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Published in:
Solid State Ionics

Link to article, DOI:
[10.1016/j.ssi.2019.115019](https://doi.org/10.1016/j.ssi.2019.115019)

Publication date:
2019

Document Version
Peer reviewed version

[Link back to DTU Orbit](#)

Citation (APA):
Simonsen, S. B., Muhl, T. T., Thydén, K. T. S., Chatzichristodoulou, C., Nielsen, J., & Sudireddy, B. R. (2019). Effect of Fe on high performing nanostructured Ni/Gd-doped ceria electrocatalysts. *Solid State Ionics*, 340, [115019]. <https://doi.org/10.1016/j.ssi.2019.115019>

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Effect of Fe on high performing nanostructured Ni/Gd-doped ceria electrocatalysts

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Keywords: SOEC, SOFC, Gd-doped ceria, CeFeO_3

ABSTRACT

Metal supported solid oxide fuel and electrolysis cells (SOFC/SOEC) impregnated with nanosized catalysts are attractive as highly efficient low cost cells operating at relatively low temperature. Recent studies have focused on catalysts based on Ni and gadolinia-doped ceria (CGO) at the fuel side of the cell, and in some cases with the addition of Fe. Here we investigate FeNi/CGO catalyst in relation to SOFC/SOEC fuel electrodes with focus on the Fe diffusion into Ni/CGO during catalyst reduction. The reduction process was followed by in-situ XRD and in situ TEM, and the experiments show that for low metal loadings the CGO nanoparticle size is unaffected by the presence of metals. However, for a high Fe loading the oxide particle size increases and Fe is widely spread in the catalyst, both, in the form of NiFe alloy and by converting most of the CGO to CeFeO_3 and GdFeO_3 .

1. Introduction

Solid oxide fuel cells (SOFC) and solid oxide electrolysis cells (SOEC) are well recognized as high efficiency electrochemical energy conversion devices. State-of-the-art SOFCs and SOECs use Ni/yttria-stabilized zirconia (Ni/YSZ) based fuel electrodes that oxidize H_2 , forming water [1]. However, Ni in these electrodes tends to agglomerate and sinter, resulting in the degradation of cell performance over time, due to loss of Ni percolation. Furthermore, the Ni-YSZ electrodes may experience significant degradation when operated with hydrocarbon based fuels, and they are prone to carbon deposition. In addition, even small amounts of impurities in the fuel, in particular sulphur, will inhibit the electrode functionality [2][3]. One solution for these challenges is to look for alternative fuel electrode materials. Gadolinium-doped Ceria (CGO) in particular has attracted large interest due to its ability to minimize carbon deposition and sulphur poisoning while activating the performance of the electrode, especially when nanosized such as in infiltration-based electrodes. Infiltration-based electrodes offer in addition the possibility of greatly improved redox robustness and

electrocatalyst design flexibility. Such electrodes are specifically interesting in the development of metal supported solid oxide fuel cells (MS-SOFCs), where the use of Ni/YSZ fuel electrodes will result in the detrimental Ni inter-diffusion with the metal support and pronounced Ni coarsening due to the processing in a reducing atmosphere [4]. Recently, a high performing Ni/CGO infiltrated FeCr/YSZ composite fuel electrode was reported [5][6][7][8] and also a Ni/CGO infiltrated $\text{La}_{0.4}\text{Sr}_{0.4}\text{Fe}_{0.03}\text{Ni}_{0.03}\text{Ti}_{0.94}\text{O}_3$ (LSFNT) [9] and $\text{Sr}(\text{Ti},\text{Nb})\text{O}_3$ [10] based MS-SOFC fuel electrode with improved corrosion resistance. Similar electrode concepts with infiltrated FeCr backbones have been explored by other groups [11][12][13][14]. In addition, Ni doped ceria electrocatalyst has due to the excellent performance been infiltrated in a wide range of electronic conducting ceramic based anode backbones [15][16][17][18][19][20][21]. However, a common observation among all these investigations is a significant performance degradation with different rates over time. The initial degradation can be attributed to the infiltrated electrocatalyst coarsening and rearrangement; however, the continuous degradation indicates that there are additional mechanisms at play. A previous detailed transmission electron microscopy (TEM) study of the FeCr/YSZ fuel electrode infiltrated with Ni/CGO electrocatalyst has revealed significant presence of Fe within the Ni/CGO electrocatalyst coating [22]. The mechanism of Fe migration into Ni/CGO was nevertheless not clearly understood. A remote possibility is the dissolution of Fe from the FeCr surface into the Ni/CGO infiltration solution during the infiltration procedure. Another possibility is the diffusion of Fe from the FeCr particles into the Ni/CGO coating during the initial periods of the MS-SOFC startup at elevated temperatures. These possible processes could explain the observations of the TEM study [22], where a gradient was also observed in Fe content from the FeCr steel and outwards. It was speculated that the diffusion of Fe into Ni/CGO coating resulted in the formation of CeFeO_3 since areas with a 1:1 ratio between Ce and Fe were identified along with the presence of Ce^{3+} from the electron energy loss spectroscopy (EELS). However, in a reducing H_2 containing atmosphere, the presence of Ce^{3+} in CGO is also expected. Presence of significant amount of Fe within the Ni/CGO electrocatalyst layer may alter the ionic conductivity and electrocatalytic properties of CGO in Ni/CGO, which is decisive for both, the cell performance and the durability. Furthermore, diffusion of Fe into Ni can result in FeNi alloying for certain Fe to Ni ratios and such alloying has been reported to improve both the performance [23][24][25] and the durability [26].

The aim of the present study is therefore to obtain a detailed understanding of Fe diffusion into the Ni/CGO electrocatalyst and the impact of such diffusion on the chemistry and functional behavior of the Ni/CGO electrocatalyst. This is attempted by detailed ex-situ and in-situ XRD and TEM studies on model Ni/CGO and FeNi/CGO electrocatalyst systems. The amount of Fe and Ni in these systems was varied in order to understand their influence on the CGO chemistry.

2. Materials and Methods

Nano-sized CGO was synthesized by dissolving both cerium (III) nitrate hexahydrate ($\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$) and gadolinium (III) nitrate hydrate ($\text{Gd}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$) in a minimum volume of deionized water (5 ml) and mixed together with a surfactant, Pluronic® P123. Samples with different weight percent of Fe and Ni, (10wt.%Ni/CGO, 1wt.%Fe-9 wt.%Ni/CGO, and 40wt.%Fe-5 wt.%Ni/CGO), were prepared using nitrate salt precursors. The weight percent refer to the final products. The appropriate amounts of iron (III) nitrate nonahydrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) or/and nickel (II) nitrate hexahydrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) were dissolved in the CGO precursor solution. Subsequently, solutions comprising of nitrate precursors were dried at 100 °C for 24 h and then calcined at 350 °C for 1 h.

The in-situ X-Ray diffraction (XRD) measurements were carried out in a Rigaku SmartLab diffractometer with Cu K α radiation, using an Anton Paar HTK 1200N high temperature oven chamber with atmosphere control. XRD patterns were recorded in the Bragg-Brentano configuration in the 2θ range 20 – 100° with a step size of 0.01° in 2θ .

Ex-situ TEM and scanning transmission electron microscopy (STEM) in combination with energy dispersive spectroscopy (EDS) was performed using a JEOL 3000F equipped with a field emission gun operated at 300 kV, a high annular angle dark field (HAADF) STEM detector, and an Oxford instruments EDS detector. The powder samples for TEM and STEM were dispersed dry on holey carbon/Cu TEM grids. From the acquired TEM images, particle sizes were measured by manually outlining the particle perimeters, using the software ImageJ and converting the measured projected particle areas to particle diameters using a circular approximation. Notice that in this context a particle can be composed of several crystallites. Quantification of the EDS spectra was performed with calculated k-factors from the INCA software.

In-situ TEM was performed using a Titan 80-300 (FEI) electron microscope equipped with a differentially pumped environmental cell [27] operated at 300 kV. Heating was facilitated by a heating holder from DENS solutions which is a chip based heating holder with temperature feedback based on a 4-point-probe resistive measurement of the micro hotplate. The holder was plasma cleaned for 5 min before mounting the chip with the 40%Fe-5%Ni/CGO sample. The 40%Fe-5%Ni/CGO was dry dispersed on the thermal chip. The in-situ experiment was performed by exposing the sample to 1.2 mbar H₂. The temperature was ramped up in steps from ca. 25 °C to 100 °C, 200 °C, 300 °C, 400 °C, 500 °C, 600 °C, 650 °C, 700 °C, and 800 °C. The temperature was ramped to the chosen temperature in ca. 1 second. Below 500 °C the temperature was only kept constant for ca. 1 minute, enough to record images of selected regions. At the higher temperatures, the temperature was maintained for a longer reduction time, specifically: 500 °C: 17 min, 600 °C: 17 min, 650 °C: 20 min, 700 °C: 10 min, 800 °C: 70 min. TEM images were recorded with 2 s total exposure time by summing and cross correlating frames for each image using a OneView camera (Gatan company). The beam current density during image acquisition was ca. 4000 e/nm²s. In addition to imaging, EELS was performed by using a Gatan 865 GIF Tridiem energy filter. High-resolution TEM (HRTEM) images recorded during the in-situ experiment were analyzed with the CrystalMatch software [28]. 10 crystals were analyzed and for all crystals at least three independent measurements were included in the analysis: two lattice distances and the angle between the planes were compared to theoretical values described in crystallographic information files (CIF) of the following structures: cubic Fe (space group Im-3m), trigonal Fe₂O₃ (space group R-3cH), cubic Fe₃O₄ (space group Fd-3mZ), cubic Ni (space group Fm-3m), cubic NiO (space group Fm-3m), trigonal NiO₂ (space group R-3mH), cubic FeNi (space group Fm-3m), cubic Fe_{0.7}Ni_{0.3} (space group Im-3m), cubic Fe₃Ni (space group Pm-3m), monoclinic FeNi (space group P1m1), cubic Ce_{0.8}Gd_{0.2}O_{1.9} (space group Fm-3m), orthorhombic CeFeO₃ (space group Pbnm), orthorhombic GdFeO₃ (space group Pbnm), and orthorhombic GdNiO₃ (space group Pbnm). A crystal was found to be consistent with a structure if all the measurements agreed with the theoretical values within estimated measurement errors of 10% for distances and 5% for angles.

3. Results

Figure 1(a-d) presents ex-situ TEM images of the four powder samples (a) CGO, (b) 10wt.%Ni/CGO, (c) 1wt.%Fe-9wt.%Ni/CGO, (d) 40wt.%Fe-5wt.%Ni/CGO after reduction at

800 °C in 5 % H₂/N₂ with 3 % H₂O for 3 hours. The particle morphology and sizes are similar for all samples except for 40wt.%Fe-5wt.%Ni/CGO, which has larger and more rounded particles. From the mass-thickness contrast dominating the TEM images it is not possible to distinguish between CGO and metals (Ni and Fe) because the densities of these materials are comparable. Thus, it was necessary to record STEM-EDS maps in order to identify each material. As an example, Figure 1(e) presents such a STEM EDS map for 40wt.%Fe-5wt.%Ni/CGO at the same region as presented in (d). For 40wt.%Fe-5wt.%Ni/CGO, Ni and CGO are separated, while Fe is distributed widely in both CGO and Ni nanoparticles. This could indicate that Fe and Ni are alloyed into FeNi nanoparticles (indicated with green ellipsis in fig. 1d) in agreement with previous studies showing that FeNi alloy nanoparticle form during reduction in H₂ at 800°C [29]. It is interesting to observe that Fe also mixes with CGO. Quantification of the EDS data show that the Fe-to-Ce atomic ratio is ca. 1 in regions with no Ni.

For the 1wt.%Fe-9wt.%Ni/CGO the concentrations of Fe appear to be highest in the Ni-rich regions. This could indicate that the diffusion of Fe into CGO regions increases when there is excess of Fe, but a firm conclusion cannot be reached, because the concentration of Fe is rather low, which makes quantitative EDS analysis uncertain.

Figure 1: (a-d) TEM images of (a) CGO, (b) 10wt.%Ni/CGO, (c) 1wt.%Fe-9wt.%Ni/CGO, (d) 40wt.%Fe-5wt.%Ni/CGO after reduction at 800 °C in 5 % H₂/N₂ with 3 % H₂O. (e) STEM-EDS map representing Fe K α (red), Ni K α (green) and Ce L α (blue) X-ray signals from 40wt.%Fe-5wt.%Ni/CGO after reduction. The region of the sample is identical in (d) and (e) and green ellipses in (d) indicate nanoparticles consisting of Ni and Fe.

By comparing STEM-EDS maps and TEM images recorded for the same regions (as exemplified by Figure 1(d-e)) it was possible to measure the sizes of oxide (containing Fe and/or Ce, Gd, and O) and metal (containing Fe and/or Ni) particles. Figure 2 presents particle diameters of the oxide and metal particles for all four samples. The spread in particle sizes is indicated by the standard deviation (Fig. 2, error bars). According to Fig. 2, the addition of 10 wt.% Ni to CGO does not influence the CGO particle size. This could perhaps be expected from the STEM-EDS maps which show that Ni does not mix with CGO during reduction at 800°C. The STEM-EDS maps show that Fe does mix with the CGO particles, and according to Figure 2 the low amount of 1 wt.% Fe does not influence the CGO particle

size while higher amounts of Fe do. The large increase in diameter of the oxide particles from ca. 40 nm with no or small amounts of Fe to ca. 150 nm for the 40wt.%Fe-5wt.%Ni/CGO sample indicates that the new phase containing Fe, Ce and O coarsens much faster during reduction at 800°C than pure CGO.

The metal particle size is unchanged by the addition of 1 wt.% Fe (Figure 2, red circles). This suggests that Fe does not significantly accelerate the coarsening of supported Ni nanoparticles in hydrogen at 800°C. The larger particle sizes observed for the 40%Fe-sample can be expected from the higher metal loading and the results therefore do not necessarily indicate a higher coarsening rate for higher Fe-to-Ni ratios.

Figure 2: Particle sizes of oxides containing Ce, Gd, O and Fe (blue squares) and metals containing Ni and Fe (red circles) presented for the four samples; CGO, 10wt.%Ni/CGO, 1wt.%Fe-9wt.%Ni/CGO and 40wt.%Fe-5wt.%Ni/CGO after reduction at 800 °C in 5 % H₂/N₂ with 3 % H₂O. The spread in particle sizes is indicated by the standard deviations (error bars).

To further investigate the possible formation of new phases in the Fe-containing samples during the reduction process, in-situ XRD experiments were undertaken on as-prepared catalyst powders, i.e. precursor solutions dried at 100 °C and calcined in air at 350 °C. In-situ XRD patterns recorded at 25 °C, 500 °C, 650 °C and 800 °C in 5 % H₂/N₂ with 3 % H₂O for 40wt.%Fe-5wt.%Ni/CGO are presented in Figure 3. At 25 °C, the main peaks in the XRD patterns are consistent with CGO and hematite (Fe₂O₃). After raising the temperature to 500 °C, some of the hematite has been reduced to form magnetite (Fe₃O₄) and the two Fe oxide

phases coexists. At 650 °C, the peaks from both Fe oxides are still observed, but in addition new peaks consistent with metallic Fe and Ni are also observed. Also, the signal from CGO has decreased and new peaks consistent with cerium orthoferrite (CeFeO_3) are observed. Finally at 800 °C, the dominating peaks can be assigned to the new phase CeFeO_3 . This result is consistent with the STEM-EDS quantification which, as mentioned above, showed an atomic Fe-to-Ce ratio of ca. 1 in the oxide particles. Both the in-situ XRD and the TEM/STEM analysis therefore suggest that an effect of Fe is to destabilize CGO in a reducing environment. The Fe is distributed in the CGO which transforms to CeFeO_3 . Previous studies have shown that CeFeO_3 forms from mixtures of CeO_2 and Fe_2O_3 at temperatures of 800-1250°C in oxidizing conditions [30] or from a mixture of CeO_2 , Fe_2O_3 and Fe fired at 800-850 °C for 48 hours [31]. Here we can observe the formation onset already at 650 °C, which suggests that a reducing environment enhances the CeFeO_3 formation. GdFeO_3 has an XRD pattern with many peaks (as shown in Figure 3), and this phase may also be present at 800 °C, but the small amount of Gd does not allow to draw a clear conclusion.

At 800 °C, in addition to peaks from CeFeO_3 , peaks are also observed from metallic Fe and Ni indicating an almost full reduction at this temperature, although there are still small peaks indicating the presence of a minor content of Fe-oxide.

Figure 3: In situ XRD patterns of the 40wt.%Fe-5wt.%Ni/CGO powder sample are presented for four different temperatures, 25 °C, 500 °C after 90 min, 650 °C after 270 min and 800 °C after 180 min as indicated in the figure. The XRD patterns were recorded in a 20 ml/min flow of 5 % H_2/N_2 with 3 % H_2O . For comparison, peak positions for CGO, Fe, Ni, Fe_3O_4 , Fe_2O_3 , CeFeO_3 and GdFeO_3 reference powder samples are presented. To guide the eye, observed peaks are related to the reference patterns by vertical dotted lines.

To follow the dynamics of the nanocrystals during reduction, an in-situ TEM experiment was performed, this method has previously been used to follow reduction processes of for example NiO/YSZ [32]. Here the calcined, but not yet reduced, 40wt.%Fe-5wt.%Ni/CGO powder sample was exposed to 1.2 mbar H_2 at elevated temperatures. Figure 4 (a-e) presents in situ TEM images of the same region of the sample at (a) 25 °C, (b) 500 °C, (c) 650 °C and (d) 800 °C, which are the same temperatures as those presented for the in situ XRD results in Figure 3. Figure 4 (e) presents the sample again at 800 °C after a reduction time of ca. 1 hour. The in-situ TEM images (a-e) show that the particle sizes increase as the temperature is raised. The growth of larger crystals appears to take place mainly near the surface of particle agglomerates, and as a result, dense (dark contrast) shells are observed around less dense

cores (brighter contrast). Several examples can be observed in (c-e). To guide the eyes, two examples of dense shells are indicated by black arrows in Figure 4 (d).

Figure 4: (a-e) in-situ TEM images of 40wt.%Fe-5wt.%Ni/CGO powder sample recorded during exposure to 1.2 mbar H_2 at (a) 25 °C, (b) 500 °C, (c) 650 °C (d) 800 °C and (e) after 60 min reduction time at 800 °C. (f) presents an in-situ HRTEM image recorded from the region marked by a white box in (e). (g) is a close-up of (f) in the region presented by a yellow box. (h) is a fast Fourier transform (FFT) of (g). The crystal in (g, h) was identified as orthorhombic $CeFeO_3$ at zone axis [010]. The miller indices for the observed lattice planes are indicated in (h) and their measured lattice distances are indicated in (g). (i) presents EELS spectra recorded at 25 °C (red) from the region marked by a red box in (a) and at 800 °C (blue) from the region marked by a blue box in (e). The $L_{3,2}$ Fe, Ni and the $M_{4,5}$ Ce edges are indicated in the figure.

To form $CeFeO_3$ and $GdFeO_3$ during the reduction process, either the Ce and Gd cations diffuse into the Fe_2O_3 or the Fe cations diffuse into CGO across the initial interface of the two materials. Likely, the diffusion rate is different for the different cations, and this could shift the position of the interface following a so-called Kirkendall process [33]. Previous in-situ TEM studies have shown the development of dense shells in the transformation of Ni to NiO by such a process [34]. The formation of high density shells, low density cores observed

in Figure 4(b-e) indicates that the outward diffusion rate is the highest. Before the in-situ reduction, calcined 40wt.%Fe-5wt.%Ni/CGO powder samples were analyzed by STEM-EDS and the results (not presented) show that relatively large FeNi oxide particles are typically surrounded by smaller CGO particles. The in-situ TEM results therefore suggest that Fe cations are diffusing into CGO to form CeFeO_3 and GdFeO_3 followed by coarsening and sintering of the new phases.

To investigate the structure of the crystals observed to grow in Figure 4(a-e) in the dense shells, high-resolution TEM (HRTEM) analysis was applied. An example of such an analysis is presented in Figure 4 (f-h). The measured lattice distances and angles between each plane of this crystal are consistent with orthorhombic CeFeO_3 and GdFeO_3 , but not with CGO, metallic or oxide forms of Fe, Ni or NiFe alloys within the estimated measuring errors. In addition, 10 other crystals were analyzed, and these were consistent with CGO in 4 cases, with Fe_3O_4 in 5 cases, with Fe_2O_3 in 1 case, but in all 10 cases the crystals were also consistent with CeFeO_3 and GdFeO_3 . These findings are consistent with the in-situ XRD results, and we conclude that the CGO phase transforms to CeFeO_3 and GdFeO_3 during reduction in H_2 in the presence of Fe.

Figure 4 (i) presents EELS spectra at 25 °C before the reduction (red) and at 800 °C during reduction (blue) recorded from the regions indicated in (a) and (e). Core loss edges for Fe, Ni and Ce are observed confirming that the crystals in the indicated region are composed of these elements.

4. Discussion

CGO is a well-known material with mixed ionic and electronic conductivity and fast oxygen exchange kinetics due to its high oxygen deficiency and diffusion coefficient in the fuel electrode environment. When CGO is infiltrated into SOC fuel electrode backbones together with transition metal electrocatalysts such as Ni, significant improvement in the electrochemical performance is observed, due to an increase in the number and activity of electrochemically active reaction sites [35]. The ionic and electronic conductivity of CGO play an essential role in the transport of oxygen ions to the electrochemical reaction sites and the transport of electrons from the electrochemical reaction sites to the current collector. Preservation of these transport properties are at the heart of the effectiveness of CGO. The present study shows that CGO can interact with Fe to form CeFeO_3 . CeFeO_3 being a semiconducting material, does not possess the same transport characteristics as CGO in the

fuel electrode environment. It can therefore be speculated that conversion of CGO into CeFeO_3 will inhibit the ionic conductivity of the electrode, reducing its activity.

A previous study, however, showed that it is possible to improve the long-term stability of Ni/CGO anodes by addition of Fe, and the enhanced performance was found to be due to an improved catalytic activity of the Ni-Fe alloy [26]. Interestingly, this previous work only reported observation of Ni-Fe alloys from XRD, but no CeFeO_3 formation. Studies of samaria-doped ceria (SDC) infiltrated with Fe and Ni also report presence of Ni, Fe and Ni-Fe alloys after reduction, but not CeFeO_3 [23,24]. On the other hand, a study of Ni-CGO infiltrated FeCr/YSZ fuel electrode backbone reports formation of a Ce-Fe-O compound having a chemical composition compatible with that of CeFeO_3 [22]. It is not clear why some previous studies do not observe such a Ce-Fe-O compound while others do. A possible reason could be differences in loading or detailed processing and operating conditions. The present XRD and TEM results, however, clearly show formation of CeFeO_3 in the SOC fuel electrode under operating temperature and this report is the first confirmation of this.

Addition of Fe to Ni/CGO may, as mentioned improve the catalytic performance. The ordered phases of NiFe, such as Ni_3Fe for example demonstrate good absorption and desorption of H_2 on their surfaces [36]. Although these intermetallic compounds are not stable at temperatures above 516 °C, which is below typical SOC operating temperatures (600-800 °C), local short range ordering cannot be ruled out. The earlier reports and the present study indicate that the fabrication procedure of Fe and/or Ni – CGO electrocatalysts or electrodes seems to have significant impact on the final chemistry. The addition of Fe to the Ni/CGO could significantly improve the initial performance of the SOCs through the formation of FeNi alloys that can have high H_2 absorption and desorption. Possibly, the formation of CeFeO_3 at SOC operating conditions with time may result in degradation of the electrochemical performance.

4. Conclusions

In this study the reduction process of FeNi/CGO catalysts in relation to SOFC/SOEC was analyzed by in situ XRD, in situ TEM and by ex situ TEM and STEM-EDS. The results show that addition of relatively low amounts of metal (10 wt.% Ni or 9 wt.% Ni + 1 wt.% Fe) to CGO did not substantially influence the mean particle size of CGO nor compromise the stability of the fluorite phase. According to STEM-EDS 1 wt.% Fe is mainly distributed in Ni. For a relatively high Fe loading (40 wt.%), Fe also appears to alloy with Ni, and in

addition, most of the CGO is converted to CeFeO_3 and possibly GdFeO_3 . We suggest that excess Fe, after formation of FeNi alloys, will migrate to CGO to form the cerium orthoferrite phase.

Acknowledgements

The A.P. Møller and ChristineMc-Kinney Møller Foundation is gratefully acknowledged for their contribution toward the establishment of the Center for Electron Nanoscopy in the Technical University of Denmark.

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