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TITLE Microwave Enhanced Diffusion?

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MICROWAVE ENHANCED DIFFUSION?

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ABSTRACT

The observation of more rapid reaction and/or sintering during microwave processing of ceramics has lead to speculation that microwave processing results in "enhanced diffusion".

The loss mechanisms by which microwaves interact with a crystal lattice have been reviewed. These mechanisms were evaluated with regard to the atomic theory of diffusion. The potential for these loss mechanisms to influence atomic diffusion, and thus produce enhancement will be discussed.

Existing evidence, both direct and indirect, regarding microwave enhanced diffusion has been reviewed and will be discussed along with recent experimental data.

INTRODUCTION

The use of microwave radiation for materials synthesis and processing is a rapidly expanding field. There have been numerous reports of ennanced diffusion during microwave processing. These reports fall into two categories. The first consists of indirect evidence of diffusion such as observations of enhanced sintering, grain growth or reaction zones[1-3]. These types of observations do not provide clear evidence of enhanced diffusion since interpretation is difficult for complex processes such as sintering, grain growth and chemical reaction.

The second body of evidence is much smaller and comprises direct measurements of diffusivites and activation energies for diffusion during microwave heating[4-6]. Fathi and Clark[4] report an increase in

width of the reaction zone of approximately 3 times for the ion exchange of potassium into a sodium-aluminum-silicate glass. This data indicates an increase in the diffusivity of approximately one order of magnitude. Patterson and McCallun[5] have implanted titanium in sapphire and studied the diffusion after conventional and 2.45 GHz microwave annealing at 1000°C. Preliminary results from this study indicate that there is no difference in the concentration profiles between the conventionally and microwave annealed samples. Janney and Kimrey[6] report activation energies 40% lower for the tracer diffusion of oxygen in alumina annealed using 28 GHz microwaves. They obtained activation energies of 710 and 410 kJ/mol for the conventional and microwave samples respectively which is equivalent to an increase of approximately two orders of magnitude in the diffusivity for the temperatures studied.

To understand how a microwave field might influence diffusion it is helpful to look at the factors which control diffusion. Substitional diffusion can be represented by the following atomistic formula:

$$D = fA_0^2N\omega \qquad (1)$$

where D is the diffusivity, f is the correlation factor, A_0 is a geometric constant, N is the concentration of vacancies (i.e., the probability that an ion has a vacant next nearest neighbor,) and ω is the jump frequency. The correlation factor corrects for the fact that only vacancy diffusion is purely random. The jumps of a diffusing ion are dependent on its previous jumps, and hence, "correlated". It follows from the above formula that a microwave field can only influence the rate of diffusion in two ways. The first and most obvious is by altering the jump frequency, ω, and the second is by changing the correlation factor, f.

Electromagnetic energy can be dissipated in a crystalline dielectric through several loss mechanisms. These mechanisms include electronic polarization, ionic vibration, ion jump relaxation, conduction and interfacial polarization.

Electronic polarization and ionic vibration are

resonance phenomenon and if operable during microwave heating would directly change the ion jump frequency. Microwave frequencies are in the range of 10^9 to 10^{10} Hz and the ion jump frequency is of the order of the Debye frequency which is about 10^{13} Hz. Application of resonance theory shows that a resonance is not possible for any reasonable damping force since these two frequencies differ by three to four orders of magnitude. This has been explained in detail by Kenkre[7]. (It will be shown later that in the unlikely event that ionic resonance did occur it would actually result in a lower diffusivity.) It can thus be concluded that electronic polarization and ionic vibration are not important loss mechanisms for microwave heating. Therefore microwave heating does not influence diffusion by altering the jump frequency.

The second way by which the diffusivity might be altered is by changing the correlation factor. This is a much more plausible way of causing an alteration in the diffusivity when considering the remaining loss mechanisms. Ion jump relaxation occurs when an aliovalent ion and vacancy form an associated pair. (An aliovalent ion is an impurity cation or anion with a valence different from that of its host sublattice.) An aliovalent ion-vacancy pair has a dipole moment associated with it which responds to the applied electric field. The vacancy is thought to jump around the aliovalent ion to align its dipole moment with the electric field[8]. Interfacial polarization occurs at a structural inhomogeneity such as a grain boundary, dislocation, or vacancy cluster. In an ionic lattice there will be a localized disruption in electroneutrality at such a structural inhomogeneity with a net dipole moment which will align itself with the applied field.

An example of ion jump relaxation might occur due to the solution of impurity $CaCl_2$ in a KCl lattice as follows:

$$CaCl_2 \xrightarrow{KCl} Ca_K^{\cdot} + V_K' + 2Cl_{Cl} \qquad (2)$$

Where $Ca_K^{\cdot}$ is a calcium ion on a potassium ion site with a +1 net charge and V_K' is a vacancy on a potassium ion site with a -1 net charge. For reasons of

electroneutrality the calcium ions and the vacancies form pairs which have a net dipole moment. This situation is illustrated in Fig. 1. For the case of no applied electric field the dipoles are randomly oriented. Figure 2 illustrates the situation after the electric field has been applied. The dipole pairs are aligned in the direction of the electric field.

Ion jump relaxation can also result from the formation of intrinsic Schottky or Frenkel pairs. An example for the case of Schottky pairs in alumina is as follows:

$$\text{null} = V_{Al}^{'''} + 1.5V_O^{\cdot\cdot} \qquad (3)$$

Where $V_{Al}^{'''}$ is an aluminium ion vacancy with -3 net charge and $V_O^{\cdot\cdot}$ is an oxygen ion vacancy with a +2 net charge. Each aluminium ion would associate with an average one and a half oxygen ion vacancies to form a dipole. The loss tangent of Coor's AD-995 alumina[9] is reproduced in Fig. 3. The loss is seen to increase exponentially with temperature. This behavior can be explained by extrinsic defects in the linear region of the curve and the formation of intrinsic Schottky type defects in the exponential region[10].

Conduction is mostly of interest at low frequencies. This type of loss mechanism occurs when vacancies are not associated with other defects, and hence are not localized. Unassociated vacancies are much more mobile than associated pairs and migrate to align themselves with the electric field.

Since both intrinsic vacancy formation and lattice jumps are thermally activated we may express them by Arrhenius type equations as follows:

$$N = \exp(-G^{f}/kT) \qquad (4)$$

$$\nu = \nu\exp(-G^{m}/kT) \qquad (5)$$

Where G^{f} and G^{m} are the Gibbs Free Energies for vacancy formation and motion respectively and ν is the Debye

frequency*. Equations 1, 4 and 5 may be combined to produce the following equation:

$$D = fA_0^2\nu\exp-[(G^f+G^m)/kT] \quad (6)$$

The Gibbs Free Energies may be expressed in terms of the enthalpies (H^f, H^m) and the entropies (S^f,S^m) for formation and motion as follows:

$$G^f = H^f - TS^f \quad (7)$$

$$G^m = H^m - TS^m \quad (8)$$

Substituting equations 7 and 8 into equation 6, we obtain the following equation for the case of intrinsic vacancy concentration controlling:

$$D = fA_0^2\nu\exp(S^f/k+S^m/k)\exp-[(H^f+H^m)/kT] \quad (9)$$

For the case where extrinsic vacancy concentration controls, the concentration of vacancies, N, is as follows:

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*The effect of an ion resonance loss mechanism would be to replace the Debye frequency with a lower primary lattice vibration frequency. The lower frequency would result in a decrease in the jump frequency (as calculated from equation 5) and a commensurate decrease in the diffusivity. Any forced oscillations induced by a microwave field can be described by an equation of the type used for a damped harmonic oscillator which is as follows:

$$d^2x/dt^2 + 2\beta dx/dt + \nu x = 0$$

where 2β is the damping factor and ν is the Debye frequency. The solution to this equation is:

$$x = x_0\exp(-Bt)\cos\nu'' t$$

where the new primary vibration frequency, $\nu'' = (\nu^2 - \nu'^2)^{1/2}$ and ν' is the frequency of the forced oscillation. If $\nu' \ll \nu$, then $\nu \approx \nu''$.

$$N = [C_i] \tag{10}$$

Where $[C_i]$ is the concentration of impurity ions. Equations 1, 5 and 10 may be combined to produce the following equation:

$$D = fA_0^2[C_i]\nu\exp(S^m/k)\exp-(H^m/kT) \tag{11}$$

Since the diffusivity has been shown on numerous occasions to be thermally activated we may express the diffusivity by an Arrhenius type equations as follows:

$$D = D_0\exp(-Q/kT) \tag{12}$$

Where D_0 is the pre-exponential factor and Q is the activation energy for diffusion. By comparing equations 9 and 12, we see that the pre-exponential factor can be expressed as follows for the intrinsic case:

$$D_0 = fA_0^2\nu\exp(S^f/k+S^m/k) \tag{13}$$

and for the extrinsic case comparing equations 11 and 12,

$$D_0 = fA_0^2[C_i]\nu\exp(S^m/k) \tag{14}$$

Similarly the activation energy for diffusion is the sum of the enthalpys for vacancy formation and motion.

$$Q = H^f+H^m \tag{15}$$

The model of the ion jump relaxation loss mechanism involves a vacancy jumping around the aliovalent ion to align its dipole moment with the electric field. Clearly such a loss mechanism would involve a change in

the correlation factor. Similarly, the interfacial polarization loss mechanism would alter the correlation factor. Conversely, these two loss mechanisms do not involve any enthalpy changes, therefore, any alteration to the diffusivity would result from changes in "D_0" the pre-exponential factor, rather than to the activation energy for diffusion.

EXPERIMENTAL

Some preliminary experiments have been performed using the alumina(Al_2O_3)-chromia(Cr_2O_3) system. This system was chosen for two reasons. First, the alumina-chromia system is ideal, and therefore, as will be shown later, the comparison of chemical and tracer diffusivities is much easier. Second, this system is something of a model system in the field of ceramics and much information is available on it including diffusion data from studies by Oishi and Kingery,[11] and by Stubican and Osenbach[12] among others.

In the alumina (or Corundum) crystal structure, the oxygen ions reside in a close packed hexagonal lattice and the smaller aluminum ions occupy 2/3 of the octahedral interstices. Since the alumina-chromia system is "ideal", it exhibits complete solid-state solubility with chromium ions substituting for aluminum ions on octahedral interstice sites.

The alumina used in this work was Sumitomo grade AKP-50*. The diffusion couples were prepared by conventionally sintering green alumina pellets in air to full density to produce 1 cm X 1 cm right circular cylinders. Chromia was then plasma sprayed onto the top surface of the cylinders. The as-sprayed layer was about 30 microns in thickness and relatively uniform.

The microwave annealing was performed under flowing argon in a facility consisting of a 2.45 GHz, 6 kilowatt microwave power supply and a cubical, 2 ft on side resonant cavity. Temperature was measured with an Accufiber Model 100 Multi-Channel Optical Fiber Thermometer§. The diffusion couples were enclosed in a low density insulation casket made from yttria

*Sumitomo Chemical Company, Ltd., Osaka, Japan.
§Accufiber, Inc., Beverton, OR.

stabilized zirconia board supplied by Zicar[5]. The insulation casket comprises a black body so temperature measurements could be made using an uncoated optical fiber.

RESULTS AND DISCUSSION

The concentration versus distance profile for an alumina-chromia diffusion couple, which has been microwave annealed at 1750°C for twenty minutes, was obtained by microprobe analysis and is presented in Fig. 4. Boundary conditions were satisfied for a Boltzmann-Matano[13,14] diffusion analysis. This type of analysis yields the interdiffusivity which was defined by Darken[15] as follows:

$$\tilde{D} = D_{Cr}N_{Al} + D_{Al}N_{Cr} \qquad (16)$$

where D_{Al} and D_{Cr} are the chemical diffusivities and N_{Al} and N_{Cr} are the mole fractions of aluminum and chromium respectively. The interdiffusivities for $N_{Al}=N_{Cr}=0.50$ obtained in this study are presented in Figure 5.

The data available in the literature for aluminum and chromium ion diffusion in alumina are for tracer diffusivities. The interdiffusivity is related to the more familiar tracer diffusivity as follows. First we define the relationship between the chemical and tracer diffusivity after Darken[15]:

$$D_{Cr} = D^{*}_{Cr}(1 + d\ln\gamma_{Cr}/d\ln N_{Cr}) \qquad (17)$$

where D^{*}_{Cr} is the tracer diffusivity and γ_{Cr} is the activity coefficient of chromium in the alumina-chromia system. Since the alumina-chromia system is ideal, $\gamma_{Al} = \gamma_{Cr} = 1$, and therefore, $\ln \gamma_{Al} = \ln \gamma_{Cr} = 0$, and equation 16 simplifies to:

$$\tilde{D} = D^{*}_{Cr}N_{Al} + D^{*}_{Al}N_{Cr} \qquad (18)$$

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[5]Zircar Products, Inc., Florida, NY.

We may now calculate the interdiffusivity for the alumina-chromia system at $N_{Al}=N_{Cr}=0.50$ using data from Oishi and Kingery, and from Stubican and Osenbach. This data is indicated by the dashed line in Fig. 4. Two interdiffusivities obtained to date in this study, appear to lie on a line parallel to the interdiffusivity calculated from the literature. The interdiffusivities measured in this study are approximately three times that of the literature values. Since the two lines are parallel the activation energy for diffusion is the same, the pre-exponential is greater for the microwave case by a factor of three.

In the unlikely event that vacancy defects are intrinsically controlled (i.e., Schottky defects dominate) the observed enhancement is due to a correlation effect. For extrinsic defects dominating, the observed enhancement simply means the concentration of extrinsic defects is three times higher.

While this preliminary data seems to indicate that a microwave field does not lead to an enhancement in diffusion it is by no means conclusive. One major criticism involves the use of a susceptor to heat the high purity alumina, which has a very low dielectric loss at room temperature, to a temperature where it will couple to the microwave field. Because of the use of a susceptor it is not certain how much of the heating was due to the microwave field. For future experiments a hybrid microwave-electric resistance furnace will be constructed. Using this furnace a diffusion couple could be heated conventionally by electric resistance elements to a temperature at which it couples to microwaves and then the resistance elements would be turned off.

CONCLUSIONS

Relaxation type loss mechanisms are thought to be operable during microwave heating of crystalline ceramics. These loss mechanisms will influence the correlation factor for diffusion. To estimate the magnitude of the change to the diffusivity, the correlation factor must be recalculated. It should be noted, however, that the correlation factor usually has a small effect on the diffusivity, less than an order

of magnitude. Any alteration to the correlation factor would show up as a change in the pre-exponential factor of the diffusivity.

In order for resonance type loss mechanisms to occur, unrealistically high damping forces would have to be present because of the large difference between the natural lattice vibration frequency and the microwave heating frequencies. For this reason resonance type loss mechanisms are not thought to occur during microwave heating.

The experimental results reported herein show a small, factor of 3 increase in the interdiffusivity of microwave annealed samples. The observed enhancement was minimal and may have been caused by an increase in the correlation factor as a result of a relaxation type loss mechanism. A more plausible explanation for the observed increase in interdiffusivity, however, is a higher concentration of extrinsic defects.

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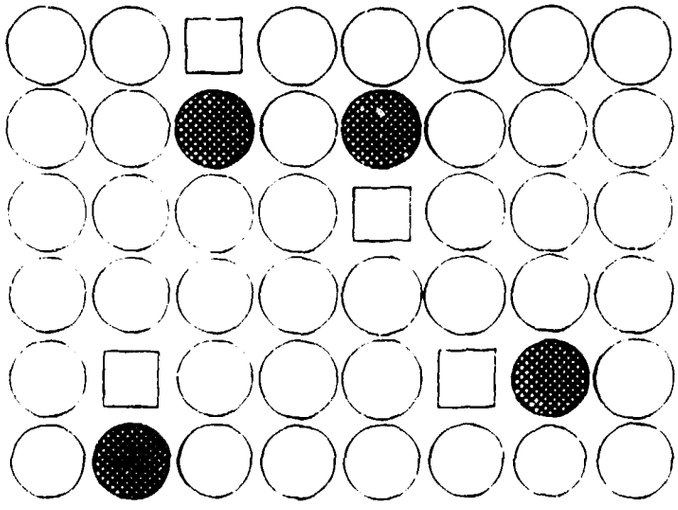

Figure 1. Schematic representation of vacancy-impurity pairs with random orientations.

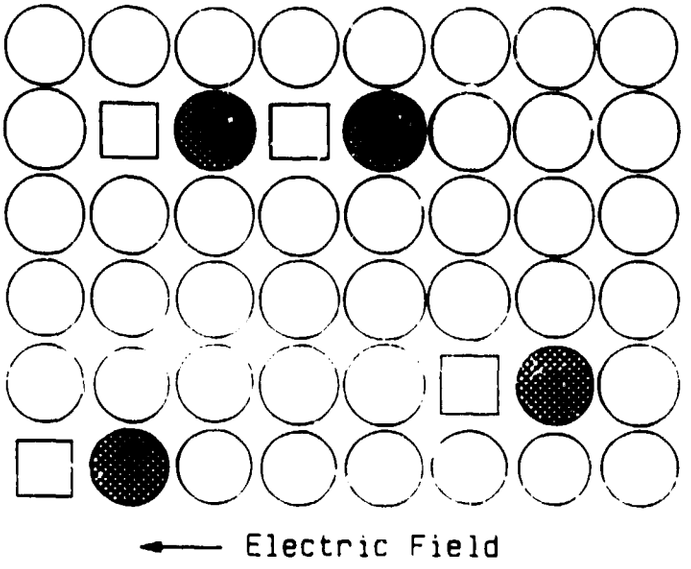

Figure 2. Schematic representation of vacancy-impurity pairs aligned with the applied electric field.

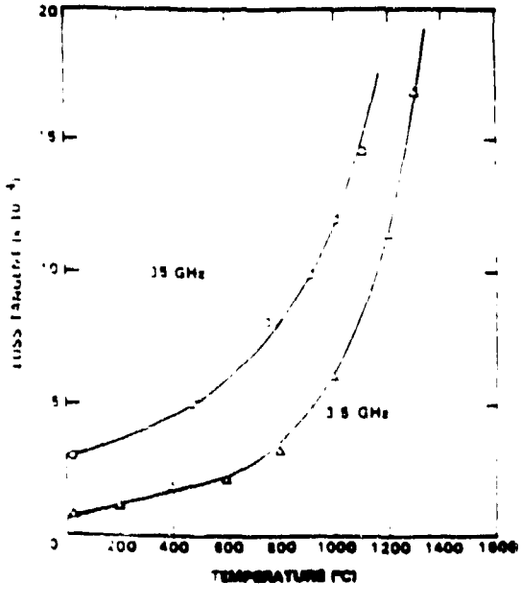

Figure 3. Loss tangent of Coor's AD-995 alumina as a function of temperature at 35 and 3.5 GHz. From reference 6.

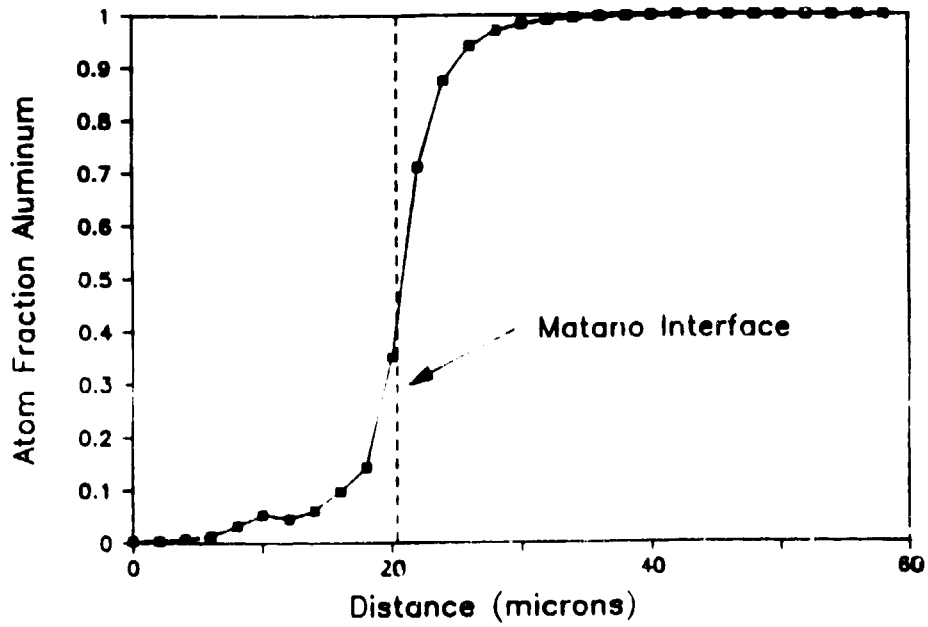

Figure 4. Concentration profile for a chromia-alumina diffusion couple microwave heated to 1750°C and held for twenty minutes.

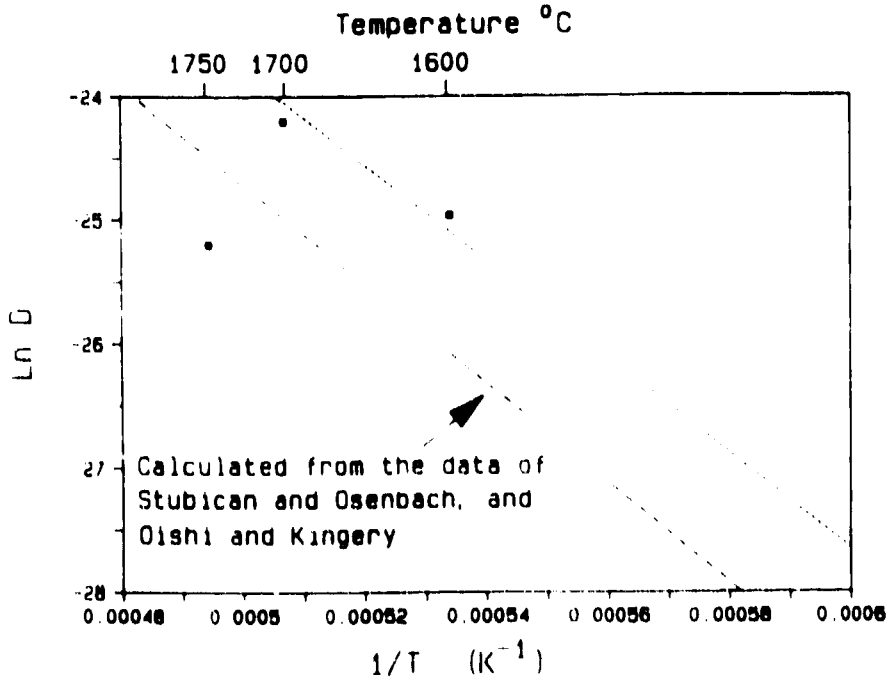

Figure 5. Calculated and measured interdiffusivities for the alumina-chromia system.