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THE SIGNIFICANCE OF STRUCTURAL FACTORS IN THERMAL DISSOCIATION OF SOLIDS

Leszek Stoch, Academy of Mining and Metallurgy
Cracow , Poland

ABSTRACT

The influence of structural factors , size and perfection of crystals on the mechanism of thermal decomposition of solids is discussed.The classification of the thermal dissociation processes according to localization of decomposition centrs and mutual relation of **parent substance and solid product** has been proposed.

Reactions of thermal decomposition of solids are of specific character , what differ them from the reactions in homogeneous , gaseous or liquid systems.The rate of isothermal reactions in homogeneous systems is determined by concentration of substrats and products exclusively. The kinetics and mechanism of thermal decomposition of solids is influenced by many different factors as:

1.Geometry of crystal lattice , kind and direction of chemical bonds and anisotropy of properties of crystals determined by them.
2.Size and morphology of crystals.
3.Macro- and microdefects of crystals.
4.Pressure of gaseous products of decomposition.
5.Dependance of mechanism and location of reaction on the conditions in which it take place and possibility of their change with the degree of decomposition of original phase in the process.

Process of thermal dissociation of solids differ in the mode of formation of products and in mutual relations of parent substance and solid product. This is the consequence of deciding role of structural factors in the course of these processes .

Taking into account criterions mentioned above , several types of processes of thermal dissociation of solids may be distinguished:

A- 1 Dissociation at the boundary : surface of the parent solid substance - gaseous products.Process leading to the complete decomposition of substance , any solid products are formed.

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Amonium salts decomposition is an example.

B- 1 Dissociation at the boundary of the phases: parent substance - solid product. Product form an outer layer , separated from parent substance with distinguish boundary.Process runs according the model of contracting sphere or disc/simple carbonates , sulphates , some hydrates etc. /.

B- 2 Dissociation at the boundary : parent substance - solid product, accompanied by recombination of gaseous products and synthesis of new compounds stable at the temperature of dissociation / decomposition of complex carbonates , dehydration of some hydrates etc. / .

C- 1 Intracrystal dissociation - decomposition centres are distributed within the whole volume of crystal of parent substance. Grains of the product are growing within crystal of parent substance and remain in topotactic relation with it $/Ca/OH/_2$ $Mg/OH/_2$ etc. / .

C- 2 Intracrystal dissociation - decomposition centres are distributed within the whole volume of crystal of parent substance.After the dissociation the essential frame-work of its structure remains preserved or new solid phase is formed inside the crystal by the transformation of structure of parent substance / layer silicates , hemimorphite , some hydrates /.

Thermal dissociation of carbonates is an example of the B-1 or B-2 process.As generaly accepted , products form a layer separated from parent phase with distinguish boundary.The dissociation takes place at the boundary. Process is usually limited by diffusion ofgaseous products through the layer of solid ones and may be described according the model of contracting sphere or disc. Partial pressure of gaseous products at the boundary determines kinetics of the process. Temperature of decomposition of simple carbonates depends on the strength of Me^{2+} cations and CO_3^{-2} group bonds . Weaker / more ionic / bond , higher the dissociation temperature , higher MeO and CO_2 chemical affinity , better reversibility of the process and higher sensitivity to the CO_2 partial pressure /$CaCO_3$, $SrCO_3$, $BaCO_3$, etc. / .

When the bond is stronger / more covalent / the $Me^{2+}$is depolarizing and weaking the bonds inside CO_3^{2-} radical and CO_2 is easy liberated.The temperature of decomposition of the as well as its reversibility is low /$MgCO_3$, $ZnCO_3$, $MnCO_3$, $FeCO_3$ etc. /.

During decomposition of complex compounds containing carbonates of the first and second group , simple carbonate of the first group may be formed /B - 2 process /. Dolomite and huntite are the example.

Dehydroxylation of hydroxides has a different mechanism /C - 1 /. During the process decomposition centres are distributed more or less evenly within a crystal and water vapour is evolved also evenly in its entire volume / 1 /. Grains of the product are growing within crystal of parent substance and remain in topotactic relation with it . Because of the distribution of decomposition centres within the crystals of parent substance this mechanism can be called intracrystaline and since the new phase is formed within the whole volume without development of a separate outer layer of products.

Dehydroxylation of layer silicates represents a peculiar type of intracrystal thermal dissociation /C - 2 /.Dehydroxylation of kaolinite is one of the best known process of this kind / 2 /.

The kinetics of intracrystal dehydroxylation is determined by parial pressure of water vapour in definite elementary volume of crystal structure - intracrystalline pressure. These volumes may be defined as termochemical domains , by analogy with the term " domain " used for minimal areas of crystal structure coherently diffracting X-ray radiation. Termoohemical domains are spaces free from structural discontinuities , bordered by dislocations , boundaries of mosaic blocks and other , along which gaseous products of reaction can escape .

Thermal dissociation process starts when intracrystalline pressure within domains exceeds the necessary value to disrupt the weakest chemical bonds. The pressure within a domain during thermal dissociation is conditioned by the resistance of diffusion on which have to be overpassed by water molecules to go out from solid. During dehydroxylation of kaolinite weakest diffusion resistance can be along interlayer space .

Contrary to the decomposition of carbonates , the pressure of gaseous products of thermal dissociation influence but slightly the kinetics of dehydroxylation of layer silicates . On the other side it is conditioned by the value of intracrystalline pressure in a given moment . This in turn depends on the size and degree of perfection of crystals / 3 /.The slow decrease of this pressure is favoured by high degree of crystallinity of mineral and consequently , by large volume of domains.

Such course of thermal dissociation is due to exceptionally distinc anisotropy of distribution of strengths of bonds in layer silicates. The anisotropy is expressed by strong ionic-covalent bonds within layer and weaker hydrogen or ionic bonds between layers.

Thus the data about kinetics of thermal dissociation may be valuable source of informations about the details of internal structure and its perfection and habit of crystals .

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