THEORY OF MICROWAVE EFFECTS ON ATOMIC DIFFUSION IN SINTERING:
BASIC CONSIDERATIONS OF THE PHENOMENON OF THERMAL RUNAWAY

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ABSTRACT

We present the results of our recent studies of the possible origin of the
reported increase in sintering efficiency brought about by the application of
microwaves. We study the phenomenon of thermal runaway in ceramic materials
undergoing microwave heating and present a theory on the basis of a simple
temperature-time equation. The nonlinear evolution inherent in the equation
arises naturally from physical considerations. The theory is applied to
experimental observations reported on several different materials including
silica, alumina, strontium titanate, zinc oxide and iron oxide, and shown to
be in good agreement with the data.

INTRODUCTION

Recently, several investigators\textsuperscript{1-3} have reported substantial effects of
microwave heating on the sintering of several materials. The effects have
included the lowering of the sintering temperature as well as of the sintering
time. Motivated by these findings, we have begun a thorough investigation of
the interaction of microwaves with ceramic materials in general. Results we
have obtained regarding one of the aspects of this interaction, viz. the
phenomenon of \textquotedblright thermal runaway\textquotedblright,\textsuperscript{1,4,5} are described below. The phenomenon is
typified by figure 1. In a number of materials, it is found during microwave
heating that the increase of temperature is found to be gentle at first but
explosive later when a threshold is reached. The sudden rise of temperature
is referred to as thermal runaway. We have carried out extensive studies of
the runaway phenomenon both at the microscopic level and the macroscopic
level, including details of the process of absorption of microwaves, the
possibility of what is termed \textquotedblright chaos\textquotedblright in the modern physics literature, and
generally nonequilibrium interaction of electromagnetic fields with matter. A
practical as well as natural description of thermal runaway has emerged in
terms of a simple nonlinear temperature-time equation. We have applied it to a
variety of materials\textsuperscript{1,4,5} as shown in figures 2 and 3 below.

THE TEMPERATURE-TIME EQUATION

We have encountered several different types of the shape of the time-
temperature curve in our study of the data on various materials. They can all
be described together by stating that, generally, there is an initial stage in
which the temperature rises relatively slowly with time, followed by a second
stage in which the rate of rise is enhanced significantly, resulting in a
steep increase of temperature, and a final stage in which the temperature
saturates to the environmental temperature. There are materials for which
only the first stage is observed, and others for which only the first and the
second are observed.
Our basic postulate is that the system consists of two species which we call the A species and the M species. The former, typified by impurities and inclusions whose relaxation times match the period of the microwaves, absorb microwaves through a Debye mechanism. These entities are absent in systems which are found to be transparent to microwaves. In such cases, the A-species entities are provided by aids which, when introduced into ceramics which are naturally transparent to microwaves, cause the absorption of radiation. This A species is responsible for the initial slow rise of temperature with respect to time. The M species consists of interstitial atoms, vacancies or bivacancies. These lie, at low temperatures, in potential wells which bind them. The energetic height of these wells is substantial, viz. of the order of eV's, and they do not absorb or do so to a negligible extent because neither their resonance frequencies nor their relaxation rates match the microwave frequencies. However, if they are let out of the binding wells, they act like relatively free particles and, as can be shown easily from microscopic considerations, absorb substantially from the microwave radiation. The fraction $f$ of the M-particles which are thus able to absorb can be modelled simply through two-state considerations:

$$f = \exp\left(-\Delta/T\right) \left[\exp\left(-\Delta/T\right) + 1\right]^{-1}$$

where $\Delta$ is a measure of the barrier which the particles must surmount to become free of their binding wells. If $n_A$ is the number of the absorbers of the A species, and $P_C$ the rate at which each absorbs energy from the microwaves, ($P$ being the microwave power) and if $n_M$ and $P_C$ are the corresponding quantities for the M-species, we can write

$$\frac{dT}{dt} = P\left[k_A + k_M f(T)\right] - \sigma_1 T^4$$

where $k_A = n_A C_A$ and $k_M = n_M C_M$, and where, following standard procedure, we have described the final saturation stage in equation 2 through the radiation-like term $\sigma_1 T^4$. Equation 2 is our starting point for the description of thermal runaway. Its important element is the term describing the contribution of the M-species. It introduces nonlinearity into the temperature evolution through the obvious feedback and makes (2) capable of describing diverse materials.

**FITS TO EXPERIMENTS ON DIVERSE MATERIALS**

If the barrier height $\Delta$ is of appropriate magnitude relative to the initial temperature, the initial time evolution of the temperature, as given by equation 2, will be a slow rise at the rate $n_A C_A$ (per unit power) decided by the A species of absorbers, e.g. the sintering aids or imperfections or natural absorbing agents. As the temperature increases, the fraction of the M-absorbers which are capable of absorbing significantly will increase and there will be a substantial increase in the time rate of temperature. Depending on the value of the saturation terms, the temperature will then reach a plateau through saturation. This plateau may not be visible for systems in which the saturation terms are relatively weak.

On the basis of equation 2, we have addressed observations for a variety of materials in figures 1 and 2. The resulting table of values of the parameters $k_A$, $k_M$, $\sigma_1$, and $\Delta$ is also presented. The values of the k's are reasonable and it is possible to fit several materials with a 3-parameter theory, omitting the A-species parameter $k_A$. The value of $\sigma_1$ is approximately the same for all materials considered. A simple relation involving the sample surface, volume, and specific heat connects $\sigma_1$ to $\sigma$, the Stephan-Boltzmann constant. The values we find lead, within experimental fluctuations, to the
known value of $\sigma$ = 5.68 x $10^{-12}$ W/cm$^2$K$^4$. This means that the traditional procedure of considering the losses to be primarily through radiation is quite appropriate. The $\Delta$'s extracted through our theory are also found to be reasonable in that they are compatible with usually accepted values of defect formation. They are not identical but do not differ by order-of-magnitude factors. The one case where $\Delta$ is found to be near zero, viz. that of iron oxide, corresponds, as it clearly should, to observations in which the temperature immediately rises (without threshold) to high values: no barrier exists to thermal runaway and the A and M species can be taken to be identical to each other.

MICROSCOPIC BASIS OF THE TEMPERATURE-TIME EQUATION

For want of space we touch upon the microscopic basis of our temperature-time equation only very briefly. The absorption of electromagnetic radiation by free charges is drastically different from that by trapped charges. When an electric field representative of the incident electromagnetic radiation is applied to the charge in question, the charge is accelerated. The movement is opposed by friction forces which increase as the velocity increases until the friction forces balance the electric force. A d.c. electric field thus brings a free charge in equilibrium to a state of non-zero velocity. The product of this non-zero velocity and the electric force is the rate at which power is absorbed by the charge from the electromagnetic field. In the case of a charge trapped in a potential well on the other hand, the velocity increase is opposed by another agent in addition to the friction force, viz. the binding force which constrains the particle to the well. In the absence of friction, an oscillation of the charge occurs around the potential minimum. This minimum is displaced from the original minimum. In the presence of friction, the oscillation decreases in amplitude until the particle comes to rest at the new potential minimum. The equilibrium state under the combined action of the electromagnetic force, the binding force and the friction force is thus that of rest in contrast to that of a constant non-zero velocity which is the case for the free absorber. Heating via electromagnetic radiation of low frequency is thus highly inefficient for a bound particle in relation to that for a free particle. If the field is a.c., it is possible to cause efficient heating even in the case of a bound particle by moving the particle repeatedly from the rest state to which it tends, i.e. by matching frequencies through resonance. Microwave frequencies are, however, very low in comparison to resonance frequencies in ceramic materials. The d.c. case is thus realized in essence for the microwave field.

At the heart of our theoretical approach to thermal runaway is the suggestion that the significant increase of absorption that is observed has the transformation of bound into free absorbers as its source. Absorbers in potential wells would be bound at low temperatures but free if the temperatures are high enough to cause them to be released from the potential well through thermal fluctuations. The characteristic temperature is the reciprocal of the Boltzmann constant times the energy barrier that the absorbers must surmount to become free. Such energy barriers are quite physical in ceramic materials and are of the order of the barriers for the formation or migration of entities such as vacancies or interstitials or, perhaps most appropriately, bivacancies.

The specific expression (1) for the fraction $f$ used in (2) is the result of the simplest assumption possible: that the M-species have access to two states only, the free state and the bound state and that their relative proportion is determined by thermal balance. This balance is affected by microwaves since their absorption increases the temperature. Absorption by the M-species can
thus be negligible at first but substantial as time goes on when the temperature becomes high enough to free the M-species.

We state without discussion or derivation that the parameters $k_A$, $k_W$, and $\Delta$ in our theory can be obtained from basic considerations from an evolution equation of the form

$$\frac{\partial^2 X}{\partial t^2} + \alpha \frac{\partial X}{\partial t} + \frac{\partial U}{\partial X} = c_1 E \cos \omega t + c_2 E^2 g(\omega, \Gamma) \left( \frac{\partial X}{\partial t} \right)^{-1}$$  \hspace{1cm} (3)

where $X$ is the absorbing coordinate of the M-species, $\alpha$ is a damping rate, the $c_1$'s are constants, $E$ is the electric field due to the microwaves, $g(\omega, \Gamma)$ is associated with the tan $\delta$ of the A-species calculated, e.g. through Debye theory, and $U(X)$ is the binding potential in which the M-species moves. The potential can be obtained experimentally or through first-principles calculations along the lines of those carried out by the present authors recently. All the parameters are thus calculable in principle.

CONCLUSIONS

We find that the simple theory of thermal runaway we have presented and applied to observations reported on a variety of materials provides a satisfactory description of the runaway phenomena. Among the advantages of our approach are a single starting point capable of describing, quite reasonably, a large variety of different materials undergoing thermal runaway; the fact that equation 2 is based on simple physical arguments and its parameters are calculable from basic considerations; and the successful treatment of quite different time-temperature curve shapes as shown in the figures. While relatively crude in the present form, the approach has considerable potential and we are in the process of developing it into a usable scheme of predictive power. We have already extended it to incorporate lattice structure and composition details into the $f(T)$ given in equation 1 and have developed a parallel theory of tan $\delta$ which has succeeded in fitting satisfactorily data on alumina at 3.5 GHz and 35 GHz for a variety of temperatures. Among the further topics currently under investigation are: (i) the full calculation of the parameters of the theory for a wide range of materials; (ii) the study of anomalous power dependence and saturation effects which are observed in several materials; (iii) the understanding of the feature common to all materials studied that the deduced value of $\Delta$ is always smaller than the barrier height as measured from defect formation and migration experiments. The fact that the deduced values of $\sigma_i$ and $\Delta$ are reasonable for the large variety of materials studied, and our parallel theory of tan $\delta$ based on the same physical considerations provides a reasonable description of experiment, lend support to our theory.

REFERENCES

Parameters deduced from the application of our theory to thermal runaway observations in a number of diverse materials

<table>
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<tr>
<th>Material</th>
<th>( k_A ) (K/min/W)</th>
<th>( k_M ) (K/min/W)</th>
<th>( \Delta ) (K)</th>
<th>( \sigma_1 ) (s*K³)^{-1}</th>
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<tr>
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<td>2600</td>
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<th>( P \cdot k_M ) (K/s)</th>
<th>( \Delta ) (K)</th>
<th>( \sigma_1 ) (s*K³)^{-1}</th>
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Figure 1 Thermal runaway observations and the application of our theory as in equation 2. The experiments carried out are for (a) strontium titanate with initial porosity 53% sintered as reported by Varadan et al., (b) silica heated at 500 W as reported by McGill et al., (c) zinc oxide and (d) iron oxide heated as reported by Sheppard, (e) silica heated at different power levels as reported by McGill et al., and (f) alumina of 50% initial porosity sintered as reported by Varadan et al.