REMOVAL OF PROCESSING AIDS FROM CERAMIC/POLYMER COMPOSITES

GREGORY C. STANGLE, DONG-JOO RHEE, AND ILHAN A. AKSAY

Department of Materials Science and Engineering, and
Advanced Materials Technology Program, Washington Technology Center
University of Washington, Seattle, WA 98195

ABSTRACT

Fundamental issues in the removal of processing aids from ceramic compacts prior to sintering have been investigated, both experimentally and theoretically. A general theoretical model has been developed that couples simultaneous momentum, heat, and mass transfer phenomena in disordered porous materials with the mechanical response predicted by an appropriate poroelasticity theory for partially saturated porous granular materials. The kinetics of pyrolytic degradation of organic processing aids were studied using a thermogravimetric analysis-mass spectrometry (TGA-MS) system.

INTRODUCTION

Net shape or near-net shape forming of flaw-free and homogeneous bodies must be possible for commercial applications to be realized. For this purpose, fabrication of ceramics by injection molding techniques is a favored approach since this technique offers the advantages of production of complex shapes and high rates of automated production [1, 2]. This approach consists of dispersing the powder and processing aids in a molten polymer, injection molding, debindering, and densifying.

Following consolidation and prior to sintering, it is necessary to remove various processing aids from the consolidated green body. This might include the organic vehicle used in dispersion, polymeric dispersant, and various binders, plasticizers, and lubricants. Approaches to the removal of processing aids include thermal degradation [3, 4], chemical degradation [5], evaporation or sublimination at ambient or reduced pressures [6], solvent extraction [7], and capillary action [8]. Thermal (or thermal plus chemical) methods are often preferred [3]. The underlying goal of any scheme to remove processing aids is to reproducibly fabricate a debindered ceramic compact without any defect creation.

This paper summarizes the results of our theoretical studies of the removal process, which include the movement of energy and material into and out of the green body, as well as the material response to internal stresses generated during the removal process. Experimental polymer degradation studies complete the picture by supplying necessary reaction rate data.

Mat. Res. Soc. Symp. Proc. Vol. 155. ©1989 Materials Research Society

MOMENTUM, HEAT, AND MASS TRANSFER

Theoretical studies of the debindering process were undertaken in order to develop predictive capabilities in the design of an improved debindering process. Further, the design of experimental debindering studies can be improved since a theoretical model, once developed and verified, can test a much larger array of variables in less time than an analogous experimental approach. The theoretical model developed describes the simultaneous momentum, heat, and mass transfer with chemical reaction in a disordered porous medium [8]. Table I summarizes the various processes responsible for the redistribution of material and energy into, out of, and within the body during the removal process. Where appropriate, the driving force for the process and the transport coefficient are listed.

Table I. Processes Responsible for Redistribution of Material and Energy.

		IMPORTANT QUANTITIES	
PHASE	PROCESS	MATERIAL	ENERGY
Gas	Diffusion	Concentration gradient Effective diffusivity	-----
	Convection	Pressure gradient Effective permeability	Temperature, pressure gradients Effective permeability
	Evaporation	Vapor pressure	Heat of vaporization
	Chemical reaction(s)	Reaction rate(s) Concentration of reactant(s)	Heat(s) of reaction
Liquid	Convection	Pressure gradient Effective permeability	Temperature, pressure gradients Effective permeability
	Evaporation	Vapor pressure	Heat of vaporization
	Chemical reaction(s)	Reaction rate(s) Concentration of reactant(s)	Heat(s) of reaction
Solid	Conduction	-----	Temperature gradient Effective conductivity

Heat transfer between the hot and cold regions of a composite depends on the amount of each phase (gas, liquid, and solid), the thermal conductivity of each phase, and the *specific spatial arrangement* of the phases. Similarly, fluid flow through such a "composite" is restricted to *available pathways*. Gas may flow (or diffuse) only through a connected network of liquid-free pores that "communicate" with the surface of the sample. Volumes occupied by solid and liquid are obviously eliminated from the allowable pathway, but so are bubble-like regions of gas that are completely enclosed by liquid and solid and thus unable to communicate with the surface of the sample. Allowable pathways for liquid flow are restricted to continuous, con-

nected networks of liquid-phase material, such that islands of liquid are incapable of capillary flow. A suitable approach is to estimate effective transport coefficients based on percolation concepts as applied to disordered media [10-13].

The more generalized form of transport equations [13,14] has been reduced to the appropriate form by Stangle and Aksay [9] for the present problem. Energy, momentum, and mass balance equations form a set of highly non-linear partial differential equations, to which the usual initial and boundary conditions apply [9]. External heat and mass transfer coefficients take into account the change in conditions external to the ceramic green body during the removal process. Profiles of temperature, gas- and liquid-phase holdup, gas-phase composition, and fluid velocities can then be predicted. Figure 1 shows a comparison of the simulated and experimental removal processes (i.e., the removal of paraffin wax from an α-Al_2O_3/paraffin compact) wherein parameters for simulation were determined *a priori*. Good agreement is seen between the predicted and experimental results and serves to validate the accuracy of the model and provides confidence that the model can be used to estimate internal stresses that are difficult to measure experimentally.

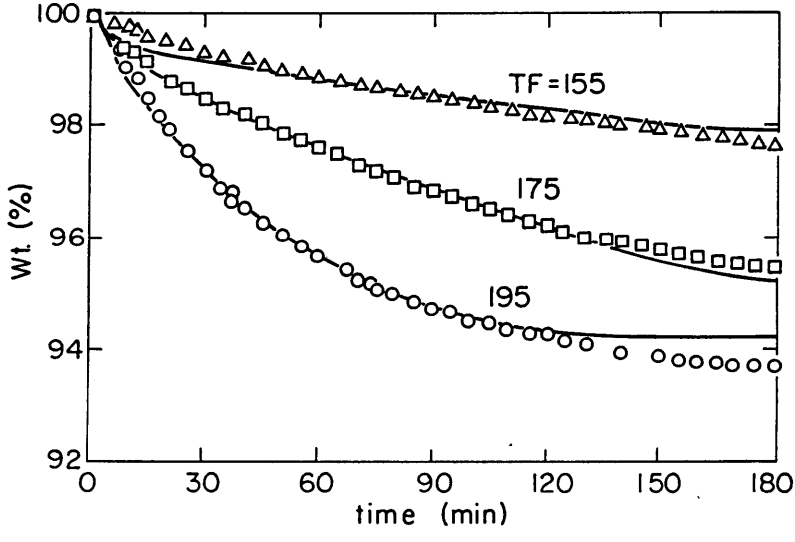

Figure 1. Comparison of model predictions with experimental thermogravimetric data. From Ref. 9.

POLYMER DEGRADATION KINETICS

Degradation of polymers by thermal and oxidative mechanisms is well documented in the literature [5,15-17] . Thermal degradation may take place by one or both of the following mechanisms: (a) depolymerization, whereby the backbone of the polymer is broken, effectively "unzipping" the polymer, or (b) removal of polymer side groups by substitution or rearrangement

processes. The former mechanism results in a decrease in molecular weight of the polymer and may leave a wide or narrow molecular weight distribution of fragments, depending upon whether the depolymerization takes place at random sites or at regularly spaced sites possessing high reactivity. The latter mechanism has little effect upon the molecular weight of the polymer. Many oxidative degradation mechanisms exhibit results similar to those of thermal degradation by depolymerization, usually differing only in the "point to attack" on the polymer chain and the oxygen-content of the resulting species. Oxidative degradation is usually more highly exothermic than thermal degradation. Two factors that are most important to the debindering of consolidated ceramic compacts are the rate at which the polymer is broken into fragments and the size of the resulting fragments. The first factor may cause the process to fall into the kinetic-limited regime, while the second influences volatility and diffusivity and hence may cause the process to fall into the diffusion-limited regime.

In our studies, we used the thermogravimetric analysis-mass spectroscopy (TGA-MS) system [18,19]. TGA-MS provides simultaneous monitoring of sample weight and complete gas-phase composition (functional group analysis and molecular weight distribution) in a real-time sampling/analysis mode. Figure 2 shows the TGA data for identical samples of paraffin wax heated in different atmospheres (air and N_2), while Figure 3 shows the mass spectra of gaseous material evolved from the samples at 80% weight loss, as detected by a triple-quadrapole mass spectrometer using an atmospheric pressure chemical ionization detector. Pyrolysis atmosphere is seen to have a profound effect on the mean fragment size and on the width of the fragment distribution. It is important to note that the generation of many low molecular weight degradation products may result in increased gas pressure and thus burnout-related cracking. Conversely, the formation of high molecular weight species may make the complete removal of binder material difficult.

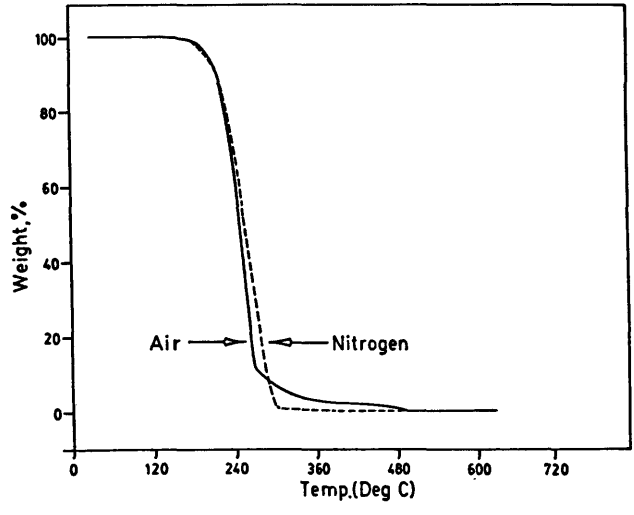

Figure 2. TGA weight loss data for paraffin wax in different furnace atmospheres.

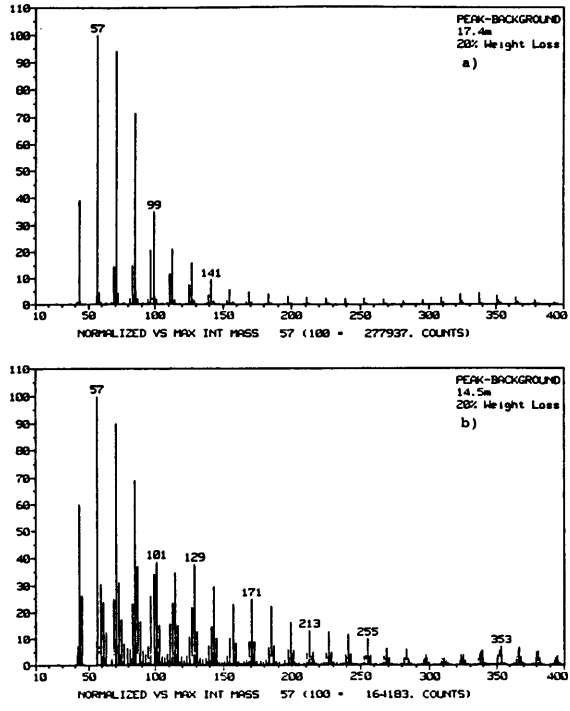

Figure 3. Mass spectra at 80% weight loss in (a) N_2 and (b) air.

MECHANICAL RESPONSE

The mechanical response of the compact throughout most of the removal process (constitutive relationship and failure criterion) is quantified by applying appropriate poroelasticity theory to a partially saturated porous granular material [9]. The geophysics and geomechanics literature is literally littered with treatment of important geological materials that are highly anisotropic and very heterogeneous, and may contain a number of solid-phase and fluid-phase materials [20-23]. A usual approach to the problem is to separate the contribution of each phase's stress to the total stress at a point. Such total stresses are related to the degree of deformation by constitutive relationships that include solid particle, drained skeleton, and liquid- and gas-phase compressibilities. Redistribution of gas, liquid, and solid may be retarded by drag forces between phases, thereby modifying mechanical response of the material. In addition, such variations in temperature as occur during the removal of processing aids require an inclusion of temperature-dependence in the relationship. Finally, a failure (or material strength) criterion is available from either micromechanical or empirical points of view [20-22]; the former can be more cumbersome than the latter but eliminates many of the simplying assumptions required by the latter.

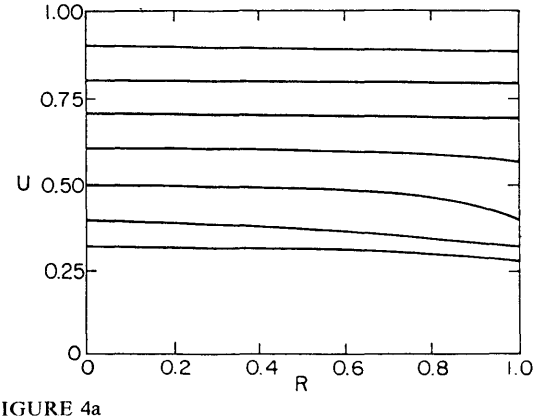

FIGURE 4a

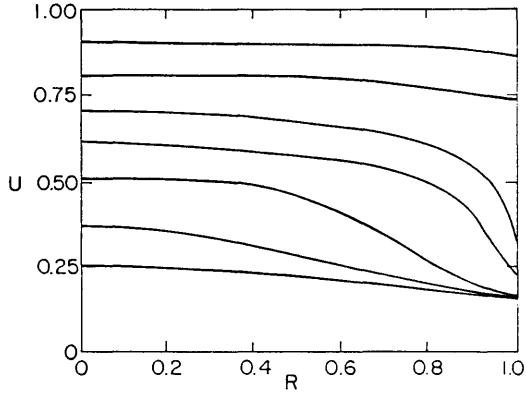

FIGURE 4b

Figure 4. Liquid saturation profiles at (a) $T_f = 155°C$ and (b) 230°C. By definition: $R = r/r_p$ = dimensionless radial coordinate; U = dimensionless saturation parameter (U = 1 when pores are full, and U = 0 when empty); and $\tau = \alpha_s t / r_p^2$ = dimensionless time. The quantities r_p and α_s are sample radius and thermal diffusivity, respectively.

Figures 4 and 5 illustrate the relationship between the temperature (T_f) at which the removal process takes place, the liquid saturation (U) profiles, and internal stress distribution [9] . For $T_f = 155°C$ (Figure 4a), the liquid saturation decreases steadily as a function of time and evenly as a function of position. For $T_f = 230°C$, on the other hand, Figure 4b shows predictions of nonuniform saturation and thus relatively steep liquid gradients, particularly between $U(0) = 0.70$ and $U(0) = 0.40$, where U(0) is the value of U at the center of the sample. Calculation of the stress profiles for both cases was undertaken and showed the largest tensile stresses occur at the surface of the sample. This is significant, since it is known that (i) partially saturated granular materials are much weaker in tension than in compression and (ii) failure

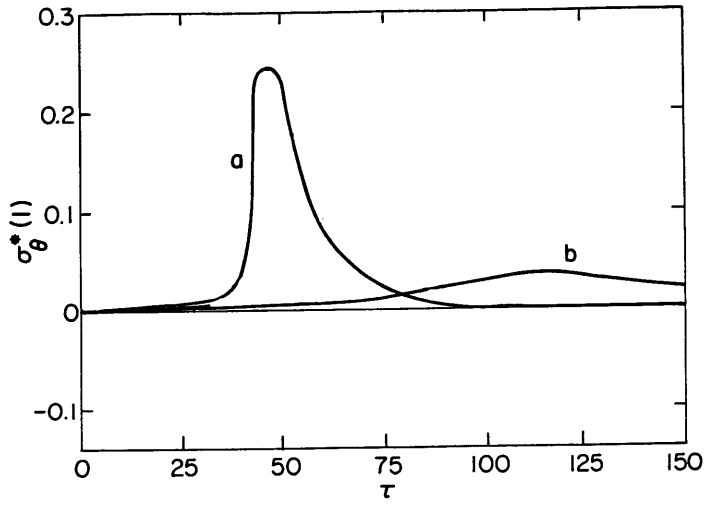

Figure 5. Internal stress profiles corresponding to saturation profiles in Figure 5. (a) $T_f = 230°C$; (b) $T_f = 155°C$.

(that is, cracking and other permanent microstructural deformation) can occur if any component of stresses locally exceeds the tensile strength of the material [24]. Curves (a) and (b) in Figure 5 illustrate the significant differences in tensile stress buildup and decay for $T_f = 230°C$ and 155°C, respectively. The magnitude of the surface tensile stress thus results from the steepness of the liquid saturation profile, which in turn derives from the relative rates of (i) convective mass transfer from the surface and (ii) that of capillary liquid flow that replenished the "drier" surface region. In addition, another possible source of sample failures is gas pressure build-up by organic vaporization. However, the results presented in Figures 4 and 5 indicate that at the indicated temperatures, stresses due to capillary forces are more significant.

CONCLUSIONS

The kinetics of pyrolytic degradation of the nonceramic processing aids was investigated with the TGA-MS technique and showed marked differences in the time-temperature-composition behavior of both solid and gas phases during decomposition. Poroelasticity theory provided a basis for quantifying the stress-strain-failure relationship. Predictions were verified by comparison with experimental removal processes. The verified theoretical model can thus be employed to improve (and possibly optimize) processing conditions in the removal of processing aids from a consolidated ceramic green body.

ACKNOWLEDGMENTS

This work was supported by the IBM Corporation as part of a block grant on the microdesigning of ceramics and ceramic/polymer composites, and the Air Force Office of

Scientific Research (AFOSR) and the Defense Advanced Research Projects Agency (DARPA) under Grant No. AFOSR-87-0114. We gratefully acknowledge R. Bruce Prime at IBM, San Jose, for conducting TGA-MS experiments.

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