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SURVEY

**Accelerated physical and chemical transformations in ceramics processing**

ERNŐ E. KISS<sup>#</sup> and SANJA N. PANIĆ<sup>\*#</sup>

*University of Novi Sad, Faculty of Technology, bul. Cara Lazara 1, 21000 Novi Sad, Serbia*

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*Abstract:* From economic and environmental points of view, solid phase chemical reactions are very important parts of modern chemistry and technology, enabling various processes to become cleaner, safer and easier to perform. This survey presents the basic concepts of solid-state transformations in ceramics processing, including notions and phenomena described in capital books on silicate chemistry, published more than 100 years ago, to the present day. During this period, scientists and practitioners in the field of ceramics processing used concepts related to the acceleration of phase transitions and chemical reactions. Today, the differences between various accelerating agents (flux agents, mineralizers and catalysts) in terms of their composition and mechanism of action are almost completely defined and clearly delimited. However, in ceramics processing, a more general term additive is preferably used instead of the previously mentioned ones. The aim of this work is to show that all accelerating agents are equally important to researchers in the field of catalysis and material science, emphasizing that the used terminology could be interpreted from different perspectives.

*Keywords:* solid-state transformations; chemical reactions; flux agents; mineralizers; catalysts.

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\* Corresponding author. E-mail: sanjar@tf.uns.ac.rs

# Serbian Chemical Society member.

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## 1. INTRODUCTION

During the physical transformations of a matter, the matter does not change its chemical identity. Boiling, melting, subliming, dissolving, sintering, allotrope and polymorph transformations, *etc.* are physical transformations. In chemical transformations, some substances disappear and new ones are formed. Physical and chemical transformations could be accelerated by bringing energy to the system (by heating, different radiations, mechanical activation) or by creating more favorable condition for proceeding these transformations (fluxing agents, mineralizers, catalysts). In ceramic processing, the most important physical and chemical transformations proceed in the solid state.

Solid phase chemical reactions are those in which the solid (crystalline) reactant or reactants react in the absence of solvents. Such reactions are advantageous from an economic and environmental point of view. The product does not have to be separated from the solvent and no solvent is a burden for the environment. Therefore, these reactions are industrially useful and can be considered as mainly green. In order to accelerate the solid phase transformations, elevated temperatures can be applied promoting movement in the crystal lattice and crystal crack defects. The same effect can be accomplished in the presence of suitable gases, since material transfer also occurs in a particular gas phase. The speed of these reactions may also be affected by the presence of other substances. The main types of diffusion processes that occur on/in a solid grain are represented in Fig. 1. During the chemical reactions, changes begin at the surface of the grain (interface). When it comes to thermal decomposition, tiny elementary particles begin to separate from the surface of the grain. After different solid particles start to react with each other, mass transfer begins with core boundary diffusion, which can further be proceeded by surface and bulk diffusion. These processes can be characterized by the Tammann temperature that is approximately equal to the half of the melting point of the material, expressed in Kelvin. At this temperature, the mobility of the tiny elementary particles becomes significant and, consequently, chemical reactions become more noticeable. The mobility of the surface atoms is significant at one-third the Tammann temperature. This value is known in the literature as the Hüttig temperature.

In solid phase reactions, the size of the interface has a significant effect on the rate of the reaction. The diffusion property of the sample is denoted numerically by the diffusion constant,  $\text{m}^2 \text{s}^{-1}$ , ranging from  $10^{-10}$  to  $10^{-14}$  for solid matter, while its value for liquids and gases is  $10^{-9}$  and  $10^{-5}$ , respectively. When

the reaction is governed by surface diffusion, the product will be located only on the surface of the reactants. If the reaction proceeds in the bulk of reactants, the product will be formed at the same location. The crystal lattice of the reactant during the reaction becomes oversaturated with product, and the product starts to separate from the bulk. Based on these considerations, three models of solid phase reactions with particular kinetic equations can be distinguished: *i*) diffusion model, *ii*) crystal growth and *iii*) phase boundary model.<sup>1</sup> Today, the literature concerning the kinetics of solid state reactions is quite rich, whereby the review paper written by Vyazovkin and Wight<sup>2</sup> could be designated as the most comprehensive one.

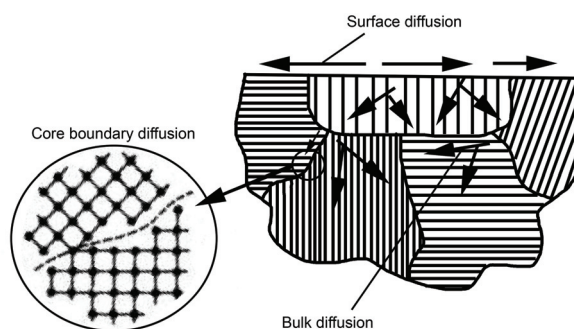


Fig. 1. Diffusion processes in a polycrystalline body.

During the investigation of the mechanism of solid phase changes or chemical reactions, the researcher can often encounter the following apprehensions: *i*) epitaxy or epitaxial growth, stranding of one layer of the matter on a single crystal of another substance, so the crystal structure of the layer is identical to the substrate; *ii*) topotaxy, the crystal orientation of the product is the same as the crystal orientation of the reactant; *iii*) structural sensitivity, the size or shape of the product may be related to the method of synthesis. The process of solid phase changes and reactions can also be explained by various effects: *i*) memory effect, the form of the product resembles the form of the starting material; *ii*) Hedvall effect, at the temperature of the polymorphic transformations, chemical reactions are usually accelerated; *iii*) Kirkendall effect, occurs at the interface due to different diffusion rates of different metals; *iv*) mineralization effect, in the reaction mixture, an admixture forms an easily melting mixture, therefore the mass transfer accelerates, but may also result in complete decomposition without any harmful end product; *v*) catalytic effect, in the presence of a catalyst, mechanism of the reaction changes substantially, such that the new barriers along the reaction coordinate are significantly lower; *vi*) Jahn–Teller effect, geometric distortion of molecules and ions. Thermal treatment of a solid system, in the absence or presence of impurities or artificially added additives, can create defects in the crystal

lattice, change the aggregate state of the components or the complete system, result in recrystallization and formation of new chemical compounds, and result in sintering as a very important phenomenon in ceramics processing. Sintering is the process of compacting and forming a solid mass of matter by heat or pressure, without melting it to the point of liquefaction. In the case of solids that form a eutectic system, during sintering with smaller amount of additives, shrinkage will be accelerated relative to the system without additives, well before reaching the eutectic temperature. This phenomenon is called activated sintering.<sup>3</sup> The presence of liquid phase can accelerate sintering and the substances that promote the appearance of a liquid phase are called flux agents.<sup>4</sup>

## 2. FLUX AGENTS, MINERALIZERS AND CATALYSTS IN CERAMICS PROCESSING

### 2.1. *Basic notions and historical background*

In ceramics processing, various additives are employed and consequently, the complexities that arise in the delimitation of the role of individual additives (flux agents, mineralizers and catalysts) still exist. Mineralizers, such as catalysts under industrial conditions, may be incorporated into the mixture of solids as natural impurities or as artificial additives. They can accelerate or retard physical or chemical changes in the solid systems. Since the presence of these additives has no influence on the stoichiometry, their required amount is usually not strictly defined. Flux agents, mineralizers and catalysts may also effect the formation of crystalline nuclei of the products, the rate of crystallization and diffusion processes, *etc.* Accordingly, it is difficult to define whether a particular additive acts as a fluxing agent, mineralizer or catalyst; however, some general rules distinguishing their roles can be established. If the matter processing has not resulted in the formation of new chemical compounds, the applied additives do not exhibit a catalytic effect. However, like catalysts, flux agents and mineralizers can also speed up the formation of new chemical compounds, but the mechanism of their action is different from the way a catalyst acts. Flux agents promote the appearance of a liquid phase where mass transfer is easier compared to solids and consequently, the formation of new chemical compounds becomes faster. Mineralizers can influence the speed of chemical compound formation by affecting the chemical equilibrium of solid-state reaction by incorporation in one or more solid phases. In contrast, a catalyst has no influence on the establishment of a new chemical equilibrium, since it affects equally the speed of the particular chemical reaction and the rate of the opposite one. The thermodynamic equilibrium constant is the same in the absence and presence of the catalyst. A catalyst speeds up or slows down the rate of chemical reaction (positive catalysis/negative catalysis), but it is not consumed during the course of chemical reaction. Additionally, it does not change permanently during the reaction, because the created intermediates are decomposed into the final product, and the catalyst is released to

repeat a new catalytic cycle.<sup>5</sup> This cannot be applied to mineralizers. Namely, in his book that is more than 100 years old, Doelter clearly indicates how an additive acts as catalyst, and as a mineralizer in silicate systems.<sup>6</sup> Mineralizers, especially carbonic acid, are not catalysts because they have a direct impact on the chemical equilibrium. Beside  $\text{CO}_3^{2-}$ , Doelter mentions even other ions, such as  $\text{F}^-$ ,  $\text{BO}_3^{3-}$  (orthoborate) and  $\text{Cl}^-$ , acting as mineralizers, and emphasizes that all these ions are acidic and highly mobile.<sup>6</sup> In one even older research, Tschermak, not only by words but also by chemical equation, shows that boron oxide acts as a mineralizer during aluminum hexafluoride transformation into corundum ( $\alpha\text{-Al}_2\text{O}_3$ ) converting to boron fluoride:  $\text{Al}_2\text{F}_6 + \text{B}_2\text{O}_3 = \text{Al}_2\text{O}_3 + 2\text{BF}_3$ .<sup>7</sup> Singer in his book “*Das Steinzeug*” describes in detail how different factors can affect the production of ceramic materials, including mineralizers and catalysts, but he does not explain the difference between these substances.<sup>8</sup> In his next book, the notions of mineralizer and catalyst are not clearly delimited, since he states that mineralizers are essential in the ceramic industry as catalysts (in the German text: “*Mineralisatoren sind für die keramische Industrie lebenswichtig als Katalysatoren für Umwandlungen*”).<sup>9</sup> Budnikov and Ginzting in their book use the term additive more often than the term mineralizer. They are reluctant to use the term catalyst and use it very rarely.<sup>10</sup> Nowadays, in ceramics processing the word additive is still widely used implying a broader concept compared to mineralizers and catalysts the individual roles of which are strictly defined by their mechanism of action.

The mineralizers and flux agents described in this survey mostly refer to those that occur in cement clinker. In order to better understand their role and mode of action governing the physical and chemical changes; it is necessary to give the basic chemical composition of cement clinker.

The main components of Portland cement clinker are tricalcium silicate (alite,  $\text{Ca}_3\text{SiO}_5/3\text{CaO}\cdot\text{SiO}_2$ , 50–70 wt. %), dicalcium silicate (belite,  $\text{Ca}_2\text{SiO}_4/2\text{CaO}\cdot\text{SiO}_2$ , 5–30 wt. %), tricalcium aluminate ( $\text{Ca}_3\text{Al}_2\text{O}_6/3\text{CaO}\cdot\text{Al}_2\text{O}_3$ , 13–20 wt. %) and calcium aluminoferrite ( $\text{Ca}_2(\text{Al}_x\text{Fe}^{1-x})_2\text{O}_5$  where  $0 < x < 0.7$ , 5–15 wt. %). Smaller amounts (<1 wt. %) include MgO (periclase),  $\text{SiO}_2$  (quartz) and CaO (burned lime in free form).<sup>4</sup> Alite, as the most common component in cement clinker, has 7 polymorphic forms, 3 triclinic (T), 3 monoclinic (M), and 1 rhombic (R). These polymorphic transformations are all reversible (Fig. 2).<sup>11</sup>

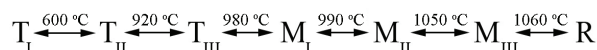


Fig. 2. Polymorphism of tricalcium silicate.<sup>11</sup>

Tricalcium silicate is stable over 1300 °C only. The  $\text{M}_{III}$  modification can be stabilized by  $\text{Mg}^{2+}$  and the rhombohedral modification by  $\text{Zn}^{2+}$ , when they are

incorporated into the place of  $\text{Ca}^{2+}$ . The creation of monoclinic  $M_I$  form of alite can be promoted by substitution of  $\text{Si}^{4+}$  in tetrahedral sites in silicate structure by  $\text{S}^{6+}$ .

Belite, as the second most common component in cement clinker, has 5 polymorphic forms, one  $\gamma$ -, one  $\beta$ - and three  $\alpha$ -forms. The  $\gamma$ -form dominates at lower temperatures. The  $\beta$ -form can be stabilized by  $\text{S}^{6+}$ . Alkaline ions and  $\text{P}^{5+}$  can easily integrate into the crystal structure of dicalcium silicate and stabilize the  $\alpha$ -form.<sup>4</sup> During heating, belite undergoes polymorphic transformations to form the high temperature  $\alpha$ -form (Fig. 3).<sup>12</sup> In his book published in 2014, Kurdowski gave a detailed study on Portland cement clinker burning process and on the kinetics of the formation of particular compounds.<sup>13</sup>

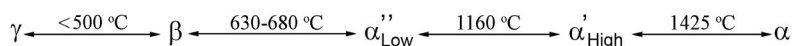


Fig. 3. Polymorphism of dicalcium silicate.<sup>12</sup>

## 2.2. Flux agents

Fluxing agents can be defined as additives that change the temperature of the appearance of the liquid phase. Thus, at a certain temperature, the quantity of the liquid phase is increased thereby promoting the reaction. These substances may also have an effect on the morphology of the crystals appearing in the solution of cement clinker. The liquid phase in the cement clinker is formed at the eutectic temperature of the substances present in the system. Mass transport is realized in this liquid phase with the rate determined by the concentration of the reactants, and the viscosity and surface tension of the liquid solution. Small amounts of impurities in the system generally reduce the temperature of the appearance of liquid phase and increase its volume. The volume increase is approximately equal to the volume of the impurities. Electropositive elements, such as  $\text{K}^+$  and  $\text{Na}^+$ , generally increase, while electronegative elements, such as  $\text{F}^-$  and  $\text{Cl}^-$ , reduce the viscosity of the liquid phase. Electropositive  $p$ -elements increase the surface tension, while electronegative ones reduce it. Conversely, if the electronegativity of the  $s$ -elements increases, the surface tension of the liquid phase will also increase. In these processes, ion exchange between the liquid and the solid phase occurs.  $\text{K}^+$ ,  $\text{Na}^+$  and  $\text{Mg}^{2+}$  replace the  $\text{Ca}^{2+}$  in the calcium silicate compounds, while  $\text{Al}^{3+}$ ,  $\text{P}^{5+}$  and  $\text{S}^{6+}$  replace the  $\text{Si}^{4+}$  in the tetrahedral position of calcium silicates.<sup>4</sup> Low values of viscosity and surface tension increase diffusivity, consequently accelerating mass transfer.

Since many additives simultaneously act as flux agents and mineralizers, their role in the process of cement clinker production, as well as their mechanism of action will be further discussed.

### 2.3. Mineralizers

A mineralizer can be defined as an agent that promotes the formation of a particular solid phase by affecting the equilibrium through its incorporation in one or more of the solid phases. Therefore, the main role of mineralizers is to reduce the burning temperature of cement clinker as it can save energy and thus make the process more environmentally friendly.

#### 2.3.1. Alkali metal oxides and alkaline earth metal oxides as mineralizers

Alkali metal oxides and alkaline earth metal oxides are very important mineralizers in cement clinker technology. In the presence of sodium, the burning temperature of belite is lowered by 100 °C. Potassium behaves similarly. Lithium accelerates the decarboxylation of CaCO<sub>3</sub>. Barium also reduces the temperature of cement clinker formation and stabilizes belite polymorphic transformations to  $\beta$ -form. Its presence in 0.5 wt. % is sufficient to accelerate alite formation by the chemical reaction of belite with CaO.<sup>14</sup>

#### 2.3.2. Transition metal oxides as mineralizers

Transition metal oxides enable the formation of higher amounts of cement clinker in the liquid phase. Accordingly, they could also be considered as flux agents. These materials, as previously mentioned, have an impact on the viscosity and surface tension of the solution. Transition metal oxides as mineralizers cause the growth of alite crystal grains. There are many different additives beside transition metal oxides that act simultaneously as mineralizers and flux agents. Without an additive, the melting temperature of cement clinker is around 1340 °C. Additives that cause a decrease of viscosity and surface tension of the liquid phase increase the mass transfer in the system. This could explain why belite reacts faster with free CaO leading to the rapid formation of alite. Timashev showed that the viscosity of the liquid phase decreases when the oxidation state of transition metals increases. If this dependence is expressed as ionic charge to radius ratio, which is equivalent to an increase in the strength of the Me–O bond, this relationship will be even more manifested (Fig. 4).<sup>15</sup> There are similar relationships with the surface tension of the melt, only the deviations are larger.<sup>15</sup>

Titanium accelerates decarboxylation, reduces the melting point of cement clinker and the amount of lime. Its effectiveness depends on concentration. Vanadium in cement clinker is present usually in the V<sub>2</sub>O<sub>5</sub> form. Vanadium ions reduce the melting point of cement clinker, accelerate the development of large alite crystals and stabilize belite in the  $\beta$ -form. Cr<sup>6+</sup> and Mn<sup>7+</sup> show similar properties. Depending on the burning conditions, chromium may appear in different oxidation states, Cr<sup>3+</sup>, Cr<sup>4+</sup>, Cr<sup>5+</sup> and Cr<sup>6+</sup>. In belite, Cr<sup>4+</sup> and Cr<sup>5+</sup> replace silicon ions in the silicate structure. When a cement is in contact with water, disproportion of the Cr<sup>4+</sup> and Cr<sup>5+</sup> occurs, forming Cr<sup>3+</sup> and Cr<sup>6+</sup>.

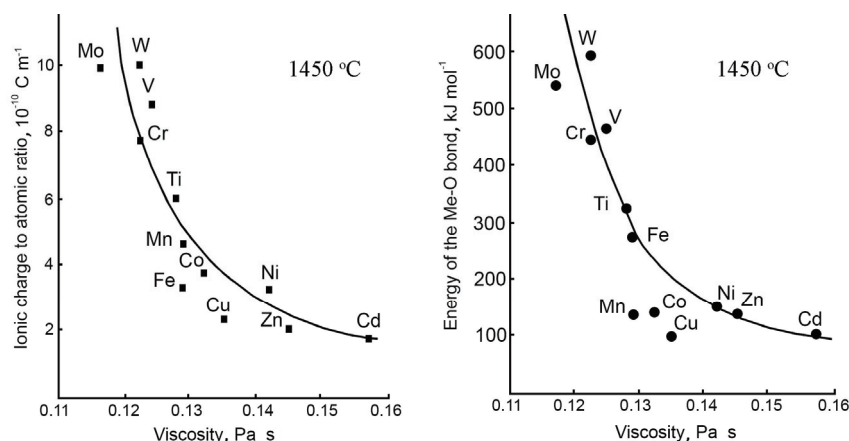


Fig. 4. Relationship between the ionic charge (left) and the energy of the Me–O transition metal bond (right) and viscosity.<sup>15</sup>

The presence of 0.5 wt. % of  $\text{Cr}^{5+}$  stabilizes the belite, consequently hindering alite formation. Generally, chromium ions increase the strength of cement, but on the other hand cause skin eczema. Due to this fact, the upper limit of their use in cement clinker today is only 0.07 wt. %.<sup>14</sup> In calcium silicates,  $\text{Mn}^{4+}$  under oxidation conditions substitute the  $\text{Si}^{4+}$  and, under reduction conditions,  $\text{Mn}^{2+}$  substitute the calcium ions. Cobalt can be accumulated in large quantities in the calcium aluminumferrite phase, where  $\text{Co}^{3+}$  exchange  $\text{Fe}^{3+}$ .<sup>14</sup> In the temperature range 1000–1300 °C copper oxide decreases the free lime content and the temperature of sintering.<sup>16</sup> Kolovos *et al.*<sup>17</sup> considered CuO as the most important mineralizer. Hou *et al.*<sup>18</sup> registered a significant mineralizing effect of CuO even at a concentration of 1 wt. %. Nickel has no significant effect on the mineralization of cement clinker.<sup>19,20</sup> According to Kakali and Parissakis,<sup>21</sup> 2–4 wt. % ZnO reduces the clinkerization temperature by 100–150 °C. Molybdenum and tungsten significantly reduce the viscosity of cement clinker melt (Fig. 4) accelerating diffusion and facilitating mass transfer.

### 2.3.3. Halogens as mineralizers

The halogens F, Cl, Br and I, are mainly introduced into cement clinker with the fuel, but they can also be introduced into the system with the raw material. Sea clay contains a lot of chlorine. As is well known, halogens have a strong oxidizing effect. The admixture of  $\text{CaCl}_2$ , in a concentration of 0.5–1.5 wt. %, facilitates the volatilization of alkali metals, and thus provides a low alkali metal clinker. Fluoride has a strong mineralization and a good fluxing effect. These effects reflect the reduction of viscosity and surface tension of the liquid phase. Fluoride also promotes alite formation. The accelerated alite formation could be explained by substitution of  $\text{O}^{2-}$  with  $\text{F}^-$ . The charge compensation is partially enabled by vacancies and interstitials. According to Shame and Glasser,<sup>22</sup> elec-



charge neutrality is actually ensured by dual ion exchange,  $\text{Al}^{3+}$  is swapped with  $\text{Si}^{4+}$ , and  $\text{O}^{2-}$  with  $\text{F}^-$ . This process results in an intensive formation of a solid solution.

#### 2.3.4. Mineralizers for activated sintering

Sintering of ceramics can be accelerated by mineralizers (activated sintering). This is one of the ways to reduce the energy expenditure in the processing of ceramics.<sup>23</sup> The effect of mineralizers will be discussed here without reference to the most important process variables of sintering (temperature, pressure, particle size, particle packing, *etc.*). However, it should be noted that the influence of mineralizer is always studied as a relative variable, *i.e.*, changes in process parameters are studied always in relation to the system in the absence of mineralizers.

Sintering can occur in the solid phase. Alumina sinters in the presence of magnesia in the solid phase, without the appearance of liquids. Very low content of magnesia (0.1–0.5 wt. %) promotes alumina sintering. During the thermal treatment of the samples,  $\text{MgAl}_2\text{O}_4$  spinel is formed. The spinel phase diffuses through the grain boundaries and pins to them leading to a decrease in the grain sizes. This process improves the quality of sintered alumina.<sup>24</sup> Magnesia-doped alumina has good strength, hardness and improved toughness.<sup>25</sup> Ytria-doped zirconia is a solid electrolyte for fuel cell applications. These types of fuel cells are prepared by sintering  $\text{ZrO}_2$  with 3–10 mol %  $\text{Y}_2\text{O}_3$  in the solid state.<sup>26</sup> Liquid phase sintering implies the coexisting of liquid and solid particles in the system during some part of the thermal treatment. It is commonly used to assist densification. The earliest uses of liquid phase sintering were in the production of building bricks from clay-based minerals. The application of barium, lead and zinc compounds as mineralizers significantly lowers the sintering temperature (by 40–60 °C), achieving considerable energy savings in the production of building ceramics.<sup>27</sup> Current application of liquid phase sintering is in the fabrication of magnesia-based refractories, and high-temperature structural ceramics, silicon nitride,  $\text{Si}_3\text{N}_4$  and silicon carbide,  $\text{SiC}$ .<sup>26</sup> The flowability and refractoriness of magnesia can be influenced by the amount of  $\text{SiO}_2$  added as microsilica.<sup>28</sup> The sintering behavior of  $\text{Si}_3\text{N}_4$  can be influenced by a liquid phase of the a ternary system of additives  $\text{Y}_2\text{O}_3$ – $\text{SiO}_2$ – $\text{Al}_2\text{O}_3$ <sup>29</sup> and binary system of additives  $\text{Y}_2\text{O}_3$ – $\text{Al}_2\text{O}_3$ .<sup>30</sup> Silicon carbide ceramic with  $\text{Y}_3\text{Al}_5\text{O}_{12}$  (yttrium aluminum garnet, YAG) additive, added by the sol–gel method, can be liquid phase sintered. The suitable sintering temperature is 1860 °C. The specimen sintered at this temperature has superior sintering and mechanical properties, having smaller crystal size and fewer microstructure defects.<sup>31</sup>

Reactive/reaction sintering implies synthesis processes in which the product results from the reaction of at least two powder components. In these processes, new compounds are usually formed and the products can be solid solutions, or a new polymorphic form of the reactants or the products. Typical representatives of

these reactions are the formation of different spinels from a divalent metal oxide and alumina,  $\text{MeO} + \text{Al}_2\text{O}_3 \rightarrow \text{MeAl}_2\text{O}_4$ , where MeO is MgO/NiO/ZnO, *etc.*<sup>32</sup> The rate of spinel formation depends on the crystal structure of alumina. On  $\gamma\text{-Al}_2\text{O}_3$ , it is much higher compared to on  $\alpha\text{-Al}_2\text{O}_3$ . Such a behavior could be explained by the topotactic effect ( $\gamma\text{-Al}_2\text{O}_3$  has a cubic spinel structure as the product), by the Hedvall effect ( $\gamma\text{-Al}_2\text{O}_3$  during the reaction suffered a series of polymorphous transformations  $\gamma \rightarrow \delta \rightarrow \theta \rightarrow \alpha\text{-Al}_2\text{O}_3$ ). At the temperatures of polymorphous transformations, the reactants are rich in energy. The surface area of  $\gamma\text{-Al}_2\text{O}_3$  is much higher compared to that of  $\alpha\text{-Al}_2\text{O}_3$ , thus the  $\gamma$ -form of the alumina provides better contact between the reactants.<sup>33</sup> SiAlONs are ceramics based on the elements Si, Al, O and N, and could be considered as solid solutions of  $\text{Si}_3\text{O}_4\text{-AlN-Al}_2\text{O}_3$ .<sup>26,34</sup> The formation of mullite in aluminum silicate systems is often cited as an example of reaction sintering.<sup>26,35</sup> This reaction may also occur during catalytic hydrodesulfurization and the presence of molybdenum in these catalysts may speed up the reaction. According to Zhu *et al.*,<sup>36</sup>  $\text{MoO}_3$  alters the mullitization reaction pathway, leading to a decrease of the initial reaction temperature by 200 °C. It also accelerates the reaction process and increases the degree of conversion.

## 2.4. Catalysts

### 2.4.1. Theoretical considerations

Catalytic reactions in solid states are not rare, and many of these reactions are very important today. In practice, the most important and the most frequently studied catalytic reaction in the solid phase is the combustion of solid ammonium perchlorate in the presence of various solid catalysts. Ammonium perchlorate,  $\text{NH}_4\text{ClO}_4$ , is a powerful oxidizer and ammonium is a beneficial fuel. These two properties could explain the usefulness of ammonium perchlorate as a rocket propellant.<sup>37</sup>

As previously mentioned, in ceramics processing, the strictly defined term catalyst is usually replaced by the more general term additive. Such cautiousness is quite justified because, in most of the cases, it is not fully known by which mechanism the additive works. In the following part of this survey, an attempt is made to find certain transformations that occur in solids during ceramics processing and are likely to occur by the catalytic mechanism.

The Jahn–Teller effect is also registered in solids, even in minerals.<sup>38</sup> Transition metals are known as good catalysts in many chemical reactions. Oxides of copper  $d^9$  ( $\text{Cu}^{2+}$ ), manganese  $d^4$  ( $\text{Mn}^{3+}$ ) or  $d^5$  ( $\text{Mn}^{2+}$ ), and iron  $d^6$  ( $\text{Fe}^{2+}$ ) or  $d^5$  ( $\text{Fe}^{3+}$ ), are given special attention for two reasons: they are good mineralizers and they provide the Jahn–Teller effect. The essence of the Jahn–Teller effect is the distortion of molecules and ions in the surroundings of corresponding transition metals, due to distribution of 3d electrons in various crystal fields.<sup>39,40</sup> From

the shape of the d-orbitals and the orientation of their lobes, it is evident that there will be substantial electrostatic repulsion between electrons in  $d z^2$  and  $d x^2-y^2$  orbitals and the charged ligands. The distortion of molecules in the sphere of influence of d-metals could be considered as a type of activated state of the molecules. The result is the splitting of d-orbitals into two sets, as in the case of octahedral coordination: higher  $d z^2$ ,  $d x^2-y^2$  ( $E_g$ ) and lower, tetrahedral,  $d xy$ ,  $d yz$  and  $d zx$  ( $T_{2g}$ ) energy level. The splitting is similar, though smaller, for tetrahedral coordination ( $\Delta_{tet} = 4/9\Delta_{oct}$ ).<sup>41</sup> For oxide ceramics derived from different forms of alumina and clay minerals, the tetrahedral sheets of silica  $SiO_4$  and octahedral sheets of aluminum  $AlO_6$  are of particular interest for these interactions. In extreme cases, the distortion of local ligand symmetry results in cooperative phase transformations of substrates.<sup>39</sup> This approach for the interpretation of accelerated transformations of polymorphic forms and chemical compounds, at least in some elements, is very similar to the catalytic mechanism. Transition of different polymorphic forms of some compounds is questionable also from the catalysis point of view. Polymorphic forms exist only in the solid state. After melting of different polymorphic forms of the same compound, the liquid phase contains only one compound, and not a solution of different stereoisomers. Stereoisomers exist both in the solid and liquid state, while the polymorphic forms of a crystalline compound exist only in the solid state.<sup>42</sup> In chemical reactions, stereoisomers give different products. A mixture of the same compound in different polymorphic forms in a solid-state reaction will give different polymeric products, but if the system was previously converted to the liquid state, *i.e.*, before the reaction, a single product will be formed.

#### 2.4.2. Experimental investigations

The significance of the Jahn–Teller effect in solid state reaction was investigated preliminary in the system of gibbsite, boehmite and  $\gamma-Al_2O_3$  in the presence of copper, zinc and magnesium oxide, alternatively.<sup>43</sup> Copper ( $Cu^{2+}$ ) has an unfilled 3d orbital, with an electron configuration of  $3d^9$ ; zinc ( $Zn^{2+}$ ) has a filled 3d orbital, with an electron configuration of  $3d^{10}$ , and magnesium is an sp element. Theoretically, the impact of the Jahn–Teller effect on physical and chemical changes could only be expected in the systems that were prepared with copper oxide. The obtained experimental results have confirmed the theoretical expectations. Accelerated polymorphic transformations of alumina occurred only in the systems that were prepared with CuO (equimolar CuO and  $Al_2O_3$ , 900 °C, 10 h, air atmosphere).<sup>43</sup> In all systems, the corresponding spinels were intensively formed. The amount of different spinels was determined by the type of the divalent metal oxide, as well as the origin of the alumina. Based on the obtained results, two other transition metal oxides (manganese and iron) were chosen as catalysts. The experimental investigations were performed on alumina (derived from boehmite,  $\gamma-AlO(OH)$ ) and on kaolinite,  $Al_2Si_2O_5(OH)_4$  containing samples.

The samples were impregnated with appropriate salts of copper, manganese and iron, so that the Me (Cu, Mn or Fe)/Al mole ratio was 1/3 in the impregnated samples. The samples were exposed to thermal treatment at 900 °C, for 10 h in air. The interaction of alumina and kaolinite with selected transition metal ions was investigated by diffuse reflectance spectroscopy (DRS) in the range 10000–45000 cm<sup>-1</sup>, at room temperature. In the DRS spectra of all systems, band splitting as the consequence of the Jahn–Teller effect<sup>44</sup>, in the range of 10800–12000 cm<sup>-1</sup> (<sup>5</sup>T<sub>2g</sub> → <sup>5</sup>E<sub>g</sub>), 15400–15600 cm<sup>-1</sup> (<sup>2</sup>T<sub>2g</sub> → <sup>2</sup>E<sub>g</sub>) and 22200–23000 cm<sup>-1</sup> (<sup>5</sup>E<sub>g</sub> → <sup>5</sup>T<sub>2g</sub>), was registered, and attributed to the octahedral coordination of d<sup>6</sup> (Fe<sup>2+</sup>), d<sup>9</sup> (Cu<sup>2+</sup>) and d<sup>4</sup> (Mn<sup>3+</sup>), respectively.<sup>45,46</sup> The phase composition of the thermal treated samples was studied by XRD, CuK $\alpha$  (Table I).

TABLE I. Phase composition of boehmite and kaolinite treated at 900 °C, for 10 h in air in the absence and presence of copper, manganese and iron ions<sup>45</sup>

Metal ion	Boehmite	Kaolinite
Copper	CuO, CuAl <sub>2</sub> O <sub>4</sub> , $\alpha$ -Al <sub>2</sub> O <sub>3</sub>	( $\alpha$ -Quartz), $\beta$ -cristobalite, mullite, CuAl <sub>2</sub> O <sub>4</sub>
Manganese	Mn <sub>2</sub> O <sub>3</sub> , Mn <sub>3</sub> O <sub>4</sub> , $\alpha$ -Al <sub>2</sub> O <sub>3</sub>	$\alpha$ -Quartz, mullite, Mn <sub>2</sub> O <sub>3</sub>
Iron	FeO, Fe <sub>2</sub> O <sub>3</sub> , $\alpha$ -Al <sub>2</sub> O <sub>3</sub>	$\alpha$ -Quartz, Fe <sub>2</sub> O <sub>3</sub> , (Fe <sub>3</sub> O <sub>4</sub> )
–	$\delta$ - and $\theta$ -Al <sub>2</sub> O <sub>3</sub>	$\alpha$ -Quartz, amorphous aluminosilicate

The reference sample of thermally treated boehmite contains low crystalline alumina,  $\delta$ -Al<sub>2</sub>O<sub>3</sub> in traces, and  $\theta$ -Al<sub>2</sub>O<sub>3</sub>. All of the applied transition metal ions strongly accelerate polymorphous phase transformations of alumina, until the formation of thermodynamically stable  $\alpha$ -form.<sup>45</sup> Ozawa *et al.*<sup>47</sup> studied the reaction between CuO and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and noticed various interfused formations. The initial CuO crystalline phase in the impregnated  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> sample disappears at 800 °C, resulting in a novel “Cu-modified Al<sub>2</sub>O<sub>3</sub>” at 830–950 °C. At a temperature of 950 °C and even lower, the Cu-modified Al<sub>2</sub>O<sub>3</sub> is transformed directly to  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> instead of  $\theta$ -type alumina. CuAl<sub>2</sub>O<sub>4</sub> spinel is formed simultaneously above 950 °C. At 1050 °C, this spinel decays with noticeable velocity and the CuO is re-precipitated starting the re-reaction with free  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> at 1100 °C.<sup>47</sup> The stability of CuAl<sub>2</sub>O<sub>4</sub> spinel depends on whether CuO or Al<sub>2</sub>O<sub>3</sub> is in excess.<sup>48</sup> These observations from the catalytic point of view have three important issues: *i*) it seems that during the thermal treatment in the presence of copper ions an unstable intermediate compound was created; *ii*) the pathway of the polymorphic transformations in the presence of copper ions was changed. There is no  $\theta$ -form of alumina on the pathway to  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> formation, since the  $\alpha$ -form was created directly; *iii*) CuO as catalyst was separated from the intermediate. These are all important steps of chemical reaction by the catalytic mechanism and therefore, this reaction could be considered as a real catalyzed reaction in the solid state (Figs. 5 and 6).

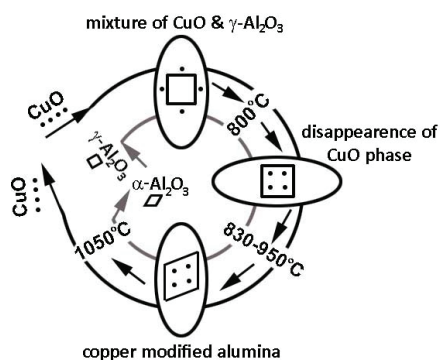


Fig. 5. The catalytic cycle of  $\gamma\text{-Al}_2\text{O}_3$  transformation into  $\alpha\text{-Al}_2\text{O}_3$  in presence of  $\text{CuO}$ .

In all of the kaolinite samples (Table I), after thermal treatment,  $\text{SiO}_2$  appears as  $\alpha$ -quartz. The formation of mullite,  $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ , proceeds in copper and manganese promoted samples, while the presence of  $\beta$ -cristobalite, only in the case of Cu promoted sample, indicates the different kinetics in these two systems. Additionally, the formation of copper–aluminum spinel,  $\text{CuAl}_2\text{O}_4$  was registered in the system with  $\text{CuO}$  as a catalyst. As already mentioned, this spinel decomposes at  $1050^\circ\text{C}$  releasing the  $\text{CuO}$  for the next catalytic cycle.<sup>47</sup> According to Martišius *et al.*<sup>50</sup> mullite is formed from kaolinite at  $1200^\circ\text{C}$  without  $\text{CuO}$ . In the presence of 5 wt. %  $\text{CuO}$ , the temperature of mullite formation is approximately  $200^\circ\text{C}$  lower. It is possible that the intensity of mullite formation increases due to the reaction of copper ions with  $\text{SiO}_2$  and consequently, a solid solution is formed. This fact may be proved by the green color of the samples heated at temperatures of  $800$  and  $850^\circ\text{C}$ . Additionally, it could be suggested that  $\text{CuO}$  interacts with the  $\text{SiO}_4$  tetrahedron and deforms the tetrahedral layer. At the end of this process, the matrix of metakaolinite becomes unstable, through the deformed and decomposed chemical combinations. Between the temperatures of  $900$  and  $1050^\circ\text{C}$ , mullite intensively begins to form surplus of amorphous silica. This crystallizes to cristobalite.<sup>50</sup> In the presence of iron ions, the absence of mullite formation could be interpreted by the weak Jahn–Teller effect of these ions.<sup>51</sup> Accelerated phase transformations and chemical reactions of metastable aluminas and kaolinite doped with copper, manganese and iron ions are accompanied with accelerated sintering.<sup>52</sup>

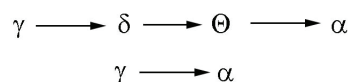


Fig. 6.  $\gamma\text{-Al}_2\text{O}_3$  phase transformations into  $\alpha\text{-Al}_2\text{O}_3$  – upper row<sup>49</sup>, and in the presence of  $\text{CuO}$  – bottom row.<sup>47</sup>

### 3. CONCLUSIONS

This survey emphasizes certain aspects of the use of common terms in the field of ceramics processing, such as flux agents, mineralizers and catalysts, all belonging to the group of accelerating agents for various physical and chemical solid-state transformations. Even today, when these terms are defined and clearly delimited, researchers and practitioners often use the term additive as a substitute for all the previously mentioned terms. The term additive is more general and has a less limited concept compared to the terms flux agents, mineralizers and catalysts. This approach of the researchers in the field of material science could be supported by the fact that, in many cases, the exact role and mechanism of action of certain additives in ceramic production systems are not completely known. Additionally, some accelerating agents can act simultaneously as mineralizers and flux agents. Even the term catalyst is much less frequently used by the scientists in the field of ceramics manufacture, although some ceramic composite ingredients very likely or certainly behave like catalysts, and not as flux agents or mineralizers. Such cautiousness is fully justified since the catalytic mechanism is much more complex compared to the mechanism of actions of flux agents and mineralizers and it is quite demanding to confirm that a particular additive acts as a catalyst. Hence, the use of different terminology here is solely related to the different scientific fields examining equally important substances, but from different perspectives.

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#### ИЗВОД

#### УБРЗАНЕ ФИЗИЧКЕ И ХЕМИЈСКЕ ТРАНСФОРМАЦИЈЕ У ПРОЦЕСИМА ОБРАДЕ КЕРАМИКЕ

ЕРНЕ Е. КИШ и САЊА Н. ПАНИЋ

*Универзитет у Новом Саду, Технолошки факултет, Булевар цара Лазара 1, 21000 Нови Саг*

Са економске и еколошке тачке гледишта, хемијске реакције у чврстој фази представљају веома важан део модерне хемије и технологије омогућавајући да многи процеси постану чистији, сигурнији и лакши за извођење. Овај прегледни рад садржи основне концепте трансформација у чврстој фази које су присутне у процесима обраде керамике, укључујући појмове и феномене описиване у капиталним књигама силикатне хемије у периоду од пре више од 100 година, па све до данашњих дана. Током овог периода, научници и стручњаци у области прераде керамике користе појмове везане за убрзање фазних прелаза и хемијских реакција. Данас су разлике између појединих агенаса за убрзање (флуks агенси, минерализатори и катализатори) у погледу њиховог састава и механизма деловања готово потпуно дефинисани и јасно разграничени. Међутим, у области прераде керамике, општи појам адитив се углавном користи уместо претходно поменутих термина. Циљ овог рада је да укаже да су сви агенси за убрзање подједнако важни и за истраживаче у области науке о материјалима, као и оне у области

катализе, при чему је различита коришћена терминологија само последица сагледавања истих феномена из различитих углова.

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