Grain Growth of Micron-Sized Grains in Undoped and Cobalt Oxide Doped Ceria Solid Solutions

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Isothermal grain growth experiments have been conducted for undoped as well as cobalt oxide doped CeO$_2$ and Ce$_{0.8}$Gd$_{0.2}$O$_{1.8}$ (CGO20). Due to the solute drag effect of the dissolved gadolinium ions, the grain boundary mobility of CGO20 was significantly lower than that of CeO$_2$. The addition of cobalt oxide increases the grain boundary mobility of CGO20. This increase is assigned to the formation of a characteristic cobalt oxide rich grain boundary film. In undoped and cobalt oxide doped CGO20, a transition from regular grain growth at high temperature in micron-sized grains to self-limited grain growth at low temperature in nanometer-sized grains occurs. As a consequence, highly stable microstructures result at lower temperatures. It is suggested that strain in amorphous grain boundary films becomes important for the self limited grain growth for very small grains at low temperatures.

Key-words : Solid oxide fuel cells, Ceria based ion conductors, Self limited grain growth, Amorphous grain boundary film

1. Introduction

Ceria-based ceramics are attractive as electrolyte materials for catalytic and for solid oxide fuel cell (SOFC) applications and have therefore been extensively studied. Their oxygen ion conductivity is superior to alternative ceramic electrolytes at intermediate temperatures. This property offers outstanding advantages as it allows operation of SOFC systems at reduced temperature and in turn decreases fabrication cost.$^{1,2}$

In particular, gadolinia doped ceria (Ce$_{0.8}$Gd$_{0.2}$O$_{1.8}$, CGO20) is among the best ceria-based electrolytes.$^{3-5}$ However, sintering of ceria-based powders is difficult, mainly due to the partial reduction of Ce$^{4+}$ to Ce$^{3+}$ atoms at high temperatures.$^7$ Various investigations have therefore aimed at fabricating ceria gadolinium oxide powders of high sinterability.$^8-12$ A well established strategy to enhance sintering is the use of dopants which promote densification while suppressing grain growth. Specific additives that enhance mass transport along grain boundaries will enhance densification while others, which facilitate mass transport across grain boundaries, will increase the grain growth rate. Unfortunately, most dopants enhance densification as well as grain growth. However, some dopants have shown to be promising sintering additives. More specifically, additions of small amounts of various transition metal oxides promote the sintering process of cerium-gadolinium-oxide.$^{11,12}$ Cobalt oxide in particular was found to be a very effective sintering aid for CeO$_2$ as well as for CGO lowering the sintering temperature by more than 200°C.$^{13,14}$ A sintering analysis of undoped as well as CoO-doped CGO20 has shown that cobalt oxide doping enhances grain boundary diffusion in CGO20 during densification. This results in lower sintering temperatures and consequently in a fine-grained microstructure.$^{15}$ Transition metal oxides, such as cobalt oxide as additives, seem not only to promote densification, but also to enhance grain growth. The comparison of cobalt oxide doped CeO$_2$ to undoped CeO$_2$ reveals larger grain sizes at all dwell temperatures upon doping.$^{16}$

Similar observations were reported by Lewis who studied the grain growth behavior in cobalt oxide doped Ce$_{0.8}$Gd$_{0.2}$O$_{1.85}$ (CGO10).$^{17}$

The present work aims at extending the experimental data for grain growth kinetics in undoped and cobalt oxide doped CGO20 over a wide range of temperatures and dwell times. In addition, an interpretation of the data on the basis of established theoretical models for grain growth is attempted.

2. Grain growth in ceramics

Grain growth in ceramics has been described in detail by Yan et al.$^{17}$ Brook$^{18}$ and Powers et al.$^{19}$ For the purpose of the present work, the most important concepts of grain boundary migration are reviewed qualitatively in the following section. For a more formal treatment, the reader is referred to the above-mentioned literature.

When a polycrystalline material is heated, a curvature-induced driving force $F_c$ causes atoms or ions to move across the grain boundary. The primary driving force for grain growth is the reduction of interfacial energy per unit volume. At steady state, the boundary moves with an average velocity $V_b$, this balances the total drag force $F_d$ acting on the boundary. $V_b$ is a function of the total drag. By normalizing the boundary velocity, the grain boundary mobility $M_b$ can be expressed as:

$$M_b = \frac{V_b}{F_d}$$

The drag force $F_d$ consists of several components. The intrinsic drag force is controlled by the diffusivities of the atoms across the boundary. Cations usually diffuse at a slower rate than anions.$^{17}$ The intrinsic grain boundary velocity is then cation-limited. This is also the case for cerium-gadolinium-oxide as it is an oxygen ion conductor.

An additional component to the total drag force can arise from a solute in the matrix. Depending on the interaction potential between grain boundary and solute, the latter will either be attracted to or repelled from the boundary. In both cases, an extra component will be generated, either diminishing or reinforcing the drag force. In the absence of an anisotropic microstructure, the grain boundary mobility is typically lowered due to a solute.

Grain boundary mobility can further be limited by an existing second phase at the boundary, i.e. pores or precipitates. The drag force of pores is usually larger than that of second-phase precipitates due to their lower mobility.$^{17}$ Two limiting cases of pore-boundary interactions need to be distinguished. Either, pores will remain attached to the boundary if the
boundary velocity equals the pore velocity. In this case, the pores will control the boundary motion. Or, pores will separate from the boundary if the boundary velocity is larger than the pore velocity. Then, intragranular pores are formed, which do not influence the boundary motion significantly. Boundary motion can also be controlled and much enhanced by a liquid film. Diffusion in liquids is much faster than in solids. If the film is sufficiently thin, diffusional transport across the film is enhanced and consequently the boundary mobility increased. Enhancement of ion transport across the boundary by a liquid phase is usually limited by the surface reaction rates, i.e. the dissolution or precipitation rate. The exact influence on the boundary mobility will also depend on the distribution of the liquid phase in the boundary, i.e. by the degree of wetting of the solid by the liquid. Wetting of the liquid film is determined by the various interfacial energies. In case the interfacial energies change during the grain growth process, in particular if a transition from wetting to non-wetting occurs, then the wetting might form isolated particles and consequently the overall grain boundary mobility is decreased. Experimentally, grain boundary mobilities are determined by measuring the average grain size of a dense sample as a function of dwell time at specific dwell temperature. The mobility values obtained are controlled by the concurrent action of solutes, pores, precipitates, abnormal grain growth, or liquid grain boundary films. It is very difficult, if not impossible, to extract the prevailing contributions on the basis of data derived from this type of experiment alone.

The grain growth rate is usually expressed as in Eq. 2,17:

$$\frac{dG}{dt} = \frac{K}{G}$$

(2)

$G$ is the average grain size at time $t$, $m$ is a constant and $K$ varies with the temperature as:

$$K = K_0 \exp \left( -\frac{Q}{kT} \right)$$

(3)

Here, $K_0$ is a pre-exponential factor, $Q$ the activation energy of the grain growth process, $k$ the Boltzmann constant and $T$ the absolute temperature. Upon integration, the familiar parabolic grain growth equation results:

$$G^2 - G_0^2 = K(t - t_0)$$

(4)

where $G_0$ is the average grain size at time $t_0 = 0$. In case of parabolic growth, $K$ equals $2M_y$, where $M$ is the grain boundary mobility and $y$ the grain boundary energy. It has been observed in various systems that grain growth data does not obey parabolic growth, so that a fit with a generalized grain growth equation is more appropriate:

$$G^m - G_0^m = K(t - t_0)$$

(5)

In this case, also a more general expression for the constant $K$ must be used for the calculation of the grain boundary mobility:

$$K = M_y y G^{m-2}$$

(6)

The grain growth exponent $m$ is related to the materials microstructure and growth mechanisms. Frequently observed values for $m$ are in the range 2-4. Parabolic grain growth ($m = 2$) is observed in very pure solids with no second phase impurities. An exponent $m = 3$ may correspond to different grain growth mechanisms, e.g. lattice diffusion when the system is either pore or boundary controlled or solute drag when a dopant is dissolved in solid solution. A value of $m = 4$ is usually assigned to grain boundary diffusion. Simultaneous contributions of several mechanisms may lead to higher values of $m$, usually not an integer.20,21 It has also been observed that $m$ varies with temperature, indicating a change in grain boundary mobility or grain boundary energy.22 It should be noted that the interpretation of experiments by the generalized grain growth law meets with an intrinsic difficulty, namely the fact that values of the exponent $m > 4$ cannot be derived from any plausible physical model. Recently, several studies have shown that the generalized grain growth law in particular fails to describe the isothermal grain growth behavior of nanocrystalline metals23 and ceramics27,28 since a limiting grain size was found after short annealing times. One may note that already in 1949, Burke observed that in many systems grain growth stopped at a fixed size. He thus modified Eq. (2) by an additional term to account for the experimental results:20

$$\frac{dG}{dt} = \frac{K}{G} - \frac{K}{G_{\text{max}}}$$

(7)

where $G_{\text{max}}$ is the grain size where the driving force for grain growth vanishes, i.e. the maximum grain size measured. Upon integration, an implicit expression for the average grain size is obtained:

$$K \frac{G_{\text{max}}}{G} t = G_0 - G(t) - \ln \left( \frac{G_{\text{max}} - G_0}{G_{\text{max}} - G(t)} \right)$$

(8)

In the following, the model of Eq. (8) will be called grain growth with impediment. It is based on the parabolic grain growth law Eq. (4). For the calculation of the grain boundary mobility, the coefficient $K$ therefore equals $2M_y$.

Very recently, Gottstein and Shvindlerman reported and modeled grain boundary motion in which grain boundary triple points possess a limited mobility.31-34 Previous theories of grain growth had assumed triple junctions with infinite mobility, so that the grain boundary mobility alone represents the rate-limiting step. However, experimental results on steady state motion of triple junctions in aluminum and zinc demonstrated that grain growth could be controlled by slowly moving triple junctions.35-37 The dimensionless criterion $A$ describes the influence of the triple junction on the motion of the boundaries and is expressed as follows:

$$A = \frac{M_y G}{M_S}$$

(9)

where $M_S$ is the mobility of the triple junction and $G$ the grain size. If $A$ is close to unity, the velocity of the boundary is controlled by the mobility of the triple junction (triple junction kinetics). If $A > 1$, the boundary mobility determines the kinetics of the system. It should be noted that $A$ depends directly on grain size. Hence, the smaller the grain size, the more the boundary motion is influenced by the triple junctions. Furthermore, in case of finite triple junction mobility, a reduced rate of grain growth can be expected and grain growth can cease if an arrangement of regular polygons is attained.34 Therefore, the approach of Gottstein and Shvindlerman is especially important for nanocrystalline microstructures of very pure materials.

In many cases the above discussed relations are still insufficient to describe grain growth, especially when the grain sizes are small, e.g., in the nanometer regime. Recently grain growth data from microcrystalline metals were described by the generalized grain growth model, whereas the grains in nanocrystalline metals grew until a certain limited grain size was reached, upon which grain growth ceased. It was shown...
that the limited grain boundary migration was due to the grain size dependent solute drag of nanocrystalline metals and by defects in the material. Nanocrystalline sputtered gold thin films showed limited grain growth being strongly affected by the amount of defects present and in ceria ceramics, the growth of grains crystalizing from an amorphous state was strongly controlled by microstrain. During isothermal annealing the grains grew as long as the microstrain decreased in both cases. Once the microstrain relaxed to a certain level in these materials, the grain growth ceased and metastable microstructures developed. This microstrain develops in the amorphous matrix due to the free volume change upon transforming amorphous material with larger volume into crystalline material with smaller volume. Some of the microstrain is also present in the grains with long range order therefore detectable by line width broadening of the X-ray diffraction patterns. The energy of the microstrain in the amorphous phase opposes further grain growth during isothermal annealings and grain growth ceases. With increasing temperatures, the amorphous material has transformed and then a transition to classical parabolic grain growth law was observed in all of these cases.

This self-limited grain growth can be described by a relaxation function where \( G_1 \) is the maximum grain size, \( t_0 \) is the incubation time for forming a nucleus of size \( G_0 \) and \( \tau \) is the relaxation time of the concentration profile (chemical equilibration) within the two-phase nanocrystal-amorphous microstructure, and \( d \) is a Kohlrausch exponent:

\[
G(t) = \frac{G_1 - G_0}{(G_1 - G_0) (1 - \exp[-(t-t_0)/\tau])} \\
G(t) = \frac{G_1 - G_0}{(G_1 - G_0) (1 - \exp[-(t-t_0)/\tau])}^{1/d}
\]

The introduction of the exponent \( d \) \((0 < d < 1)\), leading to a “stretched exponential” function \( G(t) = \exp[-(t/\tau)^{d}] \), creates a spectrum of relaxation times near the transition temperature in case of glasses, however in most cases \( d = 1 \) if nucleation and growth occur at the same time. The simplified Eq. (11) can be used as first approximation. Excellent descriptions of self limited grain growth of ceramics crystalizing from the amorphous state could be obtained by using Eq. (11) in case of nanocrystalline ceria.

3. Experimental procedures

Commercially available CeO\(_2\) powder (Nanophase, Romolville, IL, USA) with a mean particle size of 50 nm and spray-dried Ce\(_{0.8}\)Gd\(_{0.2}\)O\(_2\)_\(_x\) (CGO20) powder (Rhodia Electronics & Catalysis, France) with a mean particle size of 32 nm were used for all experiments. Detailed powder characteristics were reported earlier. The powders were doped with 2 mol\% of cobalt oxide by ultrasonic dispersion in ethanol and by addition of the desired amount of cobalt nitrate hexahydrate dissolved in ethanol. The suspension consisting of powder and cobalt nitrate was dried at 120°C and ground in an agate mortar. Calcination at 400°C for 2 h decomposed the cobalt nitrate to cobalt oxide. The undoped and cobalt oxide doped ceria-based powders were isostatically pressed at 300 MPa for 3 min and compacted to cylindrical rods with diameters of about 5 mm. Samples were heated with 1°C/min in a furnace to the desired temperature, held for the specified time and quenched in air. After measurement of the density by the method of Archimedes, the samples were ground and polished with 1 μm diamond paste. For scanning electron microscopy (SEM), the polished samples were thermally etched about 100°C below the annealing temperature. The grain size was determined by the standard method of measuring at least 300 grains in SEM micrographs. A mean intercept length to mean grain size conversion factor of 1.56 was used.

4. Results and discussion

Typical microstructures, obtained by SEM of cobalt oxide doped ceria at 1350°C and cobalt oxide doped CGO20 at 960°C after a dwell of 2 h, are shown in Fig. 1.

The pure ceria microstructure contains 8.4 vol.% porosity and pore-boundary separation can be observed, leading to the observed intragranular pores in addition to the pores at the grain boundaries. The rather high sintering temperatures required for CeO\(_2\) to achieve densities of >92% of the theoretical as well as the residual porosity were due to the agglomerates in the starting powder of the CeO\(_2\) powder from Nanophase. Hence, in the pure CeO\(_2\) materials further grain growth might be retarded by pore boundary drag.

In case of CGO20, no or only a few pores (<0.5%) located at grain boundaries were observed as shown for one example in Fig. 1(b). The spray-dried CGO20 powder from Rhodia consisted of soft agglomerates produced during the spray drying process and led to homogenous microstructures in the green bodies and hence to homogenous microstructures in the sintered materials achieving fully dense material. In addition, the presence of a solid solution of Gd\(_2\)O\(_3\) in CeO\(_2\) also helps to prevent pore–boundary separation during the later stage of sintering and hence prevents intragranular pores as already highlighted earlier by Brook.

The grain sizes after the isothermal grain growth experiments are shown in Fig. 2 for CeO\(_2\) and in Fig. 3 for CGO20. The average grain size is plotted versus the holding time in

![Fig. 1. Microstructures of CeO\(_2\) doped with 2 mol% CoO (a), dwelled at 1350°C for 2 h and CGO doped with 2 mol% CoO (b), dwelled at 960°C for 2 h.](image-url)
Fig. 2. Average grain size as a function of dwell time for CeO$_2$ undoped (a) and CeO$_2$ doped with 2 cat% cobalt oxide (b). Dashed lines represent the fits with the generalized grain growth law. Solid lines represent the fits with the grain growth model with impediment.

Fig. 3. Average grain size as a function of dwell time for CGO20 undoped (a) and CGO20 doped with 2 cat% cobalt oxide (b). Dashed lines represent the fits with the generalized grain growth law. Solid lines represent the fits with the grain growth model with impediment.

Figs. 2 and 3. Comparing Fig. 2(a) and Fig. 2(b) it is obvious that enhanced grain growth and larger grain sizes of cobalt oxide doped specimen are clearly demonstrated for pure CeO$_2$. This tendency is even more pronounced at high dwell temperatures. This also holds for the CGO20 materials. CoO doping enhances grain growth. For CGO20, a decrease in driving force for grain growth is observed at low temperatures; a limited grain size is already attained after several hours of annealing. At high temperatures, grains still grow significantly even after a dwell time of about 30 h. Hence, highly stable microstructures are found in case of CGO20 and cobalt oxide doped CGO20 at temperatures between 960 and 1100°C.

The data shown in Fig. 2 and Fig. 3 were fitted with three grain growth models presented further above (Eqs. (4), (5), and (8)). The respective fits with the generalized grain growth law (Eq. (5)) and the grain growth law with impediment (Eq. (8)) are plotted in Fig. 2 and Fig. 3 and the grain growth exponents for the generalized grain growth law are summarized in Table 1.

In case of the generalized grain growth law, the exponents $m$ with the highest correlation coefficient were chosen for each dwell temperature (see Table 1). These values of $m$ lie in the range 2–12. In case of CGO20, the exponent $m$ tends to increase for decreasing dwell temperatures. This trend has also been observed in other studies. There are a number of possible reasons why the grain growth exponent $m$ may deviate from the range 2–4. Based on Table 1, it seems obvious to attribute the large values of $m$ to a pore drag in the case of pure CeO$_2$ or to a solute drag in CGO20. However, this con-

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Table 1. Grain Growth Exponents $m$ from fit with the Generalized Grain Growth Law
The correlation coefficients as determined from fitting the data with Eq. (5) and Eq. (8) indicate that the model with impediment in general fits better the presented grain growth data as compared to the parabolic grain growth law, especially for the CGO20 materials at lower temperatures. The minimum correlation coefficient for the model with impediment is 0.97 whereas for the parabolic grain growth law, correlation coefficients as low as 0.94 have been found. This result is not surprising in view of the numerous reasons like pores or solutes that can impede grain growth in the observed microstructures. However, this consideration does not help to explain the observed highly stable microstructures at low temperatures for CGO20 and cobalt oxide doped CGO20.

The grain boundary mobility was calculated for the parabolic grain growth law (Eq. (4)) and for the grain growth law with impediment (Eq. (8)). The grain boundary mobility \( M \) is shown as a function of the reciprocal temperature in Fig. 4. A value of 0.3 J/m\(^2\) was assumed for the grain boundary energy \( \gamma \).

The obtained results for CeO\(_2\) are of the same order of magnitude as the mobility calculated by Chen et al.,\(^{45}\) applying a parabolic growth. Assuming the same value for \( \gamma \), he obtained a mobility of \( M = 3.6 \times 10^{-15} \) m\(^2\)/Ns at 1320°C. In this work, a value of \( M = 1.8 \times 10^{-14} \) m\(^2\)/Ns is found at 1350°C for parabolic grain growth. A mobility of \( M = 2.3 \times 10^{-14} \) m\(^2\)/Ns is obtained from the model with grain growth impediment. The comparison with Chen's data indicates that the mobility data obtained here are reasonable.

The relative grain boundary mobilities of the different materials shown in Fig. 4 are similar for both models (Eq. (4) and Eq. (8)). The grain boundary mobility of CGO20 is roughly three orders of magnitude smaller than that of CeO\(_2\), despite the fact that the mobility of the latter is slowed down by pore drag due to the porosity in the CeO\(_2\) sample. This clearly demonstrates the pronounced effect of the solute Gd in the ceria matrix of the CGO20 solid solution expressed by the defect equation:

\[
\text{Gd}_3\text{O}_5 \rightarrow 2\text{Gd}^{+} + 3\text{O}_2^+ + V_{\text{O}^+} \quad (12)
\]

Dissolved Gd ions are decreasing the boundary mobility by solute drag. This is put in evidence in Fig. 1, showing a microstructure without intragranular pores in CGO20 with much smaller grain size than for pure CeO\(_2\). It is therefore reasonable to assume that the grain boundary mobility is depressed due to the solute drag effect of Gd in CGO20 in line with earlier observations\(^{46}\) and recent results on SnO\(_2\).\(^{29}\)

The effect of the CoO doping in CeO\(_2\) on grain growth can be seen comparing the grain sizes in Figs. 2(a) and (b) for CeO\(_2\), and in Figs. 3(a) and (b) for CGO20.

For both materials, the CoO dopant accelerates grain growth. In case of CoO additions, one has to keep in mind that in contrast to Gd\(_2\)O\(_3\), the CoO has only a negligible solubility in CeO\(_2\) and CGO20\(^{47}\) and the CoO is concentrated in the grain boundaries, as has been reported in a previous study.\(^{13}\) The increased boundary mobility is therefore due to a second phase with cobalt and gadolinium ions in excess in the grain boundaries. Obviously, a boundary layer rich in cobalt oxide acts as a fast diffusion path parallel to the grain boundary thus enhancing shrinkage during sintering. Fast diffusion operates also perpendicular to the grain boundary, promoting grain growth.

A point of particular interest should be noticed. In the mobility data in Fig. 4, the solute drag effect of Gd persists at the boundary independent of the addition of cobalt oxide. It has been shown that the cobalt oxide grain boundary layer is sufficiently thin,\(^{48}\) so that the mass transport across the grain boundaries is not hampered. The same conclusion was drawn in several grain growth studies of zirconia as summarized by Chen.\(^{52}\)

The above considerations elucidate well the very different effects of Gd and CoO dopants on grain growth. However, the origin of the highly stable microstructures found at low temperatures for CGO20 and cobalt oxide doped CGO20 (Fig. 3) needs further considerations. In both materials, pure CeO\(_2\) as well as CGO20 at lower temperatures, a limited grain size after a short dwell time is observed. Significant pore drag is ruled out, at least in the dense CGO20.
Solute drag can also arise from background impurities. Therefore, measures of precaution were taken to avoid introduction of additional impurities. Further, sintered pellets of undoped CGO20 from this work were analyzed by means of laser ablation combined with inductively-coupled mass spectroscopy. The most important impurity found was Si, which amounted to 140 ppm. It can therefore be assumed that both undoped and cobalt oxide doped CGO20 contain an equal amount of silicon and this certainly affects the grain growth behavior. However, impurity adsorption decreases with decreasing grain size, so that the influence of silicon is considered to be marginal at the lowest dwell temperatures, where we observe the self limited grain growth.

Recent results of grain growth studies of nanocrystalline CeO2 thin films has shown a self-limited grain growth behavior at temperatures as low as 700°C due to microstrain similar to findings for SnO2. A limited grain growth behavior has also been reported for nanocrystalline tin oxide by Lai et al. Similar observations have been made in various nanocrystalline metallic systems. It was generally concluded that the traditional grain growth theory can not satisfactorily describe the behavior of nanocrystalline systems. All systems, where a self-limited grain growth behavior has been reported, have in common that the average grain size lies in the nanometer range and in some cases amorphous to crystalline transitions accompanied grain growth. The above results therefore suggest that the herein investigated dwell temperatures of CGO20 lie in a range of transition between regular grain growth at high temperature in the micrometer range and self-limited grain growth at low temperature in the nanometer range. Chen already suggested earlier that there might be additional steps involved in grain boundary migration at low temperatures. He further argued that grain growth is impeded because these steps require higher temperatures to be activated. As an example of such steps, he mentioned the movement of nodal points or nodal lines on the grain boundaries. Four-grain junctions, pore-grain boundary junctions, or three-grain junctions are examples of such nodal points and lines. The approach of Gottstein and Shvidlerman, as mentioned further above, takes into account the dynamics of nodal points and lines in grain growth of polycrystalline materials. By assigning a limited mobility to the grain boundary triple and quadruple junctions, they were able to show that the grain boundaries are effectively pinned by nodal points and lines. The approach of Gottstein and Shvidlerman further takes into account that grain growth behavior is grain size dependent. By comparing the efficiency of the different drag mechanisms, Shvidlerman and coworkers reasoned that triple junctions indeed exert a powerful retarding force on to grain growth in nanocrystalline materials. However, the drag of triple points on grain boundary mobility in their case was always demonstrated in extremely pure materials without any solutes or a grain boundary phase as in our case.

Self-limited grain growth has also been explained by structural relaxation processes of the interfaces in oxides. Similar to the approach of Gottstein and Shvidlerman, the importance of relaxation processes of interfaces increases with decreasing grain size. Assuming amorphous grain boundary material in this case, we might use Eq. (11) to model our results for the low temperature experiments. By fitting the grain growth data of undoped and cobalt oxide doped CGO20 with Eq. (11), it becomes obvious that the data for annealing temperatures between 960 and 1100°C yield good correlation coefficients. It can therefore be assumed that relaxation of interfaces are indeed of major importance in the grain growth behavior of nanoscaled sintered ceramic powders such as the CGO20 in this study similar to the data of the grain growth study of nanocrystalline CGO20 from the amorphous state. We therefore attribute the self limited grain growth behavior of CGO20 for low temperatures to microstrain in the grain boundaries as also observed in nanocrystalline doped SnO2.

5. Conclusion

Isothermal grain growth experiments have been conducted for undoped and cobalt oxide doped CeO2 and Ce0.8Gd0.2O1.9 (CGO20) and subsequently analyzed with four different grain growth models. The grain growth data could not satisfactorily be fitted with the generalized grain growth law since high values of the grain growth exponent, which are inconsistent with physical models, were found. The parabolic grain growth law for higher temperatures turned out to be the models which described best the data on hand. The grain growth law with impediment and that one taking relaxation processes into account, such as amorphous to crystalline transition of grain boundaries, fit the data at low temperatures the best.

The grain boundary mobility of CGO20 was found to be three orders of magnitude lower than the one of CeO2 due to solute drag exerted by the dissolved gadolinium ions. An accelerating effect of cobalt oxide in the grain boundaries on the grain growth rate is clearly demonstrated for CeO2 and CGO20. For the latter, the effect is more pronounced. Disordered grain boundary layers containing cobalt and gadolinium ions that enhances diffusion parallel and perpendicular to the boundary is conjectured to account for the increased grain growth rate in CeO2 and CGO20 doped with CoO. Highly stable microstructures with almost no grain growth have been observed for undoped and cobalt oxide doped CGO20 at lower temperatures. Grain growth was observed for short times followed by a limited grain size that is reached after a short dwell time. The attainment of a limiting grain size is typically observed in nanocrystalline metal and ceramic materials and is suggested here to be related to relaxation processes in the grain boundaries, similar to that one observed when transforming amorphous CGO thin films to crystalline ones. The measured grain growth data of undoped and cobalt oxide doped CGO20 describe the transition from regular grain growth at high temperatures of grains in the microcrystalline range to self-limited grain growth at lower temperatures with grains in the nanometer range and disordered grain boundaries.

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