

Contents

Acknowledgments	9
1. Introduction	11
1.1. Modern ceramics	11
1.2. The essence of the ceramics technology	13
1.3. Technology design	14
1.3.1. Economic aspect of the technological processes	14
1.3.2. Development of the material microstructure during the heat treatment ...	17
1.3.3. Selection of technology and the present book structure	19
2. Thermodynamic aspects of the high-temperature technologies used in ceramic industry	23
2.1. General notes	23
2.2. Classification and characteristics of ceramic reactions in aspect of thermodynamic function changes	25
2.2.1. Classification	25
2.2.2. Exothermic reactions developed in result of the entropy increase	27
2.2.3. Chemical reactions between solids	27
2.2.4. Exothermic reactions, developed in result of the enthalpy reduction ...	28
2.2.5. Endothermic reactions	29
2.3. Examples of the prediction of high temperature reaction course direction on the basis of thermo-dynamic data	31
2.3.1. Removal of the carbon from copper layered elements in subassemblies of micro-electronic systems	31
2.3.2. Behaviour of calcium chloride in fired ceramic material	33
2.3.3. Synthesis and decomposition of the zirconium ($ZrSiO_4$)	36
2.3.4. Thick-layered metallization of aluminum nitride bases for needs of microelectronics	37
2.3.5. Celsian synthesis	39
2.3.6. Reactions of MgO with carbonate in brickwork working zones of the oxygen converters	40
2.3.7. Mullite decomposition into corundum and SiO	42

2.4. Some reflections aimed at the entropy changes accompanying human activities (entropy concept according to Görlich's definition)	43
2.5. Additional technological interpretation	45
3. Phase systems	47
3.1. Phases in ceramic materials	47
3.1.1. General notes	47
3.1.2. Condensed phases	48
3.1.3. Role of gaseous phase in firing processes	50
3.2. Some aspects of the phase diagrams interpretation	52
3.2.1. Single and two-component systems	52
3.2.2. Three-component systems	55
3.2.3. Multi-component systems	59
3.3. Phase composition of the clayey raw materials (aluminosilicate)	60
3.3.1. Assessment of the role of admixtures	60
3.3.2. Phase composition changes due to temperature increase and interpretation	61
3.3.3. Calculation cumulated content of the liquid phase and mullite	65
3.4. Examples of technical solutions based on the composition triangles of three-component systems	67
3.4.1. Free lime in ceramic materials	67
3.4.2. Firing synthesis of minerals, which have low coefficient of thermal expansion	70
3.4.3. Phase composition of the self-disintegrating sinters in production of aluminum oxide and cement from non-bauxite raw materials	71
3.4.4. Phases formed during zirconium sand – lime high temperature reaction	72
3.5. Examples of technological problems solution on the basis of the liquid phase characteristics within two and three-component systems	73
3.5.1. Lead-sodium flux in enamel composition and Pb slag	73
3.5.2. Glassy phase in porcelain materials	74
3.5.3. Phase composition of the refractory aluminosilicate products	77
3.5.4. Phase composition and easy-melting eutectics of the basic-type refractory materials	77
3.5.5. Corrosion of aluminosilicate refractory materials – influence of sodium-calcium glass	82
3.6. Supplementary technological interpretation	83
4. Kinetic aspects of the high-temperature ceramic transformations	85
4.1. Use of the kinetic data in ceramic technologies – general notes	85
4.1.1. Character of reactions in ceramic materials	85
4.1.2. Relation between constant reaction speed and temperature	86
4.1.3. Linear kinetics	88
4.1.4. Kinetics of the diffusion controlled reactions in solid phase and with liquid phase presence	89

4.1.5. Kinetics of the reaction of the first order and fractional order reactions	91
4.1.6. Kinetics of the reactions controlled by nucleation	91
4.1.7. Selected examples	92
4.2. Kinetics and mechanism of chosen reactions between solid and gaseous phases	93
4.2.1. Graphite oxidation mechanism	93
4.2.2. Oxidation of organic admixtures in products made from clay materials	94
4.2.3. Thermal treatment of cupric thin-layer elements: kinetic aspect and mass balance	99
4.2.4. Oxidation of heating rods made of molybdenum disilicide	101
4.2.5. Oxidation of products made of silicon carbide	104
4.2.6. Nitriding of highly pure silicon	107
4.3. Kinetics and mechanism of the interactions during crystallization of the reaction product from gaseous phase	109
4.3.1. Obtaining of the layers using method of chemical deposition of the gaseous phase (CVD)	109
4.3.2. High-temperature reactions MgO + C and precipitation of solid periclase layer	114
4.4. Kinetics and mechanism of certain high-temperature transformations and oxide mineral syntheses	116
4.4.1. Transition phase of quartz-cristobalite polymorphous transformation	116
4.4.2. Gamma – alfa Al ₂ O ₃ transformation	119
4.4.3. High-temperature transformations of anhydrous aluminum silicates	120
4.4.4. Zirconium orthosilicate synthesis	121
4.4.5. Calcium zirconate synthesis	123
4.4.6. Alite synthesis in Portland cement-like compositions	126
4.5. Kinetics and mechanism of some processes occurring on a contact between molten glassy phases and solid phases	129
4.5.1. Dissolution of silica from glass-making batch in alkaline-siliceous alloys	129
4.5.2. Devitrification of silica glasses	133
4.5.3. Characteristics of the kinetics of refractory material corrosion caused by the molten glass	136
4.6. Supplementary technological interpretation	137
4.6.1. Possibility of kinetic process control by suitable selection of temperature and firing time (firing curve)	137
4.6.2. Process course and mechanism versus heat treatment	138
4.6.3. Possibilities of the process kinetics process control by the selection of right fired material properties, and/or the proper selection of the gaseous reagents composition	139
4.6.4. Some notes on technologically disadvantageous reactions	141

5. Dynamic aspect of the ceramic material microstructure formation	143
5.1. Introduction	143
5.2. Transitory and spontaneous reactions of the phase composition transformations	144
5.2.1. Typical constitutive phases occurring in various microstructure formation stages	144
5.2.2. Mullitization of clay raw materials	146
5.2.2.1. Kaolinite transformations in firing initial stage	146
5.2.2.2. Mechanism and kinetics of the mullite phase formation	147
5.2.2.3. Microstructure evolution during high temperatures heating ..	152
5.2.2.4. Metastable equilibrium states in the Al_2O_3 - SiO_2 system	153
5.2.3. Sodium-calcium glass melting and homogenization and a role of sodium sulfate being the initial material component	154
5.2.4. Synthesis of barium titanate from powdered substrates	155
5.3. Effects related with pore systems transformation	158
5.3.1. General notes	158
5.3.2. Hot pressing	160
5.3.2.1. Introduction	160
5.3.2.2. Use of the Hedvall's effect in clay raw materials hot pressing ..	160
5.3.2.3. Hot pressing of face bricks made of dusty shales	162
5.3.3. Material porosity and cohesion changes resulting from the material components interaction	163
5.3.3.1. Influence of the raw material composition and type onto building brick microstructure	163
5.3.3.2. Some aspects of the whiteware ceramics fast firing	166
5.3.4. Gaseous bubbles in ceramic materials	167
5.4. Growth of layers deposited on brickworks and refractory elements operational surfaces	171
5.5. Notes on the behavior of some ceramic materials during exploitation in both room and high-temperature conditions	173
5.6. Supplementary technological interpretation	175
6. Structural aspects of the high-temperature reactions and general characteristics of sintering processes	177
6.1. Introduction	177
6.2. Examples of the network structure influence onto technological effects	178
6.2.1. Stabilization of the Ca_2SiO_4 polymorphous transition	178
6.2.2. High-temperature reactions between ZrSiO_4 and CaO and role of the baghdadite phase	180
6.2.2.1. General characteristics of the reaction	180
6.2.2.2. Model of the reaction zone	181
6.2.2.3. Assumptions	185

6.2.3. Phases formed in refractory concretes in the MgO-Al ₂ O ₃ -SiO ₂ system . . .	186
6.2.4. Ternary Si-C-O phase in process of SiC oxidation	187
6.3. Characteristics of the sintering processes	189
6.3.1. Spontaneous process	189
6.3.1.1. Free enthalpy drop during solid phase sintering	190
6.3.2. Mass transfer processes during solid phase sintering	192
6.3.2.1. Grains rearrangement	192
6.3.2.2. Volume diffusion and diffusion on inter-granular boundaries . . .	194
6.3.2.3. Diffusion on free surfaces and diffusion via gaseous phase . . .	195
6.3.2.4. Other mechanisms	197
6.3.3. Growth of grains during solid phase sintering	197
6.3.3.1. Thermodynamic aspect	197
6.3.3.2. Grain growth mechanism and kinetics	199
6.3.4. Solid phase sintering model (Coble-Kuczyński's model)	203
6.3.5. Solid phase sintering kinetics	206
6.3.5.1. Measures of sintering advance	206
6.3.5.2. Solid phase sintering kinetics – model of spherical grains	210
6.3.5.3. Sintering kinetics – phenomenological approach	212
6.3.5.4. Kinetic effects in sintering process	213
6.3.6. Solid phase sintering of ceramic powders	216
6.3.7. Sintering with participation of liquid phase – specific sintering	219
6.3.7.1. Introduction	219
6.3.7.2. Rewetting	219
6.3.7.3. Liquid amount and viscosity	222
6.3.7.4. Sintering in conditions of perfect rewetting of the solid body with liquid phase	222
6.3.7.5. Sintering at the presence of liquid, which rewets the solid body imperfectly or poorly	232
6.3.8. Chemical sintering	234
6.4. Supplementary technological interpretation	236
7. Examples of innovative ceramic technology designs	238
7.1. Introduction	238
7.2. Examples of commonly known innovations	239
7.2.1. Low-cement refractory concretes	239
7.2.2. Magnesia – graphite refractory shapes	240
7.2.3. Self-propagating high-temperature synthesis	244
7.2.4. Aluminum nitride-based microelectronics	245
7.2.5. Chemical Vapour Deposition (CVD)	248
7.3. Examples of regional-spread and special innovations	252
7.3.1. Corrosion-resistant slag-alkaline binders	252
7.3.2. Complex conversion of poor aluminum-bearing raw materials into aluminum oxide and cement (J. Grzymek's method)	255

7.3.3. Calcia refractory obtained with semi-hot consolidation method	255
7.3.4. Immobilization of nuclear wastes with use of ceramic materials	257
7.3.5. Hydroxyapatite bio-ceramics	258
7.3.6. Modification of rice hulls into silicone carbide and silicone nitrides	260
7.3.7. New solutions of the heat resistant materials engineering	262
7.3.8. Composites based on poly-crystalline tetragonal zirconium dioxide (TZP) with granulated wolfram carbide addition	263
References	267