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Thermodynamic calculations and modeling of the hydrothermal synthesis of nickel tungstates

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Abstract

A thermodynamic model of electrolytic solutions was applied to determine the reaction conditions favoring the hydrothermal synthesis of nickel tungstate, an antiferroelectric material commonly used for catalysts and humidity sensors. Yield diagrams were constructed relating the equilibrium concentration of the chemical species as a function of temperature, pH and reagent concentration. The theoretical predictions were corroborated by experiments and we were thus able to avoid the empirical "trial-and-error" mode of synthesis. © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

The general understanding of the fundamental, scientific and engineering requirements for the successful, continuous processing of high performance ceramics is not well advanced. Complex ceramic components require bulk material properties to be optimized to provide a perfect combination of electronic, magnetic, optical, structural, chemical and/or refractory characteristics. The conventional first step in the successful processing of such "ideal" ceramics is the generation or attainment of a "good" powder. A "good" powder may be considered as one which has the required chemical purity, phase composition, and desirable processing characteristics, including controllable packing density and sinterability.[1]

Aqueous solution methods have been used for the production of powders of many ceramic types.[2] Our investigations have been in the area of hydrothermal synthesis of electroceramics.[3] This method is known as a soft solution process, or *chimie douce*, and presents the advantage of allowing shaped, sized, reacted and/or oriented ceramic materials to be fabricated in situ without firing/sintering or melting.[4] Hydrothermal processing works with closed-flow systems, which makes easy any charging, separation, cycling and recycling allows a relatively high deposition rate and presents the lowest total energy consumption among all aqueous solution processing routes.[4]

Usually, the development and optimization of materials and processes are time-consuming, and thus costly. For this reason, computer simulations from existing theoretical thermodynamic data are nowadays increasingly employed for materials production and development.[5] Recently, theoretical simulations of the hydrothermal conditions for ceramic systems were conducted by using computer software developed by OLI Systems, Inc., to model aqueous, conventional and other complex chemical phenomena.[5] The software provides a refined user interface, which includes an advanced thermodynamic framework as basis for predicting complex aqueous-based chemistry in equilibrium with vapor and solid phases at temperatures in the range 0–300°C, pressures up to 1500 bar and ionic strengths up to 30 molal. Also, an extensive thermodynamic and physical property databank verified and validated from source literature is available.[6]

Transition-metal tungstates are a technologically important group of materials with particular prominence in their potential application as materials for scintillation detectors, laser hosts, photoanodes and optical fibers. Redfern[7] studied the infrared hard-modes of the ferroelastic phase transition in $(Cu_xZn_{1-x})WO_4$ mixed crystals in order to explain local strains, order-

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disorder and related critical phenomena at structural phase transitions in this solid solution. Other tungstate materials employed in electro-optics applications were studied by Cho et al.,[8] using hydrothermal/electrochemical methods to produce polycrystalline films. Recently, Markondeya Raj[9] and Bhattacharya et al.[10] presented three independent studies on the free energy of formation of $NiWO_4$ and a study on impedance spectroscopy of these materials, respectively. In a previous work,[11] we discussed the formation of strontium tungstates under hydrothermal controlled conditions. Now, for the first time, an experimental procedure has been developed for the hydrothermal synthesis of $NiWO_4$ based on computer simulations from thermodynamic data. The theoretical predictions were corroborated by experimental results, avoiding the empirical mode of synthesis.

2. Chemistry model generation and experimental procedures

Speciation information on aqueous systems was obtained from thermodynamic multi-component modeling by using geochemical computer software from OLI Systems, Inc.[5] The electrolyte solution model was employed to simulate the chemical reactions in a nickel-tungsten hydrothermal system under a wide range of temperatures, pressures, reagent input concentrations and chemical environments. The model utilized the Pitzer's ion–ion interaction equation[5] as a basis for the calculation of the activity coefficients of ions and neutral species. The model simulated the existing experimental solubility data of high ionic strength systems based on their activity and osmotic coefficients. The approach accounted for the effects of long-range electrostatic forces as well as the short-range forces by parameterization of the virial coefficients. The standard-state properties of all solid and aqueous species were obtained from several compilations.[12–16]

To verify the theoretical predictions, hydrothermal treatments in $Na_2WO_4{\cdot}2H_2O$ and $NiSO_4{\cdot}6H_2O$ aqueous solutions (Fluka Chemie AG, Switzerland) were conducted at different pH values, input reagent concentrations and temperatures ranging from 110 to 260°C, under saturated vapor pressure. Sodium hydroxide and sulfuric acid were added when necessary in order to control the pH value. The resultant lime-green solution was loaded into stainless steel Parr® autoclaves (Model 4532) equipped with turbine-type impellers and occupied about 50% of the total volume. The autoclaves were heated at 4°C min^{-1} up to the processing temperature and maintained there for times between 1 and 4 hours under a stirring speed of 750 rpm. After synthesis, the powders were repeatedly washed with deionized water (18.2 Ω cm) in order to remove any remaining Na^+ ions and dried in an oven at 80°C.

Chemical purity as well as chemistry and phase homogeneity are critical factors for the reliable and reproducible production of electroceramics. In this work, X-ray fluorescence (Philips PW2400 sequential spectrometer, fitted with a Rhodium target end window and Philips SuperQ analytical software), energy-dispersive spectrometry with ZAF corrections (Noran- Voyager 3050 with Norvar detector window and Si–Li X-ray detector crystal), and conventional chemical analyses were employed to determine the phase homogeneity and chemistry. It was verified that the hydrothermal synthesis produced powders with adequate purity and stoichiometry with no impurities detected at the level of the techniques employed.

Morphology of the particles was determined by using scanning electron microscopy (Jeol JSM5410) at 20 kV. Very fine and agglomerated powders were seen, whose particles can only be distinguished or individually observed through advanced microscopy techniques, like atomic force microscopy (Digital-Dimension Nanoscope 3000). $NiWO_4$ identification was performed by using an X-ray diffractometer (Philips PW1830) equipped with a scintillation counter and a graphite monochromator attachment, utilizing Ni-filtered CuK_α radiation (40 kV, 20 mA). The scans were made over the 2θ range of 10–100° in $0.02°2\theta$ steps at 1 s/step.

3. Results and discussion

In the present work, the hydrothermal conditions under which the phase-pure $NiWO_4$ can be produced were predicted by thermodynamic calculations of the Gibbs free energies for the balanced relevant reactions in water as a function of pH, input reagent concentrations and temperature/pressure. This information was represented in yield diagrams (metal concentration in the aqueous solution versus pH), which show the domains of relevant aqueous species and solid compounds at a given temperature. In these yield diagrams, two kinds of boundaries can be seen: solid and dotted lines. The solid lines are the boundaries between stability areas of a solid and an aqueous species or two aqueous species. The boundary between aqueous and solid species corresponds to the existence of an infinitesimally small amount of the solid in the presence of a solution. The solid-line boundary between two aqueous species represents the conditions for which their activities are equal. The dotted lines are the boundaries between stability areas of two aqueous species that coexist with at least one solid phase. Thus, they are found only within the stability ranges of solids.

Solution pH is one of the most critical reaction parameters controlling phase composition and even morphology of the particles, since solution pH mainly determines the chemical nature of the aqueous species.[2]

Fig. 1 shows a set of yield diagrams, in which the aqueous and solid species present in our Ni–W hydrothermal system are plotted as a function of solution pH and processing temperature. The shaded areas in this figure show the regions where the precipitation of nickel tungstates occurs at a yield higher than 99%. It was observed that $NiWO_4$ can be obtained over a wide pH range, in temperatures as low as 110°C [Fig. 1(a)] and reagent concentrations as low as 10^{-5} *m* [Fig. 1(d)]. As the reagent concentration decreases, the pH range where nickel tungstate could be obtained becomes smaller. It was verified that a strong acidic condition is beneficial for the production of phase-pure $NiWO_4$. For example, when the input reagent concentration is equal to 1 *m*, the pH ranges were 2.7–7.7 at 110°C [Fig. 1(a)], 2.4–7.4 at 150°C [Fig. 1(b)], 2.0–7.3 at 200°C [Fig. 1(c)], and 1.7–7.0 at 260°C [Fig. 1(d)]. These ranges diminished as the input reagent concentration decreased. Reactions conducted below or above these values resulted in formation of undesirable metastable phases, unreacted or contaminating phases (e.g. NiO).

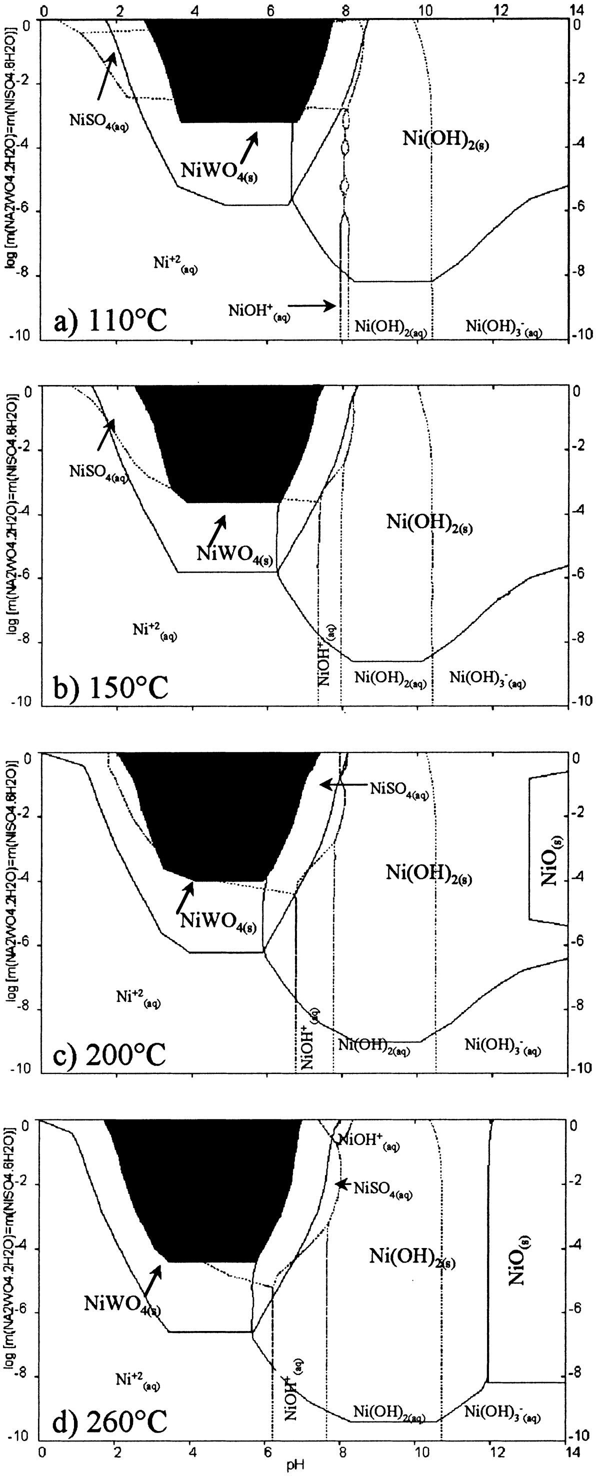

Fig. 1. Yield diagrams for $NiWO_4$ obtained after computer simulations under different pH and input reagent concentrations at (a) 110°C; (b) 150°C; (c) 200°C; and (d) 260°C.

The yield of $NiWO_4$ increased enormously when the hydrothermal temperature increased from 110°C [Fig. 1(a)] to 260°C [Fig. 1(d)], which perturbed the relative stability of the aqueous species Ni^{+2}. Also, it was observed that any excess of nickel sulfate was deleterious to the precipitation of phase-pure $NiWO_4$. The increase of the aqueous $NiSO_4$ stability can also be emphasized: for higher temperatures, we can expect that higher concentrations (in excess) of sodium tungstate hydrate will allow the precipitation of nickel tungstate powders without any loss of nickel to the mother solution during the hydrothermal synthesis. Comparing the yield diagrams displayed in [Fig. 1(a) and (b)], a pronounced change in the phase boundaries between pH 7 and 8 can be seen. An increase in the stability region of the aqueous species $NiOH^+$ can be observed when the temperature is increased from 110 to 150°C, while the phase boundary between the species $Ni(OH)_2/Ni(OH)_3^-$ remains unaltered. An important change occurred between 150 and 200°C [Fig. 1(b) and (c)]: the reduction of the stability field of Ni^{+2} was verified and can be attributed to the increase of the stability of $NiOH^+$, $Ni(OH)_2$ and $NiSO_4$, as well as of the solid species $Ni(OH)_2$ and $NiWO_4$ towards lower pH values. Also, NiO appears as a secondary phase at high pH values. The stability of this phase continues to increase for higher temperatures [Fig. 1(d)] together with the increasing of the yield of $NiWO_4$. It is necessary to remember that at 110°C the minimum input concentration was two orders of magnitude higher (10^{-3} *m*). Finally, it can be observed that the shift of the stability and yield regions of $NiWO_4$ could be due to the increase of the stability of $NiOH^+$, $Ni(OH)_2$ and NiO (completely stable at 260°C and pH > 12 in practically all reagent concentrations) associated with the decrease on the stability regions of Ni^{+2} and $Ni(OH)_3^-$.

X-ray diffraction patterns are presented in Fig. 2 for the samples produced at 200, 230 and 260°C and obtained under conditions inside [Fig. 2(a)] and outside [Fig. 2(b)] the shaded yield areas displayed in Fig. 1. The existing phases were determined according to the

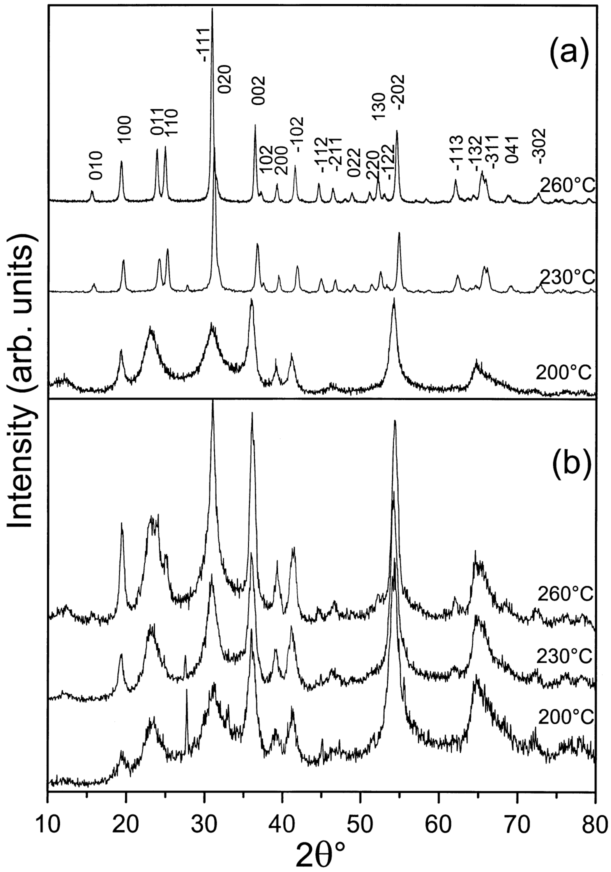

Fig. 2. X-ray diffraction patterns for the samples produced at 200, 230 and 260°C, for 4 h under hydrothermal conditions (a) inside and (b) outside the yield areas displayed in Fig. 1. The main crystallographic reflections (*hkl*) of the monoclinic structure P2/c are indicated in the figure.

Joint Committee for Powder Diffraction Standards (JCPDS No. 15-755). The results showed that the hydrothermal syntheses conducted outside the yield area lead to the precipitation of $NiWO_4$, but with poor crystallinity [Fig. 2(b)] as compared to those produced from solutions with adequate reagent concentrations and pH [Fig. 2(a)]. The effects of the hydrothermal synthesis time on the precipitation of phase-pure nickel tungstates were also studied for the temperatures considered. It was observed that the residence time have no effects on the crystallographic phases after synthesis. This result shows that although the thermodynamic simulations can fail when the time effects are not considered, the hydrothermal production of nickel tungstates is only a direct function of the temperature. Thus, it can be concluded that the electrolyte solution model is adequate to predict the phase behavior of $NiWO_4$ materials under hydrothermal conditions.

The current experimental findings are consistent with thermodynamic predictions based on the phase stability/yield diagrams. For the sample obtained at 200°C [Fig. 2(a)], it was observed that the X-ray pattern differs from those obtained for higher temperatures. It was concluded that a transition temperature for the times studied exists between 200 and 230°C. It is important to note that a crystallized material was obtained at 200°C, but with extremely fine particle size (indicated by broad X-ray diffraction peaks). This can be explained by the energy barrier for the precipitation, which is closely related to the nature of the rate-controlling step in the dominant formation process. Higher reaction temperatures accelerate the crystallization process because of greater thermal energy to overcome the energy barrier for transformation. As a consequence, materials with higher crystallinity and/or particle size can be obtained.

According to our previous studies,[3] a dissolution/recrystallization mechanism lead to the particle formation. Under the conditions studied, particle formation of $NiWO_4$ in the autoclave can be summarized as follows. First, the dissolution of nickel and tungsten hydrous complexes occurs due to increased solubility at higher temperatures (up to the hydrothermal synthesis temperature). During this stage, there is no precipitation taking place. Water evaporation at the synthesis temperature increases the supersaturation and the solute concentration reaches a value in which a rapid nucleation occurs by recrystallization. The solute concentration then decreases after a short burst of nuclei formation. Then growth of the stable nuclei proceeds by chemical reaction at the interface of the growing particles until the concentration lowers to the solubility of the Ni–W complexes. As a consequence, nearly monodispersed $NiWO_4$ particles are obtained, as verified by atomic force microscopy.

4. Conclusions

The advances in computer software for complex equilibrium calculations and the increasing availability of evaluated data for solution phases allow reliable thermodynamic simulations to be performed in all areas of materials processing and development. In the present work, theoretical simulations were carried out to design a processing route for the hydrothermal synthesis of nickel tungstates. Phase-pure and impurity free powders were produced under different hydrothermal conditions through a dissolution and precipitation mechanism.

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