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Abstract

The action of mechanical energy on solids effects changes to their structure. The resulting structural defects lead to a storage of energy in the solid, which may raise its chemical reactivity. Investigations on the mechanically induced reactivity of solids have been carried out with the specific aim of influencing reaction processes in order to obtain high yields, high reaction velocities or selective reactions. On the basis of detailed structural investigations on mechanically treated quartz and hydrargillite, the interaction of the stressed solid with the surroundings has been explored (titanite formation, zeolite formation, polymorphous transformation, gas adsorption, Na⁺-elimination and hydration of amorphous Al₂O₃).

The investigations reveal that the size reduction which occurs during mechanical activation is not the decisive reason for reactivity enhancements, but that these are caused primarily by structural changes. Apart from the structural properties of solids, however, their chemical properties as well as those of the surroundings have an influence on their reactivity.

1. Introduction

People have known since ancient times that chemical reactions can be induced by mechanical energy, e.g. by friction or impact. Thus in prehistoric times, people generated light with the aid of flint stones. Also known are the effects of pressure and shear during geological epochs in the genesis of minerals, e.g. the formation of mica from feldspar by geotectonic movements. In 1911, Ostwald¹⁾ first used the term mechano-chemistry to describe the "influence" of mechanical energy on chemical reactions. The term "tribo-chemistry", which is often regarded as a synonym, is, however, restricted to chemical and physico-chemical changes of solids under the influence of mechanical energy²⁾.

In the 1920s, Tamman³⁾ studied the influence of mechanical treatment on the reactivity of solids. In the 1930s it was primarily Fink^{4,5)} and later Bowden and Tabor⁶⁾, who investigated the effects of friction and abrasion on the oxidation reactions of metals and on their decomposition. They formulated the conception of "hot spots".

Up to the 1960s, progress was based on empiricism. Only in the 1970s were scientific investigations on the mechanism of the transfer of mechanical energy on solids begun⁷⁻¹¹⁾. The range of mechanically treated solid substances is very wide, comprises both inorganic and organic materials, and extends from oxides to phosphates and silicates, from metals to ores and raw materials, and is often used as a process step in the synthesis of compounds having great practical relevance¹²⁻²⁵⁾. Among organic substances, it is above all the polymers which aroused the interest of tribochemistry. But also, for example, the mechanical treatment of chloramphenicol-palmitate for the production of a physiologically active component is of importance²⁶⁾.

The influence of mechanical energy on solids induces a multitude of elementary physico-chemical micro and macroprocesses, which lead to a change of the structure, i.e. to the occurrence of structural defects such as changes of the surface, lattice distortions, conversion of long-range order distortions into short-range order and electronic defects. The processes taking place under the influence of mechanical energy are very complex, and depend on the kind and intensity of the mechanical stresses

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and the specific properties of the solids based on their lattice structure and, of course, their chemical nature. The mechanical energy may be transferred, e.g. by the impact of solid particles or by the induction of tensile and compressive forces in the powder mass (**Fig. 1**).

Fig. 1 Different stress mechanisms used in mechanically activating solid particles (2).
I stress between two surfaces (pressure and shearing stress)
II stressing by impact

Generally it has been established that with pressure and shear stresses, structural changes are concentrated at regions near the surface and diminish with increasing distance from the surface. With impact stresses, the size of the primary crystallite becomes smaller in the whole volume and the disturbance starts at the corners and borders^{8,9)}.

Mechanical treatment leads to a storage of energy. According to theoretical investigations by Sigrist and Fichtner²⁷⁾, it follows that apart from surface and inhomogeneous lattice distortions, homogeneous distortions may also contribute to this energy storage.

They applied their theory to experimental data from MgO and found maximum values of 30 J g^{-1} for inhomogeneous distortions, of 122 J g^{-1} for homogeneous and inhomogeneous distortions, and of 153 J g^{-1} for surface energy.

The reactivity of solids may often be considerably enhanced by mechanical treatment. Even such reactions as the formation of Au_2O_3 and C from Au and CO_2 , the formation of CuO or Cu_2O and C from Cu and CO_2 , which cannot be accomplished thermally as a result of extremely negative affinity, proceed under mechanical treatment with a measurable velocity²⁸⁾.

Investigations on the mechanically changed reactivity of solids are being carried out with the aim of deliberately influencing the reaction processes of the solids concerned. For example, in chemical syntheses, the highest possible yield, and a high velocity and selectivity are aimed at. A specific influence on the reaction processes requires a knowledge of the relation between the real structure and kinetic parameters.

By means of some examples, the influence of the mechanical treatment on the structure and reactivity of solids will be demonstrated and some conclusions of general application are given.

2. Examples of Mechanical Activation

2.1 Reactivity of Mechanically-Treated Quartz

The effect of mechanical energy on the structure of quartz has been described in detail by Steinike et al.⁸⁾. Mechanical activation leads to changes in the long and short-range order caused by lattice distortions and broken bonds. The mechanically-treated quartz is in a partially crystalline state. It still contains typical elements of the crystalline quartz structure and is characterized by the absence of long-range order (**Fig. 2**).

2.1.1 Formation of Titanite

Titanite (CaTiSiO_5) occurs in nature as a mineral and can be used for dielectric ceramics.

Fig. 2 Radial distribution function. (RDF). 1= α -quartz, 2=amorphous SiO_2 , 3= α -quartz after 70h of mechanical treatment, r =distance of an arbitrary atom from the origin (8).

There are indications that it may gain in significance in the fixation of radioactive waste^{29,30}. There are various technical methods for the preparation of titanite^{31,32}. According to Michailova et al.³³, the synthesis temperature is lowest if quartz sand is used as the SiO₂ component (**Fig. 3,a**). In the following it will be shown that in the production of titanite, quartz sand can be used and advantage may be taken of the reactivity-raising effect of its mechanical activation^{34,35,36}.

As the second reaction component, calcium titanate (synthetic perowskit) was used. With the use of calcium titanate and quartz sand the reaction at temperatures up to 1280°C leads to an incomplete transformation (**Fig. 3,b**). Higher temperatures bring about a complete transformation, but cannot be used because of the occurrence of disturbing sinter effects causing a hardening of the product. On the other hand, the use of mechanically-activated quartz sand leads to a complete titanite transformation already at 1250°C (**Fig. 3,c**). In this case, a temperature decrease of 30°C is not significant in itself, but the fact that the reaction is shifted to a temperature region in which no sinter effects occur is of critical importance.

Fig. 3 Reaction equations for the formation of CaTiSiO₅ (36).

There are optimal conditions for the reaction with regard to the mechanically-generated disturbances. The specific surface area alone is not the decisive parameter (see **Table 1**). **Table 1** contains the temperatures at which the transformation to titanite is complete. The solid reaction starts at 1050°C and is completed at 1250°C, whereby the main quantity of CaTiSiO₅ — about 90% — is already formed at 1180°C. It was not possible by the transformation of quartz into a completely amorphous state or by the use of amorphous aerosil to further lower the reaction temperature of titanate under the given conditions.

In the formation of titanite from quartz, cris-

Table 1 Dependence of the temperature T during a 100 percent transformation of titanate and quartz to titanite on the starting component.

Sample Name	t, h	s, m ² g ⁻¹	X, %	T, °C
WQS/0	0	1	100	1280
WQS/0.5	0.5	3.2	92	1250
WQS/1	1	4.1	86	1250
WQS/3	3	7.4	84	1250
WQS/5	5	9.4	74	1250
WQS/10	10	11.6	71	1250
Aerosil	—	200	0	1280

t = time of mechanical treatment

s = specific surface of the SiO₂ component

X = crystallinity (measured by X-ray diffraction)

WQS = Weferlingen quartz sand (from deposit in Germany)

tobalite occurs as an intermediate product. The lower the temperature of the transformation of quartz into cristobalite, the lower the formation temperature of titanite. (The transformation temperature of mechanically-activated quartz is >1200°C, see section 2.1.2)

The crystallites of the initial products become covered by the reaction products (**Fig. 4**). In this figure, distinct growth regions with a layer-like structure are to be seen. The "layer" heights are of the order of some 10 nm. Titanite has grown upwards on the original titanate crystals during the reaction. The diffusion of the ions involved takes place through the cover layer. Ca and Ti could be detected by element analysis.

Fig. 4 Titanate formation on titanite crystals (1200°C, 1h halt) (36).

On the basis of the results, the formation of titanite is assumed to occur via a one-sided diffusion of cations (**Fig. 5**). The Ca^{2+} and Ti^{4+} ions or the corresponding oxygen-ion complexes diffuse into the quartz lattice which is in a reactive state of transformation into cristobalite. This transformation is a reconstructive one in which Si-O bonds have to be broken. The breakage of these Si-O bonds is facilitated by the mechanically-induced bond breakages and the generated distortions and deformations of the SiO_4 -tetrahedrons with each other⁸⁾.

This also explains the formation of titanite at lower temperatures when mechanically-activated quartz is used. It is of decisive importance that the quartz lattice is in a state of transformation. The Si^{4+} ions or complexes being formed diffuse along the grain boundaries of the titanite crystallites being generated to the surface of titanite and react with titanite. From the crystal-chemical point of view, a diffusion into the titanite-lattice is not likely.

Fig. 5 Formation of titanite by one-sided diffusion of ions (36).

2.1.2 Polymorphous Quartz Transformation

Polymorphous intermediate transformations of SiO_2 , which may occur during or as a result of a complete transformation, are of great importance for the reaction of silicates because of reactivity, as shown in the case of the titanite formation. It is known from literature that mechanical deformation processes may influence the velocity, as well as the mechanism of the modification transformations^{37,38)}.

Without the influence of mechanical treatment, the polymorphous transformations of the most important SiO_2 -modifications proceed according to Fenner³⁹⁾, as shown in **Fig. 6**. Under the influence of mechanical treatment, the effect (degree) of the α - β -transformation decreases⁴⁹⁾. Strongly disturbed quartz is not transformable into the high-temperature form.

The non-appearance of the transformation effect may be accounted for by a strong disturbance of the lattice. The α - β -transformation is based on insignificant displacements of the atom positions, a deformation of the lattice. In the case of the mechanically-activated quartz, however, a growing part of the 6-ring arrangement has already been destroyed. As a result of the mechanical activation the temperature of the quartz-cristobalite transformation is strongly reduced (**Fig. 6,b**). The quartz-cristobalite transformation is, as already mentioned, a reconstructive one in which the structures have to be completely reorganized and breakage of the Si-O bonds is necessary.

Fig. 6 Polymorphous transformation of quartz. a) by Fenner (39), b) induced by mechanical treatment (40).

The breakage of Si-O bonds, and the relative distortion of the SiO_4 tetrahedrons facilitate the necessary disintegration of the structure, and play an essential role in the accelerated transformation at a lower temperature. The velocity constants k_1 and k_2 were determined from the time-dependence of the quartz-cristobalite transformation taking as a basis the mechanism derived by Mitra⁴¹⁾. On the basis of its temperature-dependence, the activation energy A_E of both partial steps may be estimated to have the values shown in **Fig. 7**. The activation energy of both partial steps is reduced by a factor of two by mechanical activation. The activation energy of the transformation leading to cristobalite is slightly higher than that of the transformation quartz $\rightarrow$ transition phase. This fact can be explained by nucleation processes. The mechanically-induced elementary defects have no influence on the transformation quartz $\rightarrow$ transition phase, i.e. on the structure of the quartz lattice, but on the new formation of cristobalite, because the activation energies for both processes are considerably lowered. Accordingly, the produced defects must still be effective in the supposed transition phase, presumably in sub-microscopic small lattice regions no longer showing any diffraction⁴¹⁾.

Activation energies A_E kJ mol⁻¹

quartz (before mech.treatment)	(1) ≈ 405	(2) ≈ 426
quartz (mech.treated, 1 and 3h, resp.)	≈ 175	≈ 226

Fig. 7 Activation energies A_E for mechanically-induced quartz-cristobalite transformation (k_1 , k_2 rate constants (40)).

2.1.3 Zeolite Formation

Zeolites are generally produced from solution containing alkaline silicates and aluminates via hydrothermal synthesis by precipitation or by a hydrogel procedure. The formation of zeolite by the reaction of quartz with aluminium oxide⁴²⁾ is also possible. In this case, the rate-determining step is the dissolution of quartz. The elementary step of the dissolution is influenced by lattice defects⁴³⁾, e.g. bond breakings, distortions and deformations normally associated with mechanical activation⁴⁴⁾.

Fig. 8 Dependence of sodium A zeolite formation from mechanically-activated quartz and α -Al₂O₃ on the reaction time t . Experimental conditions: 2m NaOH, $T=90^\circ\text{C}$, time of the mechanical mixing of quartz and α -Al₂O₃: 3h (45) (see **Table 2**). Mol ratio quartz: γ -Al₂O₃=2:1.

Fig. 8 and **Table 2** show the zeolite formation (NaA-zeolite) from mechanically-activated quartz and γ -Al₂O₃ as a function of reaction time⁴⁵⁾. The transformation to zeolite first increases with mechanical activation but then remains constant. Essentially, the transformation as a whole increases with decreasing crystallinity of quartz. X-ray investigations reveal that only the disturbed, partially crystal-

line part of the quartz dissolves and reacts with γ -Al₂O₃ during the formation of NaA-zeolite. Under the chosen circumstances, the formation of NaA-zeolite is only possible to the extent that partially crystalline quartz is available, i.e. quartz which still contains the basic elements of a crystalline structure. With the use of amorphous SiO₂, e.g. aerosil, the species B is formed.

Table 2 Characterization of the samples for the zeolite formation.

	X, %	s_1 , m ² g ⁻¹	s_2 , m ² g ⁻¹	α , %
sample 1	100	<1	11.8	ca. 20
sample 2	50	10	25	ca. 50
sample 3	45	14	17	ca. 50

X = crystallinity (measured by X-ray diffraction) of quartz

s_1 = specific surface of quartz

s_2 = specific surface of quartz/ γ -Al₂O₃-mixture

α = turnover to zeolite

2.1.4 Mechanically-Induced Adsorption of Quartz

An essential partial step in the reaction of a solid with the surroundings, e.g. a gas atmosphere, is its ability to ab- or adsorb gas. It appears that this process is also influenced by mechanical activation forces, and the structural changes of the solid associated with such activation⁴⁶⁾.

Generally, it can be stated that the amount of gas ab- and adsorbed increases with an increasing degree of the disturbance of quartz, but in a different way for the individual gases, as can be seen from **Fig. 9**. Highest is the adsorption of H₂, then follows that of CO₂ and O₂. Ar as a noble gas is not adsorbed at room temperature.

Mechanically-induced absorption primarily occurs during the action of energy. If the gas is added after the mechanical activation, there is only an adsorption at the surface and practically no diffusion of the gas molecules into the solid, i.e. the absorption is negligible.

It is assumed that during the treatment the pores are greater and that the whole lattice is loosened to a greater extent than the subsequent integral measurements reveal. The gases are absorbed both chemically and physically. The chemisorption occurs primarily on the basis of the Si-O bond breakages produced, which are determined by chemical gas -

Fig. 9 Dependence of the number of adsorbed molecules N on the amorphous part A in mechanically-treated quartz (46).

interactions^{8,46}. But far more molecules are taken up than correspond to the number of the measured centres⁴⁶, **Table 3**. The physical adsorption is mostly influenced by the following structural factors (**Table 3**).

Quartz, because of the small size of the micro-pores present, does not usually contain much gas, and only traces of H_2 can normally be detected. The gas kinetic diameter of H_2 is approximately comparable with the diameter of the quartz pores. That is why H_2 is also slightly absorbed by untreated quartz. On the other hand, the gas kinetic diameters of H_2 , O_2 and Ar are all of the same order of magnitude as the pores in mechanically-activated material, but Ar is still not absorbed. Presuming that only the size of the pores has a decisive influence on the absorption, there should be no CO_2 absorption. While the structural changes and the resulting locally generated energy states at the surface and in the disturbed quartz layer are of decisive importance, they do not completely account for the differences in the amounts of the individual gases absorbed.

Thus it must be concluded that not only the structural properties of solids, but also the chemical properties of both solid and gas play important roles with regard to ab- and adsorption of gases.

2.2 Reactivity of Mechanically-Treated Hydrargillite

Aluminium oxides are one of the main components for the production of catalytic materials and adsorbents. The starting material for the technical production of surface-rich active aluminium oxides is hydrargillite. Aluminium oxides are produced via hydrargillite by a process of dissolving and precipitation. The short-time heating of mechanically-pretreated hydrargillite is another possibility to obtain active aluminium oxides free of Na^+ .

The mechanical activation of hydrargillite has been the subject of several scientific investigations recently⁴⁷⁻⁴⁹, and has in the last few years gained in significance in connection with a short-time heating⁵⁰⁻⁵⁶.

The basic concept of this alternative procedure consists in the transformation of hydrargillite by short-time heating into a nearly X-ray amorphous aluminium oxide, being well washable regarding Na^+ ions. Synthetic hydrargillite always contains Na^+ ions as contamination caused during preparation, which adversely affect the catalytic properties of aluminum oxides, prepared from $Al(OH)_3$. Their removal is therefore necessary. The X-ray amorphous Al_2O_3 is transformed in the same washing process to pseudo-boehmite ($AlOOH$) by hydration. Hydrargillite is pretreated by a mechanical treatment for rapid disintegration.

Table 3 Mechanically-induced adsorption on quartz (period of time of mechanical treatment : 4h).

GA	$s, m^2 g^{-1}$	A, %	$N \cdot 10^{-20}, g^{-1}$	$Z \cdot 10^{-18}, g^{-1}$	N/Z	δ, nm
Ar	14	42	<0.1	5.9	—	0.37
H_2	10	48	11.3	0.9	$1 \cdot 10^2$	0.28
O_2	14	44	0.24	14.0	2	0.36
CO_2	16	64	2.6	0.9	$3 \cdot 10^2$	0.46

GA = Gas atmosphere

s = Specific surface of quartz

A = "Amorphous" content

N = Number of adsorbed gas molecules

Z = Number of radicals

δ = Diameter of the gas-molecule

Table 4 Dependence of Na^+ -elimination of X-ray amorphous Al_2O_3 on mechanical and thermal^x activation.

Hydrargillite				X-ray amorphous Al_2O_3	
Sample	t, min	do, rel. units (± 0.1)	s m^2/g ($\pm 5\%$)	s m^2/g ($\pm 5\%$)	$^{\circ}\text{Na}_2\text{O}$, mar% ± 0.005
1	5	0.7	2.9	206	0.019
2	30	0.6	10.5	169	0.017
3	60	0.4	16.0	23	0.016
4	900	0.1	27.0	11	0.011

x = Conditions of thermal activation : 0.2s, 500°C
t = Mechanical pretreatment
do = Degree of order, measured by X-ray diffraction
s = Specific surface
 $^{\circ}\text{Na}_2\text{O}$ = Na_2O content of the solid

The mechanical treatment of hydrargillite influences the thermal disintegration of hydrargillite^{56,57}. Of special interest is the fact that after a mechanical and thermal short-time heating (550°C, residence time < 10s^{55,56}) an aluminium oxide is formed, which is characterized by a very high reactivity. **Table 4** shows the Na^+ -elimination from X-ray amorphous aluminium oxides as a function of the produced degree of order do (do measured in relative units from the X-ray determined intensity of the (100) reflex) and the specific surface after the short-time heating. The Na^+ -elimination increases whereas the specific surface decreases.

Parallel to the Na^+ -elimination, a rehydration takes place. The reaction of aluminium oxides with water at 90°C yields pseudo-boehmite, which differs from crystalline boehmite with regard to the Bragg-reflexes (profile and position) and the IR spectra⁵⁶. The pseudo-boehmite content increases with the reaction time (**Fig. 10**) and reaches a final value after about 30 min. From this figure it also follows that the initial velocity of the pseudo-boehmite formation depends on the mechanical pretreatment.

The mechanical treatment of hydrargillite prior to the short-time heating increases the pseudo-boehmite yield. **Fig. 11** displays the dependence of the pseudo-boehmite-transformation on the duration of the mechanical pretreatment of hydrargillite and the degree of order do of the pretreated hydrargillite. The formation of pseudo-boehmite is also not dependent on the specific surface of aluminium

oxide since it decreases in the same measure as the pseudo-boehmite content increases (**Fig. 11**

Fig. 10 Dependence of hydration of X-ray amorphous Al_2O_3 on the time t (different mechanically-treated hydrargillite, vibration mill), $T = 90^\circ\text{C}$ do = degree of order a: do = 0.73 b: do = 0.52 c = content of pseudo-boehmite (56).

Fig. 11 Dependence of the content of pseudo-boehmite c (after short-time heating and hydration) on the duration of mechanical treatment t (a) and on the degree of order do (b, c) of hydrargillite, and the dependence of the specific surface s (after mechanical and thermal activation) on the degree of order do (b, s).

and **Table 4**). The reaction of aluminium oxide with H_2O also yields bayerite. The bayerite formation depends only slightly, however, on the mechanical pretreatment (the bayerite content rises with increased mechanical pretreatment from 0–5%). The bayerite formation is essentially determined by the temperature and reaction time. The aluminium oxides present are nearly X-ray amorphous and contain some χ - Al_2O_3 (**Table 5**). The short-range order was determined from the radial distribution function of the electron density by X-ray wide-angle investigations, **Fig. 12**⁽⁵⁸⁾. The position of the 1st peak at 0.188 nm corresponds to the Al–O distance and is independent of the method of preparation. Also the position of the other peaks remain unchanged. However, beginning from the 2nd peak ($r > 0.3$ nm), there are differences in the intensities due to distortions of the coordination polyhedrons.

Table 5 Characterization of the samples after mechanical and thermal activation.

sample name	Al_2O_3 -phase	c, % ^x
1	X + r. a. ^{xx}	40
2	X + r. a.	60
3	r. a + X	73
4	r. a + X	89

x x = X-ray amorphous

x = IR - spectroscopy, Dr. Geissler, Analytisches Zentrum Berlin

c = Degree of transformation to pseudo-boehmite

Fig. 12 Difference radial distribution function (DRDF). $DRDF = 4\pi r^2 (\rho(r) - \rho_0)$ r = distance of an arbitrary atom from the origin (sample names see **Tables 4, 5**) (58).

The greater the distortion of the polyhedrons, the higher is the degree of rehydration of aluminium oxides. The energy stored as a result of mechanically-caused distortions facilitates the formation of boehmite from aluminum oxide and water ($Al_2O_3 + H_2O \rightarrow Al(OOH)$). The reason for the distortion of the coordination polyhedrons is the mechanical pretreatment in connection with the subsequent short-time heating. The distortion increases with the length of time of the mechanical pretreatment⁽⁵⁸⁾.

3. Conclusions

Summarizing, it can be stated that under the influence of mechanical energy, solids undergo structural changes and structural defects which lead to an energy storage, which may result in an enhancement of chemical reactivity. Correlations exist between the mechanically-induced structural defects and the mechanism of the reactions.

The particle disintegration accomplished by mechanical activation and the resulting increase in surface area may be of importance for an increase of reactivity, but a number of publications have shown that the measured effect of the reactivity enhancement cannot be explained merely by these phenomena.

One of the cited examples even demonstrates that the reactivity enhancement may be inversely proportional to the increase in surface.

Table 6 contains a list of the investigated reactions as a function of structural defects. Apart from the structural properties of the solids, however, both the chemical properties of solids and those of the surroundings are of importance.

Table 6 The dependance of the reactivity of solids on their mechanically changed structure.

Reaction	Correlation with the changed structure
<u>Solid-solid</u> - α - β -quartz transformation [40] - quartz-cristobalite transformation [40] - titanite formation (mechanically-treated quartz + CaTiO ₃) [45]	partially crystalline state [8,60] partially crystalline state, with broken Si-O bonds and distortions of the SiO ₄ -tetrahedrons quartz lattice being in a state transformation into cristobalite in connection with partially crystalline state
<u>Solid-liquid</u> - dissolution of quartz [44] - Zeolithe formation (mechanically - treated quartz + γ -Al ₂ O ₃ + NaOH) [45] - CSH-formation (mechanically - treated quartz + Ca(OH) ₂ + H ₂ O) [59] - rehydration of Al ₂ O ₃ (Al ₂ O ₃ + H ₂ O $\cdots$ AlOOH) [56, 58]	partially crystalline state, with broken Si-O bonds and distortions of the SiO ₄ -tetrahedrons - // - - // - distortions of the Al ₂ O ₃ -octahedrons
<u>Solid-gas</u> mechanically-induced adsorption of quartz [46]	partially cristalline state, broken Si-O bonds, radicals and chemical defects

References

- Ostwald, W.: Handbuch der allg. Chemie I, Leipzig, 1919, 70
- Heinicke, G.; Hennig, H.-P.; Linke, E.; Steinike, U.; Thiessen, K.P.: Tribochemistry, Akademie-Verlag Berlin 1984, Carl Hanser-Verlag, München 1984. Verlag Mir, Moskau 1987 (in Russian)
- Tamman, G.: Z. Elektrochem., **35** (1929), 21
- Fink, M.: Trans. Am. Soc. f. Steel Treating, **18** (1930), 1026
- Fink, M.; Hoffmann, U.: Z. anorg. allg. Chemie, **210** (1933), 100
- Bowden, F.F.; Tabor, D.: The friction and lubrication of solids, Oxford 1958.
- Thiessen, P.A.: Abhandlungen der Dt. Akademie der Wissenschaften zu Berlin, Klasse f. Chemie, Geologie und Biologie, **5** (1966), 15
- Steinike, U.; Kretschmar, U.; Ebert, I.; Hennig, H.-P.; Barsova, L.I.; Jurik, T.K.: Reactivity of Solids, **4** (1987), 1
- Heegn, H.: Veränderung der Festkörpereigenschaften bei mechanischer Aktivierung und Feinzerkleinerung, Dissertation B, Akademie der Wissenschaften der DDR, Berlin (1986)
- Soc. of Pow. Tech., Japan: Proceedings of the Second Japan-Soviet Symp. on Mechanochemistry, 22-24 March 1988, Tokyo
- 5th Symp.: Theoretical and Technological Aspects of Comminution and Mech. Activation of Minerals: Tataraman 1988.
- Gock, E.; Asiam, E.: in (11), 60.
- Schulz, G.; Dietzel, W.: Abfall-Wirtschafts-Symp., 4-7 Dec. 1990, Berlin. I. Integrierte Abfallwirtschaftskonzepte, **3**, 265 (1990). EF-Verlag f. Energie und Umwelttechnik GmbH.
- Schultz, L.; Hellster, E.; Zorn, G.: Z. phys. Chem., NF **157** (1988), 203
- Ikeya, T.; Senna, M.: J. Non-Crystalline Solids, **113** (1989), 51
- Pavlyukhin, Yu.T.; Medikov, Ya.Yu.; Boldyrev, V.V.: J. of Solid State Chemistry, **53** (1984), 155
- Pavlyukhin, Yu.T.; Medikov, Ya.Yu.; Boldyrev, V.V.: Mat. Res. Bull. **18** (1983), 1317
- Imamura, K.; Senna, M.: Mat. Res., Bull. **19** (1984), 59
- Balaz, P.; Huhn, H.-J.; Tkacova, K.; Heegn, H.: Erzmetall, **41** (1988), 6
- Tkacova, K.; Balaz, P.; Korneva, T.A.: J.

- Therm. Anal., **34** (1988), 1031
- 21) Lin, I.J.; Nadiv, S.; Groguiian, D.J.M.: *Minerals Sci. Engng.*, **7** (1975), 313
 - 22) Tkacova, K.; Boldyrev, V.V.; Lyakhov, N.: *Proc. Indian natn. Sa. Acad.*, **55A** (1989), 778
 - 23) Tkacova, K.; Balaz, P.; Bastl, Z.: *Thermo-chimica Acta*, **170** (1990), 277
 - 24) Fubini, B.; Giamello, E.; Pugliese, L.; Volante, M.: *Solid State Ionics*, **32/33** (1989), 334
 - 25) Giamello, E.; Fubini, B.; Volante, M.; Costa, D.: *Colloids and Surface*, **45** (1990), 155
 - 26) Paudert, R. et al.: DD 222009.
 - 27) Sigrist, K.; Fichtner, H.: *Phys. Status Solidi*, **95** (1985), 473
 - 28) Thiessen, P.A.; Heinicke, G.; Schober, E.: *Z. anorg. allg. Chem.*, **377** (1970), 28
 - 29) Stäuble, J.; Bayer, G.: *Schweiz. Mineral. Petr. Mit.*, **61** (1981), 361
 - 30) White, T.J.; Segall, R.L.; Turner, P.S.: *Angew. Chem.*, **97** (1985), 369
 - 31) King, E.G.: *Amer. Chem. Soc.*, **76** (1954), 4320
 - 32) Völtzke, P.; Abicht, H.-P.; Müller, Th.; Richter, J.: *Silikatechnik*, **41** (1990), 306
 - 33) Michailova, N.A.; Vinnikova, N.S.: *Anorg. Werkstoffe*, **15** (1979), 114
 - 34) Köhler, Th.; Plötner, W.; Steinike, U.; Uecker, D.-Chr.; Schierhorn, E.: DD 263747
 - 35) Plötner, W.; Köhler, Th.; Uecker, D.-Chr.; Steinike, U.: DD 254934
 - 36) Steinike, U.; Uecker, D.-Chr.; Köhler, Th.; Plötner, W.; Schierhorn, E.; Jancke, K.; Hennig, H.-P.: *Crystal. Res. Technol.*, **26** (1991)
 - 37) Sigrist, K.; Heinicke, G.; Steinike, U.: *Kristal und Technik*, **8** (1973), 393
 - 38) Senna, M.: *KONA*, **1** (1983), 48
 - 39) Fenner, C.N.: *Amer. J. Sci.*, **36** (1913), 331
 - 40) Steinike, U.; Uecker, D.-Chr.; Sigrist, K.; Plötner, W.; Köhler, Th.: *Crystal Res. Technol.*, **22** (1987), 1255
 - 41) Mitra, S.: *Trans. and J. Brit. Ceram. Soc.*, **76** (1977), 71
 - 42) Cournager, R.A.; Kranich, W.L.; Sand, L. B.: *J. of Phys. Chem.*, **79** (1975), 1578
 - 43) Weyl, W.A.; Marboe, E.C.: *Sprechsaal*, **107** (1974), 1030
 - 44) Steinike, U.; Hennig, H.-P.; Kretzschmar, U.; Richter-Mendau, J.: *Crystal Res. Technol.*, **17** (1982), 1585
 - 45) Wutzler, R.; Klevzov, D.; Steinike, U.; Hennig, H.-P.: *Crystal Res. Technol.*, **26** (1991), 317
 - 46) Steinike, U.; Hennig, H.-P.; Ebert, I.: *Z. phys. Chem., Leipzig*, **226** (1985), 302
 - 47) Schrader, R.; Rump, H.; Sanner, G.: *Z. anorg. allg. Chem.*, **350** (1967), 130
 - 48) Pohl, K.; Haberecht, H.: DD 134365
 - 49) Pohl, K.: *Habilitationsschrift*, TU Dresden, 1970
 - 50) Vorobjev, Ju.K.; Schkrabina, R.A.; Moroz, T.D.; Fenelonov, V.B.; Zagrafskaja, R.V.; Kambarova, T.D.; Levickij, E.A.: *Kinetika i kataliz*, **22**, 6 (1981), 1595
 - 51) Zolotovskij, B.P.; Schkarin, A.V.; Krivoruchko, O.P.; Kriger, T.A.; Bujanov, R.A.: *Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Chim. Nauk*, **17** (392) 6, 36 (1984)
 - 52) Bollmann, U.; Engels, S.; Haupt, K.; Kobelke, J.; Becker, K.; Neubauer, H.-D.: *Z. Chem.*, **25** (1985), 273
 - 53) Zolotovskij, B.P.; Paramzin, S.N.; Krivoruchko, O.P.; Bujanov, R.A.: *Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Chim. Nauk* **17** (446) 6, 80 (1987)
 - 54) Steinike, U.; Becker, K.; Bollmann, U.: *Spectrum*, **7** (1988), 24
 - 55) Bollmann, U.; Becker, K.; Berger, H.-J.; Birke, P.; Engels, S.; Gruhn, G.; Jancke, K.; Kraak, P.; Lange, R.; Steinike, U.: *Cryst. Res. Technol.*, **23** (1988), 1303
 - 56) Steinike, U.; Geissler, H.; Hennig, H.-P.; Jancke, K.; Jedamzik, J.; Kretzschmar, U.; Bollmann, U.: *Z. anorg. allg. Chemie*, **590** (1990), 213
 - 57) Neissendorfer, F.; Steinike, U.; Tolochko, B.P.; Sheromov, M.A.: *Nucl. instr. and methods in Physics Res., A* **261** (1987), 219
 - 58) Kretzschmar, U.; Steinike, U.; Bollmann, U.; Lausch, H.: *Cryst. Res. Technol.*, in press
 - 59) Jedamzik, J.: *Dissertation*, Akademie der Wissenschaften der DDR, Berlin, 1982.
 - 60) Steinike, U.; Ebert, I.; Hennig, H.-P.; Müller, B.: *Cryst. Res. Technol.*, **14** (1979), 1469