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Problems of particle aggregation in ceramics☆

Kevin Kendall

Chemical Engineering, University of Birmingham, B15 2TT, UK

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Abstract

Three types of problem are presented to illustrate the thesis that small interatomic forces between ceramic particles have a major influence on the aggregates formed during processing and on the final ceramic product microstructure and strength. The first is a theoretical problem of ceramic particle aggregation to define the weak interatomic forces between spheres. The second concerns the better processing that can be applied to dispersed particles to deliver improved ceramic properties by adding polymer to ceramic dispersions to reduce particle attractions which lead to aggregation. The last is the application of polymer extrusion to make improved ceramic fuel cells which can start up in a short time to provide auxiliary power to new applications. The conclusion is that understanding and controlling weak aggregation forces between particles during powder processing can lead to better ceramic microstructures and products.

Keywords: Problems of ceramics; Contact mechanics; Polymer processing; Ceramic fuel cells

1. Introduction

Consider first the interatomic forces between ceramic particles. When two smooth elastic surfaces approach each other to attain molecular contact, there is the question of how the deformations are affected by the atomic attractions due to electromagnetic forces. This problem was solved in 1971 by considering the energy balance between two spheres under the influence of both elastic and atomic forces.[1] The results showed that the attractive forces were reduced by immersing the spheres in water and further diminished by adsorbing polymer molecules on the surface, as described in Israelachvili's book on colloidal interactions between particles.[2] Measuring the very small forces under these circumstances has now been achieved using a laser tracking technique. This illustrates how aggregates can form as a result of small attractive forces in a particle dispersion.

The second question is about the preparation of complex shaped ceramics without defects so as to produce products with better electrical and mechanical properties. This has been a fundamental problem for the manufacturer of cement, pottery and technical ceramics from the earliest times. Because ceramics are usually sintered together from compacted nanoparticles, the natural defects need to be removed in the powder mixing process if they are not to remain in the final piece to cause rejection and premature failure.[3] It turns out that, after removing extraneous contamination, these defects are aggregates caused by the weak interatomic attractions above. Adding polymer and shearing the ceramic formulation through extrusion is shown to reduce these defects considerably.

The third issue relates to the invention of new ceramic devices. In particular, the energy market requires new efficient electricity generators, for example fuel cells. The ceramic fuel cell (Solid Oxide Fuel Cell [SOFC]) is the most efficient device yet invented for converting organic fuels like methane or propane into electrical power. Yet, even though the original ceramic electrolyte was discovered by Nernst in 1897, there is still no commercial market for SOFCs in power generation, largely because the ceramic cells crack too easily during warm-up. By extruding zirconia tubes using polymer processing to get rid of aggregates,[4] better microstructures with good thermal shock resistance have been produced. These can be heated rapidly to the 700 °C operating temperature and can be applied as auxiliary power units in vehicles.

This paper shows first how the weak interparticle forces causing aggregation can be measured, goes on to prove that powder aggregates act as defects which reduce strength, and finally demonstrates improved ceramic SOFC tubes which can

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E-mail address: K.Kendall@bham.ac.uk

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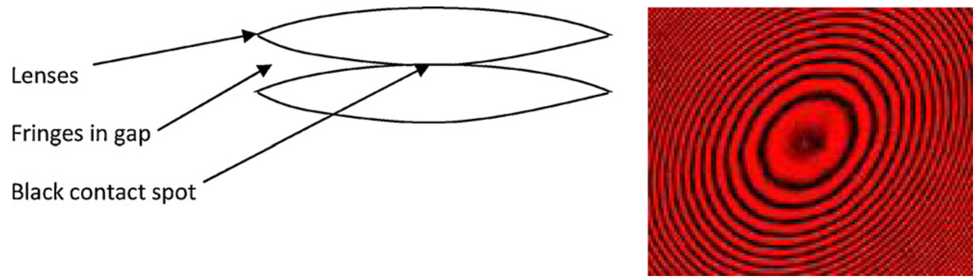

Fig. 1. The contact of glass lenses indicating the black contact spot and Newton's rings.

be heated rapidly without thermal shock to provide auxiliary power in new applications.

2. Ideas about interatomic forces

Isaac Newton used the inverse square law of gravitational attraction around 1665 but stated later that 'The Attractions of Gravity, Magnetism and Electricity. . .have been observed by vulgar Eyes. . .there may be others which reach to so small distances as hitherto escape Observation'.[5] By this he could have meant that short range interatomic forces reaching about one nanometre from the surface of a ceramic particle could make the particles aggregate. It is interesting that Newton spent about 30 years working on ceramics including antimony oxide, copper oxide, calcium carbonate, etc., far longer than he spent on gravitation and he wrote hundreds of thousands of words on these experiments, most of which were wrong because some elements such as oxygen were yet undiscovered. In 1669 he set up a furnace in Trinity College Cambridge and studied the firing of ceramic mixtures. He was also a great polisher and made lenses for his telescope. He brought two convex glass lenses together and looked at the contact which appeared as a circular black spot at the point where the glass lenses touched. He then explained the diameters of the surrounding rings, now known as Newton's rings, in terms of the geometry of the gap between the curved surfaces (Fig. 1). Newton remarked that 'I found the place in which they touched to become absolutely transparent, as if they had there been one continued piece of glass'. Based on this idea, one would expect considerable strength to be built up at the junction, making the lenses adhere. He noticed that there were scratches or dust particles in the black spot which affected molecular contact, but claimed 'Two polish'd marbles. . .by immediate contact stick together'

Hertz[6] disagreed with Newton, finding that smooth spheres pressed together exerted no adhesion and no friction. As a student in 1880, during his Christmas vacation, he produced an elastic theory of sphere contact and later verified this by measuring the black spot between equal contacting glass and metal balls. His theory assumed a hemispherical pressure distribution across the contact circle, allowing him to calculate the diameter of the black spot d in terms of the sphere diameter D, the applied force F and the elastic moduli E and ν.

$$d^3 = \frac{3(1-\nu^2)DF}{E} \tag{1}$$

This theory has been universally applied to explain the contact of ball bearings, of train wheels on rails, and of tyres on roads,[7] demonstrating that the forces of elastic deformation are dominant in many engineering situations, and that adhesion due to interatomic forces between ceramic spheres can be neglected.

However, when studying for a PhD in 1968, repeating the Newton and Hertz tests on glass lenses, but now using ultrasonics as well as optical viewing to measure the contact spot, the author[8] found that the contact spot was bigger at low loads than expected from Hertz elastic theory, as shown in Fig. 2.

Of course, there is a problem with glass and ceramics. The surfaces are very stiff and do not make molecular contact because a nanoparticle of dust can cause separations of more than 1 nm as shown in Fig. 3a. So the results shown in Fig. 2 are unreliable as Newton had remarked. On the next bench in the Cavendish Laboratory, Roberts[9] was doing similar experiments on windscreen wiper blades made from very smooth transparent rubber. This is different from glass in its compliance which allows small dust particles and scratches to be surrounded and isolated as shown in Fig. 3a. Consequently, the effect of increased contact spot diameter observed on glass lenses was revealed most clearly with the smooth rubber which deformed around the dust contamination. The resulting black spot had defects within it but was so large and clear (Fig. 3b) that the attraction of the solid surfaces pulling each other together could not be ignored.

Across Trumpington Street in Cambridge, Johnson[10] had already produced a theoretical description of the contact between adhering spheres by adding two stress distributions, the hemispherical Hertzian compressive pressure distribution for zero adhesion and the Boussinesq field derived in 1880 for a rigid punch sticking to an elastic surface by short range attractions.[7] This predicted a non-Hertzian pressure distribution across the contact spot as shown in Fig. 4b. The stress at the edge of the

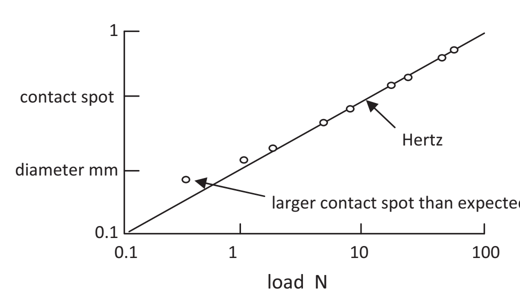

Fig. 2. Contact spot diameter between glass lenses measured optically and by ultrasonics.

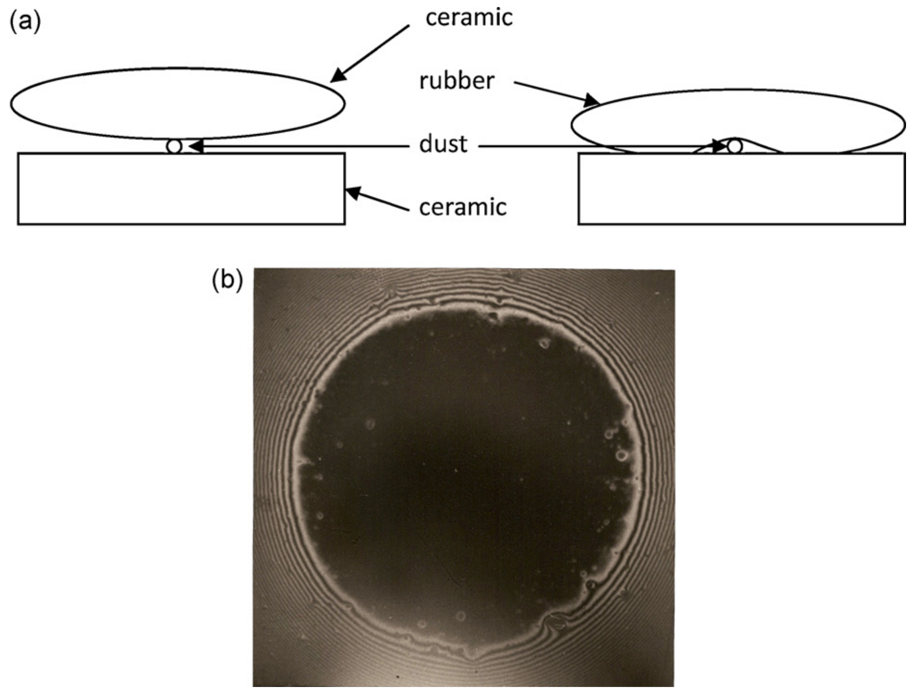

Fig. 3. (a) Effect of surface deformation on rubber contact contrasted to ceramic, showing that the rubber is compliant enough to deform around the dust contamination. (b) Newton's rings and black contact spot between rubber spheres showing the molecular contact with a few dust particles revealed as white blips.
Picture from Alan Roberts, with permission.

contact became tensile and infinite, as in a crack. This Boussinesq distribution had previously been used by Kendall[1] to explain the adhesion of a flat rigid punch to an elastic half-space, by applying a Griffith-like[11] fracture mechanics approach previously verified by Obreimoff in 1930.[12] Using the same energy balance argument to analyse the combined stress picture in Johnson's pressure distribution (Fig. 4b) allowed the Johnson Kendall Roberts (JKR) equation to be derived and compared to the experimental results.[13]

The JKR equation gave the increased diameter d of the black contact spot between two equal spheres

$$d^3 = \frac{3(1-\nu^2)D\{F + 3\pi WD/4 + [3\pi WDF/2 + (3\pi WD/4)^2]^{1/2}\}}{E} \tag{2}$$

to compare with the Hertz contact diameter where E is the Young's modulus, ν the Poisson's ratio, D the sphere diameter, F the normal load and W the work of adhesion, that is the energy required to separate 1 m^2 of contact reversibly. Clearly the work of adhesion W, the equilibrium energy of the van der Waals bonds required to separate unit contact area, is increasing the contact spot size by addition of the three extra terms to the Hertz equation.

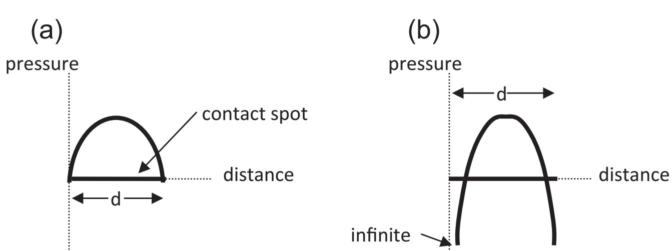

Fig. 4. Pressure distribution across black spot contact; (a) Hertz and (b) JKR.

Fig. 5b shows on linear scales how the adhesion increases the black spot diameter over the Hertz value for rubber. Fig. 5a shows on logarithmic scales how the JKR theory approaches Hertz at high loads, but levels out at low loads to give a contact spot about 0.6 mm in diameter. The value of W required for the fit was 71 mJ m^{-2} which corresponds to van der Waals forces between CH_2 groups on the rubber molecules. Although the equation does not apply very well to large glass lenses, because of surface roughness, it does apply to sub-micrometre scale ceramic particles which behave like rubber and stick very readily to cause powder process problems as shown below. Of course, for very small particles, less than 1 nm in diameter, the atomicity will cause the continuum equations above to fail, so molecular modelling is then required.[14]

Another substantial effect shown in Fig. 5a is the reduction of adhesion force when contaminant molecules are applied to the surfaces. Water reduced the work of adhesion W to 6.8 mJ m^{-2} and Sodium Dodecyl Sulphate (SDS) surfactant dropped W further to 0.7 mJ m^{-2}.

3. New method for measuring ceramic particle aggregation due to small forces

The idea that interparticle forces can be diminished by adding water and surfactants is an ancient one, used in dispersing pigments like Indian Ink.[14] Ceramists often disperse fine particles in water and detergent before filtering and compacting prior to the drying and sintering steps. But the process of observing aggregation in the particle dispersion has been unsatisfactory because

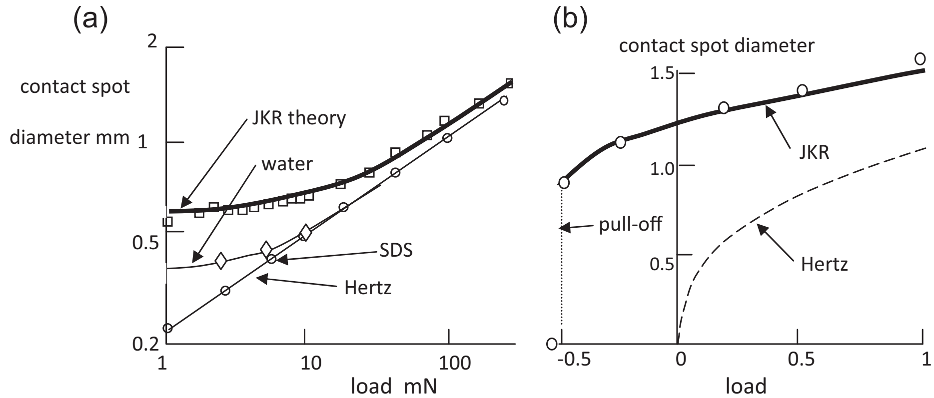

Fig. 5. (a) Results for contacts between two rubber spheres measured optically on log scale.[13] (b) Results for black spot diameter plotted on linear scale showing tensile loads.

dynamic light scattering (DLS), a commonly used method of measuring particle size distributions, has been unable to resolve doublets and triplets as the particles stick together, giving a single peak as in Fig. 6b.

A new instrument has now been used to show that such small aggregates can be seen and resolved, changing the way in which we understand ceramic aggregation. The new equipment is the Nanosight apparatus which comprises a window containing the nanoparticle dispersion viewed vertically using an optical microscope, a horizontal laser beam causing the nanoparticles to scatter light to reveal the Brownian movement of the nanoparticles, and a movie camera/computer tracking system which measures the particle diffusional random walk, then plots the size distribution calculated from Stokes–Einstein theory.[15–19] A typical track picture for 62 nm diameter (TEM result) monosize hematite particles is shown in Fig. 6a, with the computed particle size distribution shown superimposed on it. Of course, such small particles cannot be imaged using visible wavelengths, but the scattered light from each nanoparticle gives sufficient visibility for microscopic detection. The result shows that the particles display a hydrodynamic diameter about 90 nm but there is also a second peak of doublet aggregates and a third peak of triplets plus a smaller number of larger aggregates.

This is not expected because the dynamic light scattering (DLS) measurement of Fig. 6b reveals only a single peak, suggesting that the hematite particles are fully dispersed and

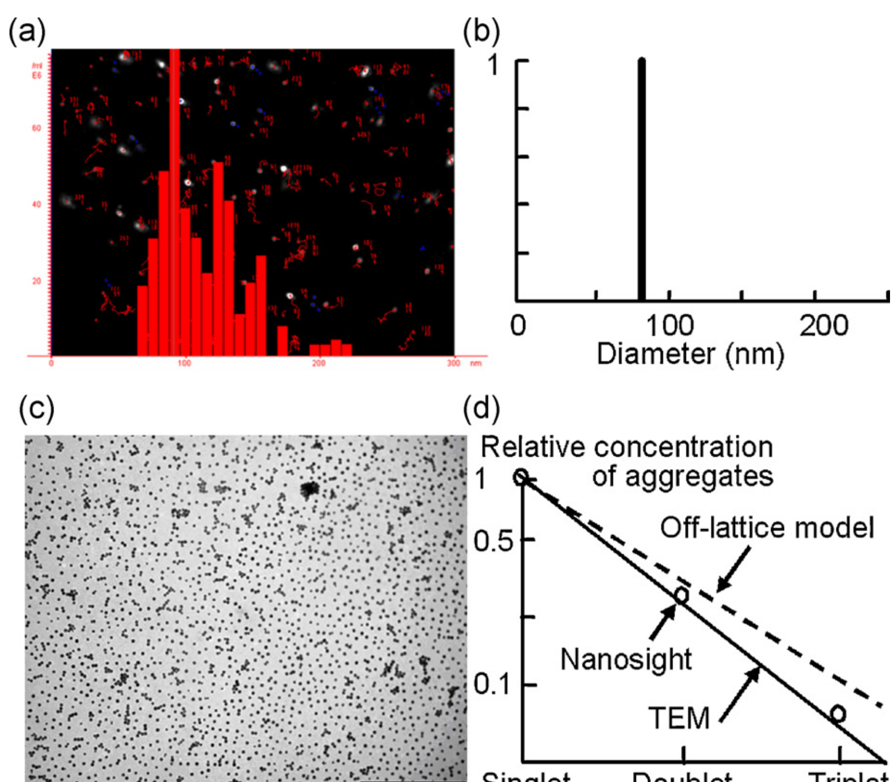

Fig. 6. (a) Nanosight results for a monosize hematite dispersion 62 nm particle diameter. (b) Dynamic light scattering result for the same dispersion. (c) Transmission electron micrograph (TEM) of the hematite. (d) Comparison of Nanosight and TEM results for singlets, doublets and triplet aggregates.

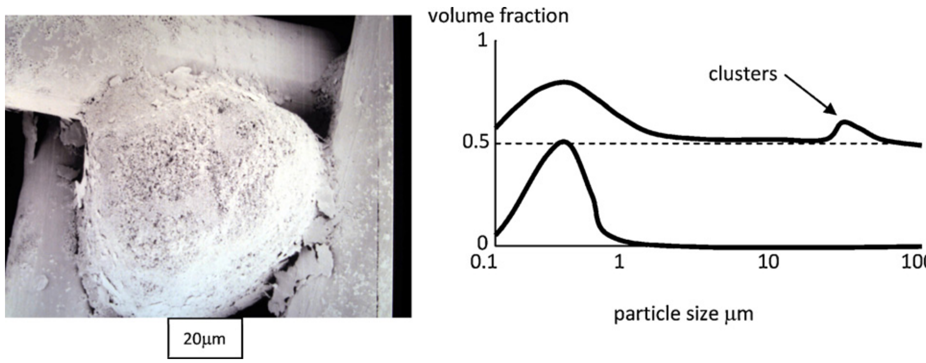

Fig. 7. Left; filtered cluster of titania formed from a perfect nanoparticle suspension by drying. Right; malvern size distributions of perfect suspension (bottom) and dried redispersion (top) showing the 60 µm clusters. The top curve has been displaced upwards for clarity.

non-aggregated. However, transmission electron microscopy (TEM, Fig. 6c) shows clearly that, although most of the particles are singlets, there is a range of doublets, triplets, etc. up to larger aggregates of 16 particles. By counting the distribution of aggregates and comparing with the numbers measured in the Nanosight instrument, Fig. 6d shows that the TEM and Nanosight results are in reasonable agreement, but slightly lower than the off-lattice model prediction based on a square well interaction potential.[20] These results, perhaps surprising because the TEM pictures are of dried dispersions which may change during the evacuation process, show that the number of doublet aggregates can be measured by this new laser scanning method in real time in real environments in contrast to DLS which cannot distinguish closely spaced aggregate peaks.[21] The conclusion from this study is that ceramic particles which seem to be fully dispersed must contain small aggregates, doublets, triplets and higher clumps. Forces as low as femto-Newtons are causing this statistical aggregation effect in competition with the thermal collisions which tend to break up the aggregates.

4. Aggregates as defects in processing of ceramics

The problem with aggregation of ceramic particles is that large clumps can grow to become embedded in the moulded compact, then form a crack during sintering as the aggregate shrinks differently from the surrounding green body. Fig. 7 shows the result of filtering a dispersion of titania particles 0.25 µm in diameter.[22] Several large agglomerates around 60 mm in size were discovered. These large clusters of the nanoparticles were detectable in the Malvern laser diffraction instrument by comparing the original perfect dispersion with a slurry formed by redispersing the dried suspension. It was evident that the primary particle peak had increased in breadth, but more noticeably, large clusters had formed around 60 µm in diameter. These clusters could act as defects in the final sintered ceramic, in addition to the contaminant defects such as lint and gas bubbles discussed in detail by Lange.[23]

In order to test the idea that aggregate defects were the principal determinants of ceramic properties, experiments were carried out on commercial alumina powders, polishing the fired surfaces to reveal the statistical distribution of aggregate defects, to compare with the Weibull distribution of bend strengths.[3] First, powder pressed alumina was tested, then polymer extruded rods were compared. Fig. 8 shows two pictures of polished surfaces of dense alumina samples. The first, powder pressed, contained large aggregate defects up to 100 µm in size when measured by image analysis. The second, polymer extruded showed much smaller defects around 10 µm in size.

The significant result was that the flaw statistics observed on polished surfaces of the ceramic corresponded to the Weibull statistics of strength measurements.[3] It was evident that powder pressing of a standard alumina (Reynolds HPBDM) left substantial flaws in the fired product, some more than 100 µm

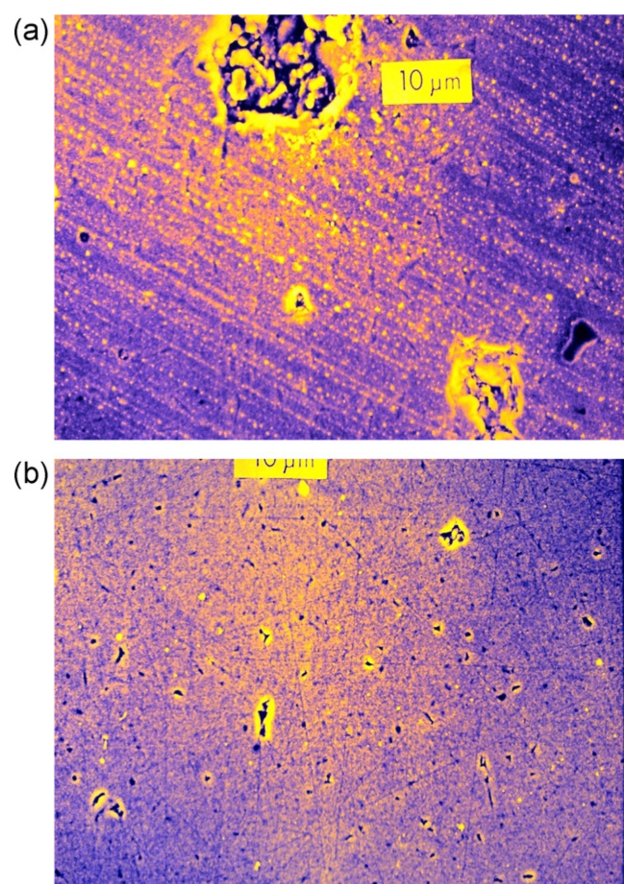

Fig. 8. (a) Polished surface of pressed alumina showing large aggregate defects. (b) Extruded alumina polished surface showing much smaller defects.

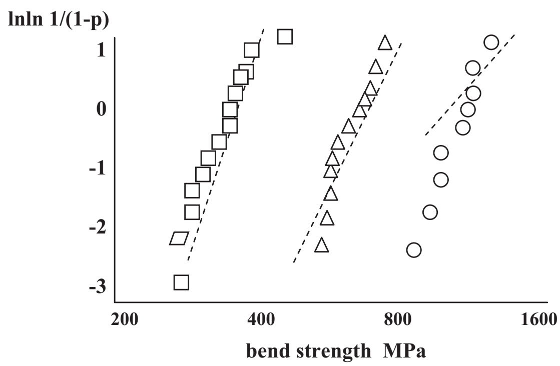

Fig. 9. Weibull plots of alumina bend strength, comparing strength (experimental points) and measured flaw statistics (broken lines). Left curve, Reynolds alumina by press compaction; middle curve, Reynolds alumina by soluble polymer addition and intense shearing at 10 MPa wall shear stress in extrusion; right curve, Sumitomo alumina by intense plastic shearing.

in length, although the individual ceramic grains were less than 1 μm. When the same material was dough mixed with 40 wt% polyvinyl alcohol aqueous solution, the same result was obtained. Slip casting gave similar flaw statistics. But when the dough mix was intensively sheared at 10 MPa shear stress by extrusion, the flaws were reduced in size as shown in Fig. 8. This indicated that large, soft agglomerates were being smashed in the plastic process. Further increase in shear stress to 20 MPa gave no further improvement, suggesting that hard agglomerates were resisting breakdown. Moving to a weaker alumina powder (Sumitomo AKP30) and using the same process showed a strength of 1042 MPa, and the flaws were much smaller. The three corresponding Weibull plots are given in Fig. 9. Our conclusion is that the flaws are aggregates in the bag of powder and that the compaction and the sintering cannot easily remove them. Consequently, the powder processing must be improved to get rid of agglomerates. Soluble polymer addition and high shear extrusion appears to be a good way of achieving this.

5. New ceramic products

Applications of ceramics in new products often require improved microstructures and properties which cannot readily be obtained by traditional processes. A typical example is the Solid Oxide Fuel Cell (SOFC) which can produce electrical power from a fuel using yttria stabilised zirconia as electrolyte in an electrochemical device. Such a device could be used to replace combustion engines to provide power twice as efficiently and with near-zero-emission. Although Nernst invented the zirconia fuel cell formulation in 1897,[4] no commercial product has yet been successful.

The need for such clean energy generators is now acute. A recent paper[24] has demonstrated that if every home in the UK used a SOFC to provide combined heat and power, 25% of the gas bill would be saved, a benefit estimated to be £10 bn/a, with additional consequences to fuel import security, plus 25 Mte/a of carbon saving.

Various attempts have been made to market SOFCs using powder pressed tubes,[25] vapour deposited layers on support tubes[26] and tape cast plates.[27] The SOFC requires thin, impermeable, long-lasting material fabricated into several layers including anode, electrolyte, cathode and interconnectors. Powder pressing gave thick and weak tubes, vapour deposition took too long, and tape-casting produced nice sheets but had difficulties of thermal shock, interconnection and sealing.

The key factors which seemed to be retarding SOFC progress in 1990 were

(1) Processing of high quality ceramic membranes
(2) Long start-up times of 2–10 h
(3) Interconnection of large numbers of cells

By making use of the plastic extrusion processes described above, it was discovered that thin-walled microtubes of yttria stabilised zirconia (YSZ) could be extruded and sintered at 1400 °C

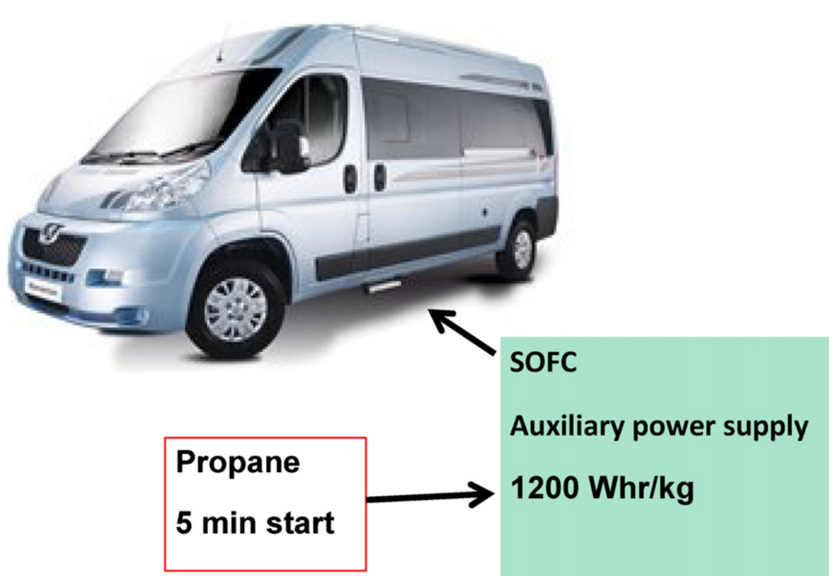

Fig. 10. Recreational vehicle with microtubular SOFC power pack running on propane.

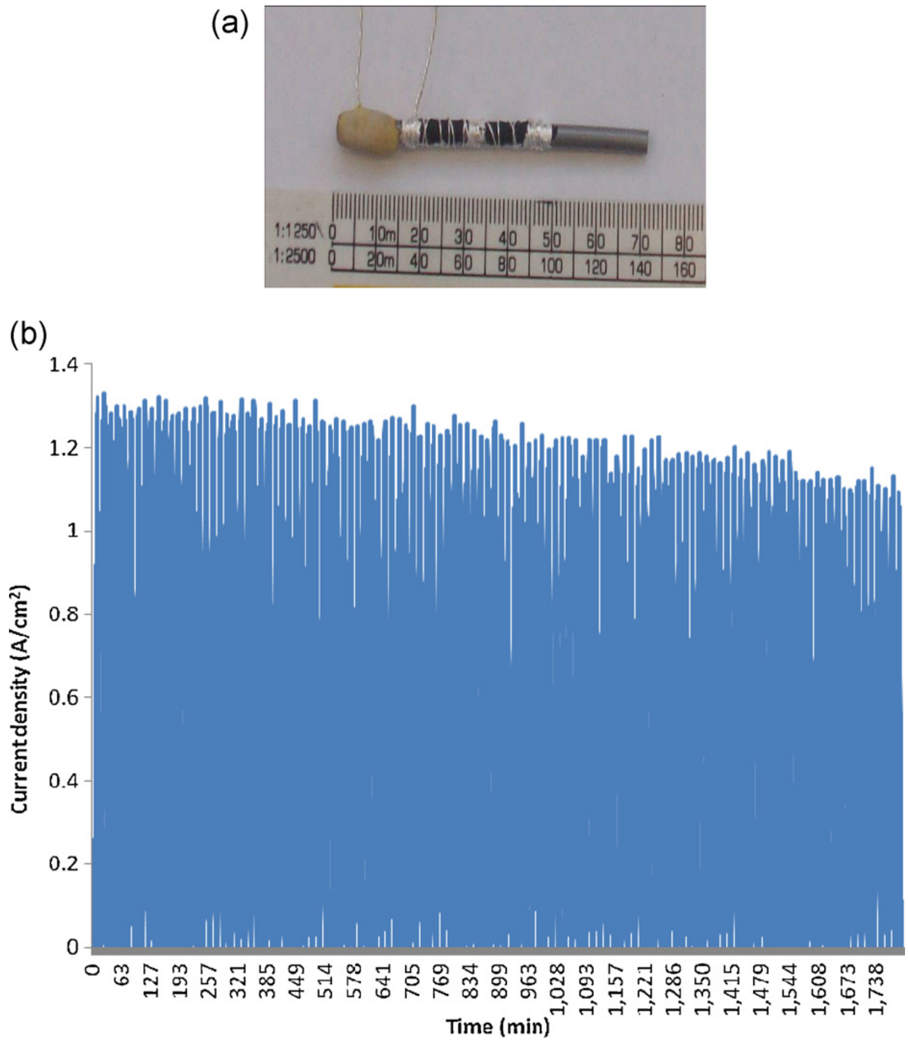

Fig. 11. (a) 2 mm diameter microtubular SOFC; (b) thermal cycling results on single cell showing slight degradation in current density.

to produce high quality cells. Moreover, cells of 2 mm diameter could be heated and cooled very rapidly without thermal shock problems to give start-up times about 10 s.[28] Co-extrusion was also demonstrated to produce a YSZ/nickel tubular anode covered by a 10 μm electrolyte layer, thin enough to give the low ionic resistance required, and a 1000 tube reactor was built to demonstrate a small combined heat and power (CHP) device running on natural gas.[29] A number of companies have picked up these ideas and are developing products for the market, including Adaptive Materials, Acumentrics, Protonex, Catator, Ezelleron.

At present, the CHP market in Europe is beginning to look attractive for 2015, but other portable power applications do seem to be needed more urgently as shown by the recreational vehicle (RV) in Fig. 10. In this application the SOFC competes with combustion engine generators which are cheap and effective but are being banned in National Parks because of noise and emissions. The SOFC is combined with a battery to give a hybrid system which can operate at low power, about 200 W continuous, yet provide peaks of 1000 W for the fridge, TV, computer and other loads.

Some research and development is still necessary on this device because the lifetime is only 1000 h and the number of start-up cycles about 100. Further improvement of the materials and system design should give higher life and cycling durability in the next few years, as described in the recent International Conference on SOFCs in Montreal.[30]

6. Conclusions

Ceramics have had an enormous influence on our view of the world, and continue to stretch our intellects in terms of the theory of material structure, the development of improved processes, and the introduction of cleaner and more efficient devices.

By considering the fundamental atomic forces, we can begin to understand how ceramic particles stick together, using equations which describe the contact stresses. It has become clear that ceramic processing is limited by such particle adhesion and that more perfect ceramic microstructures can be produced by controlling the aggregation effects during nanoparticle compaction. Having produced more perfect ceramic materials, it is then possible to make new products such as fuel cell membranes which can resist thermal cycling, as shown in Fig. 11. The 2 mm diameter tubular cell was repeatedly cycled between 200 and 800 °C, while measuring the current density at 0.5 V potential.[31] Although there was some degradation in the current density, the results showed that the cell could resist vigorous thermal cycles, suggesting that such devices might be used in rapid heating applications such as CHP and RVs.

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