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$MgAl_2O_4$ spinel synthesis by combustion and detonation reactions: A thermochemical evaluation

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Abstract

The production of $MgAl_2O_4$ spinel is evaluated using a thermochemical program, THOR, which calculates the equilibrium products resulting from the adiabatic combustion (isobaric and isochoric) or detonation of energetic materials. A classic metalized emulsion was used (ammonium nitrate, fuel oil, aluminium, water and glass microballoons), to which MgO was added. The Al/MgO proportion and the reaction regime were varied, the maximum spinel yield being achieved for the detonation of a fuel-rich emulsion with 5Al:3MgO (mol). In parallel, $MgAl_2O_4$ was experimentally synthesized by solution combustion of Al and Mg nitrates with various urea contents. The same reactions were simulated with THOR and the results obtained for products type and amounts were found to be in good agreement. Additionally, THOR simulations provided clear explanations for the experimental observations, which can be of invaluable help in the selection of fuel type and content in solution combustion synthesis of any given mixed oxide.

Keywords: Powders – chemical preparation; Spinels; Thermochemical simulation; Combustion synthesis

1. Introduction

Spinels are binary oxides with the general chemical formula AB_2O_4, where A represents a divalent metal ion (occupying FCC tetrahedral sites) such as magnesium, iron, nickel, manganese or zinc, and B represents trivalent metal ions (occupying FCC octahedral sites) such as aluminium, iron, chromium or manganese.[1]

Magnesium aluminate spinel ($MgAl_2O_4$) has a remarkable combination of interesting properties, such as high melting point (2048 K), good mechanical strength at low and high temperatures, low thermal expansion and dielectric constant, chemical inertness and good optical and catalytic properties. Thus, this spinel is suitable for a wide range of applications, in several industrial areas, as for example: insulating material in fusion reactors and refractory material in a variety of ceramic industries, sensors, catalysts supports, ceramic ultrafiltration membranes, electroinsulators and optical materials.[2–8]

The conventional method for the synthesis of $MgAl_2O_4$ is the solid-state reaction between magnesium oxide (MgO) and aluminium oxide (Al_2O_3), involving high temperature calcination (1673–1873 K) of the mixture of oxides. The main drawbacks of this method are the high energy consumption (high temperature needed), long reaction time, large particle size and broad particle size distribution, agglomeration of powders, and low product purity.[4,6–8]

The production of ceramics by detonation/combustion of metalized emulsions is an important alternative to the conventional method, which has already been up-scaled to industrial level,[9] the main advantages being the instantaneous reaction, the small size of the obtained particles and the energy savings. The combustion and detonation processes are highly exothermic,

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with rapid formation of gases and some condensed products. When a moderate and controllable power is developed, the process is generally denominated by combustion. Otherwise, when high power is involved, a supersonic shock wave is generated and the process is designated by detonation. As this process involves extreme conditions, the theoretical prediction of the final products compositions is of major interest to give guidelines in the definition of the reactant mixtures. On the other hand, related alternative synthesis methods using milder laboratorial conditions have been tried,[2,3,6,7] among which solution combustion synthesis (SCS) stands out as the simplest and most straightforward from the experimental point of view.

The main objective of this work is the simulation study of the $MgAl_2O_4$ synthesis by combustion and detonation processes and its validation by comparison with experimental results obtained in SCS, while seeking a better understanding of the difficulties found in the manipulation of an otherwise extremely simple laboratorial procedure. Full characterization and sintering behaviour of SCS spinel powders is marginal to this aim and, therefore, will not be discussed in this paper.

1.1. Prediction of spinel formation in combustion/detonation processes

Ceramic phases formation (including $MgAl_2O_4$) in combustion and detonation products from salt (oxidizer)/metal energetic emulsions may be predicted using thermochemical calculations, which are mainly based on simple energy and mass balances between the initial and final states and on well established and validated equations of state for high temperature and pressure, subjected to equally simple assumptions, like the chemical equilibrium of the products and the process restrictions.[10] The THOR thermochemical program, written in Fortran, is a versatile and valuable tool for the calculation of the equilibrium products composition and properties of reactive systems under combustion/detonation.[9,11] Its modular organization allows the easy change of data without modification of the main program. THOR uses a database named THORDB, containing the chemical and thermodynamic properties of more than 18 000 species and compounds (reactants and products) necessary for the calculation.[9,12] In addition, a graphical interface was developed in the latest version of THOR, which allows the user to introduce the problem data and edit/treat the results without a deep knowledge of the program algorithms.

The THOR code was developed, validated and extensively described in earlier works[9,11] and consists of four interconnected calculating clusters that enable the computation of the composition, *PVT* and energetic states of the combustion/detonation products, taking into account the conditions of the selected reaction regime. The first cluster includes the thermal equation of state (EoS) that allows the correlation between the products pressure and volume as a function of the temperature – *PVT* state; the second is related to the energetic equation of state, corresponding to the internal energy calculation by using thermochemical data and the Gordon and McBride polynomials applied to intermediate and final products; the third cluster is related to the conservation equations – mass, atomic species, momentum and energy, the thermodynamic equilibrium being achieved for minimum Gibbs energy; and the last cluster corresponds to the three reaction regime restrictions that may be considered: isobaric adiabatic combustion; isochoric adiabatic combustion; and Chapman–Jouguet detonation.

The composition of the combustion/detonation products in the final equilibrium state (THOR can handle 20 different products at a time) is calculated by the minimization of the Gibbs energy and considering the mass and atomic species conservation balances.[9,11]

Several *PVT* equations of state are available in THOR, namely perfect gases, Boltzmann, Percus–Yevick, BKW, Charnahan–Starling, H_9, H_{12}, H_L and JCZ3 equations. In this work, only the H_L equation of state is used. H_L equation of state (EoS) is supported by a Boltzmann EoS, but is based on physical intermolecular potential parameters of gas products instead of correlations from final experimental results. It was validated in earlier works with several energetic systems.[11,13] In THOR, the equation of state is used to calculate the gaseous products phase volume for a given temperature and pressure, which is added with volumes of each of the condensed phases that are in equilibrium with the gaseous phase at the same temperature and pressure. It also allows the introduction of corrections in the thermodynamic functions, to take into account the non ideal behaviour of the gaseous phase at high pressure and temperature.[11,14]

The evaluation of the products energetic state consists in the computation of the enthalpy, entropy and internal energy for a given temperature and pressure, considering the individual contribution of the products weighted by their molar fractions. Themochemical data (NIST-JANAF thermochemical tables[15]) and Gordon and McBride polynomial expressions[16] are needed for this purpose. In thermochemical calculations, the behaviour of condensed phases at high temperature and pressure can be described by semi-empirical models and equations (for example, Mie-Gruneisen with thermal contribution given by the Debye model, as in THOR[11]) whose parameters are known only for common and well studied products. Nevertheless, one of the simplest ways to calculate the contribution of the condensed products to thermodynamic functions is to assume Gordon–McBride's polynomials and their corresponding coefficients. This procedure allows a straightforward calculation of the energetic state of condensed species for two reasons: (i) as it is also used in the NASA-CEA Code,[16,17] the resulting Thermo Build database[17] already contains ready-to-use information on the Gordon and McBride coefficients of a wide range of products; (ii) it does not weaken the algorithms convergence due to the generalization of the polynomial formulas for gases and for condensed phases.

Despite the size of the thermodynamic property database THORDB, for some ternary compounds, like spinels, there is in the literature a lack of data necessary to calculate the contribution of these phases to the energetic state of the products. Thus, to predict the $MgAl_2O_4$ formation, it is necessary to evaluate the coefficients of the Gordon and McBride polynomials for this spinel and for all the possible combustion/detonation products with Al and Mg. It is also necessary to add the