Molecular dynamics study of the high temperature fusion of TiO_2 nanoclusters

David R. Collins, William Smith, Nicholas M. Harrison and Timothy R. Forester

CCLRC Daresbury Laboratory, Daresbury, Warrington UK, WA4 4AD

Molecular dynamics simulations of the fusion of 1245 atom nanoclusters of rutile TiO_2 at high temperature and zero pressure have been performed. Details of the collision and fusion processes, described in terms of the structure of the nanoclusters and transport properties of the constituent ions, are presented. It is shown that the fusion of TiO_2 nanoclusters is a long-timescale phenomenon facilitated by surface ion diffusion.

TiO_2 rutile is a material of major industrial importance due mainly to its effectiveness as a white pigment, though it also finds applications in catalysis and electrochemistry.[1] Powdered TiO_2 rutile has been manufactured commercially for several decades and is mostly synthesised by the 'Chloride' process[1] in which gaseous titanium tetrachloride and oxygen are burned in a flame reactor at temperatures in the range 1500–2100 K. The process conveniently deposits titanium dioxide powder directly from the reaction, with chlorine gas as a useful by-product [eqn. (1)].

$$TiCl_4(g)+O_2(g) \xrightarrow{1500\text{–}2100\ K} TiO_2(s)+2Cl_2(g) \qquad (1)$$

The production of TiO_2 powder in the Chloride process is dependent on at least three sub-processes: (*a*) nucleation; (*b*) surface growth; and (*c*) coagulation, each of which needs to be understood in detail if the optimal reaction conditions and highest quality product are to be obtained. The quality of the product is defined in terms of the desired phase (rutile), particle size distribution, and surface morphology. Through experimental studies of the Chloride process the effects of temperature and chemical additives on structural properties and particle sizes[1,2] are well known. However much of this knowledge is empirical and does not provide a complete understanding of the underlying microscopic phenomena.

A valuable way of probing and quantifying the microscopic details of the manufacturing process is computer simulation. On the macroscopic scale computational fluid dynamics (CFD) may be used to model the reaction kinetics of surface growth and coagulation,[3] however this work is dependent on the availability of empirical parameters to obtain quantitative accuracy. The basic physical chemistry underlying these parameters is not necessarily well understood, a fact which undermines any rational scheme for their adjustment. The possibility exists however, for atomistic simulation methods such as molecular dynamics (MD)[4] both to vindicate the choice of parameters and determine appropriate magnitudes. In a previous paper[5] we described a molecular dynamics study of TiO_2 nanoclusters† over the temperature range of 1000–3000 K. That initial study sought to clarify understanding of the structure of nanoclusters, about which relatively little was known. The results showed that the nanoclusters existed in the rutile phase up to a melting point of approximately 2150 K. The surface of the nanoclusters showed some tendency towards microfaceting, with significant surface disordering and surface ion mobility. The work forms an essential background to this report.

This paper continues the investigation of TiO_2 nanoclusters by MD methods. The aim in this case is to examine some aspects the fusion of two nanoclusters as a function of temperature, (the fusion being an important feature of the coagulation process, see above). The work is not claimed to be definitive, since the number of relevant variables is large and too little is known about the effects of surface contamination to permit unqualified statements. Also, as will be shown, the time scales for the full fusion of the nanoclusters are extremely long, and despite the great length of some of the simulations (*ca.* 1 ns) the fusion could not be claimed to be complete. Nevertheless the simulations do capture some important aspects of the fusion and thereby shed some much needed light on the physical chemistry underpinning the manufacturing process.

Methodology

The force field used to describe the interatomic forces in these simulations is due to Matsui and Akaogi[6] and is identical to that used in the preceding study.[5] This is a rigid ion, partial charge model ($Ti=+2.196$, $O=-1.098$) with Buckingham (exp-6) short-range terms. The initial reasons for this choice of force field are detailed by Collins *et al.*[5] but briefly, the main criteria were simplicity, ease of use and an ability to reproduce the relative stabilities of the rutile, anatase and brookite phases of bulk TiO_2.

A prerequisite for the simulation of the fusion of nanoclusters is the generation of initial nanoclusters in isolation. These, in most cases, were taken from the previous study,[5] where a selection of nanoclusters at different temperatures was available, each nanocluster representing an already well equilibrated structure. The nanoclusters consisted of 1245 atoms in a charge neutral assembly. Nanoclusters were also required at temperatures different from the earlier set and these were obtained by re-equilibration of existing structures to the desired temperatures for a period not less than 200 ps. All MD simulations were performed using the molecular simulation package DL_POLY.[7] No periodic boundary conditions were applied and all interionic interactions were calculated without imposing a cut-off. Integration of the equations of motion was performed using a Verlet algorithm with a time step of 3 fs in the NVT ensemble.

As mentioned above, the number of variables defining the collision between nanoclusters is large. We have therefore confined our study to a narrow range of possible starting conditions, which nevertheless illustrate important features of the collision process in general. We have examined the collision of two nanoclusters from an initial separation of 37 Å, with zero relative velocity and impact parameter, at temperatures ranging from 1200 to 2000 K. Two additional runs were started from 32 and 47 Å respectively, both at 1800 K. This initial configuration ensured the collision was entirely the result of

---

†In this paper we have adopted the term nanocluster in preference to the term microcluster used previously,[5] as the former term indicates the length scale more precisely.

Table 1 Summary of simulations; T = temperature, s = initial separation between nanocluster centres of mass, t = duration of simulation

run	T/K	s/Å	t/ps
A	1200	37.0	770.7
B	1400	37.0	1036.2
C	1600	37.0	658.8
D	1800	32.0	300.0
E	1800	37.0	360.0
F	1800	47.0	737.7
G	2000	37.0	751.8

interparticle forces with the motion occurring along an axis joining their respective centres of mass. The nanoclusters were initially orientated so that the (100) direction of the underlying rutile phase was parallel to the direction of motion. Both nanoclusters were originally assigned the same atomic configuration with zero angular momentum. The resulting collision could therefore be described as occurring between the (100) faces of the nanoclusters, though this simple picture is considerably complicated by the roughness of the faces. These simulations were intended to reveal the long-time aspects of nanocluster fusion and lasted several hundred picoseconds (300–1000 ps). Table 1 summarises the simulations undertaken.

Results

Visual description

A typical nanocluster collision is shown in Fig. 1, which presents a sequence of 'snapshots' from the simulation A (Table 1). From a stationary start [Fig. 1(*a*)], the nanoclusters are first drawn towards each other by mutual attraction. Contact between the surfaces is made after approximately 25–30 ps [Fig. 1(*b*)]. The collision is mediated by surface roughness, and there is visual evidence of surface distortion when the surfaces are close. The collision takes place without sign of nanocluster fracture or rebounding and the underlying phase remains rutile. Following surface contact [Fig. 1(*c*)] there is an initial rapid reduction in configuration energy (over *ca.* 30 ps). This is followed by a much longer period (several hundred ps) during which the system undergoes further energy reduction. During this phase it is apparent that the 'neck' between the nanoclusters gradually broadens [Fig. 1(*d*)].

Particle interaction

The nature of the interaction between particles of TiO_2 is of some interest in modelling the Chloride process. We have therefore examined the phenomenon of attraction between nanoclusters. Fig. 2 reveals how the centre-of-mass (COM) separation of the nanoclusters changes with time in the simulations of Table 1. All the plots show an acceleration of the nanoclusters towards each other, which is halted at a separation of *ca.* 26 Å when the surfaces make contact. Thereafter, there is a gradual closing of the separation due to long-time relaxation, which is most noticeable in the first 30 ps. Runs A, B and E show almost identical behaviour in this plot, though it appears that runs C and G halt at a significantly larger separation than the others. Runs D, F and E were all performed at 1800 K, but started from separations of 32.0, 37.0 and 47.0 Å respectively, as is clear from their different trajectories. It is interesting to note that all runs apart from C and G reveal evidence of early contact between the nanoclusters, as is shown most clearly in run D. This indicates a sensitivity to the surface features at short range.

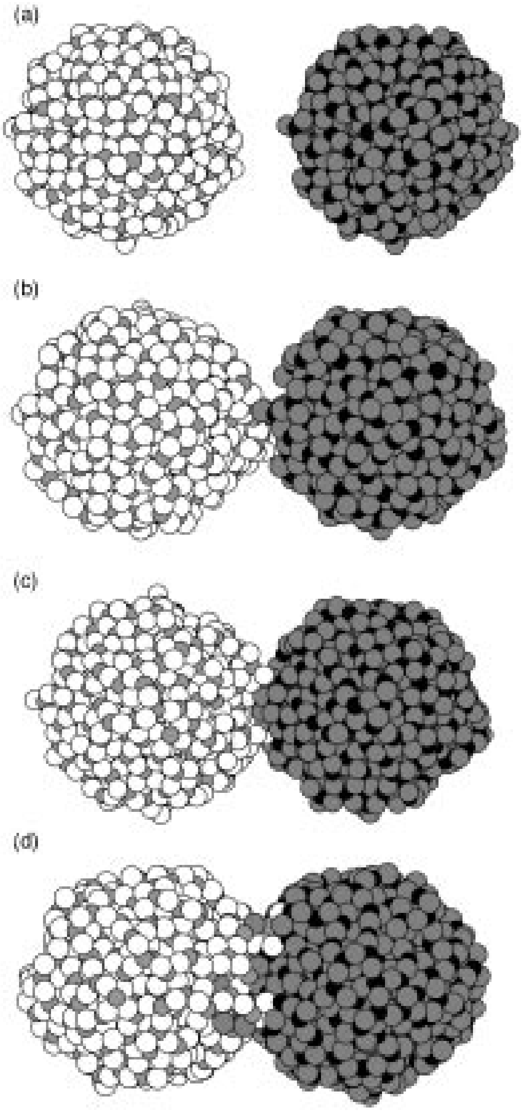

Fig. 1 Time sequence of colliding TiO_2 nanoparticles: at (a) 0.3 ps; (b) 25.5 ps; (c) 27.0 ps; and (d) 288.3 ps. White and dark grey large spheres are oxygen, black and light grey small spheres are titanium. Sequence taken from run A of Table 1.

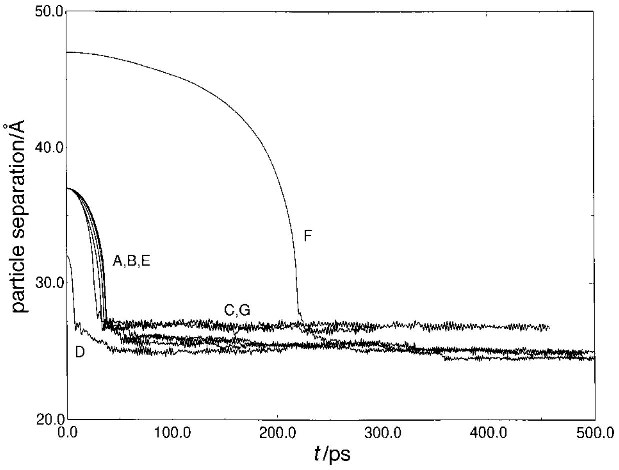

Fig. 2 Nanocluster centres of mass separation *versus* time. Runs A, B, C, E, and G commencing from 37 Å, D from 32 Å and F from 47 Å. See Table 1 for full specification of runs A–G.

Fig. 2 may be differentiated numerically to obtain the force between the nanoclusters. Fig. 3 shows the acceleration plotted as a function of nanocluster COM separation. A number of features are apparent. At long range, the force is attractive (*i.e.*

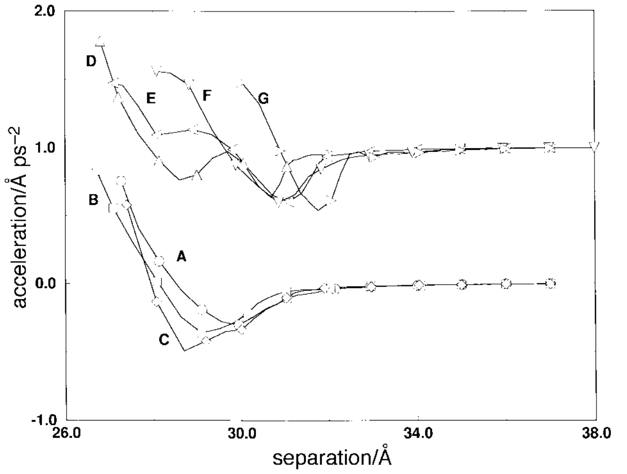

Fig. 3 Calculated inter-cluster forces *versus* nanocluster centres of mass separation, obtained from Fig. 2 by numerical differentiation. Plots for runs D, E, F and G have been raised vertically by 1 Å ps^{-2} for clarity. See Table 1 for full specification of runs A–G.

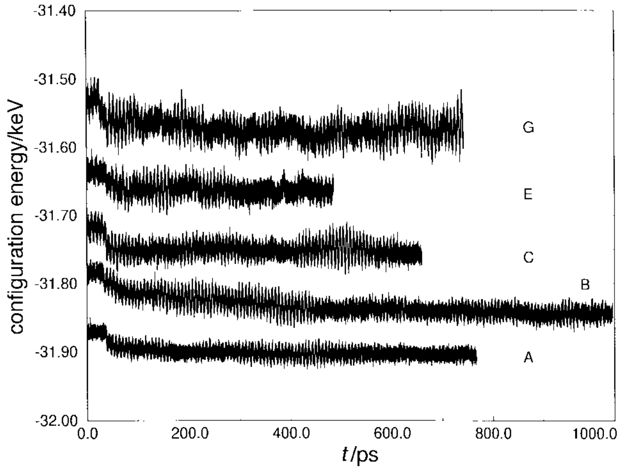

Fig. 4 Configuration energy *versus* time for fusing nanoclusters of TiO_2, taken from runs A, B, C, E and G. See Table 1 for full specification of runs A–G.

negative) and a smooth function of the separation. At short range the force is complicated by contact with the surfaces and may be alternately repulsive and attractive with decreasing separation. The higher temperature runs (D, E, F, G) show significant surface forces at a longer range than the lower temperature runs (A, B, C). It is also apparent that runs D, E, F, which differ only with respect to initial separation, exhibit effects of surface forces at separations which increase with increasing starting separation. These observations imply that the surfaces of adjacent nanoclusters are distorted by the interatomic forces, and that the effect is both time and temperature dependent, the larger initial separation provides a longer time for the surface distortion to take effect, and the higher temperatures increase the mobility of the ions, enhancing the rate of distortion and increasing surface roughness.

In an attempt to characterise the interparticle force at long range, we have fitted the acceleration plot of run F (*i.e.* with the largest initial inter-particle separation) to the function:

$$F(r) = \frac{a_0}{(r-a_1)^m} \tag{2}$$

This gave $a_0 = -12.73$, $a_1 = 28.4$ and $m = 3.6$. Clearly, parameter a_1 is a measure of the nanocluster diameter. The exponent m arises from a combination of the r^{-6} dispersion forces, integrated over the nanocluster volumes, plus any residual electrostatic effects arising from the electrostatic multipoles of the neutral clusters.

Configuration energy

In Fig. 4 we show the computed change in configuration energy with time for the simulations A, B, C, E and G, all of which commence from a cluster separation of 37 Å. The data are subject to large statistical fluctuation (including fluctuation due to the NVT thermostat), but certain features are clear.

All the plots show a sudden drop in energy when the nanoclusters first make contact. This fall we associate with the change of surface energy (*i.e.* loss of surface area) due to the meeting the nanoclusters. This is followed by an interval of *ca.* 30 ps during which configuration energy continues to fall relatively rapidly. It seems probable that this is due to reconfiguration of the surface ions in the contact area, allowing the nanoclusters to settle closer together, effectively ironing out the original surface roughness. There follows a long period of gradual reduction in configuration energy over a timescale of several hundred picoseconds. At least two mechanisms underpin this relaxation. The first is a relaxation of the underlying lattice, particularly of the former surface layers, which must occur as a consequence of the contact between two surfaces. Secondly there is strong evidence for surface ion migration into the contact region (see below), which clearly strengthens the binding between the nanoclusters and lowers the configuration energy. It should be noted that throughout these simulations, the temperature (and hence kinetic energy) showed no change, due to the action of the NVT thermostat.

It is noticeable from Fig. 4 that plot B displays a different behaviour from the others over the range 0–400 ps. It is possible that this is due to inadequate equilibration of the original nanoclusters. However it is clear that the configuration energy does eventually settle to a steady long-time average. This observation underlines the occurrence of long timescales for configurational relaxation in this system.

Notwithstanding the large statistical fluctuations in Fig. 4 and the probable incompleteness of the relaxation process, a crude estimate of the energy of fusion is possible, by subtraction of the long-time configuration energy from the starting value. Thus we obtain an average estimate of *ca.* 34 eV for all simulations excluding run B. This result is obviously dependent on the size of the fusing nanoclusters. Unfortunately statistical uncertainty prevents determination of any temperature effects in this quantity. There is however an obvious temperature dependence in the final observed relaxed energy and we estimate an average difference of 40 eV per 100 degree rise. The corresponding figure for two isolated nanoclusters of 1245 ions, obtained from the heat capacity estimated in ref. 5, is 69.7 eV, a result which indicates either (or both) insufficient equilibration of the merged nanoclusters, or the importance of finite size (and surface) effects in the heat capacity of the nanoclusters.

Effect of ion mobility

To investigate the importance of diffusion in the fusion of TiO_2 nanoclusters we have conducted the following experiment. A 'contact zone' was defined at the centre of mass of the two colliding nanoclusters, perpendicular to the direction of motion, making a slab of thickness ±3 Å either side of the centre. The number of titanium atoms entering this zone as a function of time was then computed. the results are shown in Fig. 5, for runs A, B, C, E and G.

The statistical accuracy of individual collision events is inevitably poor, but some general features are apparent. Firstly, from Fig. 5 it is seen that at first contact (*ca.* 30 ps) approximately 40 titanium atoms enter the contact zone. This number

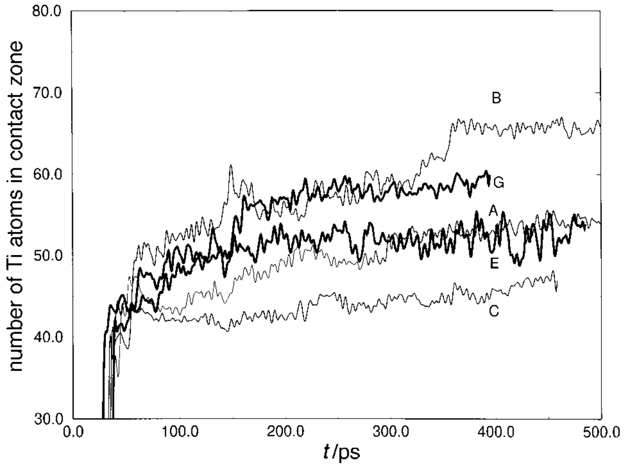

Fig. 5 Migration of titanium ions into the contact zone (±3 Å of the system COM). Plot shows number of titanium atoms in the zone *versus* time. Taken from runs A, B, C, E and G. See Table 1 for specification of runs A–G.

gradually increases, more or less linearly, thereafter, though the final total after 500 ps is different in each case. The entry of more atoms into the contact zone indicates a growth in the interface between the nanoclusters and clearly contributes to the long-term relaxation of energy observed in Fig. 4. It is evidently an important factor in increasing the cohesive energy between nanoclusters. Secondly, from visual examination of the contact zone for the several collisions studied it is apparent that most of this interfacial growth occurs on the periphery of the contact zone, where surface ions are free to enter the zone by surface diffusion. Motion of ions into the contact zone, and even onto the opposite nanocluster is apparent in Fig. 1.

The observation of surface diffusion does not rule out diffusional motion within the contact zone, where near-bulk conditions may be expected to apply. Previous work suggests that bulk diffusion is relatively low in this system,[5] but this applies to an ordered bulk structure, which the contact zone is not.

There is no obvious temperature dependence in these results, given the statistical uncertainty. It is however interesting to note that run B, which shows the most rapid relaxation in the period 0–400 ps (Fig. 4) also shows the greatest rise in the number of ions in the contact zone.

Discussion and Conclusion

The work described here provides a first look at the phenomenon of nanoparticle collision and subsequent fusion of TiO_2, such as may occur in the Chloride process. The simulations are clearly capable of revealing intricate detail of the processes involved, but at a price of high computational cost, which has limited our study to a few key variables only. We have chosen to study effects important to the fusion of nanoclusters, though this is by no means the only aspect which may have been examined.

In addition to our observations above we make the following comments.

All nanocluster collisions we observed took place without fracture or elastic rebound. This however may simply be the consequence of a zero impact parameter and the collision being between two equivalent faces. Finite impact parameters involving glancing collisions, or collisions between dissimilar faces may reveal either fracture, particle exchange or rebound, the observation of any of which would be important in macroscopic modelling of this system. Our own preliminary study of the collision between nanoclusters commencing from nonzero relative velocity[8] suggests that the nanoclusters are stable at relative velocities of up to 10 Å ps^{-1}, considerably higher than the thermal collision velocity for these particles at the temperatures studied, (which is of the order of 0.35 Å ps^{-1} for 1200 K). However the preliminary study was also confined to the (100) faces and zero impact parameter.

The fusion of the nanocluster is a long timescale phenomenon, certainly of the order of a nanosecond or longer. Even our longest simulations (of order *ca.* 1 ps) cannot be said to have equilibrated. However, the basic mechanisms for nanoparticle fusion are clear and three stages can be identified: contact, in which the nanoclusters are drawn together and held by mutual surface forces; locking, in which the reduction in surface roughness in the contact zone allows the closer approach of the nanoclusters; and fusion, in which the migration of surface ions into the contact zone increases the area of contact. Ultimately it is expected that the equilibrated fused nanoclusters adopt the structure of a single rutile nanocrystal, though clearly on a time scale beyond the limits of our simulations.

The simulations have failed to show any significant effect of temperature on the basic phenomenon of fusion. It is clear however that in the Chloride process, the 'stickiness' of TiO_2 microparticles is strongly dependent on temperature.[3] Our limited results imply that the fusion of bare nanoclusters is inevitable, regardless of temperature. However the chemistry of the Chloride process suggests that the nanocluster surfaces are probably contaminated with chlorine, which would clearly interfere with the fusion process as described here. The observed temperature dependence in the microparticle fusion may thus be a consequence of the thermochemistry of chlorine adsorption and desorption.

The description of the fusion of two nanoclusters given here is obviously relevant to the more general process of sintering under which powders can be made to fuse into a solid mass at high temperature (and/or pressure). This is a wide subject, but one in which MD simulation has a significant part to play (see *e.g.* ref. 9). In the case of TiO_2 powders it is clear that the surface mobility of ions at the grain surface, observed in our simulations, will play a important role in the sintering process.

In conclusion we have shown the collison and subsequent fusion between nanoparticles of TiO_2 to be a complex process with many subprocesses, some of which occur on the nanosecond timescale. Overall the phenomenon is amenable to detailed study by molecular dynamics, which therefore promises to yield further valuable insight into the industrial Chloride process.

The authors thank Daresbury Laboratory for computer time on the Intel iPSC/860. M. J. Westwood (Tioxide Ltd), R. J. Blake, J. Carter and D. P. Cokljat (Daresbury) are thanked for useful discussions. D.R.C. is grateful to EPSRC and Tioxide Ltd for funding under the ROPA scheme.

Referencse

1 S. Semancik and R. E. Cavuchi, *Appl. Surf. Sci.*, 1993, **70/71**, 337.
2 D. Gaskell, *Chem. Br.*, 1995, 432.
3 J. G. Carter, D. Cokljat, R. J. Blake and M. J. Westwood, *Parallel Computational Fluid Dynamics: Implementation and Results Using Parallel Computers*, ed. A. Ecer, J. Periaux, N. Satofuka and S. Taylor, Elsevier Science B.V., Amsterdam, 1995, p. 113.
4 M. P. Allen and D. J. Tildesley, *Computer Simulation of Liquids*, Clarendon Press, Oxford, 1979.
5 D. R. Collins, W. Smith, N. M. Harrison and T. R. Forester, *J. Mater. Chem.*, 1996, **6**, 1385.
6 M. Matsui and M. Akaogi, *Mol. Simul.*, 1991, **6**, 238.
7 W. Smith and T. R. Forester, *J. Mol. Graphics*, 1996, **14**, 136.
8 D. R. Collins, W. Smith, N. M. Harrison and T. R. Forester, unpublished work.
9 H. L. Zhu and R. S. Averback, *Mater. Manufact. Process.*, 1996, **11**, 905.

Paper 7/04673A; *Received* 3*rd July*, 1997