Lj. KOSTIC-GVOZDENOVIC
Faculty of Technology and Metallurgy
Belgrade University, Yugoslavia

A contribution to the consideration of the synthesis of compounds by the reaction sintering of Oxide powders*

1. INTRODUCTION

It is well known that many of chemical reactions in solid state are followed by considerable volume changes. The relation of the sum of molar volumes of reactants in the reaction to the sum of molar volumes of the reaction products determines whether the process of new phase formation by the reaction causes the shrinkage or the expansion of the system. If this relation is such that:

$$\sum_{1}^{n} V_{Mi(reactants)} < \sum_{1}^{n} V_{Mi(products)} \qquad (1)$$

the progress of the reaction causes the volume expansion. In the opposite case, as well as by sintering, the shrinkage occurs.

By the sintering of reactive compositions, that is the mixture of reactants, the processes of sintering and solid state reactions develop contemporary. The sintering of multi-component systems realized under such conditions we call the "reaction sintering". By this we mean the sintering of reactive components which will by the action of temperature, pressure and other parameters (atmosphere, defects, etc.) undergo to the mutual chemical reaction giving the new compound or the solid solution or the both together. These processes are followed with or without the formation of the liquid phase on the sintering temperature. The reaction sintering in the presence of liquid phase decreases the reaction temperature. It is the result of the intervention of the liquid phase in which the rate of diffusion is 100-1000 times greater.

Former investigations of these processes were strictly divided on two separate lines: studies of the process of sintering and solid state reactions, although at the reactive compositions these two processes are simultaneously developed and surely have the mutuai effects. Some years ago appeared the papers trying to connect these two processes in the most cases on the qualitative basis [1, 2] without any quantitative analysis, with exepction of the mathematical model of Suchet [3] .

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2. VOLUME CHANGES DURING REACTION SINTERING

The total volume change during reaction sintering is given by the sum:

$$\Delta V_{tot.} = \Delta V_r + \Delta V_s + \Delta V_t \qquad (2)$$

where it is: ΔV_r - volume change caused by chemical reaction according to relation (1)

ΔV_s - volume change caused by sintering

ΔV_t - volume changes caused by possible changes in allotropic modifications of reactants or products of the chemical reaction

The relation and the sign of some of terms in the above sum determines whether by the reaction sintering volume changes will happen at all. The sign and quantity of the total volume change will determine the system's behaviour under these conditions.

For practical applications the most interesting is the case when it is possible to achieve the conditions without any colume change ($\Delta V_{tot.} = 0$). It means that the volume of final product will not differ from the volume of green compact. In this way it is expected many problems connected with dimensions at the forming of green compacts to be solved.

Successfuly achieving this condition $\Delta V_{tot.} = 0$ requires the detailed knowledge of solid state reaction course, as well as the mechanism of sintering process of multicomponent system in which with the proceeding of reaction the number of components changes. Naturall the rigid control of the parameters of the both processes an the knowledge of phase diagram is nessecary.

About the influence of the development of chemical reaction on the sintering of multicomponent systems there are many contradictory data in the literature. By some authors [4] the formation of new phase in the system retar d the sintering process, while the another authors have the opposite opinion [5,6]

Our own experience, based on the experimental data of the following the synthesis of zinkorthotitanate by the reaction sintering of the reaction mixture consisted from TiO_2 and ZnO oxide powders in the stehiometric ratio, show that the development of chemical reaction accelerate the sintering process especially in the intermediate and final stages. In this system beside the compound Zn_2TiO_4 with the inverse spinel structure, there is a possibility of formation and the compound $Zn_2Ti_3O_8$ with the defect spinel structure. This compound causes the expansion of the system at the beginning of the reaction sintering. It is interesting that this unstable intermediate compound was not detected by the high temperature X-ray difraction analysis, althought the volume changes of the pellets at the lower temperatures and the shorter times of treatment pointed out on his presence. Owing to the defect structure and unstability of this compound the sintering process is significally accelerated as well as the formation of the only thermodinamically stable compound in this system Zn_2TiO_4.

According to Kovachev [6] this activation of the sintering process can be attributed to the imperfections of the crystal lattice of the compound just formed.

The effect of the last term in the relation[2] is also questionable according to literature data. The studing of simultaneous processes of sintering and phase transformations on the boemhite gels [7] showed that in this case the densification and phase transformation processes are the concurrent one.

In our case, by the reaction sintering of zinkorthotitanate, the process of phase transformation of TiO_2 from anatase to rutlie form accelerate, the both processes: the chemical reaction (due to the Hedvall's effect of reactivity) and the sintering process (the pure transformation is followed by appreciable shrinkage) in the investigated system.

In the case when the solid state reaction and phase transformation are exothermics processes the heat evaluated by their development gives significant contribution to the activation of the process of sintering. In the opposite case, by the endothermic processes of decomposition the sintering will be retarded. It means that the sign and the quantity of the heat of chemical reaction or phase transformation determine the effect of these processes on the sintering. In this way the observed literature misuderstandings can be explained.

3. APPLICATION OF THE REACTION SINTERING

By the reaction sintering two important processes: synthesis of the compound by the solid state reactions and sintering occure simultaneosly. In this way there is a possibility of connection of these two processes, which ussually are separately performed in the production of electrical and magnetic ceramics. It will certainly give significant savings results.

On the basis on the phenomena considered in this discussion it is obvious that some general conclision about reaction sintering cann't be drawn, as well as about the factors affecting this process and the properties of final products. Therefore the considerations of the reaction sintering process must always be connected with the determined system of components, his specific characteristics and complexity.

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