Rate of creation of the contacts between grains in a loose array of particles submitted to an uniaxial pressure

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Abstract. Macroscopic resistivity measurements have been performed on TiC/Al_2O_3 random mixtures submitted to uniaxial compression (0–95 kN). Such a random mixture exhibits an insulator-conductor transition which appears at increasing force while decreasing the conductive composition of the TiC/Al_2O_3 mixture. It is demonstrated that the conductivity behavior may be understood in the framework of a site percolation model. Finally, the rate of creation of the contacts between conductive grains is extracted from the macroscopic resistivity measurements.

PACS. 45.70.Cc Static sandpiles; granular compaction – 72.80.Tm Composite materials

1 Introduction

In most applications for powder metallurgy, concern with properties dictates that high densities be achieved in compaction. An external pressure is needed to both shape the powder and promote higher packing densities. The initial transition with pressurization is from a loose array of particles to a closer packing. The first response is rearrangement of the particles, giving a higher contact density between grains. The rearrangement portion of compaction is aided by hard particle surfaces (such as with oxides). For metals, the point contacts subsequently deform as the pressure increases (Hertz regime). Finally, metal particles undergo extensive plastic deformation. For hard materials (such as oxide or carbide), both fracture and deformation are expected. The higher pressure behavior corresponds to the fragmentation process while, in the lower pressure behavior, generally appears plastic deformation events.

As the properties of granular media are known to depend on the geometrical properties of the system, on the properties of the grains themselves, but also on the properties of contacts between grains, electrical conductivity of packings of conducting spheres submitted to uniaxial pressure has been studied by Ammi *et al.* [1].

For a packing of conducting spheres or cylinders submitted to an uniaxial pressure, the macroscopic conductivity of the system, derived from Hertz microscopic law [2], is expected to vary as $\sigma \propto F^t$. Such a law is not true on the whole range of force. At low stress, grains rearrange by rotations and local slidings and Hertz deformations play a little role. As a consequence, the power law is not valid. At intermediate stress, all possible contacts between grains are not created and the macroscopic resistivity varies because of "Hertz effect" and because of

contact density variations. At large force and for all contacts realized, one expects $t = 1/3$ (microscopic exponent derived from Hertz law). Practically, the plasticity threshold is reached long before and other processes like fracture may occur. As a consequence, the experimental exponent t varies from $1/3$ to $5/3$, depending on the powder under study. Generally, the exponent t is observed on one or two decades in pressure. Two models have been proposed to describe the electrical exponent t. In a first model, an effective medium theory which takes into account the variation of the density of randomly distributed good electrical contacts and the variation of the contact conductance with applied stress has been considered [1]. As it is known that good contacts are not at all random but rather lie along strength arms, the second model [1] deals only with the backbone of the mechanical network (strongest stresses network). The results described above only deal with packing of conducting spheres. However, interesting informations may be extracted from data registered with mixtures of insulating and conducting hard materials. In this case, compaction process mostly consists in a rearrangement of the grains. Thus, mixture conductivity depends on the arrangement state through the density of links between conducting grains (active links). From different composite compositions submitted to uniaxial pressure, one can study a model system for which the active link density depends on the volume fraction of conducting phase and on the applied force. Provided that one is able to determine the variation of the contact density with the conducting phase volume fraction, the density of contacts between conducting grains may be determined. Our goal, in this study, deals with a better understanding of the contact density variation with applied uniaxial pressure.

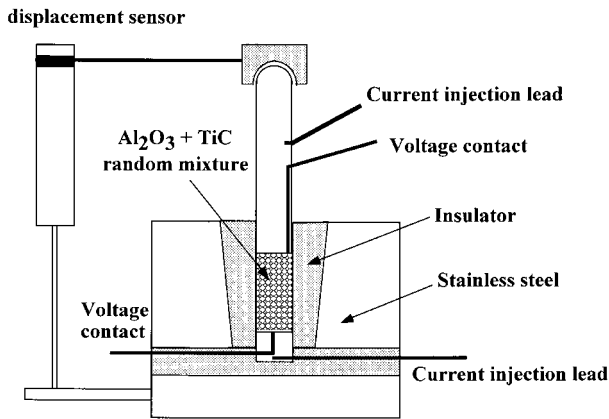[a] e-mail: `sylvain.dubois@univ-poitiers.fr`
[b] UMR 6630 CNRS

Fig. 1. Schematic representation of the home-made cell used for resistance measurements under uniaxial compression.

2 Experimental details

Conducting TiC and insulating Al_2O_3 particles of mean diameter 18 μm were used in this study. TiC and Al_2O_3 powders are weighted in order to obtain mixtures with different TiC (Al_2O_3) concentration in the solid phase $\phi_{TiC}^{(s)}$ (respectively $\phi_{Al_2O_3}^{(s)} = 1 - \phi_{TiC}^{(s)}$). Powders are then mechanically mixed in a turbula during 20 min in order to obtain random mixtures. SEM analysis was performed to check the uniformity of the mixtures; SEM micrography and X-ray cartography analysis do not indicate segregation of the two phases. As a consequence, it is assumed, in the study, that the mixture is uniform. A constant weight (0.5 g) of the mixture is packed in a cylindrical home-made cell (see Fig. 1) in order to apply uniaxial vertical pressure. The internal vertical walls are insulated with Al_2O_3 and the upper and lower walls consists in stainless steel which allows one to prevent deformation of the cell and insure electrical contacts. The samples are placed in an MTS 810 universal testing machine and a uniaxial vertical pressure is applied, growing from 0 to 95 kN. Electrical resistance measurements are performed as a function of applied force with a Keithley high performance multimeter (model 2000) which allows us to monitor either the voltage drop (current source mode), either the current flow (voltage source mode) or the resistance (ohmeter mode) depending on the resistance range to be measured. The measurements are done at increasing pressure as the force is no more uniaxial on the decreasing part of the hysteresis [3]. A displacement sensor also allows to monitor the height (h) of the pellet during uniaxial compression. As the aspect ratio of the pellet is quite large (*i.e.*: diameter over height is about 5), the inhomogeneous distribution of force in the container has been neglected. This assumption has been confirmed. Indeed, the resistance increases monotonically with the number of layers and the differential resistance (slope of the the curve $R(h)$) is constant provided that the aspect ratio of the pellet is larger than about 3. From the height of the pellet, it is also possible to determine the volume fraction of TiC (ϕ_{TiC}), the vol-

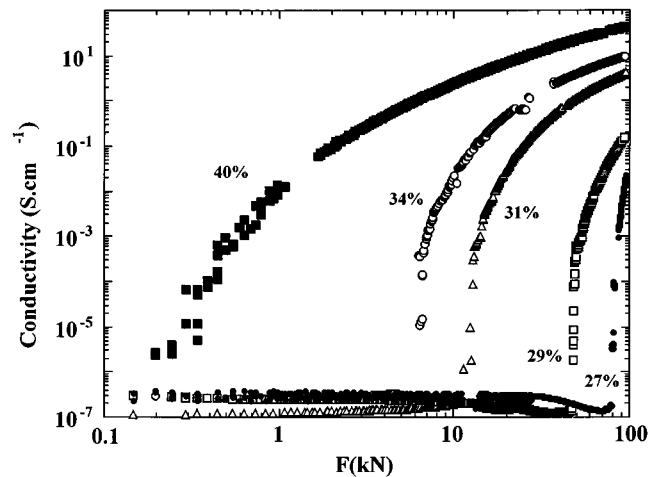**Fig. 2.** Conductivity *vs.* force applied on TiC/Al_2O_3 random mixtures with different TiC volume fraction in the solid phase ($\phi_{TiC}^{(s)}$).

ume fraction of Al_2O_3 ($\phi_{Al_2O_3}$), the porosity (ϕ_p) of the random composites and its variations with applied force.

3 Results and discussion

Figure 2 shows the conductivity as a function of the applied force for different TiC($\phi_{TiC}^{(s)}$)/$Al_2O_3(\phi_{Al_2O_3}^{(s)}$) random mixtures. For small applied force and low concentration of the conducting phase, the conductivity is about 10^{-7} S cm^{-1}; the mixture conductivity is dominated by the insulator. For larger applied force, the mixture conductivity largely increases and the random mixture becomes conductive. The force intensity (F_c) which corresponds to the insulator-conductor transition increases for decreasing concentration of TiC in the solid phase. This result is in qualitative agreement with previous data obtained on mixtures of glass spheres and silver coated glass spheres [4]. However, the power law ($\sigma \propto F^t$) extracted from a packing of conducting spheres can not give account of the experimental conductivity variation shown in Figure 2. In packings of conducting spheres, the macroscopic conductivity increases with applied stress due to the microscopic strain-stress law at the contact between two grains and to the resulting contact conductance variation. Subsequently, the point contacts between grains likely do not deform in our random mixtures which is reasonable given the TiC and Al_2O_3 hardness. In this situation, the compaction process of TiC/Al_2O_3 random mixtures consists in rearrangements from a loose array of particles to a closer packing. Such a result has also been demonstrated by Baviera *et al.* [5]. From compressibility analysis, the authors shows that compaction process of TiC powder mostly consists in a rearrangement of the grain. As a consequence, conductivity *vs.* force curves may result only in a percolation phenomenon and contact conductance variations due to Hertz's deformation of the particles may be neglected.
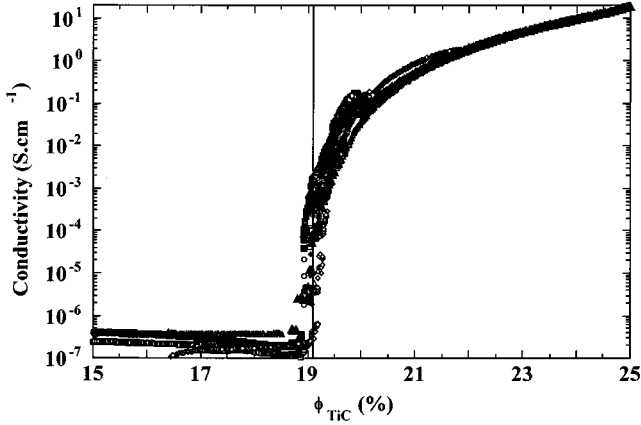
Fig. 3. Conductivity *vs.* volume fraction of TiC in the composite (ϕ_{TiC}). (ϕ_{TiC}) is calculated from the apparent volume of the pellet. Insulator-conductor transition takes place at a constant critical volume $\phi_{\text{TiC}}^{\text{c}} = 19.1\%$.

Fig. 4. Proportion of active contacts *vs.* applied force F.

Figure 3 shows the conductivity variations as a function of calculated TiC concentration in the composite (ϕ_{TiC}). The different curves are obtained for different volume fraction of TiC in the solid phase ($\phi_{\text{TiC}}^{(\text{s})}$). Figure 3 indicates that, given the ϕ_{TiC} experimental errors, the insulator-conductor transition takes place at a constant critical volume fraction of TiC in the composite ($\phi_{\text{TiC}}^{\text{c}} \approx 19.1\%$). The threshold for site percolation, well defined, appears independent of force. The application of force, which does not deform the grains, changes the contact density between TiC neighboring grains (active contacts). Accordingly, the composite behaviors may be interpreted on the basis of a percolation model of existing or non-existing contacts between grains [6] whose transition from the non conductive to the conductive state occurs at forces which may be described by some density function [$j(F)$]. At large enough force, the composite is in the conducting state if and only if there exists an infinite path of coupled TiC particles: this condition may be fulfilled if the TiC concentration at least equals the critical volume fraction $\phi_{\text{TiC}}^{\text{c}}$. At lower force, the conducting particles are decoupled and the infinite conductive path breaks down.

Let us consider a site percolation problem on a random lattice, s being the site density. The density of bonds existing between nearest neighboring sites (p) is proportional to the square of s [7], *i.e.* $p \propto s^2$. At the site percolation threshold, the site critical density is s_{c} and the bond density is p_{c} (notice that p_{c} is not the bond percolation threshold). In real materials such as the TiC/Al$_2$O$_3$ composites under study, the TiC particles are equivalent to sites and the links between conducting particles are equivalent to bonds, thus $p \propto (\phi_{\text{TiC}})^2$. At the site percolation threshold, one may write that the bond density is $p_{\text{c}} \propto (\phi_{\text{TiC}}^{\text{c}})^2$. As $\phi_{\text{TiC}}^{\text{c}}$ is the same for all composites, one can notice that the bond density is constant at the site percolation threshold (*i.e.* at $s = s_{\text{c}}$, $p = p_{\text{c}}$ for 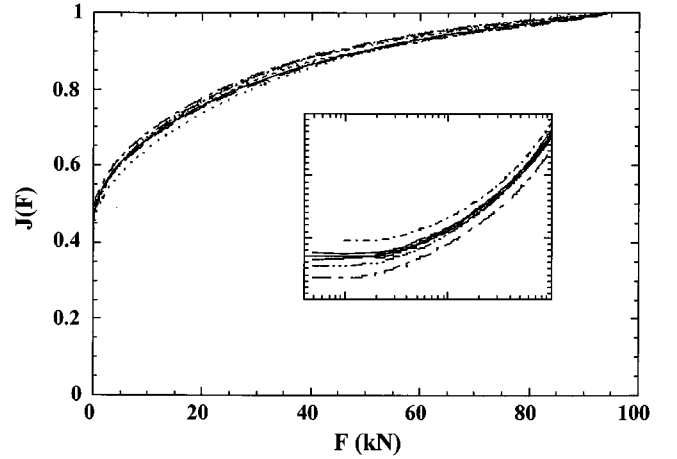all composites). Thus, one can easily deduce the ratio between the link densities $p(F, \phi_{\text{TiC}}^{(\text{s})})$ and p_{c}:

$$\frac{p(F, \phi_{\text{TiC}}^{(\text{s})})}{p_{\text{c}}} = \frac{(\phi_{\text{TiC}})^2}{(\phi_{\text{TiC}}^{\text{c}})^2} \qquad (1)$$

$p(F, \phi_{\text{TiC}}^{\text{s}})$ being the density of conductive links at applied force F and for a TiC/Al$_2$O$_3$ composite whose volume fraction of TiC in the solid phase is $\phi_{\text{TiC}}^{\text{s}}$.

One can also define the proportion $J(F)$ of active contacts at applied force F, $J(F)$ being defined by:

$$J(F) = \frac{p(F, \phi_{\text{TiC}}^{(\text{s})})}{p_\infty(\phi_{\text{TiC}}^{(\text{s})})} \qquad (2)$$

where $p_\infty(\phi_{\text{TiC}}^{(\text{s})}) \propto (\phi_{\text{TiC}}(F = 100 \text{ kN}))^2$ is the density of active contacts at the maximum applied force. Thus, one can easily deduce that:

$$J(F) = \frac{p(F, \phi_{\text{TiC}}^{(\text{s})})}{p_\infty(\phi_{\text{TiC}}^{(\text{s})})} = \left(\frac{\phi_{\text{TiC}}}{\phi_{\text{TiC}}(F = 100 \text{ kN})}\right)^2. \qquad (3)$$

We would like to mention, at this stage that although equation (3) implies that $J(F = 100 \text{ kN})$ equals 1, all contacts between TiC neighboring particles are not necessary conducting at 100 kN. Indeed, the density of active links at forces larger than 100 kN is unknown. Nevertheless, the number of active contacts likely does not change a lot for larger force as the relative density of the different composites is constant for applied forces larger than about 95 kN.

Lines shown in Figure 4 correspond to the proportion of active links $J(F)$ calculated from relation (3).

The experimental values of $J(0)$ are slightly different for composites with different compositions. Nevertheless, our values are compatible with the range [0.3–0.5] determined in the vulnerability measurements of Ottavi *et al.* [6]. It is well known that the proportion of contacts which are active from the beginning (*i.e.* $J(0) = \alpha_0$) strongly depends on the way the packing has been put
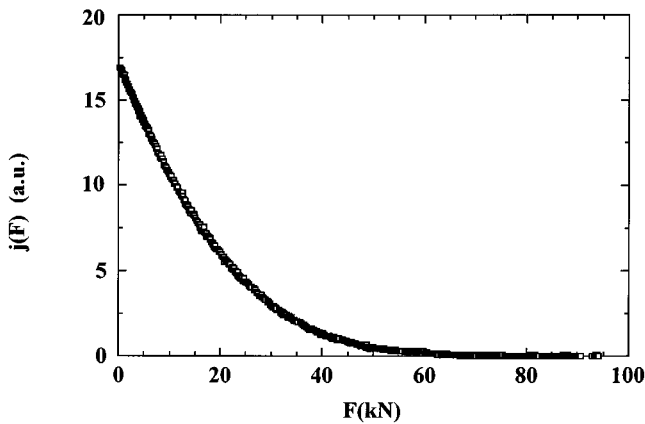
Fig. 5. Rate of creation of the contact between grains calculated from $J(F_0) = \alpha_0 + \int_0^{F_0} j(F)\mathrm{d}F$ (see text).

together and the possible forces exerted on it afterwards. It is the likely reason for our slightly different experimental values of $J(0)$.

The curves, obtained for composites with various compositions, are clearly superimposed for applied force larger than about 1 kN. Consequently, the proportion of active contacts at applied force F is the same whatever is the composition in the range 27–40%. This result can only be understood if one assumes that the conductive and non conductive contact densities vary in a same way with applied force F. In other words, it means that the $J(F)$ function also corresponds to the probability for a link between particles (whatever conductive or not) to exist at a given applied force F.

Finally, one can deduce the rate of contact creation $j(F)$ with applied force which is given by $J(F_0) = \alpha_0 + \int_0^{F_0} j(F)\mathrm{d}F$. $j(F)$ has been calculated by numerically deriving a fit of the $J(F)$ function shown in Figure 4. The resulting $j(F)$ function is plotted in Figure 5. Contacts between grains are easily created at low force (smaller than about 35 kN). This stage corresponds to a large variation of the relative density and thus to a transition from a loose array of particles to a closer packing which induces creation of a great number of new contacts between grains. In the range 50–90 kN, contacts between grains are created at a rate which decreases rapidly with applied force.

4 Conclusion

In summary, it has been shown that conductivity measurements performed on a random mixture submitted to uniaxial pressure may be understood in the framework of a site percolation model. Moreover, such a macroscopic conductivity measurement allows one to determine microscopic informations about the rate of creation of the contacts between conducting particles. Provided that the size distribution of the conductive and non conductive grains are the same, one can deduce the rate of creation of the contact between particles (whatever conductive or not). This work is a first step before studying more realistic systems used in powder metallurgy. For example, inhomogeneous distribution of pressure during compaction gives rise to product exhibiting density gradient and thus poor mechanical strength. Work is in progress to study the effect of an inhomogeneous distribution of pressure ("arching" effects). Another development concerns nanocristallized materials which consists in micron-scale particles containing nanocristallites. In these systems, porosity is not only intergranular but also intragranular which implies that contacts can be created between particles and also between nanocristallites.

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