NiO IN YTTRIA-DOPED ZIRCONIA

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ABSTRACT

The solubility of NiO in cubic ZrO₂-Y₂O₃ has been investigated for various yttria dopings. The solubility of NiO is found to be 1-2 mol%, independent of the yttria doping. The solubility is temperature activated with an activation energy of about 0.25 eV. The dissolution of NiO in low yttria-doped (6.4 mol% Y₂O₃) is found to increase the stability of the cubic phase. A single cubic phase may be produced by a sufficiently rapid cooling from 1600°C. This phase is shown to be unstable when annealing at 1200°C. The mixing of NiO with zirconia is found to decrease the sintering temperature significantly.

INTRODUCTION

NiO-ZY cermets (ZY denotes yttria-doped zirconia) are much employed anodes in SOFC (1). Usually, the anode is fabricated by printing/spraying a NiO-ZY ink onto a dense ZY electrolyte followed by ad-sintering. The sintering is typically performed at about 1300°C. During the ad-sintering Ni²⁺ may dissolve in the ZY-electrolyte. Such a dissolution of Ni²⁺ could cause changes of the lattice parameter of the ZY, thereby giving rise to mechanical stresses with subsequent possibilities for failure. The dissolution may also affect the phase stability and the ionic conductivity of the ZY.

The solubility of NiO in ZY have been investigated in recent works by Chen et al. (2-5) and Kuzjukevics et al. (6). Chen et al. find that the solubility of NiO in 5ZY (xZY denotes ZrO₂ doped with x mol% Y₂O₃) is about 3 mol% at temperatures around 1600°C, increasing with yttria doping to a solubility of 5-10 mol% NiO in 10ZY. Chen et al. have determined the solubility limit as the NiO content at which the lattice parameter of the zirconia becomes almost independent of the overall NiO content. However, the solubility limit of NiO in 10ZY is probably less than 5 mol% since a considerable amount of free NiO is still detectable in the micrographs of the NiO-ZY samples for a total NiO concentration of 5 mol% in the samples. Recently it was shown that the solubility of NiO...
in 8-10ZY is lower than 2.5 mol% at 1600°C (6). In this work we report on an investigation of the solubility of NiO in 6ZY, 8ZY and 10ZY.

Dissolution of NiO in ZY might make it possible to stabilize ZY phases. Chen et al. (4) have demonstrated that the dissolution of NiO in 5ZY is able to stabilize the cubic phase. They find that 5ZY may be fully stabilized in the cubic state after a heat treatment in air at 1600°C for 1 hour. This stabilization effect is ascribed to the introduction of oxygen vacancies in the ZY by the dissolution of Ni²⁺ (4). Here, we report on a study on the possible stabilization of a single cubic phase in 6.4ZY doped with NiO.

**EXPERIMENTAL**

Ultrafine ZY powders, both with and without NiO, were prepared by means of radio-frequency plasma synthesis, as described in detail by Grabis et al. (7). The powders were pressed into pellets with a diameter of 12 mm and 10-12 mm in height with a pressure of 25 MPa. Pellets were positioned on top of well-sintered pieces of 8ZY and sintered at temperatures between 1200°C and 1600°C with dwell times of 2 and/or 12 hours. The linear temperature ramp rates were +2 and -5 Kmin⁻¹, respectively, for increasing and decreasing temperatures. In some cases samples were quenched from 1600°C to ambient temperature by quenching in water. After quenching, selected samples were also heat treated at 1200°C for 100 hours in order to study aging phenomena.

When preparing samples for XRD only the central part of a sintered pellet was used. A thin slice was grounded in a mortar and positioned between two plastic foils. The XRD investigations were performed by using Cu-Kα₁ radiation in transmission mode in a diffractometer equipped with a Ge monochromator and position sensitive detectors. Silicon used as an internal standard for lattice parameter calculations. Least-square profile refinement were undertaken by means of the multiphase Rietveld analysis program “Fullprof” [11]. A pseudo-Voigt function with angle-dependent mixing parameter was used to refine the diffraction maxima profiles. Because of complete overlapping of the cubic phase maxima with those of the tetragonal phase maxima it was, in a few cases, necessary to use the same width parameters for the cubic and tetragonal phases. The lattice parameter of ZY-NiO solid solutions was estimated from the profile fitting of the x-ray diffractograms in the interval 2θ=68-80°. In this angle range two Si maxima, (400) and (331), and one cubic zirconium maximum, (400) is present. A step-scan with Δ2θ = 0.02° was performed with a counting time of 30-45 seconds per step. Profiles were fitted with a pseudo-Voigt function. A comparison showed that the lattice parameters determined from Rietveld analysis and profile fitting differ less than 0.00006 nm.
RESULTS AND DISCUSSION

On the Stabilization of Cubic ZY by NiO Doping

The as-prepared 6.4ZY doped with 5.3 mol% NiO (hereby denoted 6.4ZY-5.3NiO) revealed by x-ray diffraction a mixture of tetragonal and cubic zirconia phases. The estimated amount of cubic zirconia is about 69 wt%. In an undoped 6.2ZY sample the amount of the cubic phase was found to be about 50 wt.% (8). This indicates that the

Figure 1. X-ray diffractograms of 6.4ZY-5.3NiO as-prepared and after heat treatments at different temperatures in air.

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Table 1. The lattice parameters of the cubic and tetragonal phases of the 6.4ZY-5.3NiO sample as a function of sintering conditions. $I_c$ denotes the amount of the cubic phase. The data are results of Rietveld analyses.

| Sintering conditions | $a_c$ (nm) | $I_c$ (wt %) | $a_t$ (nm) | $c_t$ (nm) | $a_t/c_t$ |
|----------------------|------------|--------------|------------|------------|-----------|
| As-prepared          | 0.51335(3) | 69           | 0.511124(3)| 0.51618(5) | 1.0097    |
| 1200°C/2h            | 0.51359(2) | 54           | 0.51117(5) | 0.51661(10)| 1.0106    |
| 1300°C/2h            | 0.51348(2) | 64           | 0.51045(5) | 0.51650(9) | 1.0119    |
| 1500°C/2h            | 0.513307(1)| 71           | 0.51237(3) | 0.51458(6) | 1.0143    |
| 1600°C/12h           | 0.51263(1) | 87           | 0.51224(4) | 0.51473(6) | 1.0049    |
| 1600°C/12h quenched  | 0.51270(2) | 100          | -          | -          | -         |
| Annealed 1200°C/100h after quenching from 1600°C/12h | 0.5134 | not analysed | 0.5104 | 0.5164 | 1.012 |

The presence of NiO during the powder manufacture can have a stabilization effect on the cubic phase, i.e. it can influence the phase composition of the powders. No monoclinic phase was revealed in the XRD patterns of either the as-prepared 6.4ZY-5.3NiO or the 6.2ZY powders.

Figure 1 shows the XRD pattern of 6.4ZY-5.3NiO as-prepared and after different heat treatments between 1200°C and 1600°C. In the picked angle range the cubic phase gives rise to a single maximum, (400)$_c$, while two maxima, (400)$_t$ and (004)$_t$, will be present in the case of tetragonal zirconia. No monoclinic phase was seen in any of the investigated samples. It is clear from the x-ray diffractograms that the amount of tetragonal zirconia decreases for heat treatments above 1200°C. From the Rietveld analyses the amount of cubic zirconia and the lattice parameters of the cubic and the tetragonal phases have been determined. The results of the analyses are given in Table 1. The fraction of cubic zirconia can be seen to increase with increased sintering...
Figure 2. X-ray diffractograms of the 6.4ZY-5.3NiO sample quenched (Q) from 1600°C into water after a heat treatment in at 1600°C in air for 12 hours. The upper curve shows the diffractogram after a subsequent heat treatment at 1200°C for 100 hours.

temperature. The heat treatment at 1600°C for 12 h, followed by a conventional cooling to room temperature, resulted in about 10 wt.% in the NiO-containing samples. The NiO-free sample, 6.2ZY, had about 65 wt.% tetragonal phase for the same treatment. Hence, by doping 6ZY by NiO the amount of cubic zirconia can be significantly increased - for the given heat treatment.
Table 2. The lattice parameter of cubic ZY with various overall NiO concentrations. The amount of dissolved NiO is estimated by the use of Eq. 1.

| Sample         | \(a_c\) (nm) | \(a_c\) (nm) | Dissolved NiO in c-ZY, quenched (mol%) |
|----------------|--------------|--------------|---------------------------------------|
|                | After sintering 1600°C/12 h in air | Quenched after 1600°C/12 h in air |                                        |
| 6.4ZY-5.3NiO   | -            | 0.51270      | 1.2                                   |
| 7.9ZY-5.0NiO   | 0.51332      | 0.51327      | 1.3                                   |
| 10.3ZY-4.4NiO  | 0.51402      | 0.51392      | 1.1                                   |

It is, however, also evident that the 6.4ZY sample does not become fully stabilized in the cubic phase, in contrast to the observations by Chen et al. (4). The difference may be related to the cooling rate employed, in our case the cooling rate was controlled to be 5 Kmin\(^{-1}\) while in the case of Chen et al. the cooling between 1600°C to 1200°C took about 10 minutes, corresponding to a cooling rate of about 40 Kmin\(^{-1}\). We therefore also performed experiments where samples were rapidly quenched (within a few seconds) from 1600°C to room temperature. This resulted in a single cubic phase sample. Figure 2 shows the x-ray diffractogram after quenching. From these experiments it can therefore be concluded that 6ZY may be fully stabilized in the cubic state by doping with NiO. It should be noted that a similar quench experiment for the NiO-free 6.2ZY revealed also revealed a single phase material but all being in the tetragonal state (8). However, the single phases, tetragonal in the case of NiO-free samples and cubic in the case of NiO doped samples, are only produced when sufficiently high cooling rates are employed, as can be seen for 6.4ZY-5.3NiO in Figure 1.

In order to investigate the stability of the cubic phase produced by quenching 6.4ZY-5.3NiO from 1600°C, a subsequent annealing at 1200°C for 100 h was carried out. The x-ray diffractogram of this sample is reproduced in Figure 2. It is evident that the cubic phase decomposes into a mixture of t- and c-zirconia phases, whence the quenched-in cubic phase is unstable at 1200°C.

On NiO dissolution in cubic ZY

The amount of dissolved NiO in cubic ZY may be estimated from the change of lattice parameter (9):

\[
a_{ZY-NiO} = 0.5119 + 0.01394m_{YO1.5} - 0.0515m_{NiO},
\]

where \(a_{ZY-NiO}\) is the lattice parameter of the cubic ZY-NiO solid solution and \(m_{YO1.5}\) and \(m_{NiO}\) are the molar fraction of YO\(_{1.5}\) and NiO. The amount of dissolved NiO in the cubic
Figure 3. The calculated lattice parameter of plasma-prepared 8.1ZY-74.7NiO as a function of sintering temperature. The sintering was carried out in air. The solid line represents the best fit to an Arrhenius description of the solubility.

The zirconia phase of the quenched 6.4ZY-5.3NiO sample is thereby calculated to 1.2 mol%. By similar experiments the amount of dissolved NiO in cubic 7.9ZY and 10.3ZY has been estimated. The results are given in Table 2. It should here be noted that the estimated amount of dissolved NiO in cubic zirconia is well below the solubility limits given by Chen et al. (2-5), and that the solubility is found to be independent of the yttria doping of the zirconia. These results are in contrast to the findings by Chen et al. (2-5). That the solubility limit is about 1 mol% is confirmed by recent sintering experiments (10).

A study of the temperature dependence of the solubility of NiO in cubic zirconia has been carried for 8.1ZY-74.7NiO. In this case the overall amount of NiO is very high which should guarantee that the estimated NiO content in the zirconia matrix is that corresponding to the solubility limit. By the use of Eq. 1 the measured lattice parameters have been converted into amount of dissolved NiO. The result is seen in Figure 3. The as-prepared sample has been estimated to have about 2.9 mol% NiO dissolved in the zirconia. This corresponds to a supersaturated state which can be seen by the decrease of
the amount of dissolved NiO up to a sintering temperature of 1200°C. Above 1200°C the amount of dissolved NiO increases again, i.e. above this temperature the estimated dissolved NiO in ZY may be considered to correspond to the solubility limit for 8ZY. The solubility limit is seen to increase from about 1.1 mol% at 1200°C to about 1.7 mol% at 1600°C. This latter value is slightly larger than that estimated for the 7.9ZY-5.0NiO sample (see Table 2).

In Figure 3 the solid line represents the best fit to the data using an Arrhenius description, i.e. the dissolution is considered to be activated process. The Arrhenius description is seen to give a good representation of the data. From the curve the solubility limit of NiO in cubic 8ZY may be estimated also at lower temperatures.

**Influence of NiO on sintering of ZY**

The possible influence of NiO on the sinterability of the zirconia has been investigated for cubic 7.8ZY. The zirconia powder employed in this case was a commercial available powder from Tosoh while the NiO was prepared by the same plasma synthesis method as employed for the previously discussed samples. Powder

![Graph](image)

**Figure 4.** The rate of sintering of NiO-free 7.8ZY and 7.8ZY-0.75NiO up to 1500°C in air with a temperature increase rate 2°Cmin⁻¹.
mixtures were ball milled for 24 hours in ethanol using zirconia balls and a plastic container. The powder slurries were dried at 80°C, and then uniaxially pressed into pellets with a diameter of 12 mm and height 10-12 mm. Thereafter the pellets were cold isostatically pressed with a pressure of 200 MPa. Dilatometric measurements were performed for NiO-free 7.8ZY and for 7.8ZY-0.75NiO up to 1500°C in air with a temperature increase rate 2°C/min^{-1}. In Figure 4 is show the derivative of the length change as a function of temperature. It is evident from Figure 4 that the addition of only 0.75 mol% NiO results in a significant decrease of the sintering temperature of 7.8ZY. The maximum of sintering is at about 1215°C for 7.8ZY-0.75NiO and at about 1305°C for the NiO-free sample, i.e. a difference of 90°C. Higher NiO dopings only result in a minor decrease of the sintering temperature (10), which is in support of the above findings that the solubility limit is about 1 mol% for NiO in cubic 8ZY.

CONCLUSIONS

NiO has been found to influence the amount of tetragonal and cubic phases in yttria-doped zirconia. By a sufficiently rapid cooling from 1600°C, zirconia doped with 6.4 mol% Y₂O₃ can be produced in a single cubic phase. However, a prolonged heat treatment at 1200°C shows that the cubic phase is not fully stabilized but decomposes into a mixture of tetragonal and cubic zirconia.

The solubility of NiO in cubic zirconia doped with 6-10 mol% Y₂O₃ has been estimated to be in the 1-2 mol% range. The temperature dependence of the solubility has been investigated. The solubility is temperature activated with and found to have an activation energy of about 0.25 eV and pre-exponential of about 8.3 mol%.

The mixing of NiO with yttria-stabilized zirconia results in a significant decrease of the sintering temperature. The maximum in sintering rate is lowered by about 90°C by the addition of as little as 0.75 mol% NiO.

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