

Table of contents

1.	Preface	11
	References	12
2.	Introduction	13
	Survey-References	17
3.	Structural and physical changes of solids under mechanical energy influences	18
3.1.	Transmission of mechanical energy to solids	18
3.1.1.	Tribomechanics	18
3.1.1.1.	Triboplasma	19
3.1.1.2.	Deformation	19
3.1.1.3.	Fracture	22
3.1.2.	Effects of different triboreactors	24
3.1.2.1.	Kinds of stresses in triboreactors	24
3.1.2.2.	Mode of operation of current triboreactors	26
3.1.2.2.1.	Ball mills	26
3.1.2.2.2.	Vibrating mills	27
3.1.2.2.3.	Planetary mills	27
3.1.2.2.4.	Pinned disk mills	27
3.1.2.2.5.	Jet mills	28
3.1.2.3.	The effect of different triboreactors on changes of physical and chemical properties	29
3.2.	Changes of the solid structure by mechanical treatment	31
3.2.1.	Principle of imperfection classification	31
3.2.2.	Zero-dimensional imperfection	32
3.2.2.1.	Atomic lattice defect	32
3.2.2.2.	Electronic imperfection	33
3.2.2.3.	Energetic defect	33
3.2.3.	One-dimensional imperfection	33
3.2.4.	Two-dimensional imperfection	34
3.2.5.	Three-dimensional defect	37
3.2.6.	Primary crystallite size and lattice distortions	38
3.2.7.	On the concept of the "frozen-in lattice vibrations"	40
3.2.8.	The influence of the structural imperfections on the solid reactivity	40
3.2.9.	Methods for the measurement of imperfections	40
3.3.	Physical elementary processes in the mechanical activation of solids	42
3.3.1.	Introduction and formulation of the problem	42
3.3.2.	Mechanical activation	43
3.3.2.1.	Punctiform stress	44
3.3.2.2.	Plastic deformation	47

3.3.2.3.	Development of fractures	50
3.3.3.	Occurrence of high temperatures	54
3.3.3.1.	Friction and impact temperatures	55
3.3.3.2.	Temperatures in dislocation motions	57
3.3.3.3.	Fracture temperatures	58
3.3.4.	Tribo-induced luminescence	61
3.3.4.1.	Electroluminescence	61
3.3.4.2.	Luminescence by re-combination of mechanically excited centres	64
3.3.4.3.	Temperature radiation	66
3.3.4.4.	Chemoluminescence	67
3.3.5.	Tribo-induced electron emission	69
3.3.5.1.	Emission from mechanically excited states	69
3.3.5.2.	Photoemission with changed work function	72
3.3.5.3.	Chemoemission	74
3.3.5.4.	Thermal emission	76
3.3.5.5.	Field emission	77
3.3.5.6.	Energy of the electrons	79
3.3.6.	Electric charging processes	80
3.3.6.1.	Charging by piezoeffect	83
3.3.6.2.	Contact charging	84
3.3.6.3.	Charged fracture surfaces	84
3.3.6.4.	Charged dislocations	86
3.3.6.5.	The formation of electric double layers	86
3.3.7.	The release of lattice components	88
3.3.8.	Summary	89
	References	90
4.	Kinetics and thermodynamics of tribochemical reactions	97
4.1.	Tribochemical excitation model	97
4.2.	Experimental arrangement for kinetic and thermodynamic measurements	102
4.3.	General course of tribochemical reactions	104
4.4.	The influence of the treatment intensity on tribochemical reactions	111
4.4.1.	Relationships between reaction velocity and intensity of the treatment	111
4.4.2.	On the efficiency of tribochemical reactions	117
4.5.	The dependence of tribochemical reactions on temperature	120
4.6.	The pressure-dependence of tribochemical reactions	129
4.7.	Kinetics of the tribosorption	136
4.7.1.	The detection of the triboabsorption	136
4.7.2.	Kinetics of the triboabsorption	139
4.7.3.	Factors influencing the tribosorption	141
4.7.4.	Penetration profile of triboabsorbed gases	143
4.7.5.	Desorption of the tribosorbate	145
4.7.6.	Relations between triboabsorption and triboreaction	146
4.7.7.	Tribokinetic model	148
4.8.	The thermodynamics of tribochemical reactions	149
4.8.1.	Thermodynamic characterization of mechanically disturbed solids	149
4.8.2.	Application of irreversible thermodynamics to tribochemical processes	159
4.8.3.	Tribochemical equilibrium	163

4.9.	Tribochemical modification transformation	169
	References	175
5.	On the causes of reactions in tribochemistry	181
5.1.	Chemical effects of tribo-plasma	181
5.2.	The role of elastic stresses in tribochemical reactions	182
5.2.1.	Tribochemical reactions influenced by constant stresses	182
5.2.2.	Tribochemical reactions influenced by altering mechanical stresses	187
5.3.	The role of temperature in tribochemical processes	189
5.4.	Chemical effects of triboelectric processes	203
5.4.1.	On supercharging disperse substances in milling equipments	203
5.4.2.	The influence of tribo-induced electrostatic charges on chemical processes	205
5.4.3.	The release of chemical reactions by tribo-induced discharges	209
5.4.4.	The release of chemical reactions by fast electrons	211
5.5.	The dependence of tribochemical reactions on the surface area	214
5.5.1.	The importance of the surface area for the solid reactivity	214
5.5.2.	Several kinds of solid surfaces	214
5.5.3.	Change in primary crystallite sizes by mechanical treatment and its importance for the solid reactivity	215
5.5.4.	Change in the inner and outer surface through mechanical stress	218
5.5.4.1.	Surface changes in dependence on the system of substances	218
5.5.4.2.	The HÜTTIG milling equilibrium	219
5.5.4.3.	The influence of the outer medium on the milling equilibrium	223
5.5.5.	The importance of the outer and inner surfaces for solid reactivity	226
5.6.	Fresh surface and transport effects as factors accelerating tribochemical reactions	229
5.6.1.	Sorption and reaction of gases on mechanically developed fresh surfaces	229
5.6.2.	The sorption of gaseous mixtures to mechanically developed fresh surfaces	235
5.6.3.	Tribomechanically induced displacement sorption	238
5.6.4.	Fresh surface reactions in liquid phase	239
5.6.5.	Fresh surface reactions caused by the transport effect between solid phases	239
5.7.	The tribodiffusion mechanism of gases	242
5.8.	The influence of top layers on tribochemical reactions (top-layer-effect)	249
5.9.	The effect of tribomechanically caused structural changes on the solid reactivity	251
5.9.1.	The influence of crystal imperfections on the solid reactivity	251
5.9.1.1.	The influence of the degree of disorder on the reactivity	251
5.9.1.2.	The reaction behaviour of solids in dependence on the distribution of crystal imperfections	255
5.9.1.3.	Structure—reactivity correlations in the presence of several crystal imperfections in the solid	257
5.9.2.	Correlations between individual structural imperfections and reactivity of solids	259
5.9.2.1.	The influence of dislocations on the reactivity of solids	260
5.9.2.2.	The influence of atomic lattice defects on the course of tribochemical reactions	262
5.9.2.3.	The importance of radical states for the course of tribochemical reactions	263
	References	267
6.	Tribochemical reactions in special systems	273
6.1.	Tribochemical reactions in solids with different bond character	273
6.1.1.	Tribochemistry of silicon carbide	273

6.1.1.1.	Structure and reaction behaviour of silicon carbide	273
6.1.1.2.	Changes in structure of SiC by tribochemical treatment	273
6.1.1.3.	Tribosorption at SiC	276
6.1.1.4.	Tribochemical reactions at SiC	279
6.1.1.5.	Extension of the statistical reaction model to other solids	285
6.1.2.	Tribochemistry of quartz	287
6.1.2.1.	Structure and properties of quartz	288
6.1.2.2.	Changes in structure of quartz by tribomechanical treatment	289
6.1.2.3.	Structure — reactivity correlations at mechanically treated quartz	294
6.1.2.3.1.	The solubility of mechanically treated quartz	295
6.1.2.3.2.	Interaction of mechanically treated quartz with gases	299
6.1.3.	Tribochemistry of apatites	303
6.1.3.1.	Structure of apatites	303
6.1.3.2.	Tribomechanically caused changes in structure and reactivity of apatites	305
6.1.3.3.	Dissolution kinetics of activated apatites	313
6.2.	Tribocatalysis	315
6.2.1.	Catalysts by means of tribochemical reactions	317
6.2.2.	The influence of tribomechanical treatment on the catalytically active surface area	320
6.2.2.1.	Changes in surface size by mechanical stress	320
6.2.2.2.	Tribomechanically caused changes in the catalytically active surface	320
6.2.3.	The relation between disorder and catalytic activity of tribomechanically stressed catalysts	322
6.2.4.	Changes in catalytic activity by tribomechanically effected secondary structural changes	326
6.2.5.	Summary	326
6.3.	Tribochemistry of polymers	328
6.3.1.	Introduction	328
6.3.2.	Kinds of mechanical influences on polymers	329
6.3.3.	Changes in polymer structure and texture by the action of mechanical energy	329
6.3.3.1.	Comminution of polymers	330
6.3.3.2.	Tribochemical degradation of polymers	331
6.3.4.	Mechanism of the tribochemical degradation	333
6.3.5.	Modification reactions at the tribochemical degradation	335
6.3.5.1.	Modification reactions in the polymer-polymer system	335
6.3.5.2.	Modification reactions in the polymer-monomer system	338
6.4.	Triboanalysis	341
6.5.	Tribochemical reactions for preparation purposes	344
6.6.	Tribochemistry of solid state electrode	346
6.6.1.	Introduction	346
6.6.2.	Thermodynamics	347
6.6.2.1.	Integral processes	347
6.6.2.1.1.	Processes at solid state electrodes	347
6.6.2.1.2.	Static or dynamic application of mechanical energy by macroscopic deformation	347
6.6.2.1.3.	Dynamic supply of mechanical energy by multiple impacts	350
6.6.2.2.	Local processes	351
6.6.2.2.1.	Local elements produced by impact: "Disturbed interface layer/less disturbed interface layer"	351
6.6.2.2.2.	Analysis of the mechanism of the formation of impact produced local elements	352
6.6.2.2.3.	Interaction between local and integral processes	353
6.6.2.2.4.	Reactions of impact-produced local elements	354

6.6.3.	Kinetics	356
6.6.3.1.	Effect of the impact treatment of solid state electrodes on the electrolytes, side diffusion conditions in the phase boundary layer	356
6.6.3.2.	The effect of the impact treatment of solid state electrodes on the electrocrystallization of metals	359
6.6.3.3.	The effect of macroscopic deformation on the electrode kinetic of the dissolution of metals	362
6.6.3.3.1.	Fresh surface effects on solid state electrodes	365
6.6.3.4.	Tribodiffusion in the solid part of the interface layer	365
6.6.3.4.1.	Metal/metal tribodiffusion at room temperature under the influence of impact	365
6.6.4.	Tribochemistry of solid state electrodes in engineering	367
6.6.4.1.	Mechanically activated galvanic precipitation	368
6.6.4.2.	Cutting processes on metals in the presence of electrolytic media	369
6.6.4.3.	Electrochemical tribocorrosion	370
6.6.4.3.1.	Stress-corrosion cracking	371
6.6.4.3.2.	Corrosion fatigue	372
6.6.5.	Final remarks	373
	References	374
7.	Application of tribochemistry in technology	384
7.1.	Introduction	384
7.2.	Tribochemical processes in the material-changing industry	386
7.2.1.	Process engineering aspects in tribochemical processes	386
7.2.1.1.	Triboreactors and activation sets for tribochemical processes	386
7.2.1.2.	Particularities of tribochemical processes in the material-changing industry	387
7.2.2.	The importance of tribochemistry in the chemical and metallurgical industries	391
7.2.2.1.	Tribochemical processes in the gas-solid system	391
7.2.2.2.	Tribochemical processes in the liquid-solid system	395
7.2.2.2.1.	Kinetics and thermodynamics of tribochemical dissolution processes	395
7.2.2.2.2.	Dissolution processes in the preparation of raw materials	397
7.2.2.2.3.	Tribochemical cementation reactions	400
7.2.2.2.4.	Tribochemical solubilization of rock phosphates	401
7.2.2.3.	Tribochemical processes in the solid-solid system	405
7.2.2.4.	Tribochemical reactions of inorganic solids with organic reactants	406
7.2.2.4.1.	The importance of modification reactions for the manufacturing of composites	406
7.2.2.4.2.	Tribochemical modification	408
7.2.2.4.3.	Technological application of tribochemical modification	408
7.2.2.5.	Summary	411
7.2.3.	Tribochemistry of building materials	411
7.2.3.1.	Tribochemical activation of SiO_2 for the manufacture of silicate concretes	411
7.2.3.1.1.	Introduction	411
7.2.3.1.2.	Chemical processes in the hydrothermal hardening	412
7.2.3.1.3.	The mechanical activation of SiO_2	413
7.2.3.1.4.	The importance of the tribochemical activation for the manufacture of silicate concretes	418
7.2.3.2.	Tribomechanical activation of cement and cement aggregates	420
7.2.3.3.	The formation of binders from tribomechanically activated raw materials	423
7.2.3.4.	The sintering of mechanically activated solids	425
7.3.	The ignition of metal fires by tribochemical reactions	430
7.3.1.	Metal fires in engineering	430

7.3.2.	The mechanism of metal fires	431
7.3.3.	Reasons for the ignition of metal fires	432
7.3.4.	Tribochemical fire ignition	433
7.3.4.1.	Fire ignition during the treatment of metals in vibration mills	433
7.3.4.2.	Tribochemical fire ignition in technical plants	536
7.3.5.	Conclusions on the prevention of metal fires	438
7.4.	The importance of tribochemical reactions in friction, lubrication, and wearing processes	438
7.4.1.	The technical importance of friction, lubrication, and wear	438
7.4.2.	Tribochemistry as a subsection of tribology	439
7.4.3.	The tribochemical dissipation model	440
7.4.4.	The effect of tribochemical reactions on friction and wearing processes	445
7.4.4.1.	The formation of friction- and wear-reducing on protective layers by tribochemical processes solid surfaces	445
7.4.4.1.1.	Triboadhesion	445
7.4.4.1.2.	The formation of protective layers by tribosorption	445
7.4.4.1.3.	Oxidic protective layers	446
7.4.4.1.4.	The formation of protective layers through chemisorption and reaction of surface-active substances	447
7.4.4.1.5.	Protective layers by EP additives	448
7.4.4.1.6.	High-temperature protective layers	450
7.4.4.1.7.	The co-operation of tribochemical reactions in the formation of protective layers by means of solid lubricants	451
7.4.4.1.8.	Polymeric protective layers	453
7.4.4.1.9.	Protective layers trough selective material transfer (GARKUNOV effect)	453
7.4.4.1.10.	Summary	454
7.4.4.2.	Tribocorrosion	455
7.4.4.2.1.	Forms of manifestation of tribocorrosion	455
7.4.4.2.2.	Tribocorrosion as a fundamental wear mechanism	456
7.4.4.2.3.	Causes of tribocorrosion	457
7.4.4.3.	The effect of tribosorption and triboreaction on fatigue wear	459
7.4.4.4.	Tribochemical effects of water on friction and wear processes	463
7.4.5.	The effect of tribochemical reactions on energy exchange processes	465
7.5.	Final remarks	465
	References	466
8.	Tribochemical reactions by geomechanical processes	474
8.1.	Geomechanics	474
8.2.	The role of tribochemical reactions in the origin of life on earth	475
8.3.	The importance of tribochemical reactions in the development of deposits	476
	References	480
	<i>Acknowledgements</i>	481
	<i>Subject Index</i>	482