Thermochimica Acta, 133 (1988) 197–201
Elsevier Science Publishers B.V., Amsterdam

THE RELATION BETWEEN THE STRUCTURE AND THERMAL REACTIONS OF SOLIDS

L. STOCH
Acadamy of Mining and Metallurgy, Krakow (Poland)

ABSTRACT

Results of comparative studies on structural changes accompanying the thermal reactions of solids are presented. Reactions of some crystalline and X-ray amorphous borates and silica are considered.

INTRODUCTION

Thermal reactions of solids are governed by external factors (temperature, pressure etc), as well as intrinsic ones (crystal structure and its imperfections) and also by morphological factors (grain size and habit). The influence of grain size and habit has not been sufficiently recognized so far. For this reason the description of reactions which occur during the heating of solids and their real mechanism by kinetic equations worked out so far, proved to be incorrect [1].

Modern thermal analysis, employing electron microscopy, spectroscopy as well as X-ray and other diffraction methods have revealed the real mechanism of thermal processes and the precursor-product mutual relation. There is at present sufficient data on different substances to enable one to undertake the search for general principles which determine the thermal reactions of solids.

TOPOCHEMICAL AND INTRAFRAMEWORK PROCESSES

From the specific features of the thermal reactions of solids one of the most important is the localization of the reaction centres visualized in the mutual relation: parent substance - solid product [2]. Taking these factors as a criterion, solid state reactions can be divided into: 1. topochemical reactions, 2. intraframework reations.

Thermal Analysis Proc. 9th ICTA Congress, Jerusalem, Israel, 21–25 Aug. 1988
0040-6031/88/$03.50

As a topochemical reaction we shall consider the reaction which occurs on the surface of the parent substance. The solid product of the reaction is separated from the parent substance by a distinct interphase boundary. The rate of these reactions is limited by the rate of the chemical interaction in the reaction centers, localized at the boundary or by the transport of the gaseous products through the layer of the solid product.

In solids one can also observe reactions occurring in the entire volume of the crystal grain. The solid product of the reaction is formed inside the parent substance and its structure usually remains in topotactic relation with respect to the structure of the parent substance. The special character of these reactions is disctinct enough to define them with a special term "intracrystalline reactions", and in a wider sense, if one wishes to include amorphous solids as well, the term "intraframework reactions" is to be used [2,3].

The intraframework thermal reactions include: 1. thermal dissociation 2. processes of internal structure rebuilding (such as (a) synthesis of new phases and segregation of components; (b) thermal amorphisation of crystal solids; (c) the glassy state transformation; (d) crystallization of amorphous solids) 3. oxidation reduction reactions.

The factor determining their kinetics is usually the rate of migration of the atoms, ions and molecules through the framework of the parent solid, which in crystalline bodies is an important process. It may also be limited by breaking of the chemical bonds.

THERMAL DISSOCIATION

Topochemical thermal dissociation is one of the better known reactions, e.g. decomposition of simple carbonates, sulphates, complex compounds of metals, some hydrates, etc. Such a dissociation belongs to a contracting volume process. The topochemical thermal dissociation is sensitive to the partial pressure of the gaseous decomposition products on the phase boundary and\or in a layer of the solid product of the reaction. The reactions or individual stages of multi-stage processes, consisting in breaking one type of the metal-ligand bonds belong to this category. Many of them have been described in the literature.

The intraframework thermal dissociation is characteristic of substances of which the structural framework remains preserved after the process is completed or is only partly damaged. The substances undergoing intraframework thermal decomposition, are ususally those whose structure contains elements formed of polymerized coordination polyhedra with strong bonds (layers, chains) such as silicates, borates, phosphates, organic polymers, etc. The process takes place in the bulk volume of the substance and the decomposition centres are distributed uniformly within the whole grain.

This reaction is made up of two partial processes: 1 - breaking of bonds between atoms, ions or molecules (H, OH, H_2O, CO_2, etc.) and formation of free molecules of gaseous decomposition products; 2-removal of the gas molecules from the framework of the solid product. The temperatures of these two processes may be considerably shifted with respect to each other [3,4].

Removal of the gas molecules occurs when their intraframework pressure exceeds the value necessary to disrupt the weaker chemical bonds of the structural framework. The volume and shape of the solid often does not change during the process. This occurs occasionally in a rapid way and it is then connected with a step-like increase of the volume. The intraframework decomposition process is hardly sensitive to changes of pressure of the gaseous decomposition products. The intraframework decomposition has been investigated on several layer silicates [4]. Recent investigations of the borates confirmed the above concept.

The decomposition of colemanite, a borate with a chain structure, proceeds as follows:

$$Ca_2\left[B_6O_8\right](OH)_6 \cdot 2H_2O \xrightarrow[-19.7]{340^\circ} Ca_2\left[B_6O_{11}\right] \cdot 2H_2O + 3H_2O_{if} \xrightarrow[-53.9]{368^\circ}$$

$$Ca_2\left[B_6O_{11}\right] + 5H_2O_{if} \xrightarrow[-40.2]{386^\circ} Ca_2\left[B_6O_{11}\right]\text{amorph} + H_2O_{vap}$$

The DTA peak temperature (°C) and the enthalpy (kJ/g) of the successive stages of decomposition are given above and below the arrows, respectively.

The decomposition begins with splitting-off of OH groups and the formation of H_2O molecules. Next, H_2O bound with strong hydrogen bonds to the borate chains, splits off. The water molecules liberated in both stages remain captured in the voids of the framework (H_2O_{if}). When the intraframework pressure of H_2O exceeds the strength of the bonds, the framework breaks and the water vapour escapes with an explosion. This process is irreversible and independent on presure changes which has been demonstrated by Q-TG. An X-ray amorphous solid substance is formed. it has numerous pores and small channels with a diameter of less than 1 µm, arranged parallel to the borate chains, where the H_2O molecules concentrated. They are visible in an electron scanning microsope.

Layer borate, pandermite $Ca_2[B_5O_8](OH)_3$ decomposes in several stages loosing at the temperatures 300°, and 360°C each time 1.5 moles of H_2O. The first stage of dehydration does not result in any structural change. At 390°C, recrystallization (exothermic peak) takes place and in the next step the OH groups as 3 moles of H_2O are removed (endothermic peak 465°C). These processes are accompanied by the delamination of crystals parallel to the lattice layers under the action of evolving water vapour. The resulting anhydrous substance is X-ray amorphous. As can be seen the successive steps and the way in which water is removed from both borates are determined by their structure.

PROCESSES OF FRAMEWORK REBUILDING

The processes of framework rebuilding are discussed in connection with amorphisation of crystalline solids by heat treatment below the temperature of melting (thermal amorphisation). Crystallization of these X-ray amorphous solids is also considered.

In the framework of glasses, which are the best known amorphous solids, there are regions with chemical composition and ordering close to that of the corresponding crystal substance (submicroregions, clusters, paracrystals, domains, etc.). A great similarity of behaviour of the thermal amorphised layer sillicates and silicate glasses has been observed, in spite of different character and origin of these substances [3].

The DTA curves of the X-ray amorphous solids of both kinds show a weak endothermic peak. The beginning of the DTA peak of glass is close to its T_g temperature.

The peak corresponds to the rebuilding of the framework, is connected with the breaking off of certain bonds and formation of nuclei of the crystal phase by ordering of submicroregions. Next, the exothermic peak of the crystal growth appears.

With respect to the its chemical composition and structure, the first product of the crystallization is close to the submicroregions in the framework of amorphous substance. The substance tends to attain its equilibrium state through gradual rearrangment of structure and\or segregation of the chemical componenets in submicroregions.

Our latest investigations on colemanite and panderite have shown that analogeous processes take place in them. The anhydrous amorphous colemanite shows the endothermic peak at 650° followed by crystallization of $2CaO. 3B_2O_3$ (exothermic peak at 740°C). During the heating of pandermite the endothermic peak of the X-ray amorphous substance apears at 560° and then $CaO. B_2O_3$ crystallizes (745°C) and subsequently $CaO.2B_2O_3$ is formed (800°C).

Pure quartz at temperature above 1100°C changes into an X-ray amorphous substance. It is formed after prolonged heating, the time necessary to break off part of the oxygen bridges between SiO_4 tetrahedrons. The broken bonds appear at 604 cm^{-1} in the Raman spectrum of the sample. X-ray amorphous substance is formed considerably below the melting temperature of quartz. The amorphous substance crystallizes into cristobalite. For the pure rock crystal a 2h period of heating at 1500°C is required before the amorphous substance occurs. After another 2h of heating the crystallization of the cristobalite begins.

Thermal amorphisation of quartz is greatly influenced by trace quantities of isomorphous substitutions. The alkalies accelerate its amorphisation. Aluminum inhibits the crystallization of cristobalite, increasing the range of stability of amorphous substance.

A comparable study of crystallization of silica glass obtained by melting the samples of quartz of different purity at 1800° and cooling the melt has been undertaken. It crystallizes at 1000°C into quartz and a small admixture of cristobalits. At 1200°C somewhat larger amounts of cristobalite than at 1000°C were formed at the expense of quartz. The aluminium impurities inhibited, as before, the crystallization of the glass.

The process shows analogy with the previous one. The newly-formed quartz which is also unstable, changes into cristobalite. It may be presumed that quartz is formed as the first, due to existence of elements with a structure similar to the quarz structure in the glass framework, which are ordered by heating. Closer is the crystallization temperature to the temperature range of the quartz stability, the more quartz is formed.

CONCLUSIONS

Many seemingly different thermal reactions of solids run according the same scheme of structural changes. They cannot be described by the traditional kinetic models and new formal approach to their mechanism is necessary.

REFERENCES

1. M. Maciejewski and A. Reller, Thermochim. Acta, 110 (1987) 145.
2. L. Stoch, Thermochim. Acta, 110 (1987) 359.
3. L. Stoch, J. Thermal Anal., 32 (1987) 1651.
4. L. Stoch, J. Thermal Anal., 29 (1984) 919.
5. I. Waclawaska, L. Stoch, J. Paulik and F. Paulik, Thermochim, Acta, 126 (1988) 307.