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Theory of microwave interactions in ceramic materials: the phenomenon of thermal runaway

V. M. KENKRE,* L. SKALA,* M. W. WEISER ‡
*Center for Microengineered Ceramics, *Department of Physics and *Mechanical Engineering Department, University of New Mexico, Albuquerque, NM 87131, USA*

J. D. KATZ
Los Alamos National Laboratory, Los Alamos, NM 87545, USA

A theory of the phenomenon of thermal runaway in ceramic materials undergoing microwave heating is presented on the basis of a simple temperature–time equation. The non-linear evolution inherent in the equation is shown to arise naturally from physical arguments and it is shown how the parameters of the theory may be calculated from the microscopic absorption processes and information about the material under consideration. The theory is applied to experimental observations reported on several different materials and shown to be in good agreement with the data.

1. Introduction

The purpose of this paper is the understanding of the interaction of microwaves with ceramic materials in general, and the phenomenon of thermal runaway in particular. One of the reasons for the interest in the interaction of microwaves with ceramics is the observation, reported by several investigators in the recent literature [1–3], that microwave heating can lower the sintering temperature in several materials by several hundreds of degrees and shorten the sintering time by several hours. It appears that microwaves not only increase the heating efficiency by concentrating the heating process within the material rather than in the furnace in which the material is placed, but also have basic consequences such as more efficient atomic diffusion within the material. The study of microwave heating from the point of view of basic effects is clearly of crucial importance at the moment, both from the practical and the fundamental point of view.

Foremost among the interesting phenomena associated with microwave heating of ceramics is "thermal runaway" [1, 4, 5]. This phenomenon is typified by Fig. 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. It is clear that a theory of the interaction of microwaves with ceramics must address this phenomenon in as thorough a way as possible. To attempt this in a manner which includes a practical description as well as a basic understanding is the focus of this paper.

We have carried out extensive studies of various aspects of the runaway phenomenon both at the microscopic level and the macroscopic level. In the context of the former we have considered the details of the process of absorption of microwaves, the possibility of what is termed "chaos" in the modern physics literature, and generally non-equilibrium interaction of electromagnetic fields with matter. As a result of our various efforts we have found that a practical as well as natural description of thermal runaway can be given in terms of a simple non-linear temperature–time equation. We have found that the equation provides a single starting point capable of describing, quite reasonably, a large variety of different materials undergoing thermal runaway; that it is based on simple physical arguments; that its parameters are calculable from basic considerations; and that it explains widely differing time–temperature curve shapes as will be shown in Figs 2 and 3.

The rest of this paper is outlined as follows. In

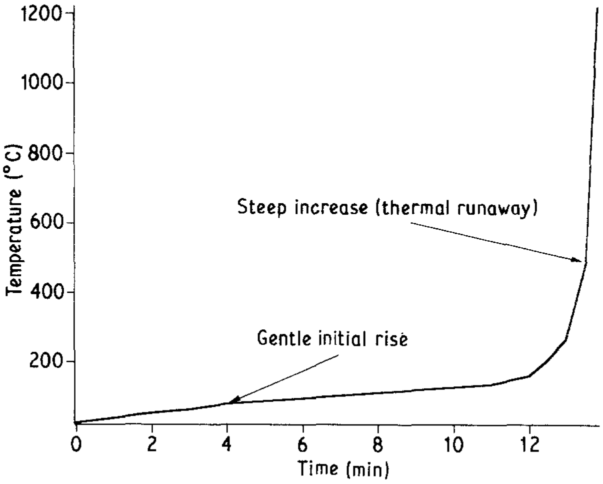

Figure 1 The thermal runaway phenomenon under microwave heating showing the gentle initial rise of temperature followed by a steep increase. The data is from observations on chromia for 500 W reported in [1].

Section 2 we present our temperature–time equation and a brief discussion of its parameters. In Section 3 we use the equation to describe experiments and show how it fits the observed data on zinc oxide, alumina, strontium titanate, iron oxide, and silica. The observations are those reported by McGill *et al.* [5], Sheppard [1], and Varadan *et al.* [4]. In Section 4 we discuss, in essential detail, how we arrive at our suggested equation from microscopic considerations. We also outline how the parameters of our equation can be calculated for any given material. Section 5 contains concluding comments.

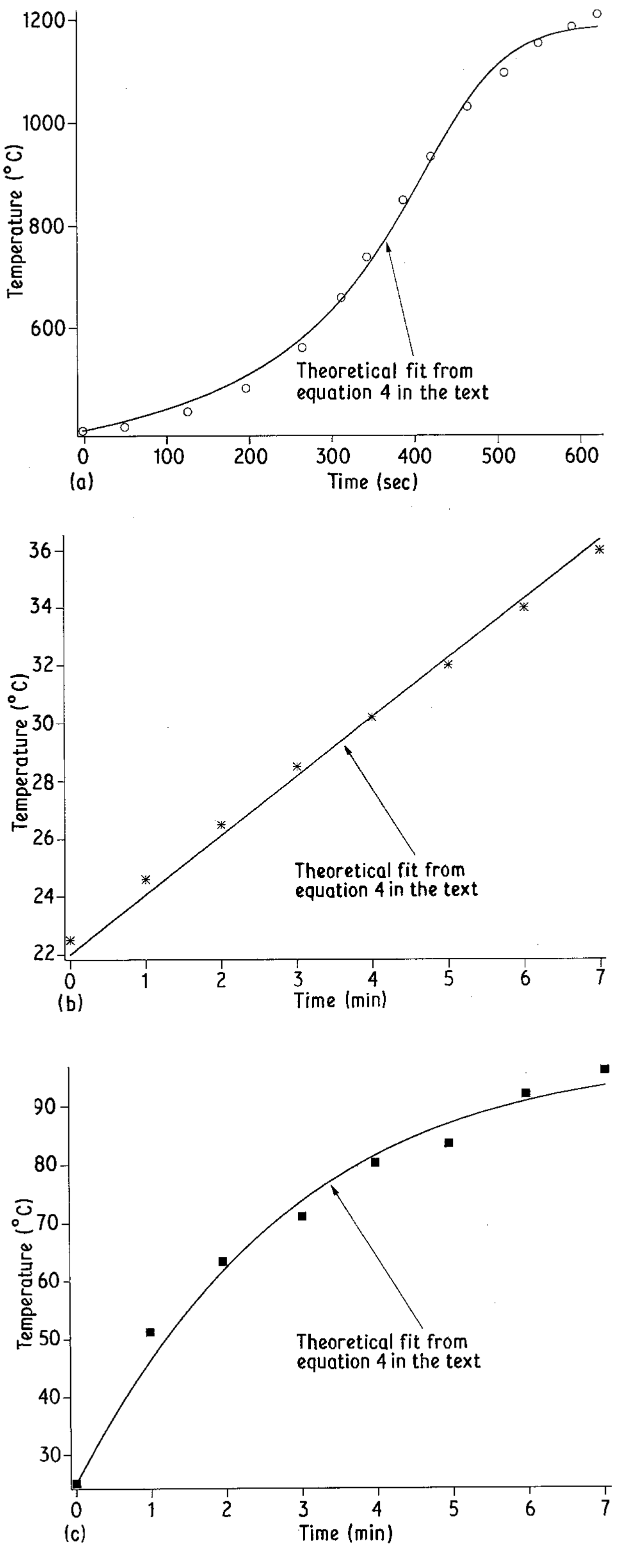

Figure 2 Thermal runaway observations and the application of our theory as in Equation 4. The experiments carried out are for (a) strontium titanate with initial porosity 53% undergoing microwave sintering as reported by Varadan *et al.* [4], (b) silica undergoing microwave heating at 500 W as reported by McGill *et al.* [5], and (c) zinc oxide undergoing microwave heating as described by Sheppard [1]. Our theory is represented by solid lines.

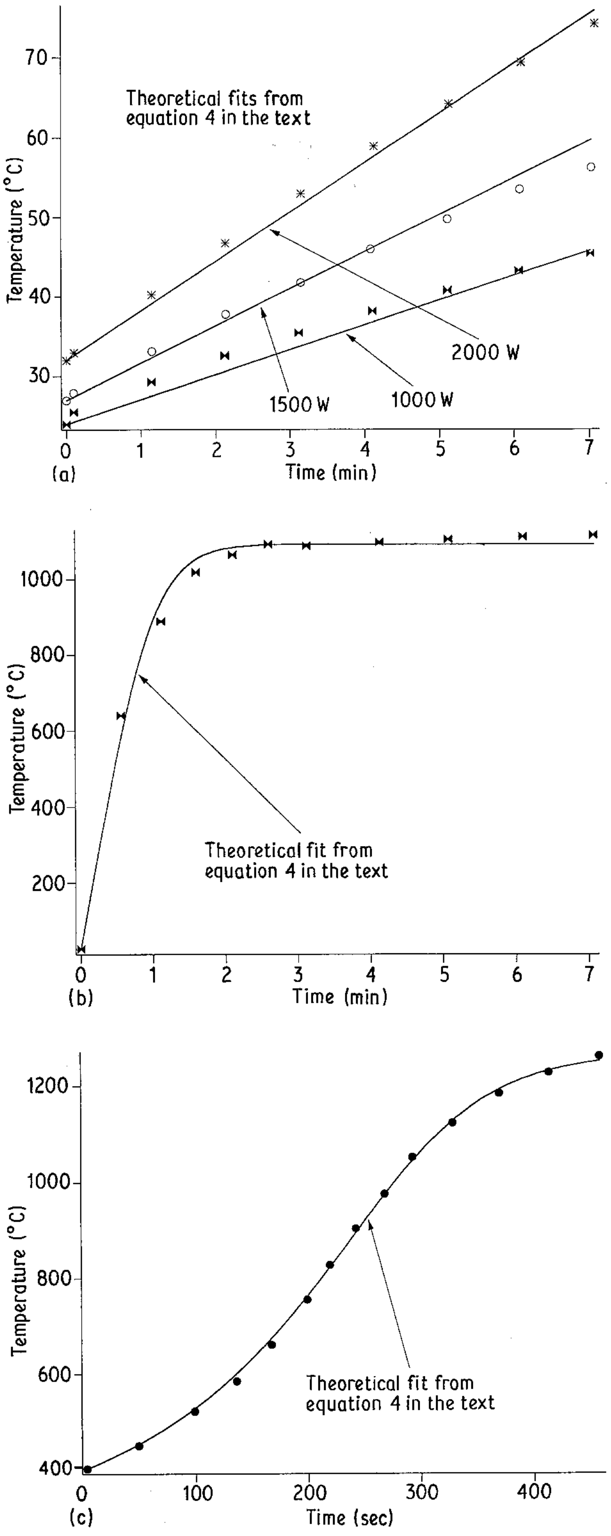

Figure 3 Thermal runaway observations to further materials and the application of our theory as in Equation 4. The materials studied are (a) silica undergoing microwave heating at different power levels (as shown) as reported by McGill *et al.* [5], (b) iron oxide undergoing microwave heating as shown by Sheppard [1] and (c) alumina of initial porosity 50% undergoing microwave sintering as reported by Varadan *et al.* [4]. As in Fig. 2, our theory is represented by solid lines.

2. The temperature–time equation

We have encountered four different types of the shape of the time–temperature curve in our study of the data on various materials. Type 1 is seen in Fig. 1 and is characterized by a dramatically sudden increase in temperature and no saturation within the reported observations. Type 2 shows only a slight effect, i.e. a near-linear rise of temperature. Type 3 is characterized by a rise followed by temperature saturation and type 4 combines these effects into an S-shaped curve which includes the gentle rise, the steep increase and the saturation. Types 2–4 can be found in Figs 2 and 3. The essential features of the observed runaway are thus 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 an explosive (or at least 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. It is therefore helpful to regard the runaway phenomenon as consisting of the three stages in general and to consider the materials in which particular stages are not observed as being ones in which the relevant processes are absent as a result of parameter magnitudes.

Our basic postulate is that the system consists of two species which we call the A species and the M species. The former consists of absorbing entities and is typified by impurities and inclusions whose relaxation times (not resonance times) match the period of the microwaves and which therefore absorb microwave radiation through what is sometimes known as a Debye mechanism (see e.g. [6]). 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. It is also the absorption by this A species that leads to the initial slow rise of temperature with respect to time, which we have called the first stage above. If n_A is the number of the absorbers of the A species, and Pc_A the rate at which each absorbs energy from the microwaves (P being the microwave power), this initial stage of temperature evolution is described by

$$\frac{dT}{dt} = Pk_A \qquad (1)$$

where $k_A = n_A c_A$. The final saturation stage is usually [7] described by a radiation-like term $-\sigma_1 T^4$ so that the combined equation appears as

$$\frac{dT}{dt} = Pk_A - \sigma_1 T^4 \qquad (2)$$

Although the justification of the fourth power of temperature in the saturation term above is not clear because the losses responsible for saturation are not only radiative but arise from other sources as well, we will maintain the form to conform to standard procedures. In cases wherein the standard description is not applicable the loss term in Equation 2 should be changed appropriately. Equation 2 would also apply formally if the heating is in a conventional furnace, i.e. without microwaves, the term Pk_A then being simply the rate at which the conventional furnace supplies heat to the sample. The important additional term with which Equation 2 must be augmented is the one responsible for the explosive acquisition of energy. Our study of various aspects, microscopic as well as observational, of the thermal runaway phenomenon have led us to suggest the following simple model for the additional term. Interstitial atoms or vacancies lie, at low temperatures, in potential wells which bind them. The energetic height of these wells is substantial, namely of the order of eVs. These vacancies or interstitials are our species M. They do not absorb, or do so to a negligible extent, because neither their resonance frequencies nor their relaxation rates match the gigahertz frequencies of the microwaves. However, if they are let out of the binding wells, they act like relatively free particles and absorb from the microwave radiation. The details of why carriers thus freed from their binding wells absorb to a much greater extent than bound carriers will be explained in Section 4 below from a microscopic analysis. Here we merely note the fact that the fraction f of the M-particles which are able to absorb will be given by

$$f = \exp(-\Delta/T)[\exp(-\Delta/T) + 1]^{-1} \qquad (3)$$

where Δ is a measure of the barrier which the particles must surmount to become free of their binding wells. The form that Equation 2 must take to incorporate the above is now clear

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

where $k_M = n_M c_M$ and the quantities n_M and c_M refer to the M species but have the same meaning as the corresponding A quantities.

Equation 4 is our starting point in the description of thermal runaway.

3. Fits to experimental observations on diverse materials

The basic evolution of temperature described by Equation 4 should be evident. If the barrier height Δ for the material under discussion is of appropriate magnitude relative to the initial temperature, the initial time evolution of the temperature 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.

TABLE I Parameters deduced from the application of our theory (Equation 4) to thermal runaway observations on diverse materials

Material	k_A [deg/min/W]	k_M [deg/min/W]	Δ [deg]	σ_1 [1/s/deg^3]
zinc oxide (500 W)	9×10^{-2}	30	2800	0.46×10^{-12}
iron oxide (500 W)	1.6	0.96	1.7×10^{-3}	0.5×10^{-12}
silica (500 W)	3.9×10^{-2}	8.5	5400	0.35×10^{-12}
silica (1000 W, 1500 W, 2000 W)	1.8×10^{-2}	8.8	5600	0.35×10^{-12}

Material	Pk_A [deg/s]	Pk_M [deg/s]	Δ [deg]	σ_1 [1/s/deg^3]
alumina (50% I.P.)	8.1×10^{-6}	72	2600	1.9×10^{-12}
strontium titanate (53% I.P.)	1.1×10^{-2}	230	3600	4.1×10^{-12}

Equation 4 can be solved to quadratures as

$$t + \text{constant} = \int \mathrm{d}T h(T) \quad (5)$$

$$h(T) = \{P[n_A c_A + f(T) n_M c_M] - \sigma T^4\}^{-1} \quad (6)$$

Either through the use of expression 5 or by fitting Equation 4 directly to observations it is possible to address experimental data. This is done for a variety of materials in Figs 2 and 3, and the resulting values of the parameters k_A, k_M, σ_1, and Δ are shown in Table I. It is remarkable that the agreement obtained for the widely different materials is excellent, that the value of σ_1 is approximately the same for all materials considered and is compatible with the value of the Stephan–Boltzmann constant σ along with sample parameter values, and that the Δs extracted through our theory are not disparate in orders of magnitude relative to the barrier heights for defect formation in the materials.

In Fig. 2a we see data, reported by Varadan *et al.* [4], on the time–temperature evolution of strontium titanate of initial porosity 53% during the process of sintering via microwave heating. The time–temperature curve is of type 4 discussed above in that it includes all three processes mentioned: a gentle initial rise, a subsequent steep increase and a tendency towards saturation. The temperature range is from 400 °C to 1200 °C and heating data has been collected for 600 s. The description by our Equation 4 is very satisfactory and the parameter values obtained are as follows: the trapped–free barrier Δ (measured as a temperature) is 3600 deg, σ_1 is $4.1 \times 10^{-12}\,\mathrm{s^{-1}\,deg^{-3}}$, and the product of power P and the absorption rate k in deg s^{-1} is 1.1×10^{-2} for the A species and 230 for the M species.

Fig. 2b shows observations of McGill *et al.* [5] on silica for microwave heating at a power of 500 W for 7 min. The temperature rise is only from 22 °C to less than 35 °C, the curve is of type 2, i.e. is near-linear, but shows a slight saturation tendency. Our fits result in the following parameter values: the barrier Δ is 5400 deg, σ_1 is $0.35 \times 10^{-12}\,\mathrm{s^{-1}\,deg^{-3}}$, and the absorption rate k in deg W^{-1} min^{-1} is 3.9×10^{-2} for the A species and 8.5 for the M species.

In Fig. 2c we see a curve of type 3 – exhibiting a rise and clear saturation – in zinc oxide from Sheppard [1]. The heating time is 7 min, the temperature range is from room temperature to about 100 °C, and our Equation 4 provides a satisfactory fit with parameter values as follows: the barrier Δ is 2800 deg, σ_1 is $0.46 \times 10^{-12}\,\mathrm{s^{-1}\,deg^{-3}}$, and the absorption rate k in deg W^{-1} min^{-1} is 9×10^{-2} for the A species and 30 for the M species.

Simultaneous description of data for various power levels is shown in Fig. 3a. The curve is of type 2, the material is silica as in Fig. 2b, and the three curves correspond to power levels of 1000 W, 1500 W, and 2000 W, respectively [5]. Our fits result in the following values: the barrier Δ is 5600 deg, σ_1 is $0.35 \times 10^{-12}\,\mathrm{s^{-1}\,deg^{-3}}$, and the absorption rate k in deg W^{-1} min^{-1} is 1.8×10^{-2} for the A species and 8.8 for the M species.

Another type 3 curve but with very steep rise followed by very clear saturation is seen in Fig. 3b where our theory provides a good fit to the data on iron oxide given by Sheppard [1]. The temperature rise is dramatic in the first 3 min (the range being larger than 1000 °C) and saturation behaviour is seen in the next 4 min. Our deduced parameter values are: the barrier Δ is essentially absent, i.e. equals 1.7×10^{-3} deg, σ_1 is $0.5 \times 10^{-12}\,\mathrm{s^{-1}\,deg^{-3}}$, and the absorption rate k in deg W^{-1} min^{-1} is 1.6 for the A species and 0.96 for the M species.

A type 4 curve – S-shaped incorporating all aspects – is seen again in Fig. 3c. The material is alumina of initial porosity 50% undergoing microwave sintering [4]. Almost 900 °C are covered in about 500 s and our fit is excellent with resulting parameter values as follows: the barrier Δ is 2600 deg, σ_1 is $1.9 \times 10^{-12}\,\mathrm{s^{-1}\,deg^{-3}}$, and the product of power P and the absorption rate k in deg s^{-1} is 8.1×10^{-6} for the A species and 72 for the M species.

It is interesting to note that σ_1 has been found to be essentially the same in all the samples studied.

Indeed, our σ_1 may be taken to be related to the Stephan–Boltzmann constant σ through the equation

$$\sigma_1 = \left(\frac{S}{V}\right)\left(\frac{1}{C_v}\right)\sigma \tag{7}$$

where S and V are the surface and volume of the sample and C_v is its specific heat. The magnitude of σ is known through the well-known relation (see, e.g. [10])

$$\begin{aligned} \sigma &= (2\pi^5 k^4)(15c^2h^3)^{-1} \\ &= 5.68 \times 10^{-12}\ \mathrm{W/cm^2\,deg^4} \end{aligned} \tag{8}$$

the quantities k, c and h being universal constants (the Boltzmann constant, the speed of light and the Planck constant, respectively). Although the parameter σ_1 in our theory would change from sample to sample (as indeed it does), and although the details of the surface, volume and specific heat of the samples used in the experiments we have analysed are not available to us, we would like to point out the following simple calculation. If we take the C_v characteristic of alumina to be 3 $\mathrm{J/cm^3}$ deg and assume that the surface–volume ratio is 1 $\mathrm{cm^{-1}}$, we obtain σ_1 to be $2 \times 10^{-12}\ \mathrm{s^{-1}\,deg^{-3}}$. The value deduced from the application of our theory to the data of Varadan *et al.* is (see Fig. 3 and Table I) $1.9 \times 10^{-12}\ \mathrm{s^{-1}\,deg^{-3}}$. This agreement is closer than one might expect from the level of description proposed. However, it supports the view in the literature that the loss of heat by radiation is indeed the major factor responsible for temperature saturation in thermal runaway. We also see that the deduced magnitudes of Δ appear 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 Δ 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 well be identical to each other.

4. Microscopic origin of the temperature–time equation

In order to understand the considerations which lead to Equation 4 for the evolution of temperature which we have suggested above and which, as we have seen, provides a rather satisfactory description of thermal runaway in a wide variety of materials, it is necessary to first note several important features of microwave absorption in general.

We begin by pointing out that absorption of electromagnetic radiation by free charges is very 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 effect is different. The velocity increases under the action of the electric field but this increase is opposed by another agent in addition to the friction force, namely 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 which 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 was 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.

In the light of the above considerations, it is natural to suggest that the significant increase of absorption that occurs in the phenomenon of thermal runaway has the transformation of bound into free absorbers as its source. Indeed, absorbers lying 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 clearly 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 picture behind our suggested equation is thus as follows. There would be no absorption and no heating whatsoever if the ceramic were totally transparent to microwaves. Absorbers which are either responsible for partial absorption by the material itself, or by impurities or other inclusions, give rise to the first term in Equation 4 which describes linear evolution of temperature, i.e. heating at a constant rate. We have called these absorbers the A species, as stated in Section 2. The bound entities described above, which can become free when the temperature is sufficiently high, form what we have called the M species. The fraction of them responsible for absorption – and therefore for changing the rate of increase of temperature – is itself dependent on temperature. It therefore gives rise to the second term in Equation 4 and results in a non-linear evolution of temperature. The specific expression 3 for the fraction f used in Equation 4 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.

In all the above, it is to be noted that absorption of microwaves in ceramics cannot occur by the resonance mechanism but rather by a relaxation mechanism [6]. The simplest way to understand the distinction is to consider a damped harmonic oscillator driven by an external sinusoidal field. In the absence of damping, or in the presence of small damping, the external field has the greatest influence on the dynamics of the oscillator when the field frequency matches the natural frequency of the oscillator. This is resonance. Let us use the term "optimum frequency" to denote the frequency at which the external field has the maximum effect. As damping increases in magnitude, only a minor shift in the optimum frequency occurs. However on further increasing the damping rate, the optimum frequency moves rapidly away from the natural frequency of the oscillator and approaches a "relaxation frequency" which equals the ratio of the square of the natural frequency and the damping rate. This is relaxation absorption. It is important to observe that, in this limit, absorption can thus occur at field frequencies which cannot be identified with, and are much lower than, all frequencies in the system except the quantity we have called the relaxation frequency. The terminology arises because the physical origin of the absorption is through a matching of the field period to a time characteristic of the relaxation process that the oscillator undergoes under the combined action of damping and natural oscillatory tendencies. This mechanism appears to have been first invoked by Debye [6].

The procedure to calculate the parameters involved in our theory from microscopic considerations is not difficult. While we are not interested in carrying out such a calculation in the present paper, we will sketch the procedure briefly by showing some details regarding the M species. Their representative coordinate x would have undergone the following equation of motion in the absence of the temperature rise

$$\frac{d^2x}{dt^2} + \frac{\alpha\,dx}{dt} + \frac{dU}{dx} = c_1 E \cos\omega t \qquad (9)$$

where $U(x)$ is a spatially periodic potential typified by $A(1 - \cos ax)$ where a describes the spatial variation of the potential and A is a constant; α is a damping rate arising from interactions of various sorts with the rest of the solid; E and ω are the magnitude and frequency of the microwave field, respectively; and c_1 is an appropriate constant. However, the temperature rise causes a stochastic perturbation of the kinetic energy of the M species. To obtain the appropriate terms that should be added to Equation 9 to describe the temperature rise in as simple a manner as possible (without turning Equation 9 into a stochastic differential equation of motion), we rewrite the consequence of Equation 9 for the evolution of the energy $\mathcal{E}$, namely

$$\frac{d\mathcal{E}}{dt} = (c_1 E \cos\omega t)\left(\frac{dx}{dt}\right) - \frac{1}{2}\alpha\left(\frac{dx}{dt}\right)^2 \qquad (10)$$

and append to it a source term arising from the absorption by the A species. The result is

$$\frac{d\mathcal{E}}{dt} = (c_1 E \cos\omega t)\left(\frac{dx}{dt}\right) - \frac{1}{2}\alpha\left(\frac{dx}{dt}\right)^2 + c_2\left\langle\left(\frac{dy}{dt}\right)(E\cos\omega t)\right\rangle \qquad (11)$$

where y is the coordinate of the A species absorber, the symbol $\langle\ \rangle$ denotes an average over a cycle, and c_2 is an appropriate constant appearing in the relaxation equation characteristic of the absorption of microwaves by the A species. The relaxation equation is typically

$$\frac{dy}{dt} + \Gamma y = c_3 E \cos\omega t \qquad (12)$$

where c_3 is an appropriate constant and Γ is a relaxation rate, and can be used to calculate the last term in Equation 11 as a time average. Denoting that term by $c_2E^2g(\omega, \Gamma)$ where the dependence on the second power of the electric field magnitude has been made explicit, we see that Equation 9 is now to be augmented into the form

$$\frac{d^2x}{dt^2} + \alpha\frac{dx}{dt} + \frac{dU}{dx} = c_1 E \cos\omega t + c_2E^2g(\omega, \Gamma)\left(\frac{dx}{dt}\right)^{-1} \qquad (13)$$

The microscopic parameters of the M-absorbers go into the potential U which can be obtained experimentally or through first-principles calculations along the lines of those carried out by the present authors recently [11], into the damping rate α and the constant c_1. The A-absorbers make their presence felt through c_3 and $g(\omega, \Gamma)$ which is closely related to the absorption coefficient or $\tan\delta$ of the A species. The parameters k_A, k_M and Δ are thus all calculable in principle. A microscopic theory based on such calculations will be presented elsewhere.

5. Conclusions

We have presented a simple theory of thermal runaway and applied it to experimental observations reported on a variety of materials. We have found that the theory provides a good description of the runaway phenomena. The essential idea behind our theory is simple and is provided by Equation 4. The microscopic origin of Equation 4 is explained in Section 4 and it is made clear that the parameters of the theory are calculable. As stated in the introduction, the following are the advantages of our approach:

1. The equation proposed provides a single starting point capable of describing, quite reasonably, a large variety of different materials undergoing thermal runaway.

2. The equation is based on simple physical arguments and its parameters are calculable from basic considerations.

3. The approach succeeds in explaining quite different time–temperature curve shapes as in Figs 2 and 3.

Although the approach is relatively crude in the present form, it has considerable potential and we are in the process of developing it into a usable scheme of predictive power. Among the 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 the materials studied, that the deduced value of Δ is always smaller than the barrier height as measured from defect formation and migration experiments. The fact that the deduced values of σ_1 and Δ are reasonable for the large variety of materials studied, and that the observed $\tan\delta$ in many materials [8] also shows Arrhenius dependence on temperature as in our expression 3 for f, lend support to our theory.

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