSILICATE)	CARBON	40	Continuous	195	680	25.7*	3.4	1000°C
SODA GLASS	CARBON	45	Continuous	216	570	30.5*	4.3	700°C
LAS	SiC	45	Continuous	138	830	17.0	2.1	
PYREX	CARBON (3mm)	20	Random	102	48	6.0*	0.35	(700°C to
PYREX	CARBON (3mm)	30	Random	120	40	6.5	0.35	1000°C)
BORO-SILICATE	SiC	35	Continuous	188	830	18.9	1.90	1150°C
CEMENTITIOUS MATERIALS								
MORTAR	STEEL FIBER	1	Random	30	6	6*	1.20	
MDF	NYLON A	5.4	Continuous	46.9	120	2.99	15.9	
MDF	NYLON C	5.2	Continuous	48.3	54	2.78	44.4	
MDF	KEVLAR 29B	9.0	Continuous	37.4	94	5.25	78.6	

* K_{1C} OR G_F VALUES WITH (*) ARE ESTIMATED FROM THE OTHER VALUE THROUGH $EG = K^2$

TABLE 4 FEATURES OF OMNI-MIXER IN RELATION TO PROCESSING PROCEDURE

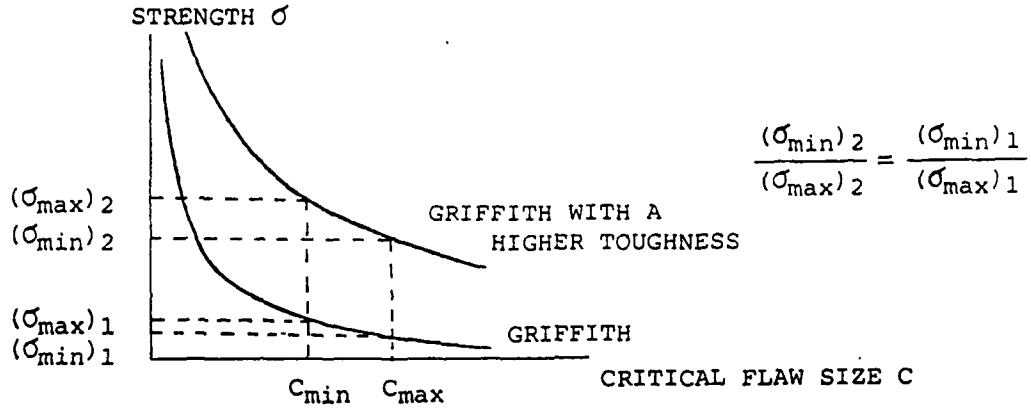
FEATURE	UTILIZATION IN THIS PROJECT
(1) Mixing without blades	(a) Reduce fiber "balling up" at blade (b) Mixer easier to clean
(2) Vacuum Control	(a) Help remove entrapped air in dry mixing (b) Assist evaporation of liquid media in wet mixing

TABLE 5 FEATURES OF MTP-14 PRESS IN RELATION TO PROCESSING PROCEDURE

FEATURE	UTILIZATION IN THIS PROJECT
(i) Feedback Control of Force , Temp. and their Rates	Accurate Control of Processing Variables
(ii) Extra Thermo-couple	Can use temperature of Manufactured part for feedback control
(iii) Water Cooling Option	Wider range of cooling rate
(iv) Bump Cycle	Removal of entrapped air
(v) Digigraph	Graphical output of Force & Temperature - easy process monitoring

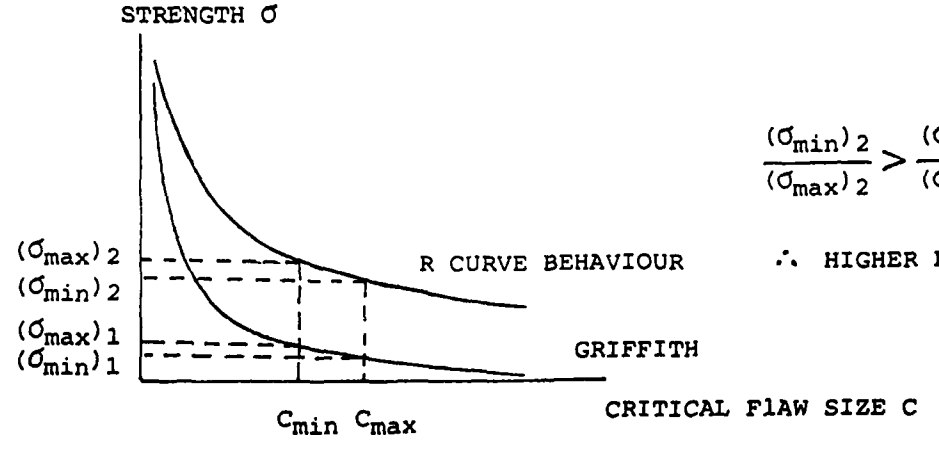
WEIBULL MODULUS $\propto \ln(\sigma_{min}/\sigma_{max})$

(A) HIGHER TOUGHNESS BUT NO R-CURVE BEHAVIOUR



$$\frac{(\sigma_{min})_2}{(\sigma_{max})_2} = \frac{(\sigma_{min})_1}{(\sigma_{max})_1}$$

(B) HIGHER TOUGHNESS AND WITH R-CURVE BEHAVIOUR



$$\frac{(\sigma_{min})_2}{(\sigma_{max})_2} > \frac{(\sigma_{min})_1}{(\sigma_{max})_1}$$

$\therefore$ HIGHER RELIABILITY

FIG. 1 Illustration of the improvement of Reliability through R-Curve Behaviour

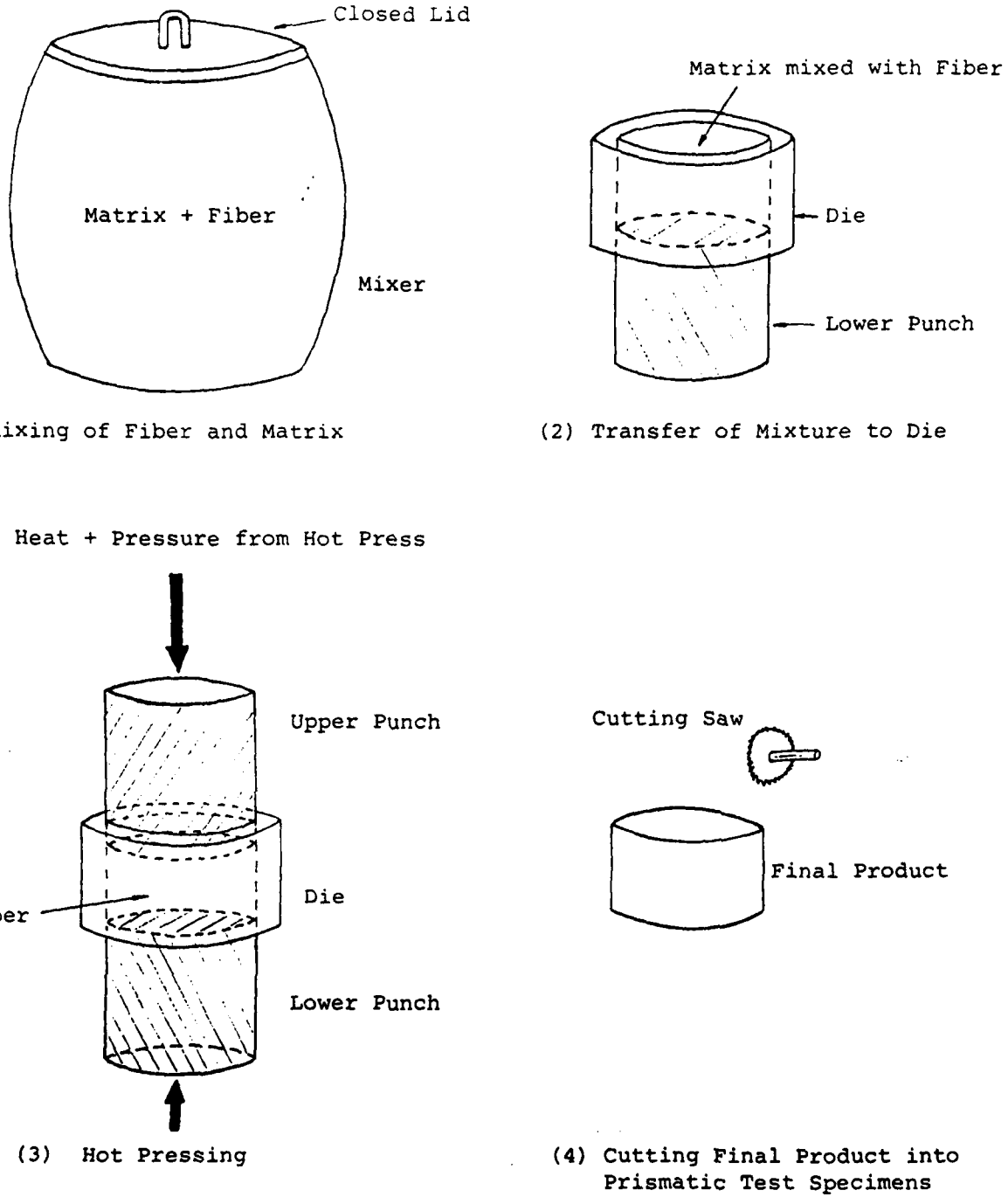


FIG. 2 A Schematic Showing Steps in the Processing Procedure

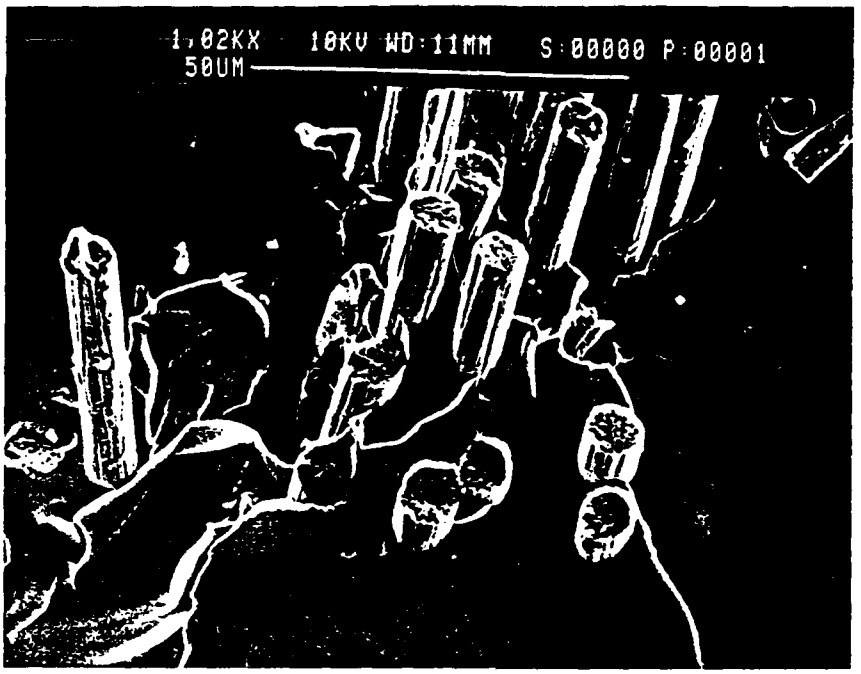


Fig. 3 Micrograph showing Fiber Breakage and Pull-out on a Fracture Surface

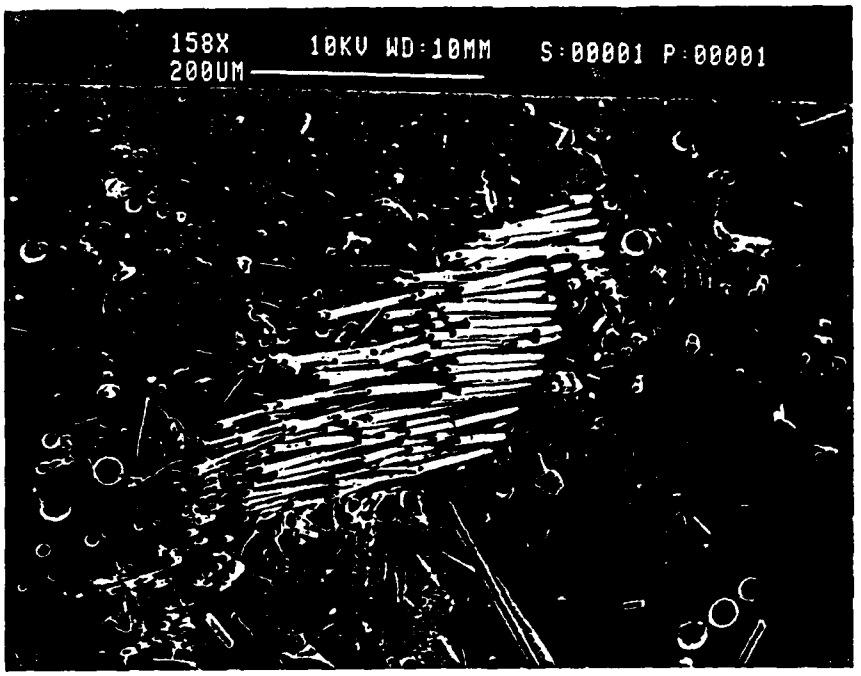


Fig. 4 Micrograph showing a Bundle of Fiber on a Fracture Surface