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Analysis of the polymorphic transformation of nano- and microcrystalline zirconia doped with CaO and MgO during reaction-sintering process by neutron thermodiffraction. A thermodynamic approach

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Abstract

Polymorphic transformation of zirconia during reaction-sintering process in nano- and microcrystalline mixtures of monoclinic zirconia and dolomite was analyzed using neutron thermodiffraction experiments. This is being the first time that such an approach has been applied in the analysis of these materials. Taking into account the isoplethal section $CaO{\cdot}MgO–ZrO_2$, the composition, which allows doped CaO/MgO cubic zirconia to be obtained at the lowest temperature, was chosen to carry out the experimental studies.

The comparison of the results in both samples, in terms of their thermodynamic and kinetic aspects makes it possible to analyze the effect of the particle-size on the reaction behavior and temperatures of phase transitions.

Keywords: Thermodynamic calculation; Neutron thermodiffraction; Zirconia; Nanoparticles; Reaction sintering

1. Introduction

The synthesis of materials with new properties by means of microstructures controlled through their manipulation at nanometers level is an emerging interdisciplinary field based on solid-state physics, chemistry, biology and materials science. In recent years, there have been many changes, especially in the design and production of advanced ceramics using nanosized powders.[1] These advanced ceramic materials are based on the use of raw or synthetic materials with ultrafine particle size, in the range of nanometers (10^{-9} m), which are more intimately and homogeneously blended in order to obtain nanocrystalline ceramic materials.[1] Currently, there is a growing interest in the study and attainment of these types of materials due to the observation in them of new and/or superior properties (extremely low thermal conductivity, high refractivity, increased resistance in fatigue test, high hardness, superplasticity, *etc.*)[2] to those existing at micron scale. For example, nanophase ceramics are more ductile and more easily formed than conventional ceramics.[3]

Ceramic nanocomposites have been of interest because of the possibility of superior mechanical and functional properties.[4] Nano/nano-type composites are composed of a matrix with dispersed grains of nanometric size and have generally been made from amorphous material or ultrafine powders.[5] These novel nanophase materials have grain-size dependent mechanical properties that are significantly different from those of their coarser-grained counterparts.[3] These composites have been studied to probe new functions such as superplasticity and machinability. In this regard, the characteristic machinability and quasiplasticity behavior of $CaZrO_3$/MgO nanocomposites have recently been described.[6]

In the production of nanosized ceramic powder, a number of synthesis techniques[1] are currently available. Important examples are: precipitation methods,[7] the sol–gel technology,[8] spray pyrolysis,[9] hydrothermal synthesis,[10] flame spraying,[11] rapid solidification[12] and inert gas condensation.[13,14]

Considering that somewhat complicated processes and relatively high costs are involved in the production of such nanomaterials, simple and economical alternative techniques are desirable. The high energy milling of mixtures induces heavy cyclic deformation in powders, especially if at least one component contains a carbonate group. Water or hydroxyl groups, have

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been demonstrated as an alternative method to obtain nanostructured materials.[15] The mechanical activation during high-energy milling reduces the particle size and introduces a high concentration of defects in the material (dislocations, high-angle grain boundaries, *etc.*). The effect obtained is a substantial increase in the superficial free energy of the particles, resulting in causing an increase in the reactivity of the powders produced in this way. The sintering process is activated and consequently the necessary temperature and time for the densification of the material are reduced, thereby providing more control over the grain growth in the final dense material.

The low particle size has important consequences in the relative stability of the phases giving rise to the appearance of metastable phases in the materials. Several authors[16,17] confirm these points and report observations of metastable phases in various materials such as alumina[18] and graphite.[19] In the case of zirconia materials, particle size also affects the polymorphic transformations. In this regard, micrometric particles of monoclinic-zirconia (m-ZrO_2) go through a reversible first order phase transition at about 1170 °C toward a tetragonal phase[20] that cannot be quenched at room temperature.[21,22] Nevertheless, it is well known that this tetragonal phase can be observed at room temperature in zirconia nanoparticles of less than 30 nm diameter.[23] The stabilization of nanocrystalline tetragonal zirconia is generally understood in terms of a surface free energy lower than in the normal phase.[23–25] However, this explanation is not generally accepted[26] and some authors report either the appearance of 6 nm diameter monoclinic zirconia nanoparticles[27] or they do not relate the decreasing of the tetragonal phase to the increase in the grain size of zirconia nanoparticles.[16] The main reasons for these controversies are usually related to extrinsic factors such as the presence of impurities[28,29] and to the existence of residual stresses in the nanoparticle agglomerates.[30]

The last objective principal objective of this paper is to obtain nanocrystalline cubic-zirconia (Ca,Mg-PSZ) by the solid-state sintering method, from commercial monoclinic zirconia and a raw material of high purity and low cost such as dolomite (Ca,Mg$(CO_3)_2$). Dolomite simultaneously contributes with CaO and MgO, which are well-known stabilizers for c-ZrO_2.[31,32] The low particle size of the raw materials obtained by high energy mill also has an influence on the decomposition process of dolomite and the polymorphic transitions of zirconia. In this regard, the second objective of this paper is to establish the combined effect of both stabilizing oxides as well as particle size on the phase transition temperatures, which is essential to control the design of zirconia based materials. Finally, a thermodynamic calculation of the polymorphic transformation of zirconia as a function of both effects, solid solutions of CaO/MgO and particle size, has been also carried out and the results were compared with experimental results.

Phase equilibrium diagrams have for many years been a basic tool to understand the effect of numerous dopants on the phase transitions of zirconia. The previous thermodynamic studies of ZrO_2–CaO–MgO system[33–37] provide a very friable calculation of the isoplethal section MgO·CaO–ZrO_2, essential to select the composition of interest. Moreover, current computational tools allow the reaction path in the subject materials to be foreseen by thermodynamic simulation. However, the contribution of the particle size and surface free energy should be taken into account in the thermodynamic description of the phases, especially when low particle size and/or high specific surface raw materials are used.

In the present study, neutron thermodiffraction was used as tool to study the reaction process between dolomite and m-zirconia. The first advantage of using the Neutron Diffraction technique is related to its high penetration capabilities, which make it possible to examine the bulk of the material. Experimental data collected from the reaction in a bulk sample are truly representative, because the diffraction signal comes from the whole specimen and not the surface layer alone. The intensity of the neutron source used for measurement provided a time resolution of ~1 min, enough to follow the solid-state reactions. All these factors allowed an *in situ* observation of the processes that occur in the sample. On the other hand, the high intensity of neutron diffraction peaks at high angle makes it possible to distinguish between the different polymorphic forms of ZrO_2. Moreover, the high scattering factors of light atoms, such as Ca and Mg, are very useful when these are, as in this case, minority components in the sample. By neutron thermodiffraction, it was possible to establish “in situ” the mechanism of formation of cubic-zirconia in two samples of the same composition but different particle size. A critical comparative study of the results obtained in nanometric powders with respect to the micrometric, in light of thermodynamic calculations, allows us to analyze the influence of the particle size on the reaction process.

2. Experimental procedure

2.1. Sample preparation

The starting materials were high-purity powders of m-ZrO_2 (TZ-0, 99.9 wt%, Tosoh Corp., Tokyo, Japan) with an average size $d_{50} < 0.87$ μm and a specific surface area of 13.5 m^2/g and high-purity dolomite (MgCa$(CO_3)_2$) (Micro15, 99.9 wt%, Prodomasa, Málaga, Spain) with $d_{50} < 4.87$ μm and with a specific surface area of 2.05 m^2/g.

The studied compositions were selected in light of the isoplethal section Mg·CaO–ZrO_2 proposed by the present authors from thermodynamic calculations.[37] According to this isoplethal section, the composition 84.2 m-ZrO_2/7.9 CaO/7.9 MgO (mol%), named Z3 allows monophasic c-ZrO_2 materials to be obtained from mixtures of m-zirconia and dolomite at the lowest temperature.

A mixture of 84.2 m-ZrO_2/15.8 CaMg$(CO_3)_2$ mol% was milled in a high-energy attritor, with a rotation speed of 1350 rpm, for 2 h with zirconia balls (zirconia milling balls Y-stabilized ZrO_2 (YTZ Ceramic Ball (Tosoh)) with 1 mm diameter), dried at 60 °C overnight followed by 63 μm sieving in order to obtaining the sample Z3MICRO.

In order to obtain nanometric raw materials, the original m-zirconia and dolomite, were also milled separately in a high-energy attritor, with a rotation speed of 1350 rpm, for 50 h with zirconia balls, dried at 60 °C overnight followed by 63 μm