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Direct synthesis of Mg–Ni compounds from their oxides

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ABSTRACT

A study was carried out on the synthesis of Mg–Ni compounds as well as on the extraction of pure Ni and Mg from their oxides using the method of electro-deoxidation. The oxides sintered at 1200 °C were in the form of discrete phases NiO and MgO, suitably proportioned to yield Ni, $MgNi_2$, Mg_2Ni and Mg. The oxides were electrolyzed at 3.2 V in a eutectic mixture of $CaCl_2$–NaCl solution maintained at a constant temperature (900–600 °C), using a graphite anode. The study has shown that NiO rich mixture, MgO:NiO = 1:2, can be reduced successfully to metallic state. Some loss of Mg was apparent in the latter, with the result that the product was far from the target composition $MgNi_2$. The electroreduction of MgO rich mixtures was difficult to achieve. The mixture MgO:NiO = 2:1 when electrolyzed at 725 °C for 24 h, could be reduced to metallic phases only in small proportions (18 wt.%). In pure MgO, no trace of reduction was observed during the electrolysis at 600 °C. Difficulties in the electroreduction of MgO and MgO rich mixtures were partially attributed to low conductivity of MgO.

1. Introduction

Solid state electroreduction of oxides has been an area of intense research during the last decade [1–4]. The method was used not only to extract metals from their oxides [1] but also to synthesize alloys and compounds from the oxide mixtures [2]. In this method, pellets of oxide powders used as the cathode were deoxidized by the application of a potential against graphite without decomposing the electrolyte, a molten salt that is capable of dissolving and transporting oxygen ions. During electrolysis, while oxygen ions are removed from the pellets and transported to the anode to form either CO and/or CO_2, metallic constituents are left behind in the cathode, which via in situ reactions may yield alloys or compounds. The method has the advantage that when inert anodes are used, the electrolysis leads to oxygen generation rather than CO or CO_2 emission [5].

A number of factors affect the ease with which the reduction is achieved in the electro-deoxidation process. It has been reported that, oxides of low reduction potentials, e.g. NiO, Cr_2O_3, Fe_2O_3, are deoxidized faster than others, e.g. rare earth oxides [6]. The ease of reduction is also affected by the oxygen diffusivity in the solid state. Oxides such as TiO_2 and ZrO_2 are reduced relatively easily in the early stages, but as pointed out by Chen et al. [7], once the metallic state is achieved, the rate slows down, since the diffusion of oxygen is extremely slow in the metallic lattices. Insulating oxides such as SiO_2 was also difficult to reduce and required the number of contacting points in the cathode to be increased [8]. Here the reduction is claimed to proceed via the propagation of conductor–insulator–electrolyte triple interline [9,10]. Similarly, the deoxidation of some oxides, such as MgO and Al_2O_3, has been found to be complicated due to difficulties in the initial metallization of the oxide pellets as well as due to the fact that the corresponding metals have low melting points [11].

The reduction of oxide mixtures is often more complicated than their pure counterparts. The mixtures, such as Tb_2O_3–NiO [12], Fe_2O_3–TiO_2 [13] and TiO_2–NiO [14], have been successfully deoxidized to yield the respective intermetallic compounds, i.e. $TbNi_5$, FeTi, and TiNi. The complication often arises because the oxides are reduced at different rates which may give rise to separate individual phases rather than to the compounds themselves. Yong et al. [14] reported that the use of a higher reduction potential may reduce the differences in the reduction rates and could thus promote the compound formation. In this context, the pre-compounding of the oxide mixtures as well as the optimization of the porosity in the pellets could be beneficial to have more complete reduction of the oxides to the required stoichiometry. The reduction of the oxide mixtures also has its advantages. For instance, compounds, such as Ni_2MnGa [15] and Nb_3Sn [16], have been successfully synthesized in the solid state at temperatures higher than the melting points of some of their constituent metals. Furthermore, Qui et al. [17] points out that the reducibility of the oxide mixture could be improved by fast reduction of one of the oxide phases and the formation of metallic particles in situ may enhance the reduction of the other oxide constituents.

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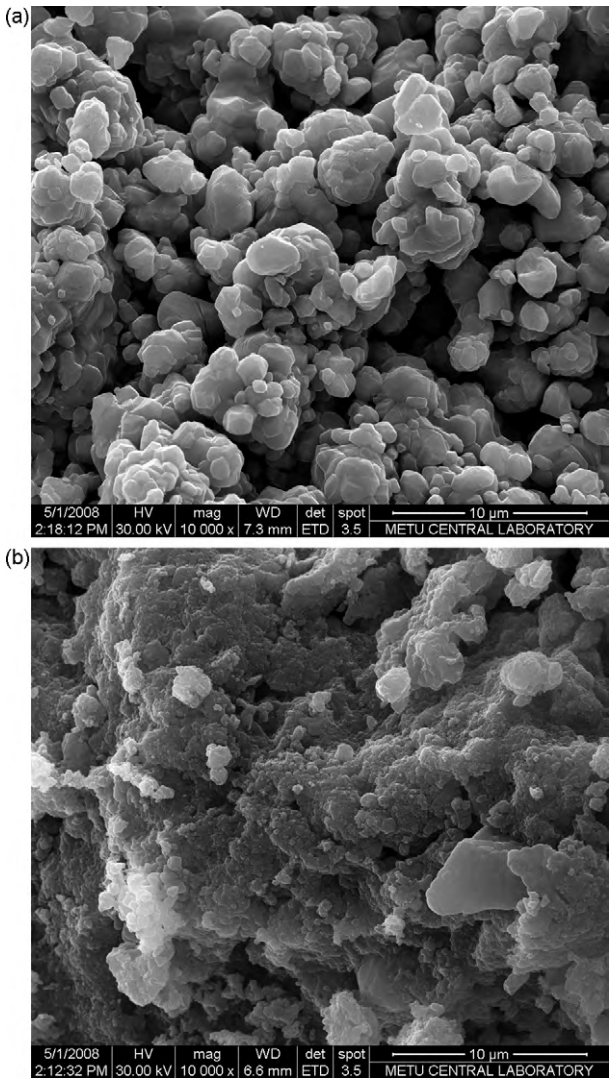

Fig. 1. SEM images of oxide powders; (a) NiO and (b) MgO used in the experiments.

The current work deals with synthesis of Mg–Ni compounds as well as the extraction of pure Ni and Mg from their oxides. The study is of particular interest since the system involves oxides, MgO and NiO, which have widely different physical, such as electrical conductivity and oxygen diffusivity, and thermodynamic properties. Therefore, electro-deoxidation of these oxides, either on their own or as mixtures, are of considerable significance. Moreover, Mg_2Ni, one of the target compounds has a considerable potential as hydrogen storage alloy [18].

2. Experimental

Starting materials were NiO (99%, Alfa Aeser) and MgO (99%, Merck) powders. NiO powders were irregular in shape and 1.20 μm in size, Fig. 1(a). MgO particles were much finer, i.e. sub-micron in size, Fig. 1(b). Both powders, in the as-supplied form, were agglomerated to larger granules with average sizes, measured by a laser diffraction technique, of D_{50} of 18 μm and 30 μm for NiO and MgO, respectively.

Oxide powders were mixed in fixed proportions corresponding to metallic compositions: Ni, $MgNi_2$, Mg_2Ni and Mg. The mixing was carried out for 30 min in a Spex Mill at ball-to-powder ratio (B/P) of 1. The mixtures were further hand mixed with some PVA solution and allowed to air dry for 24 h. They were then cold-compacted under a pressure of 110 MPa to cylindrical pellets of 15 mm in diameter and 4–7 mm in height. All pellets were heated to 1200 °C with a heating rate of 5 °C/min and sintered for 6 h.

Deoxidation experiments were conducted in a stainless steel reactor placed in a vertical furnace. The reactor comprises a stainless steel crucible for holding molten electrolyte and has a lid with retractable electrodes immersible into the electrolyte. Two sets of electrodes were available, one set (auxiliary) for pre-electrolysis and the other (working electrodes) for electro-deoxidation, Fig. 2. Anode-to-cathode distance in both pairs was 25 mm. Anodes were graphite rods, 13 mm of diameter and 40 mm in length, and were connected to a stainless steel current collector. The cathodes were stainless steel wire of 4 mm in diameter, which in the case of working electrode was connected to the oxide pellet. The reactor was sealed, allowing electrolysis in an argon atmosphere (99.995% purity) maintained at a flow rate of 150–250 ml/min.

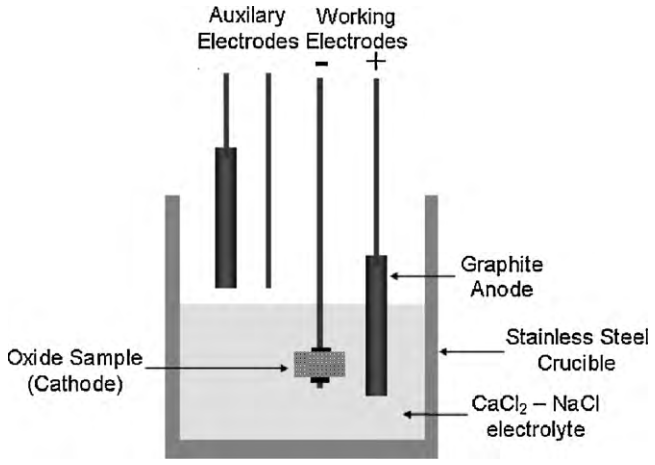

Fig. 2. Schematic drawing of an electrolytic cell used in the deoxidation experiments.

A eutectic mixture of $CaCl_2$–NaCl was used as the electrolyte, which has a melting point of about 505 °C. Approximately 1 kg of electrolyte was used for each experiment. The salt mixture was heated slowly to the electrolysis temperature to reduce its moisture content. The electrolyte was further purified by pre-electrolysis using the auxiliary electrodes at a potential of 3.0 V for a minimum of 6 h. Following the pre-electrolysis, the auxiliary electrodes were lifted above the electrolyte, and the electrolysis was initiated by immersing the working electrodes, i.e. oxide pellet (cathode) and a fresh graphite rod (anode) into the salt bath. During electrolysis, current-time data was collected by a computer connected to the power supply.

At the end of each experiment, the electrodes were disconnected from the electrical supply and both the graphite anode and the reduced sample were removed from the electrolyte by positioning them above the melt. After cooling to room temperature under a continuous flow of argon gas, the reactor lid was opened and the sample with its stainless steel connector was removed. The sample was washed in a hot methanol–ethanol–water mixture and all undissolved material was collected for XRD and SEM analysis.

Volumetric porosities of the oxide pellets after sintering were determined from geometric dimensions and the mass of the pellets, making use of specific density values of the constituent oxides. Phase make-up of the samples was determined via X-ray diffraction. The quantity of phases was determined following Rietveld refinements of the powder diffraction patterns using the software MAUD [19].

3. Results and discussion

The oxides following the sintering treatment yielded pellets with porosity values varying between 37 and 57%. An X-ray diffractogram of a sintered pellet of mixed oxide MgO:NiO = 1:2 is given in Fig. 3(a). Since MgO and NiO have the same crystal structure and very similar lattice parameters, the peaks are very close to one another showing considerable overlapping. Still, the peaks of MgO and NiO are differentiated from each other, indicating that the mixed oxides have a two-phase structure rather than a single-phase solid solution. Considering that the sintering was carried out at 1200 °C this is somewhat surprising and could be due to insufficient mixing of the oxides in the SPEX mill. This has been further verified via SEM imaging in backscattered mode. Regions of two different contrasts were apparent, see Fig. 3(b), in compliance with the presence of two-phase structure. Grains in the sintered samples had sizes (mean intercept value) of 1.9 μm and 3.2 μm for MgO and NiO respectively.

The process of electroreduction leads to the discharging of oxygen from the cathode thus leaving the metallic constituents behind. More specifically, under the applied potential, the oxygen is ionized