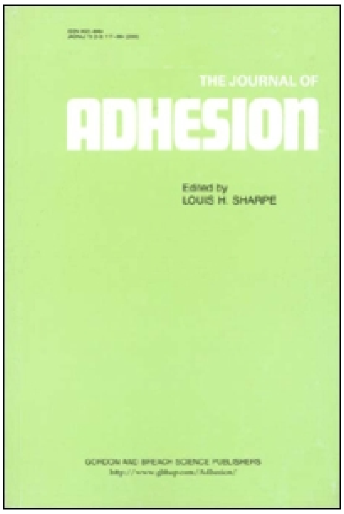

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Adhesion Effects of Intermediate Layers on the Densification of Ceramic Powders†

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In the ceramic technology the first step to produce sintered bodies is the manufacturing of powders which then are densified. The adhesion mechanisms between the single particles and the agglomerates produced from them determine the densification process. Starting from theoretical considerations adhesion mechanisms, such as solid bridge formation, adhesive bonding and glide-promoting effects, are discussed in principle. Subsequently, the effects of surface-active substances on the densification behaviour of clay-ceramics and oxide-ceramic bodies are discussed. Further, the evaluation of the action of additives to the powder mixtures on the microstructure of the compacts, such as porsity and texture, leads to a compaction equation which describes the transition from the powder pile to a densified green body.

KEY WORDS Adhesion of layers; adhesion mechanisms; ceramic powders; densification; effect of surfactants; structure of compacts.

1 INTRODUCTION

In the clay–ceramic technology the workability of the starting mixtures, containing quartz, feldspar and clay, is determined significantly by the plasticity of the clays. This is particularly valid for the more and more used dry-pressing-technique, which starts in

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contrast to the slip-casting from spray-dried or granulated powders with low moisture contents. The deposits of high-plastic clays are decreasing worldwide, so that the application of so-called poor clays in the process engineering causes some difficulties attributed to very low adhesion in the compacts.

In principle, the initial substances for the production of engineering-ceramic products without exception are very brittle materials as alumina or silicon carbide. They are produced either by slip-casting or, increasingly, by the dry-pressing technique. The absence of plastic portions leads to a restricted adhesion ability in the compact and thereby to a very small stability of the green body.

Thus, in clay-ceramics and engineering-ceramic products, higher values for the strength of powder agglomerates are reached by increasing the adhesion between the individual particles, with the result that the rejection of unfired green bodies is essentially decreased in the process line.

2 ADHESIVE LAYERS AND ADHESION MECHANISMS

Investigations by Rumpf[1] on the dependence of the transferable tensile strength on the particle size in agglomerates resulted in an increasing of the strength of the compacts by addition of additives (Figure 1). However, in the technology it must be considered that, on the one hand, the application of large quantities of additives can be expensive. On the other hand, the quantitive removal of the added substances, for example by burning out, leads to problems because of changes in the properties of the sintered bodies.

According to the diagram of Rumpf the highest strength for small grain sizes is reached by building up characteristic solid bridges between the primary particles. In Figure 2 the reaction scheme of the system silicates–trichloromethylsilane (TCMS) is given as an example for the formation of a characteristic adhesive layer between powder particles.[2] After mixed sorption of silane and water molecules, the silanol groups of the silicate surfaces are integrated into a stabile network between the single particles by spalling hydrochloric acid. Thus, a high specific strength of the single contacts is reached, yet leading to a blocking of gliding processes during the compaction of a powder bed. What follows is a

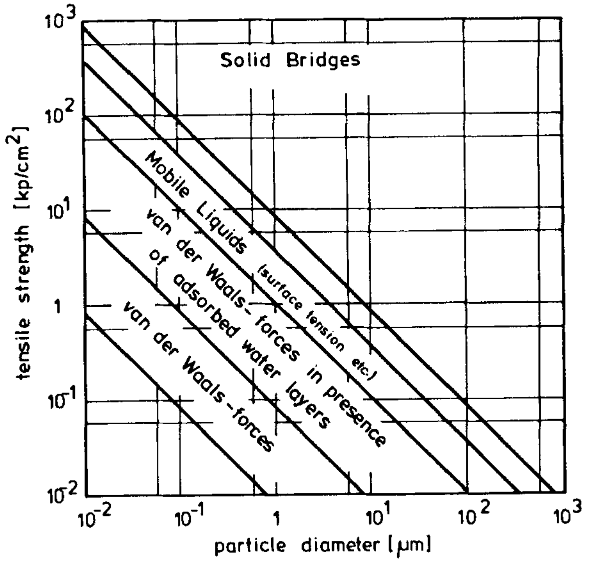

FIGURE 1 Dependence of theoretical tensile strength of agglomerates on the primary particle size for different bond types.

pressing with high strength but with an apparent density insufficient for optimal sintering. Consequently, there results the claim for the dry-pressing technique, that during compacting of powders a sufficient green density is reached by particle gliding simultaneously with an as high-as-possible adhesion between the particles.

In principle, this claim is fulfilled by the use of polar surface-active molecules. After the theory of Fowkes[3] the interaction potentials, which determine the total surface energy, are superimposed additively, so that the following equation is valid:

$$\gamma = \gamma_D + \gamma_P$$

with γ_D = the non-polar part, determined by the dispersion forces
λ_P = the polar part determined by the dipole forces

Within the meaning of adhesion an efficient substance is characterized by a very high polar energy term. According to the results of Fowkes, Michel[4] gives a systematic listing of the adhesion mechanisms for sticking processes on polymers for different adhesive material combinations.

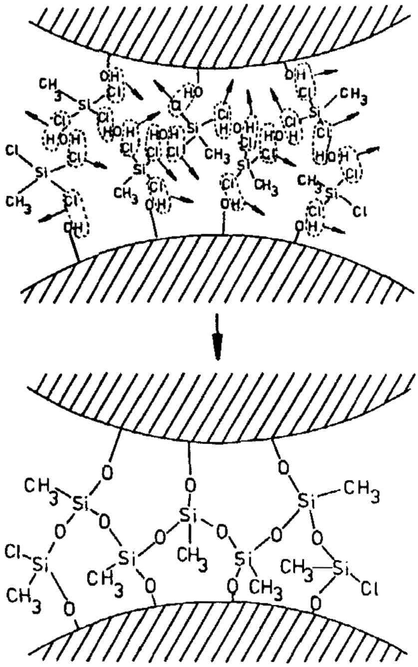

FIGURE 2 Formation of solid bridges on powder surfaces with hydroxylic ions.

The application of polar molecules as adhesion- and glide-promoting substances for compaction of powder piles is determined by the strength of the dipole forces and the number of the active dipoles per molecule. For monopolar substances like water the adsorption causes a saturation of the surface potentials as shown in Figure 3. From this, density-promoting glide processes with a lubrication effect result, whereas the adhesion forces are small. Hereby, the number and the size of the adhesive surfaces increase with simultaneous increase of the total strength and, furthermore, of the compacts' apparent density.

For the adsorption of bipolar molecules, according to their structure, two principally different orientations are possible. In the case of a limited mobility of the molecule, for instance by reason of a double linking, bridges between the particles are formed, caused by polar interaction at the opposite contacting areas (Figure 4a).

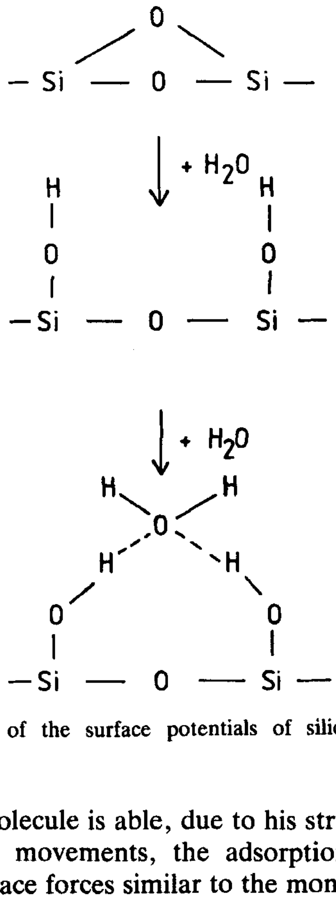

FIGURE 3 Screening of the surface potentials of silicate surfaces by water (Ref. 12).

Against that, if a molecule is able, due to his structure, to carry out turning or bending movements, the adsorption produces only a shielding of the surface forces similar to the monopolar case (Figure 4b). The first process leads to a "strutting" of the powder frame by the adhesive and, therefore, to a glide-hindering effect. In comparison with this, gliding processes between the particles are favored by turning and bending movements.

3 EXPERIMENTAL PROOF OF ADHESIVE LAYERS

In the following, the principal applicability of the different adhesion mechanisms on the compacting of powders are discussed using examples from the ceramic technology.

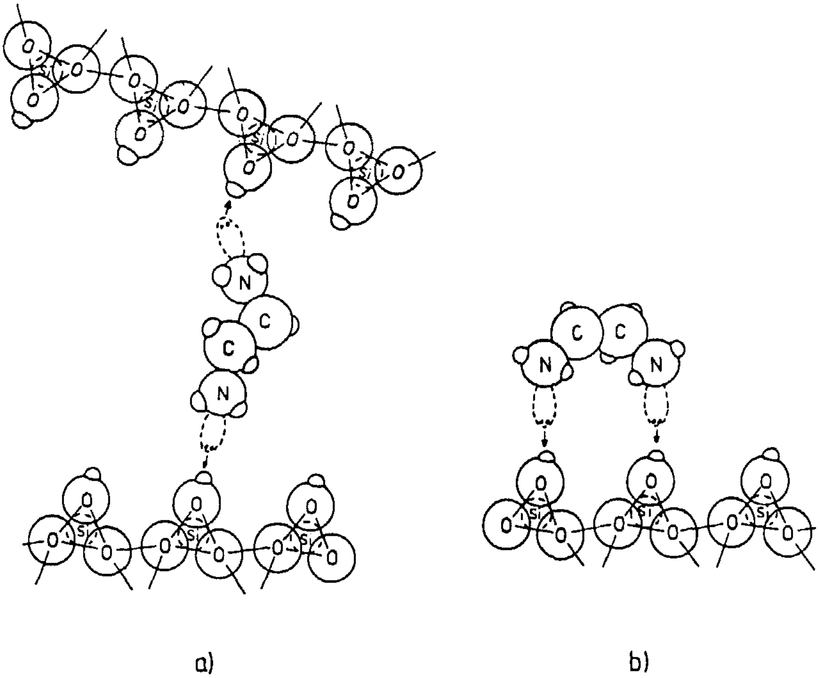

FIGURE 4 Adsorption of bipolar amines on kaolinite.

If spray-dried clay–ceramic batches are pressed without additives, an increasing compacting pressure increases the apparent density. According to Figure 5, the number of contacts raised thereby results in an increasing compression strength of the green bodies.[5] The adsorption of trichloromethylsilane on the hydroxylic surfaces and the resulting reaction producing hydrochloric acid, after Figure 2, enables the construction of characteristic ideal solid bridges as the sturdiest constellation of the adhesion between the particles. It is possible to reach values for the compression strength, which are more than twice as high as those for powders with equal apparent density but no surface-active additives.

An example for the glide-promoting and the adhesive effect of molecules, is given in Figure 6, for clay–ceramic sprayed grains with a constant apparent density and, therefore, with a constant number of particles in the sample volume.[2] With increasing water content

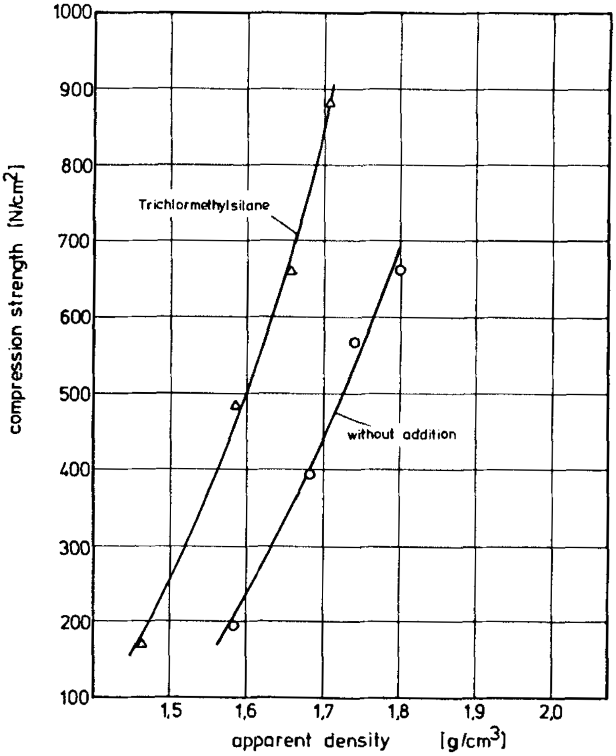

FIGURE 5 Influence of the apparent density on the compression pressure of clay-ceramic spary-dried batches caused by surface-active substances.

the compression pressure of the green bodies drops to a constant value. This trend is typical for the glide-promoting effect of adsorbed molecules, which diminish the surface forces.

In contrast to this, a surface-specific addition of di-iso-propanolamine (DIPA) strengthens the powder frame into the compact, resulting in a doubling of the strength, an effect opposite to that of water addition. (The measured decrease of the apparent density of the stabilized pressing should be compensated by using a higher compacting pressure.) The competing effect of water (gliding) and DIPA (adhesive) is verified in Figure 6 by the middle curve for the addition of a 1:1 mixing of both substances.

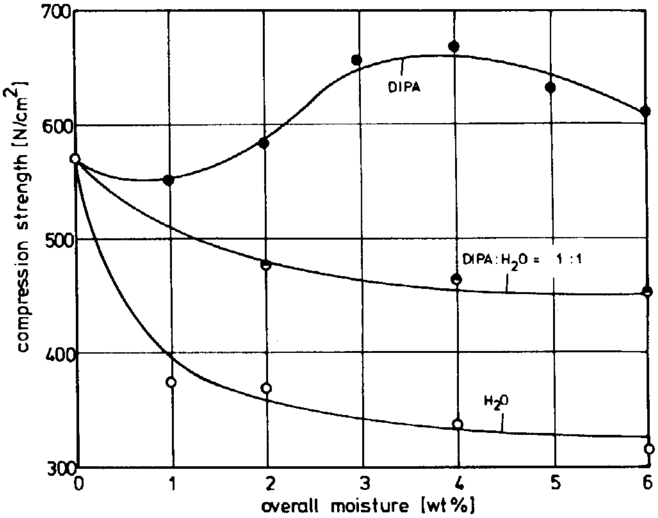

FIGURE 6 Dependence of the compression pressure and the total moisture for clay-ceramic batches.

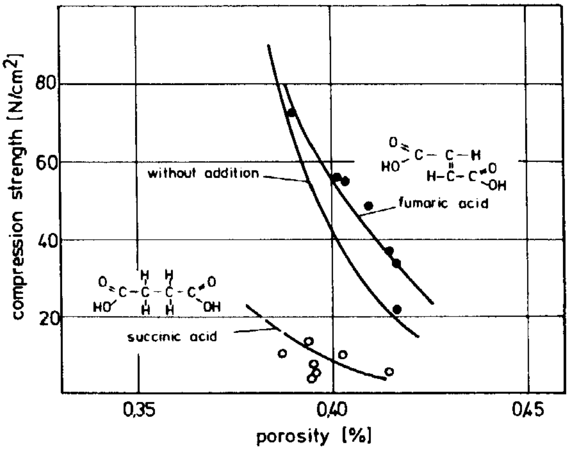

FIGURE 7 Influence of the surface coverage on the compression pressure and the porosity of compacted alumina powders.

The respective stabilizing or destabilizing character of dicarboxylic acids with different molecular mobility was proved for alumina compacts.[6] According to Figure 7, the stability of a compact produced from dry powder, containing no neck-water but adsorbed water, is guaranteed by the action of the surface adhesive forces between the particles. If a freely revolving molecule such as succinic acid is adsorbed on alumina particles, a continued screening of the adhesion forces gives rise to a drastic decrease in strength. On the other hand, the fumaric acid (isomeric to the succinic acid) causes a distinct strengthening of the frame by adhesion mechanisms. This adhesion is made possible by reason of the central double bond.

4 ADHESION JUNCTION BETWEEN POWDER PARTICLES AND THE STRUCTURE OF COMPACTS

The different adhesion mechanisms between single particles in a ceramic powder are followed by qualitative and quantitative effects on the microstructure of the compacts produced.

The following results are valid for clay-ceramic batches, which were produced from well-defined spray-dried powders as initial material.[7] Their particles shape is shown in Figure 8.

During compaction with a pressure of 62 N/mm^2, the microstructure of a spray-dried granulate with addition of water is destroyed (Figure 9a). On the contrary, it was observed, that the adhesive-stabilizing effect of DIPA causes a molding of the agglomerates without destruction of their inner coherence (Figure 9b). The stabilization effect of TCMS is so strong that the spray-dried agglomerates are partially undeformed after compaction, this being caused by the characteristic solid bridges between the primary particles (Figure 9c).

We shall now discuss the quantitative, measurable properties for the characterization of the adhesive effects of additives on the microstructure of compacts. A measure for the arrangement of the powder particles in the compact is given by the X-ray texture, using the (001) and (020) interferences of the kaolinite.[8] In accordance with Figure 10, the texture index I for spray-dried, water-containing batches is increased with the compaction pressure. This indicates a

FIGURE 8 SEM-micrograph of clay-ceramic spray grains.

gliding of the kaolinite particles into a new space-saving configuration. After passing over the maximum of the curve the index decreases, indicating fracture or bending of the individual particles.

The maintenance of the inner microstructure of the secondary grains by adding adhesive substances like DIPA causes a smaller texture index at low compaction pressures. This demonstrates that an orthogonal orientation of the flat kaolinite particles relative to the compaction pressure is hindered by the adhesion between them. The higher index level after the turning point is attributed to a destruction of small agglomerates in the necks of the greater grains, which are polygonized by the compaction pressure.

A further quantitative microstructural parameter for the compaction process is the mean pore width caused by the particle orientation. This so-called mean hydraulic pore width is defined as:

$$d_{\text{hydr.}} = 2\frac{V_{\text{green body}} - V_{\text{theoret.}}}{A_{\text{spec.}}}$$

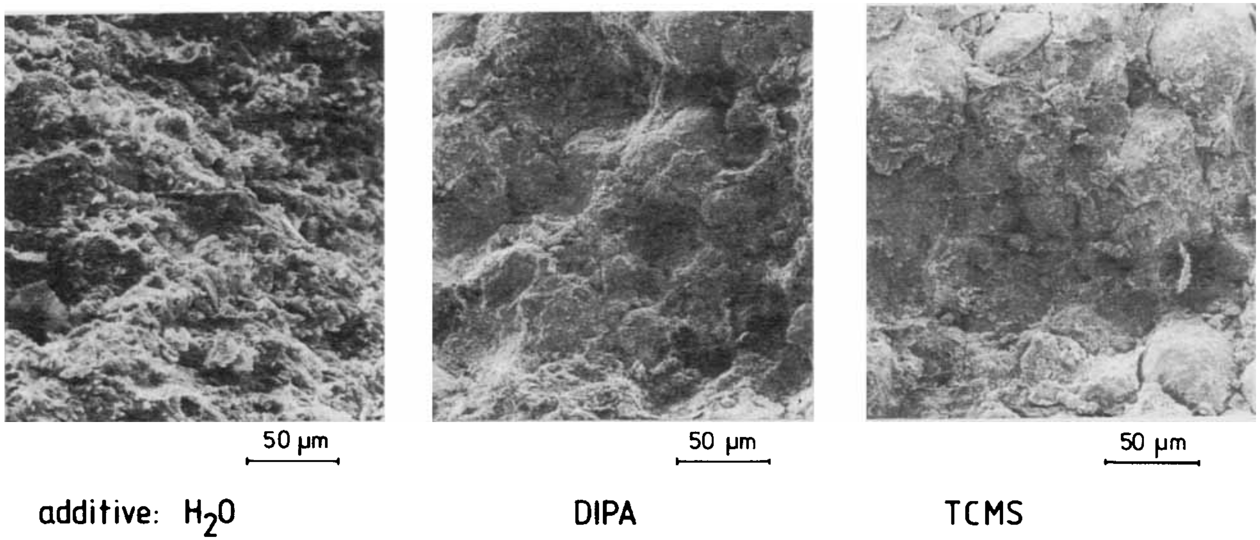

FIGURE 9 SEM-micrographs of the stabilizing effect of surface active substances in the compaction of clay-ceramics (compaction pressure: 62 N/mm^2).

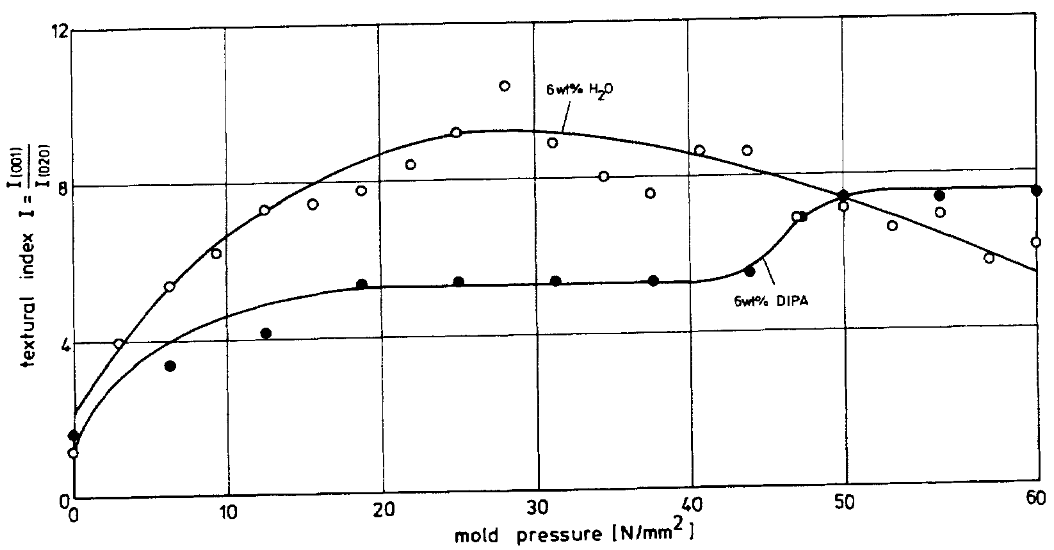

FIGURE 10 Influence of the compaction pressure on the texture index of clay–ceramic compacts.

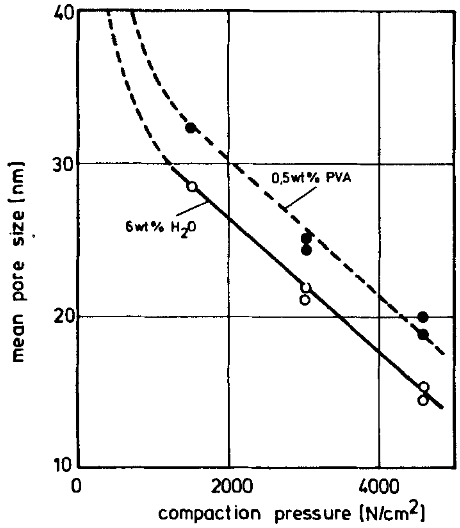

FIGURE 11 Mean hydraulic pore width dependence on the compaction pressure of clay-ceramics.

with

$$V_{\text{green body}} - V_{\text{theoret.}} = \text{pore volume}$$

$$A_{\text{spec.}} = \text{specific surface area}$$

The hydraulic pore width for compacts from clay-ceramic batches depends linearly on the compaction pressure as shown in Figure 11, independent of the pressing aid used.[9] However, the addition of 0.5 wt% polyvinylalcohol (PVA) causes, over the entire compaction pressure range, a mean pore width which is, in comparison with water addition, more than 10 percent higher. The pore structure is stabilized by the adhesive effect of PVA.

In ceramic technology for producing green bodies, a strength of the compacts as high as possible is demanded for good handling of the products. On the other hand, the sintering process is accelerated by a minimal porosity of the compact. New investigations[10] have demonstrated, that a hyperbolic dependence exists for the compression pressure and the pore volume independent of the kind of compaction process (*e.g.* simple compaction with high pressure or multiple compaction with low pressure). The dependence is given

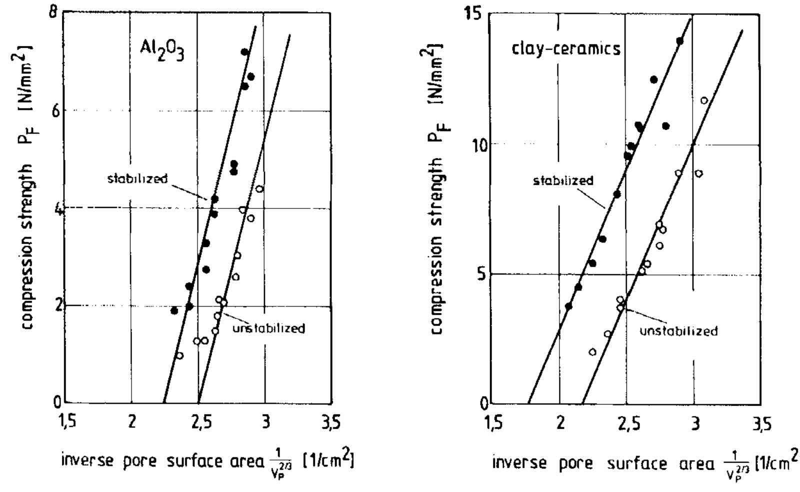

FIGURE 12 Dependence of the compression pressure on the reciprocal pore surface for clay-ceramics and alumina compacts.

by the relation:

$$P_F = \frac{C_i}{V_P^{2/3}} + d_i$$

with

P_F = compression pressure
V_p = pore volume
C_i, d_i = mass specific constants.

Figure 12 shows this relation for oxide– and clay–ceramic pressings. On the one hand, the compression pressure for both of these, relative to their plastic quantities extremely different materials, is proportional to $V_P^{-2/3}$. This indicates the increasing transition of inactive free pore surface to active adhesive area. On the other hand, the covering of the contact area by multipolar adhesive molecules leads to an increased strength. The adhesion of thin, probably monomolecular layers, results in an increase of 4.4 N/mm² for clay–ceramics and 2.7 N/mm² for alumina compacts with respect to water addition. Similar effects may also be expected for other surface-active and adhesive pressing aids.[11]

The discussed results of the influence of intermediate layers on the densification of ceramic powders do not correspond to the diagram of Rumpf without contradiction. However, it must be considered that the entire number of particles in the specimen volume and, therefore, the number of contacts, is specific for the adhesion mechanisms including the typical effects of additives at the solid surfaces. But this is not included in the diagram of Rumpf.

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