Journal of Thermal Analysis, Vol. 38 (1992)131-139

INTERNAL STRUCTURE REBUILDING REACTIONS OF CRYSTALLINE AND AMORPHOUS SOLIDS

L. Stoch

ACADEMY OF MINING AND METALLURGY, 30-059 CRACOW, POLAND

Structural mechanism of the internal thermal reactions of dehydration and dehydroxylation as of solids well as crystallization of their amorphous products and glasses are considered. They are multi-stage processes, realized through small translative displacements of polymerized anion network elements and diffusional shift of cations. It is the way to equilibrium state of the lowest energy consumption and the least energetic barrier to overcome.

Keywords: amorphous solids, crystalline, structural mechanism

Introduction

The inheritance of structural and morphological features of the substrate by the product of reaction is frequently observed in solid bodies and it is referred to as topotaxy. An example here is the decomposition of $Mg(OH)_2$ to MgO [1] and α-FeOOH to α-Fe_2O_3 [2]. Many other examples can be found in the papers of Oswald and coworkers [3, 4].

The topotactic reations of this type are possible when the structures of the substrate and the product are of great similarity. According to [1] such reactions as $Mg(OH)_2$ decomposition consist of small correlated displacements of the anion sublattice, to which the relatively mobile cations adjust their positions. This mechanism is similar to that of so-called diffusionless phase transformations of the martensitic type. The transformation proceeds through correlated shifting of many atoms resembling the shearing deformation. It enables the formation of coherent, i.e. crystallographycally consistent interface, between the substrate and the product with a common lattice plane and with the minimal excess of free energy.

The described topotactic reactions represent a relatively simple example of reactions realized by the rebuilding of the substrate (precursor) internal

John Wiley & Sons, Limited, Chichester
Akadémiai Kiadó, Budapest

structure. The solid product of the reaction is a monophase and its chemical composition corresponds to that substrate.

More complex reactions of internal rebuilding connected with the redistribution and segregation of the chemical components are known. The result of these reactions are solid products of various chemical composition and structure. These reactions are characteristic of substances built of polymerized coordination polyhedra such as silicates, borates and phosphates; hydrates, sulphates and many other crystalline substances of more simple composition also undergo these reactions.

The specific character of reactions is distinct enough to call them the therm 'intracrystal reactions' and in a wider sense, including amorphous solids, the term 'intraframework' or a shorter one 'internal' processes can be used [5, 6].

The internal processes include those phase transformations as well as chemical reactions realized by the rebuilding of solid substrate internal structure and proceed within the whole bulk of the solid grain. The solid product of these processes are formed inside the structural framework of the parent substance remaining in mutual correlation with respect to the primary structure.

Internal reactions are realized by the displacement of the structural elements inside the rigid structure of the precursor. Transport in solids is slow and directional, depending on the anisotropy of their internal structure. The consequence is a multistage course of these reactions and a step-by-step mode of establishing the equilibrium state.

The regularities governing the internal thermal reactions will be discussed in the example of thermal dehydration and dehydroxylation and the processes of crystallization of multicomponent amorphous solids.

Internal thermal dehydration and dehydroxylation

Previously published data referring to the dehydroxylation of layer silicates of the kaolinite group [5–8] as well as the results of the investigations of some borates/colemanite $Ca_2B_6(OH)_6 \cdot 2H_2O$ [9] ulexite $NaCaB_5O_6 \cdot 5H_2O$ [10] and others [11] including also the results obtained by other authors allow to formulate the following opinion about the mechanism of the internal decomposition of solids.

The process of the formation of water molecules from the OH groups and the decomposition beginning, consists of the dissociation of some of the OH groups and the liberation of protons which join the other OH groups. It is preceded by the predehydroxylation state with increased proton mobility as it has been recognized by kaolinite $Al_2Si_2(OH)_4$ investigations [12].

The process described above consists of single events in which individual ions and molecules take part. It can be assumed that the atoms participating in these events are located uniformly in the bulk of the solid body and deviations from this uniformity are only due to the anisotropy and their localisation in the structure. This stage of thermal decomposition seems to be analogous to the reactions in a homogeneous system with the only difference that it takes place in the structure of a solid, acting as a medium in which the reacting ions are subject to displacements. This medium can moderate the velocity and the direction of the displacements.

This stage may be defined a homogeneous-like stage of the thermal decomposition. It should be reversible as it is indicated by the results of experiments with the rehydratation of some silicates [8].

The subsequent stage can be defined as the stage of the phase separation (solid phase and gaseous phase). The newly formed free molecules of the gaseous reaction products become located in the empty voids of the framework. They also accumulate along the macro and microdefects of the grains. Some of them make an attempt to escape outwards through the structure discontinuities.

The possibility of such accumulation and shifting of the process of the gas molecules liberation to a temperature higher than at which they have been formed has been proved by the studies of the decomposition of colemanite and other borates (Table 1), [9–11].

The stage of the liberation of the accumulated gaseous products takes place when, as a result of temperature increase, their pressure exceeds the critical value, required to break the weakest bonds, e.g. perpendicular to the cleavage planes, and then the enclosed gaseous products escape, sometimes in a sudden way (explosive dehydroxylation) [13].

Few water molecules and OH groups remaining enclosed in the solid matrix migrate with temperature increase outwards. This is the diffusional release of the rest of the gaseous components. This stage as well as the previous ones are irreversible and represent the heterogeneous stage of the decomposition reaction.

The above stages of the thermal decomposition can be easily distinguished by means of Q-derivatograph and other methods of constant rate thermal analysis [13, 14].

A sealed box with compressed gaseous products inside, may represent a model of internal thermal decomposition reactions described above [13, 14]. The wall are the forces counteracting of the diffusional migration of the gas molecules. The box walls are impermeable (perfect crystals) or partly permeable (defected crystals) to the gas molecules.

The sealed box volume corresponds to the mean volume of a uniform parts of the structure of solid, free of any discontinuities, bordered by boundaries of mosaic blocks, dislocations or other imperfections along which gases can escape. An ideal crystal represents on this volume – thermal domain. Real crystals are a set of the domains.

Table 1 Stages of the thermal decomposition of borates

Colemanite

$Ca_2B_6O_8(OH)_6 \cdot 2H_2O \xrightarrow[\text{endo}]{340^{\circ}} Ca_2B_6O_{11} \cdot 2H_2O \mid 3H_2O_{\text{int.}} \mid \xrightarrow[\text{endo}]{363^{\circ}}$

cryst. cryst.

$Ca_2B_6O_{11} \mid 5H_2O_{\text{int.}} \mid \xrightarrow[\text{endo}]{378^{\circ}} Ca_2B_6O_{11} \mid 4.5H_2O_{\text{int.}} \mid + 0.5H_2O \uparrow \xrightarrow[\text{endo}]{378-650^{\circ}}$

cryst. expl. cryst.

$Ca_2B_6O_{11} + 4.5H_2O \uparrow \xrightarrow[\text{endo}]{652^{\circ}} Ca_2B_6O_{11} \xrightarrow[\text{exo}]{741^{\circ}} Ca_2B_6O_{11} \xrightarrow[\text{endo}]{951^{\circ}} Ca_2B_6O_{11}$

amorph. I amorph. II cryst. melt

Ulexite

$NaCaB_5O_6(OH)_6 \cdot 5H_2O \xrightarrow[\text{endo}]{118^{\circ}} NaCaB_5O_6\,(OH)_6 \mid 0.5H_2O_{\text{int.}} \mid 3H_2O + 1.5H_2O \uparrow$

cryst. cryst.

$\xrightarrow[\text{endo}]{144^{\circ}} NaCaB_5O_6(OH)_6 \cdot 3H_2O + 0.5H_2O \uparrow \xrightarrow[\text{endo}]{152^{\circ}} NaCaB_5O_6(OH)_6 \cdot 0.5H_2O + 2.5H_2O \uparrow$

expl.

$\xrightarrow[\text{endo}]{152-260^{\circ}} [\mid 0.5CaB_2O_4 + 0.25Ca_2B_2O_5 \mid \mid NaB_{3.4}O_{3.7}(OH)_{3.8} \mid] + 1.5H_2O \uparrow$

cryst. cryst. amorph.matrix

$\xrightarrow[\text{exo}]{624^{\circ}} [\mid NaB_3O_5 \mid \mid (Ca_2B_2O_4)_{0.5}(Ca_2B_2O_5)_{0.25}(B_2O_3)_{0.2} \mid] + 2H_2O \uparrow$

cryst. amorphous matrix

$\xrightarrow[\text{exo}]{700^{\circ}} [\mid NaCaBO_3 \mid \mid (B_2O_3)_2 \mid] \xrightarrow[\text{endo}]{854^{\circ}} NaCaB_5O_9$

cryst. amorph. melt

Temperatures according Q–TG, Q–DTG and Q–DTA curves [9, 10].

When the internal pressure in the sealed box exceeds the tensil strength of its walls, disruption of the box and release of the gas occur. It may be accompanied by disintegration of solid grains by ejected gas – explosive decomposition. Sealed box may domain or promoting the formation of specific intermediate decomposition products. Decomposition of some Al-hydroxides seems to be the example.

High pressure DTA of kaolinite [15] has revealed that the increase of external pressure up to 1024 bars causes an increase of the dehydroxylation temperature and the process proceeds very quickly (the DTA peak becomes very sharp). This can be explained as being due to the diminished permeability of the 'sealed box' until the moment its walls burst. Phenomena like this were interpreted traditionally as side condensation of H_2O molecules.

The sealed box model explains the divergencies in measurements of the decomposition kinetics by the TG method. Rate of the decomposition is measured here by the loss of mass due to gaseous products escape, but in fact they are the separate processes or cover partly, depending on the structural and textural factors.

The tearing-off of a greater number of water molecules or OH groups sometimes results in the rebuilding of the structure. Investigations of the dehydration of $Pb_2P_4O_{12}\cdot 4H_2O$ [16] have revealed that this may proceed by way of rather small displacements of the structural elements. This refers mainly to the flexible complexes of PO_4 tetrahedrons, while the rigid chains of PbO_x polyhedra undergo small changes.

The rebuilding of the structure associated with the tearing-off of water molecules or the OH groups has thus the character of diffusionless displacements of the structural elements including whole complexes of atoms or coordination polyhedra. The factors inducing these displacements are, as it may be assumed, internal strains of the framework, caused by the breaking of a part of the bonds and the liberation of the H_2O molecules and the OH groups.

Total dehydration and dehydroxylation usually involve considerable destruction of the primary structure which must undergo rebuilding and recrystallization. This follows immediately, as in the case of sepiolite $Mg_4Si_6(OH)_2\cdot 4H_2O$, the structure of which becomes transformed into the chain structure of enstatite $MgSiO_3$ with a release of SiO_2 excess. According to [17] this rebuilding proceeds by way of a displacement of large elements of the primary structure.

In general, however, the product of total dehydration and dehydroxylation is an amorphous solid body.

Internal structure rebuilding and the crystallization of amorphous solids

In the course of heating amorphous solid bodies and some glasses there take place the processes tending towards their transition to a crystalline state. The way along which these processes proceed leads through metastable intermediate stages being the result of rearrangement of the precursor structure.

The components of glasses are formally divided into network formers such as SiO_2, B_2O_3, P_2O_5 etc. and network modifiers, localized out of the network (alkali, alkaline earthes etc.). The above distinction may be valid for amorphous solids formed through thermal decomposition too.

The ways of attaining the equilibrium state through the rearrangement of internal structure are various and complex.

An example of a simple rebuilding process is that of colemanite (Table 1). The X-ray amorphous product of its decomposition shows at 650°C and endothermal DTA peak similar to that occurring during heating of glasses above the so-called vitrification temperature (T_g). Its nature is not quite clear; it may be assumed to be the effect of breaking of part of the bonds of the deformed and strained framework undergoing relaxation. An amorphous solid becomes fully recrystallized at 741°C into a compound $2CaO \cdot 3B_2O_3$ of identical composition. Its melting temperature is 950°C, thus the crystallization of the amorphous precursor is completed in a solid phase.

The rebuilding of the structure of ulexite has a particularly complex course. The removal of water from the molecules causes the crystallization of $2CaO \cdot B_2O_3$ and $CaO \cdot B_2O_3$ and the amorphous matrix $NaB_{3.4}O_{3.7}(OH)_{3.8}$ formation. Removal of the OH groups from it induces a reaction of matrix and earlier crystallized borates and as a final effect the formation of the compounds $NaCaBO_3$ and B_2O_3 (Table 1).

The data collected in [8] indicate that the layer silicates can also supply interesting examples of the rebuilding of the amorphous structure into an equilibrium phase composition.

Migration of Mg begins the crystallization of $MgSiO_3$ in dehydrated talc and formation of Mg_2SiO_4 in serpentines.

The excess of SiO_2 forms an amorphous phase doped with Mg which subsequently is recrystallized into pure SiO_2 cristobalite.

In metakaolinite the first to crystallize is γ-Al_2O_3 or (Al, Si) spinal phase; next the layers of the SiO_4 tetrahedra fall apart forming defected mullite I, which at higher temperatures recrystallizes into well crystallized mullite $3Al_2O_3 \cdot 2SiO_2$ of different orientation than that of mullite I, not parallel to the 001 plane of kaolinite.

The amorphous solids being the results of thermal decomposition retain fragments of the structure of the parent substance, which subsequently affects the type and sequence of the compounds derived from them. During the heating of amorphous pandermite first to be formed is $CaO \cdot B_2O_3$ (745°C) and later $CaO\cdot 2B_2O_3$ (800°C) crystallizes. During heating of synthetized glass of the anhydrous pandermite composition the first to crystallize is $CaO\cdot 2B_2O_3$ and almost concurrently $CaO\cdot B_2O_3$, both processes taking place at a higher temperature (870°C). Thus the process of rebuilding of the structure proceeds in a different way.

The crystallization of such amorphous solids which are the result of decomposition starts with diffusional displacements of the cations localizes out of the network. Simultaneously gradual rebuilding or decomposition of the anion network begins but it proceeds at a slower rate. As a result the first to crystallize are the compounds containing fewer network-forming component in comparison with those formed later on. At higher temperatures when the diffusion processes are intensive enough, the decomposition of the previously formed metastable phases, the redistribution of the chemical compounds and the formation of equilibrium crystal phases take place.

The crystallization of inorganic glasses has been the subject of intensive research in connection with the production of new glass-ceramic materials. More information on this subject can be found in [18]. In the light of these data the following general regularities referring to the process of glass crystallization may be formed.

Depending on the composition of glass the first to crystallize are usually the compounds of simple composition made up of components occupying the structural positions outside the SiO_4 network or if they enter into the composition of the network, spinel $MgO\cdot Al_2O_3$ or $Al_2Ti_2O_7$ in glasses rich in aluminium and magnesium and containing an admixture of TiO_2 etc. are crystallized. Completion of the crystallization of these compounds usually initiates spontaneous bulk crystallization, in the course of which substances of complex composition are formed having the character of a solid solution rather far from their natural composition.

To such substances there belong the solid solutions with the structure of quartz $Li_{2-2(x+y)}Mg_xZn_yO\cdot Al_2O_3\cdot zSiO_2$ quartz (s.s.). At higher temperature there follows the ordering of the structure of these solutions connected with the segregation and redistribution of the chemical compounds, and their composition is gradually transformed into the composition of a crystal phase proper for a glass of a given chemical composition.

In glasses in the system SiO_2–Al_2O_3–LiO_2 the first to form is quartz (s.s.), and with the passage of time and/or temperature increase is transformed into spodumene (s.s.), and next into sodumene $Li_2O\cdot Al_2O_3\cdot 4SiO_2$. In glasses with the composition of cordierite the first to form is quartz (s.s.), and subsequently, by way of successive rearrangement of structure, sapphirine and fine cordierite $2MgO\cdot 2Al_2O_3\cdot 5SiO_2$.

In glasses from the system SiO_2–Al_2O_3–CaO–Na_2O the crystallization of wollastonite with the composition $Na_xAl_x(CaMg)_{1-2x}(O, F) \cdot SiO_2$ instead of $CaO \cdot SiO_2$ takes place. Such examples are numerous, and indicate that in some cases bulk crystallization of glasses beginning with the formation of crystalline substances whose composition and structure are as close as possible to the structure of glass. Small translations and the reorientation of the coordination polyhedra of the network as well as small diffusive displacements of cations are sufficient for their formation.

When the temperature is close to the softening point and the mobility of the cations-modifiers as well as the network forming components is high, it is possible that a considerable part of the framework bonds becomes broken and all chemical components undergo displacement. This leads to the decomposition of the transitional metastable phases and then well crystallized compounds are formed corresponding to the state of equilibrium.

Crystallization of glasses by way of gradual transformation of structure and crystallization of amorphous solids formed by thermal decomposition have the similar stages. They are:

1. Diffusional rearrangement of the weakly bound and most mobile components of the structure-modifiers (simple compounds like oxides, titanates, fluorides crystallize).
2. Translative diffusionless rebuilding of the framework (formation of crystal phases of the parent substance-like composition).
3. Translative diffusive transformations (crystallization of metastable compounds of various composition).
4. Diffusive transformations (recrystallization of metastable compounds formed earlier, and crystallization of stable compounds proper for the equilibrium state).

The driving force of the diffusionless translations may be the strains of framework and that of diffusive displacements – the local differences of the chemical potentials.

The above discussed processes satisfy the principles of succession, structural similarity and synchronized rearrangements characterizing directions and structural mechanism of the processes of internal rebuilding [6, 18].

Final remarks

The examples presented here indicate that the processes which may be referred to as the internal structure rebuilding, in spite of their great variety, have numerous features in common, one of them is that they attain the state of equilibrium through a series of intermediate states that are attained by was of possibly small changes in structure and thereby requiring only small expense of energy. In this way the high energy barrier needed to create the interface is omitted. According to the classical theory of crystallization this barrier hampers nuclei growth in liquids and melts.

Processes of the internal rebuilding take the path to equilibrium of the lowest energy consumption and least energetic barriers to overcome.

As a result of internal rebuilding, the formation of crystal phases at lower temperatures and having non-conventional composition becomes possible. The manufacturing glass-ceramics materials is an example. It appears the technology of nonequilibrium, intermediate phases.

References

1 R. Pampuch, Bull. Grup. France Argiles, 23 (1971) 107.
2 S. Yariv and E. Mendelovici, Appl. Spect., 33 (1979) 410.
3 H. R. Oswald, Thermochim. Acta, 135 (1988) 3.
4 H. R. Oswald and A. Reller, J. Thermal Anal., 29 (1988) 67.
5 L. Stoch, J. Thermal Anal., 29 (1984) 919.
6 L. Stoch, J. Thermal Anal., 32 (1987) 1651.
7 L. Stoch, Thermochim. Acta, 110 (1987) 359.
8 G. W. Brindley and J. Lamaitre, in Chemistry of Clays and Clay Minerals, A. C. D. Newman Ed., Mineralogical Soc. Monograph, London 1987, p. 319.
9 I. Waclawska, L. Stoch, J. Paulik and F. Paulik, Thermochim. Acta, 133 (1988) 263.
10 L. Stoch and I. Waclawska, J. Thermal Anal., 36 (1990) 2045.
11 L. Stoch and I. Waclawska, Thermochim. Acta, (in press).
12 R. Pampuch, M. Kawalska and W. Ptak, Pol. Acad. Sci. Kracow Div., Pr. Kom. Ceram., 17 (1971) 63.
13 L. Stoch, J. Thermal Anal., 37 (1991).
14 L. Stoch, Thermochim. Acta, (in press).
15 F. Koster van Gross, Proc. 9th Clay Conf., Strasbourg 1989, Sci. Geol. Mem., 89 (1990) 123.
16 H. Worzala, Z. Anorg. Allg. Chem., 445 (1987) 27.
17 H. Nagata, S. Shimoda and T. Sudo, Clays and Clay Minerals, 22 (1974) 285.
18 Z. Strnad, Glass-Ceramics Materials, Elsevier, Amsterdam 1989.
19 L. Stoch, in Advanced Solid State Chemistry, Proc. 2nd Int. Symp. on Solid State Chem., Pardubice 1989, M. Frumar, V. Cerny and L. Tichy Eds., Elsevier, Amsterdam 1989, p. 298.

Zusammenfassung — Es werden Strukturmechanismen von internen thermischen Reaktionen von Dehydratation und Dehydroxylierung sowie der Kristallisierung der entstehenden amorphen Reaktionsprodukte betrachtet. Dabei handelt es sich um mehrstufige Prozesse, die über kleine translative Verschiebungen von polimerisierten Elementen des Anionennetzwerkes und durch Diffusionsverschiebung von Kationen ablaufen. Dies ist der Weg zum Gleichgewichtszustand mit dem geringsten Energieverbrauch und der niedrigsten, zu überwindenden Energiebarriere.