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Problems of particle aggregation in ceramics☆

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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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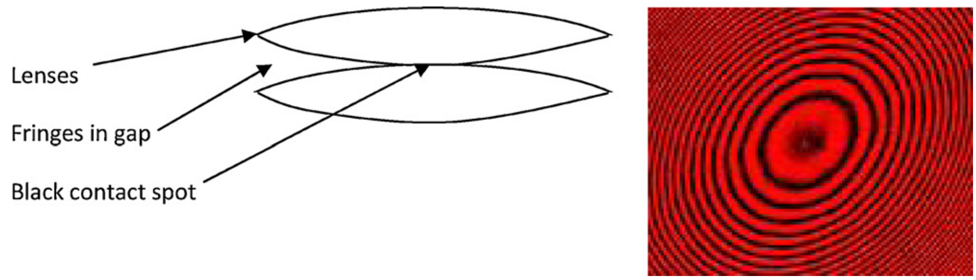

Fig. 1. The contact of glass lenses indicating the black contact spot and Newton's rings.

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

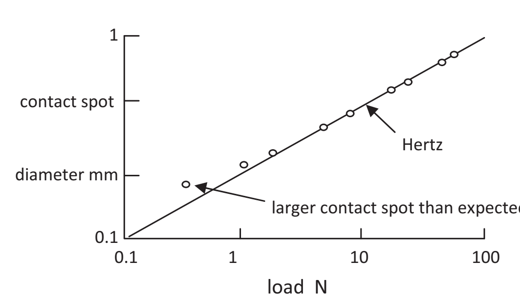

Fig. 2. Contact spot diameter between glass lenses measured optically and by ultrasonics.