

ON THE ORIGIN OF INCREASED ACTIVITY IN MECHANOCHEMISTRY OF SOLIDS

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ABSTRACT

In form of a review is dealt with important topics of above mentioned problem. With this also was considered earlier, but fundamental knowledge in this field. The importance of mechanochemistry is analysed. Main topic is the energetics of mechanochemical processes. Briefly is reported on kinetics of processes as well as on mechanically activated solids. This review is completed with a detailed overview of references especially from Comecon states.

RÉSUMÉ

Cet article traite des points essentiels du problème mentionné. Il tient également compte de découvertes antérieures, mais fondamentales dans ce domaine. L'importance de la mécano-chimie y est évaluée. Le sujet principal porte sur les caractéristiques énergétiques des processus mécano-chimiques. La cinétique des processus ainsi que les propriétés des solides mécaniquement activés y sont brièvement étudiées. Cet aperçu est complété par une bibliographie détaillée, concernant surtout les travaux réalisés dans les Etats du Comecon.

1. Introduction

To write on the origin of increased activity in mechanochemistry of solids in a limited paper demands quite some effort. During the last 30 years an extensive accumulation of detailed knowledge has developed in this field which causes difficulties to list all proposed theories. Due to many schools, there are numerous hypotheses supported by physicochemical experience. The main obstacle is the lack of compatible results owing the noncompatibility of experimental conditions. Secondly, a common scientific language and general definitions are missing in this field. Thus, one group of authors⁽²⁰⁾ uses the term "tribochemistry" for mechanochemistry of solids while another group uses the same conception for the chemical aspect of tribology (friction, wear and lubrication)⁽⁶⁾. Also, the terms mechanical activation and mechanochemical activity are used according to every author's own will. On the other hand, with respect to the manifold physical processes and physicochemical consequences, the number of possible mechanisms via which the increased chemical activity is released by mechanical energy is not even currently fully known.

We have to answer the top question: In which way does mechanical energy act as the available energy in chemical processes — either directly or subsequent to transformation into other energy forms.

Mechanochemistry is now an established field in the topic of reactivity of solids. Ostwald's proposition⁽³⁰⁾ is now fulfilled in two ways: *Mechanochemistry* as the science of a system's changes of reactivity by and after the action of mechanical energy and *chemomechanics* as the science of environmentally sensitive mechanical behaviour of materials. Both mentioned branches of nonthermal physicochemical activity of systems are intensively connected and interacting.

Mechanochemical reactions became important in the improved understanding of solid reactivity as well as in technology. In the latter field, the knowledge on mechanical activation provides for better optimisation of comminution processes, since this stage of manufacto-

ring of raw materials depends not so much on a maximum of dispergation but rather on the maximum overall activity. On the other hand, it is dangerous to over-estimate mechanochemical technologies: Mechanical energy is very expensive and mechanical activation is of very low-grade energy efficiency in many systems. The installation of technically activating facilities is also very difficult since a great decrease in reactivity is observed in comparison to laboratory aggregates, except industrial disintegrators^(31,32). Therefore, hitherto only several mechanochemical technologies have been realized, e.g. silicate concretes⁽³³⁾, rock-phosphate fertilizers⁽³⁴⁾ and mechanical alloying^(35,34). In contrast, however, investigations into the mechanochemical destruction of materials are of some great technological importance, e.g. erosion corrosion, corrosion fatigue, and stress corrosion cracking⁽²⁰⁾, mechanochemically initiated metal fires⁽²⁰⁾, and manifold mechanically induced degradation of polymers⁽¹⁰⁾.

Centres of mechanochemical research are inter alia: In the Soviet Union Novosibirsk⁽¹⁸⁾, Moscow^(5,19), Tallinn⁽³²⁾, in the UK Cambridge⁽³⁶⁾, in France Dijon⁽³⁷⁾, in Israel Haifa^(16,33), in Japan Yokohama⁽³⁸⁾, in the FRG Karlsruhe⁽³⁹⁾, Aachen⁽⁴⁰⁾, and in the GDR Berlin⁽²⁰⁾ and Freiberg^(82,41). A vast number of monographs was published by these research centres, e.g. ^(1,29,32).

2. General observations in mechanochemistry

The *general course* of an overall (integral) mechanochemical reaction is described on Figure 1^(20,42). Before the beginning of mechanochemical treatment (phase 1) the reaction is determined by thermal activation and therefore is a function of the reaction temperature. However, at room temperature most solid reactions proceed immeasurably slowly. Application of mechanical energy generally results in a significant increase of the solid reaction velocity, frequently amounting to some orders of magnitude (phase 2). The formation velocity of Ni(CO)₄ from Ni and CO, for instance, rises

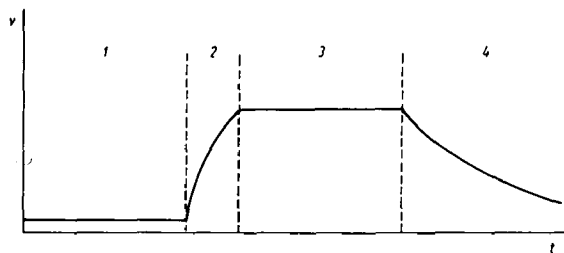


Fig. 1. — Diagram of a tribochemical reaction course⁽²⁰⁾, v — reaction velocity, t — time; (1) — reaction on the untreated solid, (2) — rising activity, (3) — steady state reaction, (4) — decaying activity.

from $5 \cdot 10^{-7}$ mole. \cdot h $^{-1}$ up to $3 \cdot 10^{-5}$ mole. \cdot h $^{-1}$ at 298 K⁽⁴⁵⁾. Phase 3 shows the typical steady state reaction velocity with steady state mechanical activation conditions. In reality, this phase is characterized by an overlap of individual reaction outbursts in the micro to millisecond range released by mechanical impacts^(18,43,44). The decay of reaction velocity after interruption of mechanical treatment (phase 4) depends on the thermal or non-thermal character of the mechanochemical reaction. In the case of a process with negative affinity, the decay occurs instantaneously. In the case of partial thermal activation the decay function can be characterized via the assumption of the lifetime of "active centres" and their consumption by mechanochemical processes⁽⁴⁰⁾.

In many examples the reactivity of solids remains much higher after mechanical treatment than the primary reactivity prior to mechanical treatment. This is caused by the higher energy content of a solid subsequent to the action of mechanical energy onto it. This fact is reflecting the modifications of morphology of the structure and the storage of energy caused by surface and structural defects⁽⁵⁰⁾. This effect is called "mechanical activation of solids" by many authors. It is the subject of most of the listed papers due to the relative simplicity of the investigation of this effect. In contrast, the processes during the action of mechanical energy (in statu deformandi⁽⁴⁶⁾) appear to be less simple.

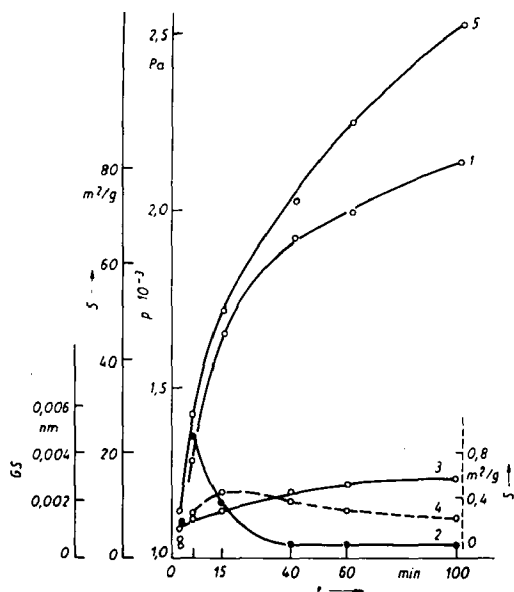


Fig. 2. — Changes in the physico-chemical properties of milled Calcite⁽²⁰⁾. 1 — specific surface area (S) of the primary crystallites, 2 — lattice imperfections (GS), 3 — specific surface area (S) by BET, 4 — specific surface area of secondary particles (S) by sedimentation, 5 — equilibrium pressure (p) of carbon dioxide at 973 K.

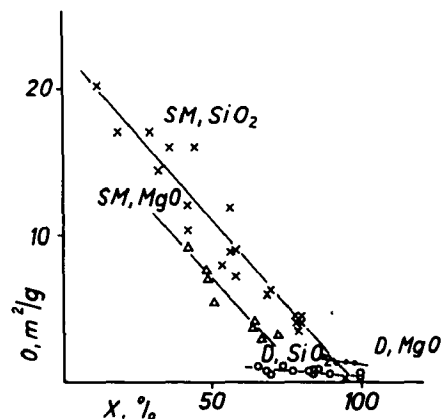


Fig. 3. — Correlation between specific surface (O) and crystallinity (X)⁽⁴⁷⁾. SM — vibration mill; D — disintegrator.

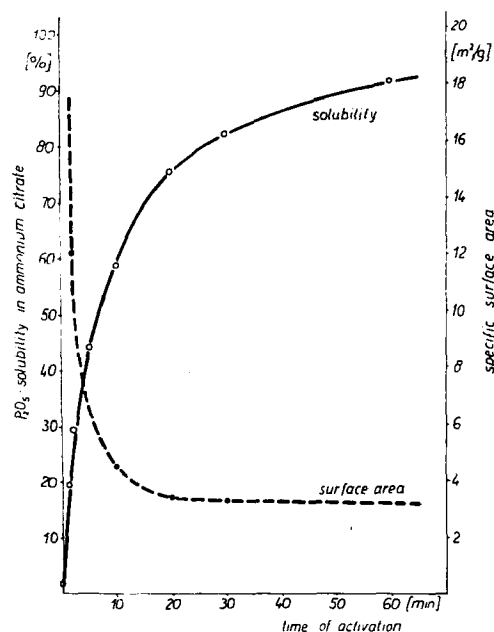


Fig. 4. — Influence of mechanical activation of Maroc rock phosphate on solubility in ammonium citrate solution and specific surface area (BET)⁽⁸²⁾.

A rather classical approach in order to intensify the reactivity of solids involves the *enlargement of surface area* by dispergation. In many cases, the reactivity of solids is determined by the specific surface area of the primary crystallites (Fig. 2⁽⁷⁾), where the latter frequently is lineally connected with the crystallinity (or amorphization) (Fig. 3⁽⁴⁷⁾). However, Figure 4⁽⁸²⁾ indicates that the increase in reactivity can continue after a constant value of dispergation is reached. This shows the effect of lattice defects on reactivity, e.g. the energy storage by homogenous and inhomogenous lattice distortions⁽⁵⁰⁾ etc. It must be emphasized that the remaining reactivity is the real mechanical activation of solids^(18,32) after the subtraction of surface area induced part.

The relatively simple dependence of the overall reaction velocity of mechanochemical processes on the intensity of mechanical treatment⁽²⁰⁾ is frequently observed. In vibration mills, the reaction velocity of many processes such as carbonyl formation from nickel, hydration of silicon carbide, oxidation of iron, depends lineally on the second power of frequency or amplitude

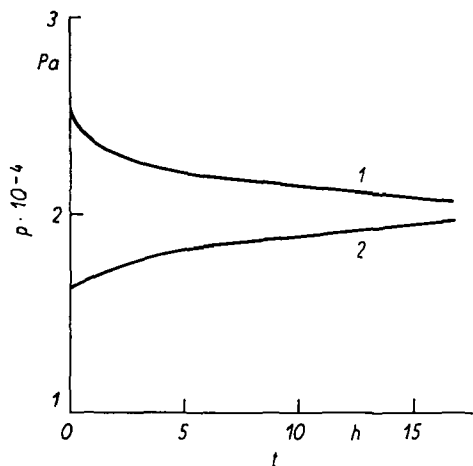


Fig. 5. — Dependence of the CO₂ pressure p on the time t of mechanical treatment for the formation (1) and decomposition (2) of CdCO₃ (²⁰).

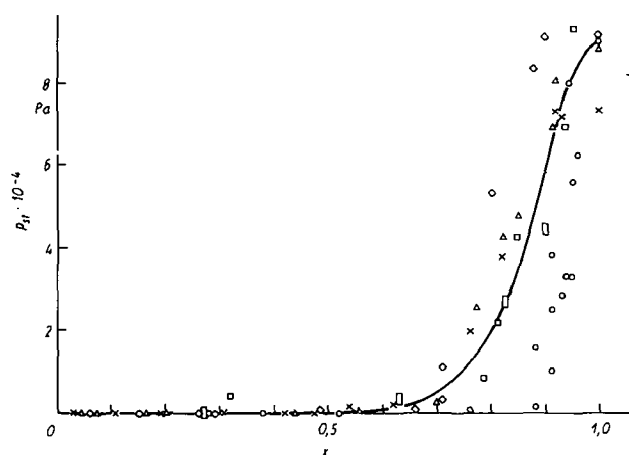


Fig. 6. — Dependence of the steady state CO₂ pressure p_{st} on the composition of solid phase in closed vibration vessels (mole fraction x of carbonates in MeO/MeCO₃ and Me₂O/Me₂CO₃ systems resp.) (²⁰). Me: O — Mg, Δ — Cd, x — Li, □, ◇ — Zn.

of the mill vessel during mechanical treatment, that is on the acting mechanical energy.

One of the most interesting observations in the field of mechanochemistry is the drastic elimination of temperature dependence on reaction velocity. In (²⁰) a great number of mechanochemical processes is listed with no or only very low activation energy.

At least one more specific effect of mechanochemical processes must be mentioned which is the so called "tribochemical equilibrium" (^{20,83}). In a series of tribochemical processes in closed vessels under steady state mechanical conditions, such as the decomposition of cadmium carbonate, a decline of the reaction velocity is observed when a certain concentration of the reactants is reached. If this concentration is varied by the application of one reactant in said system, then again a reaction occurs toward the re-establishment of the initial state.

Figure 5 shows the dependence of the CO₂ pressure on treatment time as an example for formation and decomposition of cadmium carbonate. According to this the same steady state appears from both formation and decomposition (⁵¹).

In mechanochemical reactions of systems such as



it is of significant peculiarity that established steady states ("tribochemical equilibria") are dependent on the

composition of solid components, in other words on the mole fraction ratio of oxide to carbonate (Fig. 6 (⁴⁹)). This effect contradicts Gibbs phase law. In (²⁰) many mechanochemical processes are listed that lead to steady states with an overall zero reaction velocity, inclusive adsorption/desorption processes, modification transformations, and reactions of polymorphs (⁸³).

It was necessary to state these relatively simple though significant observations made 15 years ago before going into detail with respect to different approaches.

3. Energetic approach

Energetics of mechanochemical processes are connected with the dissipation of mechanical energy in the complex system solid/chemically active environment. A multistep model of spacial and temporal dissipation of energy including the respective consequences to the reactivity of the said system is reproduced in Figure 7 (^{44,52}), based on the heuristical "magma-plasma-model" (^{1,7,20,53}):

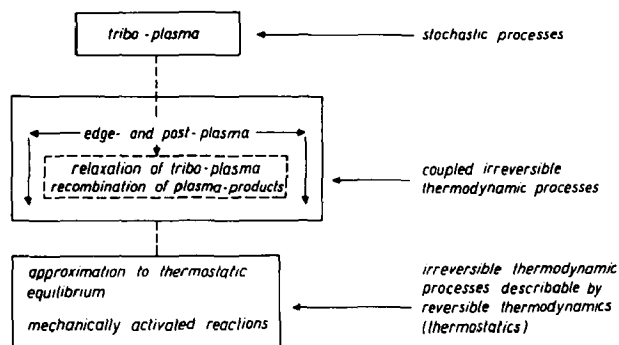


Fig. 7. — Step diagram of the energy dissipation on solids stressed by impact (⁵²).

Triboplasmas are the highest step in this "hierarchy". They cause an energy excess within an ultra-short time (10^{-11} to 10^{-7} s) by the finite speed of disturbances propagation in the real discontinuum and extend to submicroscopic lattic parts. This energy excess can be evaluated from the energy application which is, calculated according to Hertz (⁵⁴) by impact braking as well as from the experimentally observed deformation volume (^{55,56}). Triboplasmas are characterized by an extremely disturbed solid structure as well as by non-steady high-excited fragments of the solid and of the surrounding chemical reaction sphere by means of lattice components such as ions, free electrons (^{57,58}), molecular sublimation (⁵⁹), material exchange between impacting body and target (^{1,60,25}), and also photon emission (^{61,62}). The short lifetime of the triboplasmas causes no Maxwell-Boltzmann distribution. Thus, the conception of a "temperature" is of no sense and the chemical process that takes place in this excitation phase cannot be described by the laws of thermodynamics. Conversions in triboplasmas are of stochastic nature. This first step in the hierarchy of energy dissipation coincides with conceptions — mentioned elsewhere (^{19,63-65}) — on relaxation of vibrational excitation states and conversion into heat. The kinetic temperature due to this process is very high ($> 10^4$ K). It is suggested here that the lifetime of those excitation "states" (10^{-10} — 10^{-9} s) is not sufficient for bimolecular reactions but only for reactions with decomposition of solids (for instance dehydration (³⁷)).

The highest stage of excitation dynamically changes into the next step characterized by relaxation of the plasma "states" and termed "edge and postplasma" (Fig. 7) (resp. to the spacial and temporal dissipation). This process is caused by the recombination of the plasma products as well as by the relaxation of lattice disturbances. It is a necessary consequence of energetic "quenching" of the system. This step is characterized by high reaction velocities, energy, and entropy production. These recombination processes with high energy excess and reaction cross-section play an important role. They produce a great share of the chemically available energy of the post plasma "state" and thus bear the *function of an energy transformer* of mechanical energy to chemical energy in mechanochemical processes. Besides, a number of physical processes take place at this stage of energy dissipation, such as emission of photons and electrons, static electrification, electrostatic discharges, change of electrical conductivity, formation and migration of lattice and electron defects e.g. dislocation generation and motion or F-centres, fresh surface effects, fracture processes⁽²⁰⁾.

Since the individual processes have an essentially longer lifetime than the triboplasmas, such conditions can be generally expected for this "state" that lead to an equidistribution of the energy of the molecules and permit the use of the thermodynamic definition of entropy⁽⁶⁶⁾. Hence it is possible to apply the thermodynamics of irreversible processes to the reactions occurring at this step of energy dissipation^(11,52,67).

Thus, for instance, reactions having a negative affinity appear during mechanical treatment of solids (Table I)⁽²⁰⁾. The so called "tribogalvanic effect"^(43,44), that is the mechanically induced metal deposition without an external current "ageinst" the electromotive series is also a chemical reaction with a minimum affinity of $-300 \text{ kJ mole}^{-1}$ ⁽⁶⁸⁾. It could be shown that the mentioned reactions of the postplasma type (Fig. 7) are thermodynamically coupled with the dissipation processes of mechanical energy, especially with recombination processes of higher excited impact induced "states"^(20,52).

For the dissipation function ψ is valid:

$$\psi = T \cdot dS_i/dt = \sum_k J_k X_k > 0 \quad (1)$$

(T — temperature, ds_i/dt — generation of entropy per unit of time, J_k — generalized flux, X_k — generalized force). When considering that both scalar and vectorial fluxes and forces can appear, than equ. (1) changes into

$$\psi = T \cdot dS_i/dt = \sum_{k=1}^{n_1} J_k X_k + \sum_{j=1}^{n_2} \vec{J}_j \vec{X}_j \quad (2)$$

(J_i, X_i — scalar generalized fluxes and forces, \vec{J}_j, \vec{X}_j — vectorial generalized fluxes and forces). The left addend can be called chemical term and takes into account the coupling of scalar quantities, e.g. of reaction velocities with affinities and of scalar heat fluxes with scalar differences in temperature, which partially occur in recombination processes of triboplasmas. The right addend can be called electro-mechano-caloric term coupling directed matter fluxes with field gradients. In this is involved the coupling of *electric currents* with the electrochemical affinities (as in mechanically induced corrosion processes), *dislocation fluxes* with microscopic and macroscopic stresses, and of "normal" *heat fluxes* with the temperature gradient. Under certain conditions both terms do not couple with one another. Therefore each term has to be defined positively separately acc. to equ. (1). Within each term coupling is possible. If only one single mechanochemical reaction with the velocity v and the affinity A is regarded in the system and if the part $V \cdot A$ is separated from $\sum J_k \cdot X_k$ then there results:

$$\psi = v \cdot A + \sum_{i=1}^m J_i X_i + \sum_{j=1}^{n_2} \vec{J}_j \vec{X}_j \quad (3)$$

As follows from the above formulated conditions:

$$\left(v \cdot A + \sum_{i=1}^m J_i X_i \right) > 0; \quad \sum_{j=1}^{n_2} \vec{J}_j \vec{X}_j > 0 \quad (4)$$

Then under condition (4) can be

$$V \cdot A < 0 \quad (5)$$

if

$$|V \cdot A| < \left| \sum_{i=1}^m J_i X_i \right| \quad (6)$$

TABLE I

Mechanochemical reactions with negative affinity A

No	Reaction	$A_{298 \text{ K}}$ kJ/mole
1	$\text{C} + 2 \text{H}_2\text{O} \rightarrow \text{CO}_2 + 2 \text{H}_2$	- 62,4
2	$2 \text{Cu} + \text{CO}_2 \rightarrow 2 \text{CuO} + \text{C}$	- 140,2
3	$\text{Au} + 3/4 \text{CO}_2 \rightarrow 1/2 \text{Au}_2\text{O}_3 + 3/4 \text{C}$	- 311,5
4	$\text{SiC} + 2 \text{H}_2 \rightarrow \text{Si} + \text{CH}_4$	- 58,9
5	$\text{BaO}_2 \rightarrow \text{BaO} + 1/2 \text{O}_2$	- 55,2
6	$\text{Fe}_3\text{O}_4 + 2 \text{C} \rightarrow 2 \text{CO}_2 + 3 \text{Fe}$	- 330,2
7	$2 \text{MgO} + \text{C} \rightarrow \text{CO}_2 + \text{Mg}$	- 744,9

It is evident from equ. (4) to (6) that partial mechanochemical processes with positive free enthalpy or negative affinity by mechanical energy input thermodynamically coupled with many other processes on-line, e.g. recombination processes of higher excited "states", can proceed with an overall positive entropy output.

Relation (6) is valid for many examined experimentally mechanochemical systems⁽⁴⁸⁾. Thus, mechanochemical reactions with negative affinity occur through thermodynamical coupling, and hence there is an explanation for the reactions listed above.

In order to connect velocity and affinity with sufficiently small A-values⁽⁵²⁾ there can be calculated

$$V = L_{11} A + \sum_{i=1}^{n_2} L_{1i} X_i \quad (7)$$

(L_{11} , L_{1i} — phenomenological coefficients).

In the steady state of mechanical treatment the 2nd term of equ. (7) is constant, so that equ. (7) yields

$$V = aA + b \quad (8)$$

(a , b — constants)

which can be proved experimentally, e.g. Figure 8⁽⁶⁷⁾.

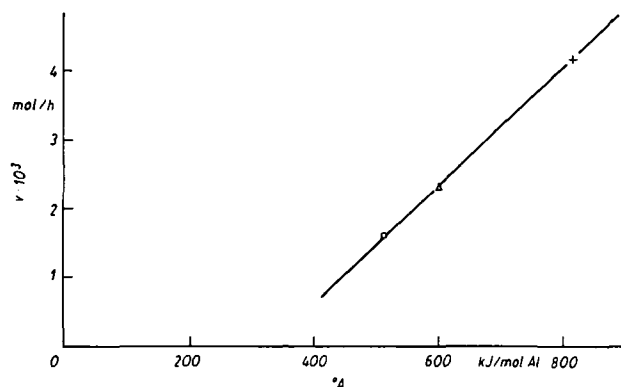


Fig. 8. — Dependence of the reaction velocity v on the basic affinity A for aluminium⁽²⁰⁾.

X — reaction with O_2 , Δ — reaction with CO , o — reaction with CO_2 .

As defined in irreversible thermodynamics, a steady state appears by virtue of the fact, that a number of fluxes drop to zero by maintaining determined forces constantly in time. In the case of mechanical treatment in a closed milling set such as a vibration mill, steady states appear after an incubation period which lead to the appearance of forces constant in time. If the $(n + 1)^{th}$ flux vanishes with maintenance of n forces then a n^{th} order steady state is present. In the consideration of a mechanochemical process the "tribochemical equilibrium" represents such a state, following the Le Chatelier-Braun-principle. Upon identification of the "tribochemical equilibrium" as a steady state of n^{th} order, steady state mechanochemical reactions could be proved to run *isoaffinely*⁽⁵²⁾. This is evidence that an open thermodynamic system is present in the case of mechanochemical reactions during the action of mechanical energy. This means, that the thermal reaction system (post plasma) is subjected to a permanent matter and energy input from the higher excitation states of the system (triboplasmas). Equ. (8) for $v = 0$ changes during steady state into

$$-A = \frac{b}{a} = A_0 \quad (9)$$

Consequently, the steady state affinity takes on a finite value ($A_0 \neq 0$) in the steady state. It is established⁽⁴⁴⁾, that experimentally measurable and frequently measured⁽²⁰⁾ steady state negative deviations of integral

electrode potentials during mechanical treatment of metals are identically with steady state affinity of mechanochemical processes in the sense of equ. (9).

The causal connection between the production of lattice disorders in metal as a result of the macroscopic supply of mechanical energy e.g. by strain, the appearance of dislocations at the interface and the special electrochemical reactions thus caused, represents a simple example for the thermodynamic coupling of mechanical and chemical processes. Dislocation current and electric current are both vectorial processes capable of thermodynamic coupling (equ. (2), (3)). Thus the mechanochemical process may be written as (while neglecting adsorption effects)⁽¹¹⁾:

$$T\sigma = J \frac{n\Delta\mathcal{A}}{\bar{\alpha}} + I \cdot \tilde{A} \quad (10)$$

(T — temperature, σ — entropy production, J — dislocation current, n — number of dislocations in a planar accumulation, $\Delta\mathcal{A}$ — macroscopic stress difference (strain hardening), I — electric current, \tilde{A} — electrochemical affinity, $\bar{\alpha}$ — dislocation concentration).

The product $\frac{n\Delta\mathcal{A}}{\bar{\alpha}}$ represents the affinity of the "chemical" reaction for the generation of dislocations. From equ. (10) the lineal phenomenological equations for the currents yield:

$$J = L_{11} \frac{n\Delta\mathcal{A}}{\bar{\alpha}} + L_{12} \tilde{A} \quad (11)$$

$$I = L_{21} \frac{n\Delta\mathcal{A}}{\bar{\alpha}} + L_{22} \tilde{A} \quad (12)$$

The phenomenological linearity coefficients L_{12} and L_{21} are equal according to Onsager. Some effects that provide interesting physical interpretations can be derived from equations (11) and (12):

- the electric current per unit of dislocation current in electrochemical equilibrium ($A = 0$) which characterizes the mechanical activation of corrosion processes by macroscopic deformation,
- the dislocation current per unit of corrosion current in the absence of mechanical stresses ($\Delta\mathcal{A} = 0$) or electroosmosis of dislocations, the so-called "chemomechanical effect", rediscovered later by the name "chemostress coefficient"⁽⁷⁶⁾, a kind of environment sensitive behaviour of materials,
- the electrochemical potential difference per unit of mechanical stress difference in absence of corrosion current ($I = 0$), the transfer potential of dislocations connected with the negative shift of electrode potentials by deformation of solid electrodes,
- the mechanical stress difference per unit of electrochemical affinity in the absence of dislocation currents ($J = 0$) as electroosmotic pressure of dislocations.

The effects mentioned represent complete analogues to the known electrokinetic phenomena.

For a long time the opinion was held that temperature peaks during the transmission of mechanical energy to solids were the only cause to release mechanochemical reactions⁽⁶⁹⁾. The Bowden-Tabor theory of "hot spots" based on extensive experimental material^(36,70) has been an important factor in this.

Thus, it was found that during solid friction temperatures of more than 1 000 K can appear in small areas of $10^{-1} - 10 \mu m^2$ with a duration of 10^{-4} to 10^{-3} s. Comprehensive theoretical interpretation and calculation formulas of mechanical energy in thermal energy are given in⁽²⁰⁾. The causes can be impact and friction temperatures in the range of 750 K while temperatures in dislocation range up to some 100 K. Fracture temperatures at

some distance (10^{-9} m) from the crack tip are in the range of some 100 K up to the heat generation caused by the above mentioned relaxation of elastic energy, e.g. after mechanically released breaking of macromolecular chains. The latter example shows that thermal effects of the "hot spots" type also occur in the network of dissipation processes and represent one of the possible excitation "states". However, they do not belong to the highest in the hierarchy of dissipating energy.

Thus, "hot spots" and other mentioned thermal effects are characteristic of the dissipation step of post and edge plasmas (Fig. 7). Moreover, they are one of the possible yet not necessary forms of chemically available energy of relaxation processes in high excited primary processes caused by mechanical treatment of solids.

The approximation to the thermostatic equilibrium has to be regarded as the last step of the energy dissipation hierarchy (Fig. 7). Part of the dissipating energy remains in the solid as the so-called excess free enthalpy. As mentioned above, this is bound up, with morphological and electronic defects and is of a long life, especially at low temperatures (mechanically activated solids). The flow of excess free enthalpy is an irreversible process which occurs so slowly, with respect to the chemical reaction in the solid, that in many cases the activated "state" is adapting itself and can be regarded as quasistatic and thus described with sufficient approximation by the use of reversible thermodynamics laws⁽⁴³⁾.

The excess free enthalpy is defined by equation (13)⁽⁷¹⁾:

$$\Delta G = G_{\dagger}^* - G_{\tau} \quad (13)$$

(G_{\dagger}^* — free enthalpy of the active solid, G_{τ} — free enthalpy of that substance at the initial state at temperature T).

Experimentally it can be directly determined by use of the equilibrium constants of reactions with active (K_p) and nonactive (K_p) solids, resp.⁽⁷²⁾:

$$\Delta G = RT (\ln K_p - \ln K_p) \quad (14)$$

In contrast, it is not correct to derive ΔG from the integrally measured emf. of mechanically stressed solid electrodes due to a deviation of results by local electrode processes^(20,43,44,73-75).

Experimental determination of excess free enthalpy by calorimetry or DTA is very difficult because of the arduousness to measure the entropy difference between active and nonactive solid.

4. Kinetic approach

The cited monographs⁽¹⁻²⁹⁾ present inter alia an accumulation of facts and theories on changed kinetics of chemical processes due to the action of mechanical energy on solid/medium systems. Beyond the remarks on kinetics of mechanochemical reactions mentioned above, significant factors in this field are: Sorption and desorption processes, transport processes in the phase boundary layer, including reaction layers and fresh-surface effects, and transport processes in the solid.

The "tribokinetic model" (Fig. 9)⁽⁷⁷⁾ of interaction of CO_2 with Cu can serve as an example for gas/solid interaction with mechanical treatment. This model obviously describes the interaction of mechanically influenced adsorption, desorption, absorption, and reaction on the surface, as well as in the bulk of solid. The mechanism of mechanically induced chemisorption as a consequence of lattice disorder on the surface of SiO_2 and MgO is reported in detail in⁽¹⁹⁾.

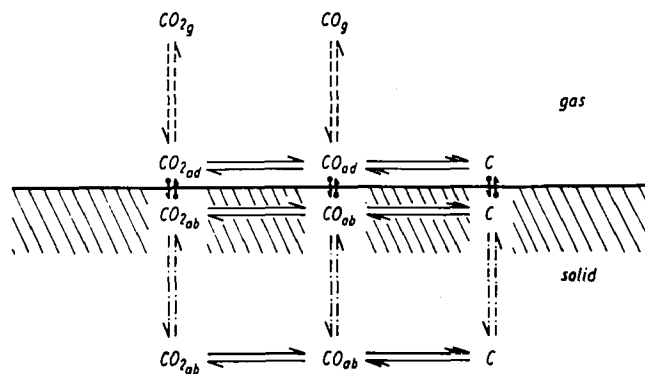


Fig. 9. — "Tribokinetic" model in the CO_2/Cu system⁽⁸¹⁾. CO_{2g} , CO_g — gaseous state, CO_{2ad} , CO_{ad} — adsorbed state, CO_{2ab} , CO_{ab} — absorbed state. \rightleftharpoons — chemical reaction: $\text{CO}_2 + \text{Me} \rightleftharpoons \text{CO} + \text{MeO}$; \rightleftharpoons — chemical reaction: $\text{CO} + \text{Me} \rightleftharpoons \text{C} + \text{MeO}$; $\circ \rightleftharpoons$ — absorption, $\delta \rightleftharpoons$ — desorption, \updownarrow — diffusion, $////$ — phase boundary layer disturbed by mechanical treatment.

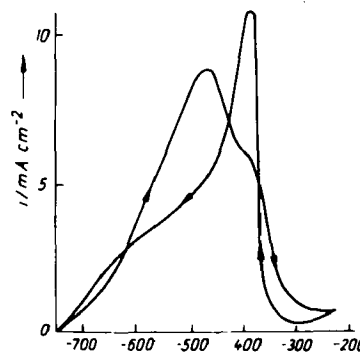
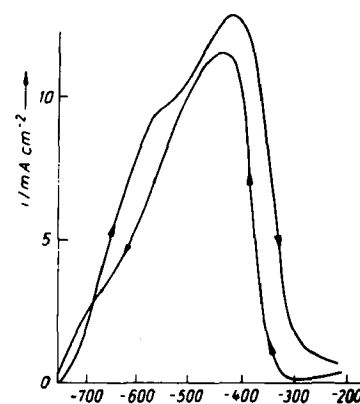


Fig. 10. — Potentiodynamic current density vs. electrode potential curves of iron in phosphate electrolytes. a) without mechanical treatment, b) with mechanical treatment⁽⁷⁸⁾.

As an interesting example of changed kinetics in the phase boundary layer solid/liquid, the mechanically induced formation of phosphate layers on iron, indicated by electrochemical measurements is described in^(78,79) (Fig. 10). A diagram of current density vs. electrode potential (Fig. 10) describes in metal/electrolyte systems a reaction velocity vs. the electrochemical affinity function. Thus, changes in reaction kinetics can be clearly demonstrated. Under potentiodynamic conditions, a reaction layer is formed by mechanical treatment of high purity iron (glass-bead impingement on rotating disc electrode at 3000 r.p.m.) in an electrolyte containing phosphate anions prior to the common passivating layer formation. This effect is indicated in Figure 10 as a deviation of the current density

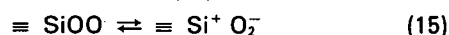
maximum to more negative potentials and as a very narrow current density peak after reactivation of the passive electrode. By measurements of the current density vs. time a two-dimensional progressive nucleation of reaction layer could be established that is caused by direct reaction of freshly generated iron surfaces with the electrolyte. The active centres of nucleation may appear as dislocations on the interface owing to an impact deformation of the solid. Local damages of said reaction layer ($m \text{ FeHPO}_4 \cdot n \text{ Fe}_2\text{O}_3$)⁽⁸⁴⁾ result upon the action of shear forces that in turn are given rise to by tensile or compressive strain due to surface erosion. In this, conditions for pit nucleation are established. Thus was found pitting corrosion of iron released from "non pitting" phosphate anions under mechanical impact treatment.

A detailed kinetic model for solid/solid reactions in dispergation facilities is given in⁽¹³⁾. Many examples of changed kinetics and of mechanically induced diffusion processes in solids are described elsewhere⁽²⁰⁾.

As was shown by the investigation of zinc impact-induced "diffusion" into a copper matrix at ambient temperature⁽⁸⁰⁾ with a formal increase of diffusion coefficient by three orders of magnitude the number of lattice defects per se is not responsible for the abnormal mechanically released diffusion behaviour. However, the process depends on the *motion* of defects, e.g. dislocations, grain boundaries⁽⁸¹⁾ etc. The above mentioned effect is an example of an important factor in mechanochemistry the so-called "lattice dynamics"⁽¹⁹⁾. The solid's structure is not only formed due to deformation, but is also "breathing". By the action of defects *while* they move, the *mobility* of structure releases a very high reactivity during the deformation process of solids.

5. Activated solids

As mentioned above, the increase of reactivity due to stable changes of structure of solids is called mechanical activation, and thus said solids are activated solids. A comprehensive review on mechanically activated periclase (MgO) and quartz (SiO₂) is given in⁽⁴⁷⁾. The comminution of both oxides results in crushing and smashing of initial agglomerates, respectively, and in structural changes, which are specified by the primary particle diameter and lattice distortions (the latter could not be established in quartz). Significant differences due to the stress mechanism occur (Fig. 3): A relatively high decrease of crystallinity can be reached by shock treatment (disintegrator) without sufficient changes in specific surface of primary crystallites; by pressure and shearing treatment (vibration mill) the decrease of crystallinity is connected with a sufficient increase of specific surface. Zero, one, two, and three-dimensional defects are generated. Regions near the surface are mainly disturbed where interactions are possible of the induced defects with the gas atmosphere. Thus, in periclase F⁺-centres (trapped electrons in mechanically induced anion vacancies) are generated as well as O₃⁻ centres by the interaction with oxygen. During mechanical treatment of quartz, Si-O bonds are broken, and by this radicals are created. = Si-radicals were detected as so-called E'-centres. Oxygen defect electron centres (ODE) are formed by reaction (15) in the



presence of oxygen. In quartz mechanical energy causes an essentially stronger structural perturbation than in periclase. Yet, the penetration depth of distortion is greater in the latter compound. In summary there can

be stated that the distribution of detected defects in activated solids mainly depends on the mechanism of treatment; whereas kind, concentration, and penetration depth depend on the material-specific features of the substances.

Another important structural-dependent physical property of activated solids, the electrical conduction mechanism, is also changed. To give an example, recently the influence of mechanical treatment on the capacitance of passivated iron electrodes was investigated⁽⁸⁵⁾. In this a significant change of parameters could be established. Such parameters determine the semiconductor properties of passive layers by action of mechanical impacts as e.g. the dielectric constant, the donor concentration, the flatband potential etc.

In conclusion there can be stated, if the deformation released by these processes is the first response of solids to the action of mechanical forces, then the lattice perturbation that remained stable after deformation is the final expression due to the origin of increased reactivity of solids in mechanochemistry.

References

- (1) P.A. Thiessen, K. Meyer, G. Heinicke. — "Grundlagen der Tribochemie", *Abh. dtsh. Akad. Wiss., Kl. Chem. Geol. u. Biol.* Nr. 1, 1966.
- (2) T. Kubo. — *Mechanochemistry*, Tokyo 1971.
- (3) P.J. Butyaguin. — *Uspekhi khimii*, 1971, 40, 1935.
- (4) V.V. Boldyrev, E.G. Avvakumov. — *Uspekhi khimii*, 1971, 40, 1835.
- (5) B.V. Derjagain, N.A. Krotova, V.P. Smilga. — *Adgesya tverdikh tel*, Moscow 1973.
- (6) Committee on Tribology. — *The introduction of a new technology*, London 1973.
- (7) V.V. Boldyrev, K. Meyer. — *Festkörperchemie*, Leipzig, 1973.
- (8) G.S. Khodakov. — *Fizika izmelcheniya*, Moscow 1972.
- (9) P.G. Fox. — *J. Mater. Sci.*, 1975, 10, 340.
- (10) N.K. Baramboim. — *Mekhanokkimiya Vysokomolekulyarnikh soyedinenii*, Moscow 1978.
- (11) E.M. Gutman. — *Mekhanokhimiya metallov u sachita ot korrosii*, Moscow 1974.
- (12) V.P. Regel, A.I. Slutsker, E.E. Tomashevski. — *Kineticheskaya teorya prochnosti tverdikh tel*, Moscow 1974.
- (13) E.G. Avvakumov. — *Mekhanicheskoye metody aktivatsii khimicheskikh protsessov*, Novosibirsk 1986.
- (14) M.W. Vlasova, N.G. Kakassey. — *Electronnyi paramagnitnyi resonans v mekhanicheskoy razrushennykh tverdikh telakh*, Kiev, 1979.
- (15) V.A. Radtsig. — In *Kinetika i mekhanizm khimicheskikh reaktsii v tverdikh telakh*, Chernogolovka, 1981.
- (16) J.I. Lin, S. Nadiv. — *Mater. Sci. Engng.*, 1979, 39, 193.
- (17) N.S. Enikolopov. — *Tezisy dokl. Mezdunerodnyi simpozium po khimicheskoi fizike*, Moscow 1981, p. 83.
- (18) V.V. Boldyrev. — *Eksperimentalnye metody v mekhanokhimiya neorganicheskikh vechestv*, Novosibirsk 1983.
- (19) P.J. Butyaguin. — *Uspekhi khimii*, 1983, 53, 1769.
- (20) G. Heinicke. — *Tribochemistry*, Berlin, 1984.
- (21) 1. Simpozium: *Mekhanokhimiya i mekhanokhimiya protsessy v tverdikh telakh*, Voronez 1968, Tezisy.
- (22) 2. Simpozium: *Mekhanokhimiya i mekhanokhimiya tverdikh tel*, Materialy, Frunze 1969.
- (23) 3. Simpozium: *Triboemission und Tribochemie*, Berlin 1971, Thesen.
- (24) 4. Simpozium: *Mekhanokhimiya i mekhanokhimiya tverdikh tel*, Irkutsk 1973, Tezisy.
- (25) 5. Simpozium: *M.i.m.tv.t.*, Tallinn 1975, Materialy, Tallinn 1977.
- (26) 6. Simpozium: *Mechanoemission und Mechanochemie*, Berlin 1977, Thesen.
- (27) 7. Simpozium: *M.i.m.tv.t.*, Tashkent 1977, Tezisy, Doklady Tashkent 1979.
- (28) 8. Simpozium: *M.i.m.tv.t.*, Tallinn 1981, Tezisy.
- (29) 9. Simpozium: *Mechanoemission und Mechanochemie*, Berlin 1983, Kurzreferate.
- (30) W. Ostwald. — *Die chemische Literatur und die Organisation der Wissenschaft*, Leipzig 1919.
- (31) J. Hint. — *Aufber. — Techn.*, 1971, 12, 96.
- (32) J. Hint. — *UDA-tehnologiya*, Tallinn 1981.
- (33) J. Hint. — *Osnovy proizvodstva silikalitsnykh izdeliy*, Leningrad, Moscow 1962.
- (34) H. Harenz, R. Paudert, S. Müller, E. Linke, H. Müller. — *Arch. Acker- und Pflanzenbau u. Bodenkunde*, 1979, 23, 707.

- (35) J.S. Benjamin. — *US Pat. Nr. 3723 092*, 1973.
- (36) F.P. Bowden, D. Tabor. — *Reibung und Schmierung fester Körper*, Berlin 1959.
- (37) J.C. Mutin. — *10th Intern. Symp. Reactivity of Solids*, Dijon 1984, Extended Abstracts, p. 424.
- (38) M. Senna. — *Proceedings of Intern. Symp. on Powder Technology*, Kyoto 1981, p. 457.
- (39) H. Rumpf. — *Aufber. — Techn.*, 1973, 14, 59.
- (40) R. Schöne. — *Chem. Ing. Techn.*, 1969, 41, 287.
- (41) K.H. Heegn. — *Diss. AdW Freiberg*, 1986.
- (42) G. Heinicke. — *Kolloidn. Z.*, 1969, 31, 596.
- (43) K.P. Thiessen. — *Z. Chem.*, 1974, 14, 135.
- (44) K.P. Thiessen. — *Diss., AdW Berlin*, 1983.
- (45) G. Heinicke, H. Harenz, K. Sigrüst. — *Z. anorg. allg. Chem.*, 1967, 352, 178.
- (46) L. Graf. — *Z. Metallkde.* 1975, 66, 749.
- (47) U. Steinike, K. Kretschmar, L.I. Barsova, I. Ebert, K.P. Hennig, T.K. Jurik. — *Reactivity of solids*, to be published.
- (48) G. Heinicke, R. Riedel, H. Harenz. — *Z. phys. Chem.*, Leipzig, 1974, 227, 62.
- (49) G. Heinicke, K. Sigrüst. — *Z. Chem.*, 1971, 11, 226.
- (50) K. Sigrüst, H. Fichtner. — *Phys. stat. solidi* (in press).
- (51) G. Heinicke, K. Sigrüst. — *Mber. Dt. Akad. Wiss.*, 1969, 11, 44.
- (52) K.P. Thiessen, K. Sieber. — *Z. phys. Chem.* (Leipzig), 1979, 260, 403, 410, 417.
- (53) P.A. Thiessen. — *Z. Chem.*, 1965, 5, 168.
- (54) H. Hertz. — *Ges. Werke*, Bd. 1, p. 155, Leipzig 1895.
- (55) K. Meyer, E. Gragert. — *Phys. stat. sol.*, 1964, 6, 803.
- (56) H.J. Spangenberg. — *Mber. Dt. Akad. Wiss.*, 1971, 13, 130.
- (57) K. Meyer, M. Rossberg. — *Z. Chem.*, 1971, 11, 202.
- (58) E. Linke. — *Z. angew. Phys.*, 1970, 29, 241.
- (59) P.A. Thiessen, E. Franke, H. Florek. — *Mber. Dt. Akad. Wiss.*, 1965, 7, 371.
- (60) K.P. Thiessen, W. Hübner, R. Jung, A. Pinkowski, A. Rommel, W. Siegling, P. Spitzer. — *Die Technik*, 1976, 31, 5, 326.
- (61) E.P. Schober. — *Diss. HU Berlin*, 1970.
- (62) K. Meyer, P. Obrikat, M. Rossberg. — *Kristall und Technik*, 1970, 5, 181.
- (63) P.G. Fox, I. Soria-Ruiz. — *Proc. Roy. Soc.*, 1970, 79.
- (64) V.V. Boldyrev. — *Kinetika i kataliz*, 1972, 13, 1 414.
- (65) F.C. Urakæev, V.V. Boldyrev, O.F. Pozdnyakov, V.R. Regel. — *Kinetika i kataliz*, 1977, 18, 350.
- (66) J. Prigogine, R. Defay. — *Chemische Thermodynamik*, Leipzig 1962.
- (67) K. Sigrüst. — *Diss. HU Berlin*, 1967.
- (68) K.P. Thiessen. — *Z. Chem.*, 1976, 16, 9.
- (69) L. Gilbert. In K. Peters. — *Symposium Zerkleinern*, Weinheim 1962, p. 94.
- (70) A. Knappwost. — *Schmiertechnik und Tribologie*, 1970, 17, 166.
- (71) G.F. Hüttig. — *Handbuch der Katalyse*, VI, 3, p. 318, Wien 1943.
- (72) G. Heinicke, H. Harenz, J. Richter-Menda. — *Kristall u. Technik*, 1969, 4, 78.
- (73) M. Clarke. — *Corr. Sci.*, 1970, 10, 671.
- (74) K.P. Thiessen. — *Z. Chem.*, 1976, 16, 9.
- (75) E. Leitel, W. Hübner, K.P. Thiessen. — *Schmierungstechnik*, Berlin 1986, 17, 47.
- (76) M. Ciftan, E. Saibel. — *Solid state comm.*, 1978, 27, 435.
- (77) G. Heinicke, E. Schober. — *Z. Chem.*, 1971, 11, 219.
- (78) E. Leitel, W. Hübner, P. Czaja, K.P. Thiessen. — *Werkst. Korros.*, 1983, 34, 613.
- (79) E. Leitel, W. Hübner, A. Rommel, K.P. Thiessen. — *Werkst. Korros.*, 1985, 36, 79.
- (80) W. Hübner, K.P. Thiessen. — *Wear*, 1979, 55, 305, R 5.
- (81) K. Smidoda, W. Gottschalk, H. Gleiber. — *Acta met.*, 1978, 26, 1833.
- (82) R. Paudert, H. Harenz, R. Vogt. — *Fachtagung, Zerkleinerung und Tribochemie*, Preprints, p. 203, Freibert 1981.
- (83) S. Nadiv., I.J. Lin. — *10th Intern. Symp. Reactivity of Solids*, Dijon 1984, Extended Abstracts, p. 421.
- (84) J.B. Makaricev, A.G. Akimov, E. Leitel, W. Hübner, K.P. Thiessen. — *Poverchnost*, in press.
- (85) A. Pinkowski, K.P. Thiessen. — *Z. phys. Chemie* (Leipzig), 1985, 266, 513.