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The possible role of the pre-exponential factor in explaining the increased reaction rates observed during the microwave synthesis of titanium carbide

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Reaction rates observed during the microwave synthesis of titanium carbide powder via the carbothermal reduction of the oxide are more than three times faster than those observed during conventional processing at the same temperature. Although not dissimilar to other reports of "microwave effects" in the literature, this result is of interest because the microwave heating mechanism is quite different compared to work using ionic ceramics. The initial powder mix consisted of low dielectric loss titania mixed intimately with very fine carbon black powder. It is the latter phase which couples with the microwaves via a conventional ohmic dissipation mechanism. Calculations have shown that the faster diffusion rates might be explained by an increase in the Arrhenius pre-exponential factor *A*, with no change in the activation energy.

1. Introduction

Over recent years several investigators have reported unexpected effects resulting from the use of microwave radiation as an alternative energy source during the processing of materials. This has included apparent evidence for enhanced sintering of ceramic powder compacts, including lower sintering temperatures [1, 2], accelerated kinetics for a range of processes in ceramic, polymeric and organic systems [3–11] and reduced activation energies [1, 3–5]. For example, researchers at Oak Ridge National Laboratories, USA, have performed a whole series of comparative experiments involving microwave and conventional heating of alumina ceramics [3]. They report activation energies of 160 and 575 $\text{kJ}\,\text{mol}^{-1}$ for microwave and conventional sintering, 480 and 590 $\text{kJ}\,\text{mol}^{-1}$ for grain growth using microwave and conventional annealing, and 410 and 710 $\text{kJ}\,\text{mol}^{-1}$ for ^{18}O tracer diffusion in alumina, using microwave and conventional heating, respectively. They argue that the different changes in activation energy observed are indicative of the different processes involved in each of the three experiments. During the sintering experiments, for example, they observed differences both in the structural evolution and the kinetics of the processes. This, they concluded, meant that microwave and conventional sintering were two distinctly different processes [3]. Conversely, the approximate similarity in effect for the grain growth and ^{18}O tracer diffusion experiments suggested to them that the structural processes were essentially the same for microwave and conventional annealing [4].

It is not just sintering and annealing which has been found to be enhanced. For example, Willert-Porada *et al.* [8] found that pyrolysis of metallorganics was observed at lower temperatures with microwave heating than in conventional heating, resulting in enhanced reactivity of the ceramic powders generated. Boch *et al.* [9] used microwave heating to reaction sinter $Al_2O_3 + SiO_2$ and $Al_2O_3 + TiO_2$ powder mixtures to prepare mullite and aluminium titanate ceramics, respectively. In comparison with conventional heating, microwave heating led to a decrease in the required temperature of 50–100 °C. Fathi *et al.* [10] observed enhanced exchange of K^+ ions for Na^+ ions in sodium alumino-silicate glasses when microwave heating was used leading to deeper penetration and higher surface concentrations of the K^+ ion.

A number of theories have been put forward to explain the above effects [10–13]. Fathi *et al.* [10] attributed the enhanced diffusion to increased vibrational frequency of the ions caused by the electric field of the microwave radiation. Booske *et al.* [11, 12] initially proposed that the effect of the microwaves would be to excite a non-thermal phonon distribution in the polycrystalline lattice. This would translate into a non-thermal energy distribution, thereby enhancing the mobility of crystal lattice ions. The authors themselves subsequently proved that the effect was too small to explain the observed data under practical conditions. A similar fate awaited a later theory based on quasi-static polarization of the lattice near point defects [13]. The most recent theory [14, 15], developed by scientists at the Russian Academy of Sciences Institute of Applied Physics, suggests that the observed effects arise from the ponderomotive (time-averaged, non-zero) action of the high-frequency electric field on charged vacancies in the ionic crystal lattice. That is, it is the *driving force* which is affected, not the atomic *mobility*. Whilst this theory looks plausible, a number of significantly simplifying assumptions have had to be made, and it does not account for the "microwave effects" seen in non-ionic systems such as polymers (assuming that it is the same effect which is operational in these systems).

An underlying, and by no means insignificant, factor which has been all too often ignored in the experimental analyses, is the inherent difficulty of measuring temperature in a microwave field. The arguments surrounding the use of thermocouples, including shielded thermocouples, and optical pyrometers have presented before [16] and will not be rehearsed again here. Suffice it to say that those individuals who question temperature measurement put the inaccuracy at up to 100 °C – approximately the same value often quoted for the "microwave effect". Recent evidence from Freeman *et al.* [17, 18] however, provides evidence of a microwave-induced ionic current in sodium chloride in which questions of temperature measurement inaccuracies were irrelevant. In this case the with/without microwave comparison was done *in situ* and instantaneously. The results suggested two conclusions: (i) that a pre-requisite for the microwave effect is a pre-existing chemical potential gradient (which is a condition that applies to the experimental conditions associated with previously reported microwave effect observations); but (ii) that microwave fields do *not* change activation energies or any other parameter associated with ionic mobility. Rather, the evidence was believed [18] to support the ponderomotive theory suggested by Rybakov and Semenov [14, 15]. However, it has been questioned [19] whether the microwave pulse is actually effecting the kinetics of atom motion or the chemical potential of the charged vacancies.

During a recent experimental investigation into the microwave synthesis of two refractory metal carbides [20] by carbothermal reduction of the respective oxides, further evidence of a "microwave effect" was observed. This took the form of much faster reaction rates being observed with higher yields being obtained at lower temperatures and in shorter times when using microwave heating compared to equivalent experiments conducted using conventional heating. This work is of interest because the microwave heating mechanism will be quite different in this system compared to work using ionic ceramics. The initial powder mix consisted of low dielectric loss titania mixed intimately with very fine carbon black powder. It is the latter phase which couples with the microwaves via a conventional ohmic dissipation mechanism [16]. Even though the penetration depth of 2.45 GHz microwaves into carbon is minimal [21], because the carbon black is extremely fine (0.3 μm) the diameter of the carbon particles is very much smaller than the penetration depth of the microwaves, allowing rapid volumetric heating.

This paper reports some calculations which suggest that, if atomic mobility is indeed enhanced by the presence of a microwave field, then it is the pre-exponential factor which is enhanced rather than the activation energy which is decreased.

2. Experimental procedure

Stoichiometric mixes of TiO_2 and carbon black powders were heated in alumina crucibles using a 2.45 GHz multimode-controlled atmosphere microwave applicator to generate the reaction

$$TiO_2 + 3C \rightarrow TiC + 2CO\uparrow \qquad (1)$$

Microwave power was smoothly controllable between 500 W and 5 kW and the reaction zone was purged with argon to maintain an inert atmosphere. The reaction crucible was insulated within the microwave cavity using low dielectric loss alumina fibreboard to minimize heat losses and generate as uniform a temperature as possible within the powder mix. Temperatures were monitored using an optical fibre thermometer (Accufibre, Beaverton, OR) buried deep in the powder mix. Holding temperatures of 1300, 1400 and 1550 °C were used, with holding time at temperature being varied in the range 0.5–120 min. A heating rate of 20 °C min^{-1} was used for all experiments. The experimental arrangement is shown schematically in Fig. 1. Some of the above experiments were duplicated using a conventional controlled-atmosphere furnace with silicon carbide heating elements but an otherwise similar experimental arrangement.

The powders were weighed before and after heating to enable the extent of reaction to be determined. Assuming that all weight loss is due to evolution of carbon monoxide, a loss of 48.32% indicates that the reaction has gone to completion. Powder products were characterized by a range of techniques including X-ray diffraction (XRD), to determine the phase composition, and particle-size analysis and scanning electron microscopy to study particle size and particle-size distribution. In addition, the total and free carbon content as well as the oxygen and nitrogen content could be monitored if required. Further experimental details can be found elsewhere [20].

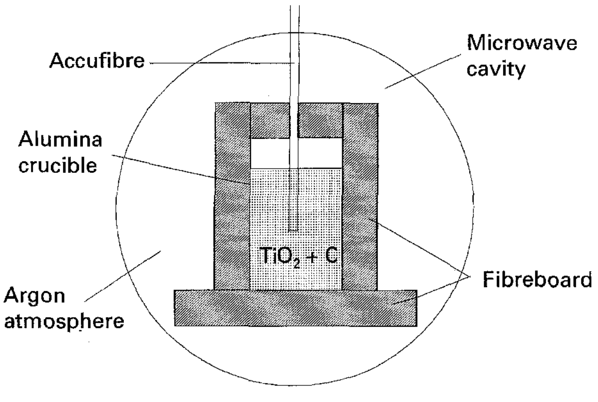

Figure 1 A schematic diagram of the experimental arrangement for heating TiO_2/C powder mixtures using microwave energy (not to scale).

3. Results and discussion

Plots of weight loss versus total reaction time for both the microwave and conventionally heated $TiO_2 + C$ mixtures are presented in Fig. 2. The total reaction time, t_{react}, that the samples had undergone was assumed to be given by

$$t_{\text{react}} = t_{\text{hold}} + \left(\frac{t_{\text{heat}}}{2}\right) + \left(\frac{t_{\text{cool}}}{2}\right) \qquad (2)$$

where t_{hold} is the holding time at temperature, t_{heat} the time spent during heating between the minimum temperature for any reaction to occur and the holding temperature, and t_{cool} the time spent during cooling between the holding temperature and the minimum temperature for any reaction to occur. Preliminary work had indicated that the minimum temperature for any reaction to occur was 1050 °C for the microwave heating case and 1200 °C for the conventional heating situation. The results show that both sets of data satisfy a parabolic model indicating that diffusion is the rate-controlling step in the reaction [22].

The feature of greatest interest in Fig. 2 is the evidence for faster diffusion rates using microwave heating compared with conventional heating. This is demonstrated more quantitatively in Table I, which presents the reaction (diffusion) rate constant, k, from the parabolic model

$$\text{degree of reaction } (= \text{weight loss}) = (kt_{\text{react}})^{1/2} \qquad (3)$$

It can be seen that the diffusion rates using microwaves are more than treble those achieved using conventional heating.

If we assume that this is due to enhanced mobility of the atoms then we can investigate the origins of this behaviour by considering the Arrhenius equation

$$k = A\exp\left(-\frac{Q}{RT}\right) \qquad (4)$$

where k is the diffusion rate constant, Q the activation energy, R the gas constant, T the absolute temperature, and A the pre-exponential factor.

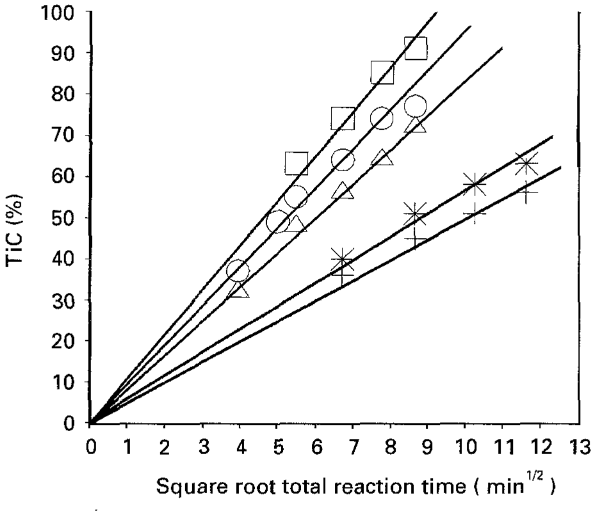

Figure 2 Weight loss versus reaction time for microwave and conventionally heated carbothermal reductions (error in weight loss is ± 0.2%). (□) MW 1550 °C, (○) MW 1400 °C, (△) MW 1300 °C, (∗) conv 1400 °C, (+) conv 1300 °C.

TABLE I Reaction rates achieved by microwave and conventional heating (error in reaction rate constant is ± 0.5 min^{-1})

Holding temp. (°C)	Heating method	Reaction rate constant, k(min^{-1})	Ratio $k_{\text{mw}}/k_{\text{conv}}$
1300	Microwave	15.8	3.3
1300	Conventional	4.8	
1400	Microwave	21.8	3.4
1400	Conventional	6.5	
1550	Microwave	28.4	–

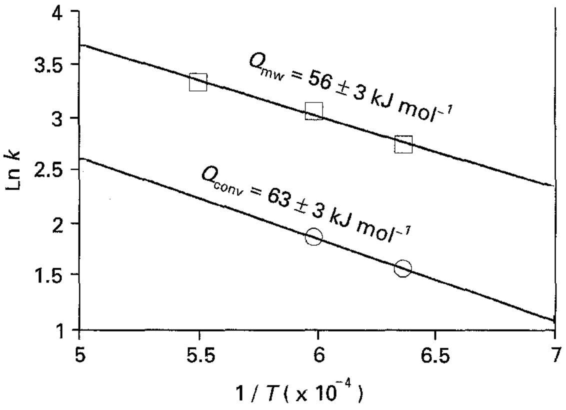

Figure 3 Activation energies for microwave and conventionally heated carbothermal reductions (error in ln k values is ± 0.04).

Plotting ln k versus $1/T$ yields the activation energies, Q (see Fig. 3), for the microwave and conventional heating cases. These are 56 ± 3 and 63 ± 3 kJ mol^{-1}, respectively; leading to an apparent 10% reduction in activation energy for microwave heating. However, given the small number of experimental points considered and the errors associated with the above values, it seems not unreasonable to assume that the activation energies are actually the same for the two types of heating. On this basis, and using an intermediate value of 60 kJ mol^{-1}, calculations yield values for the pre-exponential factor of approximately 1650 and 500 min^{-1} for the microwave and conventional heating cases, respectively. Thus the use of microwaves has resulted in an apparent increase in the pre-exponential factor by a factor of 3.3. These results support those of Katz *et al.* [7] who found a factor of 3 increase in the pre-exponential factor and no reduction in the activation energy for interdiffusivity in the alumina–chromia system when using microwave heating.

An alternative explanation for the observed increase in reaction rate could be the well known difficulties in measuring temperature in a microwave environment [16]. To investigate this, let us assume that our microwave temperature measurements are, in fact, in error and that $Q_{\text{mw}} = Q_{\text{conv}} = 60$ kJ mol^{-1} and $A_{\text{mw}} = A_{\text{conv}} = 500$ min^{-1} over the temperature range

1300–1550 °C. Then:
at 1300 °C

$$\ln 15.8 \;=\; 6.21 - \frac{60000}{8.31 \times T_1} \qquad (5)$$

yielding $T_1 = 1820\,^{\circ}\mathrm{C}$;
at 1400 °C

$$\ln 21.8 \;=\; 6.21 - \frac{60000}{8.31 \times T_2} \qquad (6)$$

yielding $T_2 = 2035\,^{\circ}\mathrm{C}$;
at 1550 °C

$$\ln 28.4 \;=\; 6.21 - \frac{60000}{8.31 \times T_3} \qquad (7)$$

yielding $T_3 = 2250\,^{\circ}\mathrm{C}$.

These calculations show that a temperature inaccuracy of between 500 and 700 °C would be required to account for the trebling of the reaction rate when microwaves are used as the source of energy. It is believed that a variation of the magnitude required would most certainly have been detected.

The only other possibility is that electrical discharges or sparking occurred between the carbon particles yielding very high temperatures on a local scale. However, as the sparks would be expected to generate very similar local temperatures irrespective of measured temperature, such a phenomenon would not be expected to yield the three clearly defined slopes for microwave heating seen in Fig. 2.

In this context it is interesting to reconsider the results of the Oak Ridge grain-growth experiments discussed in Section 1 where the activation energies were about 20% different. In the original paper [3] there is some confusion between the use of natural and base 10 logarithms and also in what constitutes the pre-exponential factor (i.e. whether it is A or the logarithm of A). This led to the conclusion that the pre-exponential factors were similar. However, if instead we assume that, within the limits of accuracy of measurement, the activation energies were the same at 535 $\mathrm{kJ\,mol^{-1}}$ (the average of the two values reported), then we find that the exponential factors are significantly different, supporting the view that it may be the pre-exponential factor, rather than the activation energy, which is being changed by the presence of microwaves.

The Arrhenius pre-exponential factor, A, is dependent on a small number of materials' factors by an equation of the general form [23]

$$A \;=\; \gamma\lambda^2\Gamma \qquad (8)$$

where γ is a geometric factor which includes the number of nearest-neighbour jump sites, λ the distance between adjacent lattice planes, i.e. the jump distance, and Γ the jump frequency. Of these, it might be reasonably assumed that γ and λ will not be affected by the presence of microwaves, because they are determined by the crystal structure of the material. Thus it appears that the most likely candidate for being affected by microwaves is the jump frequency, Γ. This is given by [23]

$$\Gamma \;=\; \nu \exp\left(\frac{-\Delta G^{+}}{kT}\right) \qquad (9)$$

where ν is the natural vibration frequency of the atoms, and ΔG^{+} is the activation energy. Because the latter appears not to be affected in many cases, it would seem that the microwave field is somehow affecting ν. For bulk crystals a value for ν which is often quoted is $10^{13}\,\mathrm{s^{-1}}$. This makes a change in ν difficult to understand, because the microwave frequencies used are $10^{-9}\,\mathrm{s^{-1}}$ and hence resonance effects would be unexpected. Nevertheless, the possibility of some change in ν cannot be discounted at this stage, especially for phenomena relying on diffusion along grain boundaries or across surfaces where frequency factors are less well defined.

4. Conclusion

Experiments involving the synthesis of titanium carbide via the carbothermal reduction of the oxide resulted in higher yields being obtained at lower temperatures and in shorter times when microwaves were used as the source of energy compared to conventional heating. This is of interest because the microwave heating mechanism is based on ohmic dissipation in an ultra-fine carbon phase and hence is quite different to that obtained in ionic ceramics. Analysis of the results indicates that the microwave reaction rates were 3.3–3.4 times faster. It would appear that the phenomenon can be explained by a 3.3-fold increase in the Arrhenius pre-exponential factor, A, with no change in the activation energy. The pre-exponential factor is dependent on the vibration frequency of the atoms at the reaction interface and hence it could be postulated that this might be being affected by the microwave field. Attempts to explain the increased reaction rates in terms of faulty temperature measurement were unsuccessful.

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