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THE EFFECT OF TEMPERATURE DEPENDENT FACTORS UPON THE MECHANICAL AND SURFACE PROPERTIES OF SOLIDS

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ABSTRACT

The effect of temperature dependent factors upon the mechanical and surface properties of solids depends on the competing forces of activation and sintering. In decomposition from the solid phase the state of the resultant solid produced is determined by the stresses imposed by these competing forces. This in turn is reflected in measurements of the kinetics of solid state decomposition, the surface texture, and the thermo-mechanical properties which result. All these measurements can involve thermal analysis equipment. The crucial factor which differentiates organic, polymer and inorganic behavior is that temperature, called by various names, which indicates that the solid structure is no longer rigid. Above this temperature the strains induced by the stress of volume change and altered solid state lattice positions can be dissipated usually without micellar diminution whereas below this temperature the stress is relieved by micellar diminution which does not necessarily match completed solid state decomposition. All solid materials on heat treatment are subject to sintering which is a temperature and time dependent process and complicates the simpler picture built up on the consideration of only activation. There are numerous applications in industry where these considerations have to be applied and the major tools in investigative techniques for this purpose are those of thermal analysis.

INTRODUCTION

The subject of the manner in which mechanical and surface properties of solids vary with heat treatment takes two divergent paths. In the first the concern is for the property that results at the temperature which is applied. This is typified by the use of thermomechanical analysis units and thermodilatometry where the concern is for the mechanical property or the dimensional change at the temperature of measurement. However, there are fields of application where the measurement of concern is that which results when the material under study is brought back down to its normal operating temperature, usually but not always ambient. Most texture measurements are of this kind, for the simple reason that many methods of texture, e.g. surface area, porosity, etc. are only able to be measured effectively at ambient or even lower temperature. In presenting this topic the author is aware that the imaginative research of others with whom he has worked has played an important part in shaping his ideas. The early years spent at Exeter University - then the University College of the South West brought him under the influence of Dr. S.J. Gregg whose creative research and fertile mind and love of the

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subject brought out the best in all his students. The general theory of activation and sintering of solids (1) propounded by Dr. S.J. Gregg remains as a key paper to be studied by all interested in the topic. The 27 years spent by the present author at Salford University bought him into contact with real problems that could be solved by a general extension of the principles laid down by Gregg and allowed excursions into the fields of coal chemistry, cement technology, glass manufacture, polymer science, carbon behavior, as well as allowing some refinements of the general case. The 6 years at the University of Toledo has provided further contact with these topics and have indicated fresh avenues of approach and provided new fields of geology and pharmacy in which to pursue the subject.

GENERAL CONCEPT OF ACTIVATION

The general concept of activation of solids arises from the fact that in a reaction of the general type

$$\text{Solid A} \xrightarrow{\text{heat}} \text{Solid B} + \text{Gas} \qquad (1)$$

there is involved movement of constituent species or derived species from positions occupied in the solid lattice of the reactant to the new positions occupied in the solid lattice of the product. There is also an attendant alteration in volume. Both the movement of species within the solid lattice and the alteration in volume are opposed by the general property of the solid phase to exhibit a rigid structure. Now this is of course a generalization and the higher the temperature of a solid the less rigid it is, as will be seen later. The definition of "activity" as outlined here is that it refers to an increase in those properties dependent upon the surface area. This presupposes a reduction in crystallite or micelle size. Gregg uses the term "micelle" because he believes the term "crystallite" implies a perfect lattice. Thus if a unit cm^3 of a solid density ρ is rendered more active by reduction of micellar size to cubes of side l then the specific surface, S, (m^2g^{-1}) is given by

$$S = \frac{6}{\rho l} \qquad (2)$$

It will be shown that this kind of reduction takes place due to the imposition of strain caused by the two factors already mentioned, i.e. the alteration of the lattice distances and the change in volume (and hence density) as the material changes from solid reactant to solid product.

There is a kinetic aspect to this conversion which forms the basis of most of the kinetic models which are tested in the rising temperature kinetic analysis utilized in the programs provided with most dedicated computer work stations for thermal analysis units (2). These are generally based on the concept of nucleation, growth of nuclei and the progress of a reaction interface. The nucleation aspect becomes more important as micellar size decreases; that is in smaller volumes fewer nuclei are needed to ensure complete decomposition. The initial models put forward for the progress of the reaction interface were based simply on the geometry of the decomposing micelle (3). However this tends to break down as the stress involved by movement of species in the lattice structure and the volume changes bring about the diminution in micellar size (4).

This diminution in micellar size also brings about a general weakening of compacted structures which affects the mechanical properties (5,6). The measurement of strength in the absence of activation is influenced by temperature solely through the process of sintering which is both time and temperature dependent. The processes which cause sintering to occur and its temperature dependance will be discussed next.

SINTERING

If a material is subjected to heat treatment without decomposition it undergoes sintering. This can be defined by citing what happens and what causes the effect, namely, a reduction in particle size, with a consequent decrease in surface area, caused by the combined effects of time and temperature. The effect can easily be demonstrated by noting how oxide particles can be sintered and zinc oxide serves as a good example (7). Using surface area as the "probe measurement" it can be shown that in isothermal heating runs there is a decrease in surface area towards an equilibrium value determined by the initial state of the particles and the temperature of the isothermal run (Figure 1). Basically a diffusion mechanism is involved with a coalescence of adjacent particles leading to a decrease in their number. On the basis of a constant rate of growth per unit area under isothermal conditions, and assuming the process of diffusion remains the same over a given temperature range then the Arrhenius equation can be used to give the activation energy for the sintering mechanism. However, the process of diffusion can alter. Huttig (8) on the basis of work mainly on metal powders formulated general conclusions regarding the mechanism of sintering in terms of the temperature, expressed as $\tau = \frac{T}{Tm}$, where T is the absolute temperature of the solid and Tm is absolute melting point. Jones (9) summarized Huttigs conclusions as:

1. Below $\tau = 0.23$, a process of adhesion between particles occurs with a consequent reduction in surface area. It the process is significant at ambient temperatures it is referred to as aging.
2. In the region $\tau = 0.23 - 0.36$ surface diffusion occurs leading to an initial increase in surface activity when both surface area and capillaries are enlarged.
3. In the region $\tau = 0.33 - 0.45$ the surface diffusion results in sintering.
4. In the region $\tau = 0.37 - 0.53$ internal lattice diffusion occurs and may initially lead to activation. In this region the last traces of occluded volatile materials are often expelled.
5. In the region $\tau = 0.45 - 0.80$ lattice diffusion produces further sintering. It is the region in which single crystals may be formed.

6. Above $\tau = 0.8$, a slight reactivation may precede melting.

The processes of sintering with reference to oxides may be further condensed as follows:

1. Below $\tau = 0.33$, sintering takes place by adhesion between particles leading to the formation of permanent junctions at the points of contact.
2. In the region $\tau = 0.33 - 0.45$ sintering occurs by surface diffusion in which coalescence of particles occurs by movement of chemical species along the surface.
3. In the region above $\tau = 0.5$ sintering occurs by diffusion of chemical species through the bulk material.

These shortened statements can be correlated with the more detailed observations of Huttig on the basis that in oxide systems the small rearrangements leading to reactivation are often absent.

Although it is probably that there is a relaxation effect in sintering quite good agreement with experimental data is reported in the region where diffusion is expected (10,11) by expressions of the kind

$$\frac{dS_t}{dt} = -k_s(S_t - S_f) \tag{3}$$

in isothermal experiments, where S_t is the surface area at any time t and S_f is the surface

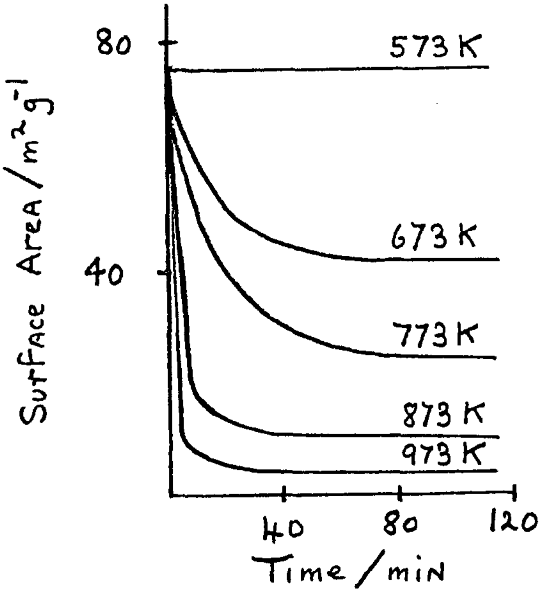

Figure 1 - Isothermal Sintering of Zinc Oxide under 8 KN m^{-2} nitrogen (Ref. 7)

area at $t = \infty$ when the rate has diminished to zero and k_s is the rate constant. Integration gives:

$$\ln(S_t - S_f) = -k_s t + \text{const} \tag{4}$$

This kind of expression applies to the sintering of zinc oxide (7). The data is often collected in terms of particle size but this can be related to the above relationship via the expression

$$r = \frac{3}{S\rho} \tag{5}$$

where r = radius of the particle

S = specific surface area and

ρ = density of oxide phase.

In cases where the experimental observations span both the region where surface and bulk diffusion occurs, then each region is characterized by its own energy of activation (12). The temperature which differentiates between these two regions ($\tau = 0.5$) is seen to be important and in many cases is easier to identify than the melting point. It is often referred to as the Tammann temperature after the man who did much to establish that this was a well characterized temperature (13).

In other fields of study, e.g. in polymers and glasses a similar temperature is characterized, termed the glass-transition (T_g point), below which the solid phase is brittle and above which it is plastic, rubbery or liquid like. However, the comparison may be superficial and the T_g point has to be regarded as a second-order transition based on a relationship associated with the super-cooled glassy state (14). Nevertheless, the fact remains that below the T_g point there is little transitional motion of the polymer molecular or movement of the segments of the chain. Motion of the constituent atoms is presumably restricted to movement of a very few atoms in the main chain or of side groups together with vibrations of the atoms about the equilibrium position. Above the T_g point transitional motion of the entire molecule is possible together with movement of segments of the chain to allow flexing and uncoiling. Stated in this way and on the basis of observed behavior there then appears a reasonable resemblance between the Tamman temperature and the glass-transition temperature.

COMBINED EFFECT OF ACTIVATION AND SINTERING

The combined effect of activation and sintering is best discussed by reference to the reaction given by Equation 1. A typical example would be the decomposition of calcium carbonate (15)

$$CaCO_3(s) \text{ --> } CaO(s) + CO_2 \tag{6}$$

but there are hundreds of other examples (2). The possibility of reaction with the atmosphere must always be considered. This occurs with oxalate decompositions (16). Thus to quote just one example (17) zinc oxalate decomposes endothermically in nitrogen and exothermically in air. In both instances the reaction is

$$ZnC_2O_4 \dashrightarrow ZnO + CO + CO_2 \qquad (7)$$

However in air the catalytic reaction

$$CO + O_2 \dashrightarrow CO_2 \qquad (8)$$

over the product solid zinc oxide, a very efficient catalyst, gives an exothermic character to the basic endothermic reaction (Figure 2).

It should be noted that the reaction interface is rarely identified with the surface area. In the case cited for calcium carbonate, a layer of product oxide is built up covering the reaction interface as decomposition continues. Thus real consideration must be given to diffusion problems as the product gas must diffuse away from the reaction interface through the layer of product calcium oxide, (or other solid product in the general case). Further complications arise because of the change in volume, due to differences in density between reactant oxysalts and the product oxide. This causes a distortion of the geometrical system leading to a break-down into many smaller particles under the strain imposed on the system by this process (18). The diminution of the particle or micelle size results in an increase in the total number of micelles in the system giving an increase

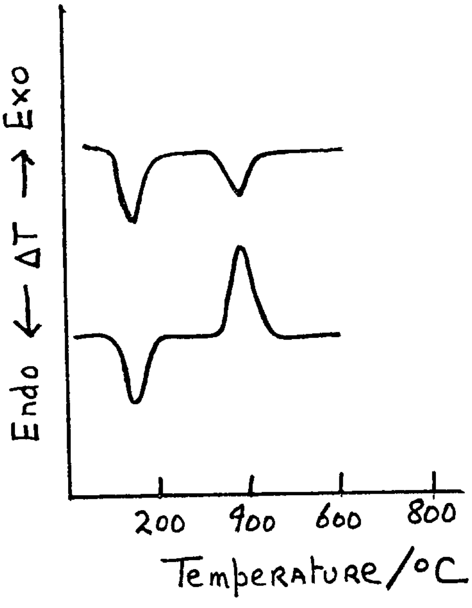

Figure 2 - DTA curve for zinc oxalate dihydrate in nitrogen and oxygen (Ref. 17)

A. Nitrogen:	109°-156°C	endo dehydration
	342°-373°	endo decomposition to oxide
B. Oxygen:	109°-156°C	endo dehydration
	342°-389°C	exo decomposition to oxide

1st temp:Initial Temp. 2nd temp:Peak Temp.

in specific surface area. However sintering decreases this surface area often producing a plot of surface area against time or temperature of treatment showing a maximum surface area finally diminished by the sintering process. This maximum occurs when the strain cannot be contained within the original lattice structure and this does not necessarily coincide with the point where the reaction is complete.

The process can be set down more specifically (10,11,19). Let the surface area due to activation be denoted by S_a, then one can write

$$S_a = k_1\alpha \qquad (9)$$

where α = fraction decomposed, k_1 is a constant.

In a typical case one may suppose a contracting sphere equation describes the kinetics

$$1 - (1 - \alpha)^{1/3} = k_2t \qquad (10)$$

Rearrangement gives

$$\alpha = 1 - (1 - k_2t)^3 \qquad (11)$$

then

$$\begin{aligned} S_a &= k_1[1 - (1 - k_2t)^3] \\ &= k_1k_2t(3 - 3k_2t + k_2^2t^2) \qquad (12) \end{aligned}$$

Differentiation gives

$$\begin{aligned} \frac{dS_a}{dt} &= k_1k_2(3 - 6k_2t + 3k_2^2t^2) \\ &= 3k_1k_2(1 - k_2t)^2 \qquad (13) \end{aligned}$$

The sintering process can be described by

$$\frac{dS_s}{dt} = -k_4S \qquad (14)$$

Both the kinetics may be different and alternate sintering expressions may be utilized (20).

The overall rate of change of surface area is then

$$\begin{aligned} \frac{dS}{dt} &= 3\,k_1k_2\,(1 - k_2t)^2 - k_4S \\ &= A\,(1 - Bt)^2 - CS \qquad (15) \end{aligned}$$

(Here A, B and C are substituted for the various functions of K)

This can be rewritten as:

$$\frac{dS}{dt} + CS = A\,(1 - Bt)^2 \qquad (16)$$

After integration this gives

$$S = A'\,[E - Ft + Gt^2] + \text{constant} \qquad (17)$$

(Here again A', E, F, and G are substituted for various functions of k)

The combination of density and surface area can be used to show the effect of the increase in the number of particles brought about by the activation process (18, 21, 22).

Simple geometric calculations show that if in the decomposition process the n_1 original particles of oxysalt produce n_2 particles of product then

$$\frac{V_1}{V_2} = \left[\frac{S_1}{S_2}\right]^{3/2} \bullet \left[\frac{n_2}{n_1}\right]^{1/2} \tag{18}$$

where V_1 is the molar volume of the solid, reactant, V_2 is the equivalent volume of the solid product, S_1 is the molar surface area of the solid reactant, S_2 the equivalent molar surface area of the solid product, and n_2 is the number of particles of solid product produced from n_1 particles of the solid reactant. If the number of particles remain the same

$$\frac{V_1}{V_2} = \left[\frac{S_1}{S_2}\right]^{3/2} \tag{19}$$

Equation (18) can be used to follow the combined effects of activation and sintering during the thermal decomposition (21,22) for V_1 can be expressed in terms of density (ρ_1), and average particles radius (r_1);

$$V_1 = \frac{M_1}{\rho_1} = \frac{4\,\pi n_1 r^3}{3} \tag{20}$$

where M_1 is the gram molecular weight. There is a similar expression for the solid product. This gives:

$$\frac{M_1\rho_2}{M_2\rho_1} = \left[\frac{S_1}{S_2}\right]^{3/2} \bullet \left[\frac{n_2}{n_1}\right]^{1/2} \tag{21}$$

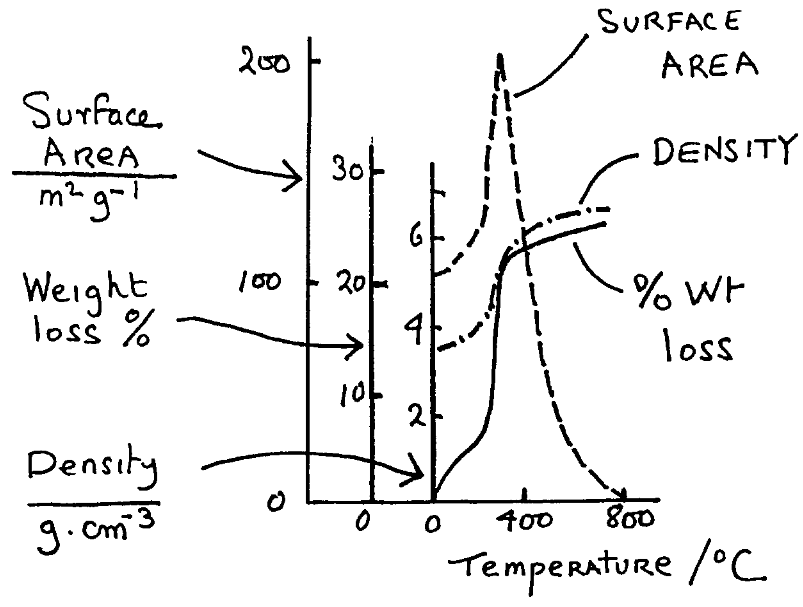

Figure 3 - Density, Surface Area and % Weight Loss on heat treated nickel hydroxide (Ref. 21)

or

$$\frac{r_1}{r_2} = \left[\frac{S_1}{S_2}\right]^{1/2} \bullet \left[\frac{n_2}{n_1}\right]^{1/2} \qquad (22)$$

The expression can thus be utilized using molar volumes, density or average radius measurements. If the molecular weight of the original reactant material is designated as M_1, and of the final product as M_3, then the "effective" molecular weight of the partially reacted material M_2 can be estimated as:

$$M_2 = (1 - \alpha)\, M_1 + \alpha\, M_3 \qquad (23)$$

where α is the fraction decomposed. The molar surface area of the partially reacted material is then given by

$$S_2 = s_2\, \{(1 - \alpha)\, M_1 + \alpha\, M_3\} \qquad (24)$$

where s_2 is the experimental surface area in m^2g^{-1}. This allows the variation in the ratio of particles (n_2/n_1) to be measured during an isothermal or a thermogravimetry experiment. Typical experimental data is shown in Figure 3 and expressed as the ratio (n_2/n_1) in Figure 4.

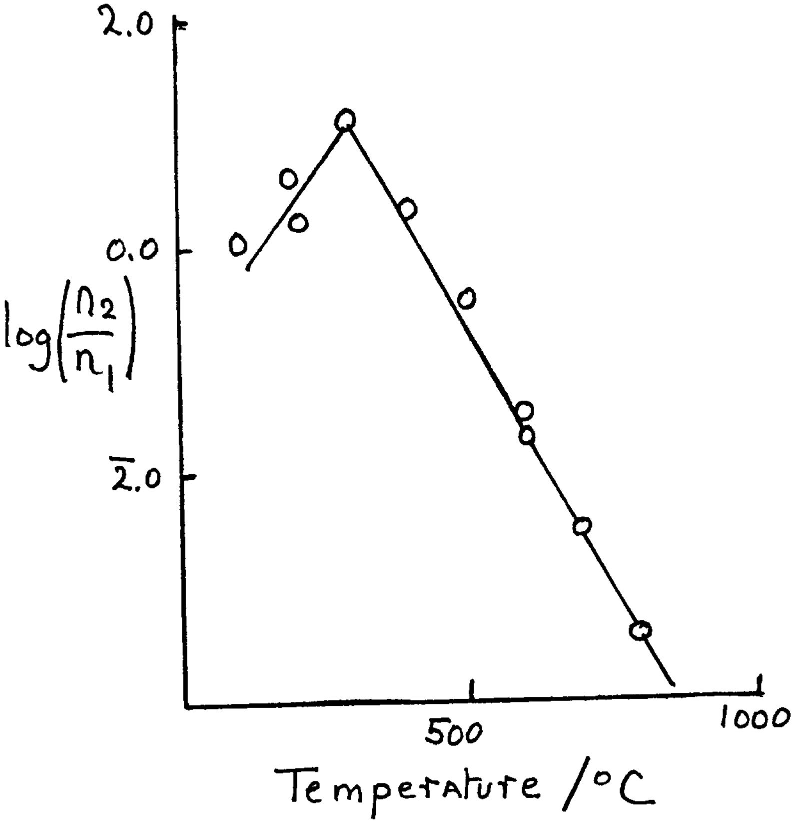

Figure 4 - Logarithmic Relation Between Number of Product Particles (n_2) formed from the number of Particles of Reactant (n_1) for nickel hydroxide (Ref. 21)

MECHANICAL FEATURES

The most direct and in many ways the most pertinent mechanical measurement is that of the strength of an aggregate or compact. The most obvious effect of sintering is simply that the coalescence of particles will lead to an increase in the mechanical strength of an aggregate or compact of powdered materials. The effect of the activation process on a compact of powdered material will be to weaken the compact or shatter it completely through the sudden production of many more particles and the alteration in volume consequent upon the formation of the product solid phase. The variation in the strength of compacted powders is susceptible to environmental factors such as adsorption (23,24,25,26). The Griffith Flaw theory can be used to explain this behavior (27). Adsorption generally causes a decrease in strength. The determination of strength under vacuum most often given an experimental strength value which is considerably higher than data obtained under atmospheric conditions. The difficulty is that even under vacuum, experimentally determined strengths are less than the theoretical strengths often by a factor of severalfold. Griffiths explained this on the basis of a stress concentration behavior at the apex of flaws orientated in the direction of applied stress. This also explains the importance of texture in such measurements and the fact that standard deviation data indicates a wide devergence in any one set of results. To narrow the standard deviation data the flaws or pores present would have to be all orientated in the direction of applied stress and perfectly repeatable. Griffith related the modulus of rupture (R) of a compact with the surface energy (γ) by the expression:

$$R = \left[\frac{2Y\gamma}{\pi C}\right]^{1/2} \tag{25}$$

where Y is Youngs modules for the solid and 2C is the length of the crack at which failure occurs. The Gibbs adsorption equation can be utilized to calculate the decrease in the surface energy ($\Delta\gamma$) from the adsorption isotherm, and it is this decreased value which should be introduced into equation 25 (28,29). This concept explains with some modification all the observed facts relating to the selective effect of adsorption upon the strength (26). The effect of adsorption must be stressed, as the measurement of strength is most often reported on samples already containing adsorbed material and hence any subsequent effect of temperature often is superimposed upon the effect of adsorption already present. There are three areas where the strength may be influenced by the temperature (5). The first factor is the degassing conditions imposed on the compact before the strength measurements, the second is the prior effect of temperature on the powders prior to the aggregation process needed to form the compact and finally the direct effect of heat upon the compact itself. In the study on magnesium hydroxide (5), the TG results showed that carbonation occurred on storing (about 2-3%) giving the main decomposition

$$Mg(OH)_2 \dashrightarrow MgO + H_2O$$

in the region 350-500°C followed by loss of carbonate at some higher temperature. The effect of the degassing temperature on the strength showed a wide variation but that degassing at 200°C gave the most reproducible results. The irregular results below this temperature could be attributed to insufficient and irregular loss of moisture during degassing. In the heat treatment of powders of magnesium hydroxide between 250°-800°C a correlation could be obtained between the surface area, the chemical identity of the powder and the strength (Figure 5). The effect between 400° and 800°C is that as the strength increased, the measured surface area decreased. This is explained by noting that sintering reduces the number of discrete particles. When a given pressure is applied to a fixed mass of powder the number of points of contact reduces so the pressure at each point increases enabling the particles to be pressed closer together, thus increasing the strength through better adhesion between particles. The chemical effect may be noted in the case of magnesium hydroxide by observing that the surface area of the material heated at 800°C and at 200°C is approximately the same but the strength of the compact of material where the powder had been heated to 800°C is two and a half times as great. The TG data however shows that at 200°C we are compacting hydroxyl groups while at

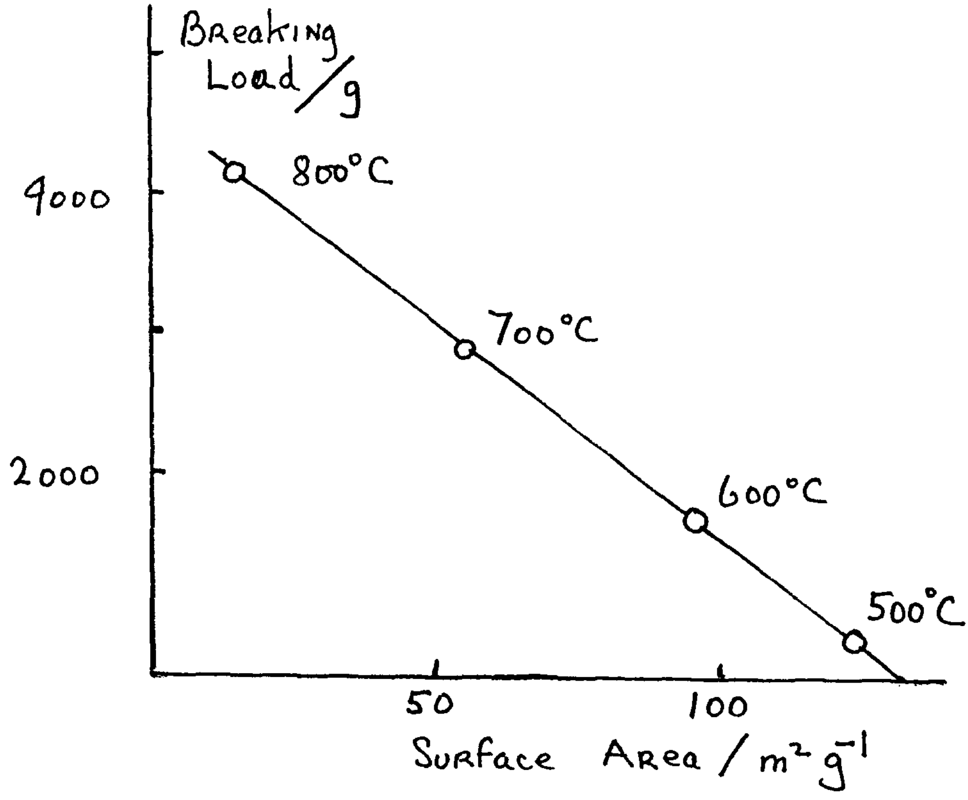

Figure 5 - Plot of Breaking Load Against Surface Area of Powder From Which Discs of $Mg(OH)_2$ were prepared. Temperature of treatment noted on graph (Ref. 5)

800°C we have a pure magnesium oxide surface producing a compact of much higher strength.

All this data refers to measurements carried out at room temperature after the heat treatment had been received. Measurement of mechanical properties at the temperature of treatment is a more common practice among thermal analysts (30). Thermomechanical methods include thermodilatometry (TDA), thermomechanical analysis (TMA) and dynamic thermomechanometry (DMA). Here the onset of surface diffusion and bulk diffusion at specific temperatures should become marked. In application to polymer systems the method becomes important in locating the glass transition temperature.

APPLICATIONS

Application of the factors and relationships outlined, to inorganic systems can easily be made. However in studying organic compounds several modifying features are apparent. Most organic compounds melt below 300°C and so decomposition of solid organic materials occurs in temperature ranges where bulk diffusion takes place. Furthermore many organic decompositions take place with partial or complete liquefaction. With bulk diffusion as the operative sintering mechanism it is therefore not surprising that adsorption experiments find limited use in giving information on the decomposition process for many organic compounds.

Polymer systems like other organic systems are probably subject to degradation from the solid state in temperature regions where bulk diffusion is taking place. However where chain scission takes place to give a resultant carbon then the product carbon may show large adsorptive capacities due to the formation of amorphously structured carbon

Table 1

Comparison of Rates of Oxidation of
Carbon Blacks at 744K (Ref 34)

ASTM Designation	Surface Area m^2g^{-1}	Rate per unit Area $g\ m^{-2}$	Rate per unit area relative to Sample N774
N774	29	5.2×10^{-5}	1.00
N660	35	5.0×10^{-5}	0.96
N650	38	8.8×10^{-5}	1.69
N550	42	2.4×10^{-5}	0.46
N326	84	3.5×10^{-5}	0.67
N330	103	1.9×10^{-5}	0.36
N234	126	3.5×10^{-5}	0.67
N110	143	0.7×10^{-5}	0.13

(31). Here we are starting from a system subject to bulk diffusion through to a system where sintering is very restricted. Thus is seen in the gasification studies on the resultant carbons (32). Such studies, for example, gasification of carbon by oxygen, water vapor or carbon dioxide might be used as models where the reaction interface can be identified with the surface area as measured by adsorption (33). However it appears that only part of the carbon surface is effectively rate determining in the gasification in air or oxygen. Thus in the comparison of oxidation rates of carbon blacks (Table 1) carbons with lower surface areas showed a faster oxidation rate per unit area then carbons with higher areas (34). This arises because the rate of oxidation of carbon crystallites is about 17 times faster in the direction parallel to the basal planes (i.e. oxidation of edge atoms) than

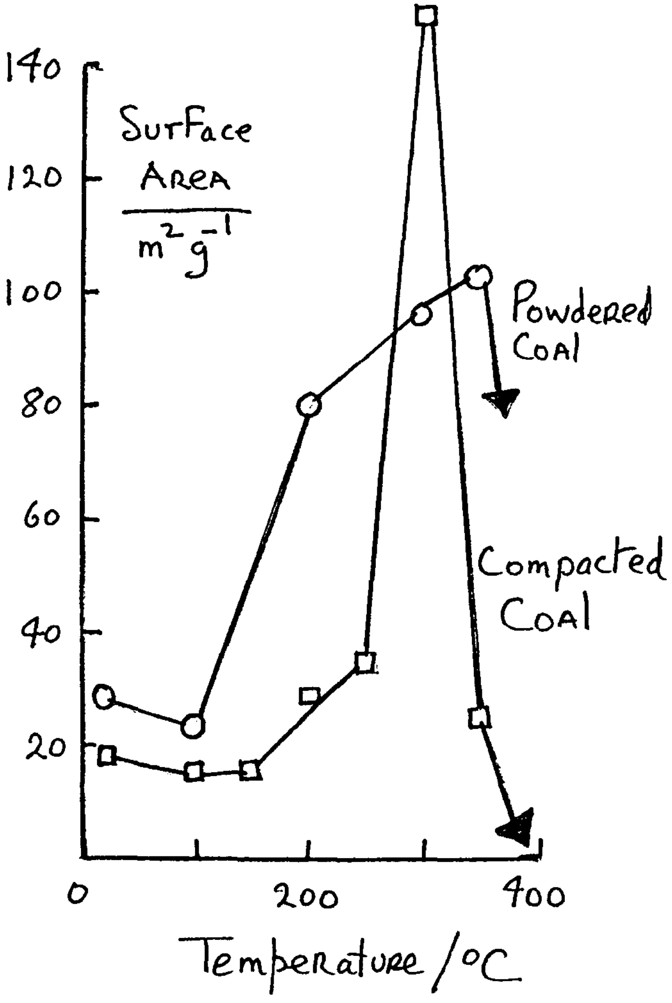

Figure 6 - Surface Area of Mansfield High Hazel Coal Against Temperature of Heating.

perpendicular to them (35,36). The inference must then be that the lower surface area carbon blacks have a greater proportion of their surface consisting of "edge" carbon atoms whilst the higher area carbon blacks expose a larger proportion of the relatively inactive basal plane carbon atoms.

There are other applications of the general theory of activation and sintering outlined in this presentation. It can, for example, be applied with some modification to the variation in strength and surface area of coal compacts prepared under pressure and subjected to heat treatment (37). Figure 6 shows the variation of surface area with temperature of heating for a middle rank coal. It can be seen that the process of activation can be discerned and is more apparent in the compacted material then in the powdered coal. There was a catastrophic failure in the strength of the compacts at 300°C where the activation is a maximum.

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