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 triboplasma	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

Acknowledgements . . . 481

Subject Index . . . 482