Grain growth in NiO-MgO and its dependence on faceting and the equilibrium crystal shape

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Abstract

The impact of faceting on grain growth was approached by model experiments in NiO-MgO. Grain growth rates were found to be 10 times higher in NiO compared to MgO. As the self-diffusion coefficients differ by a factor of 250, grain growth in NiO is unexpectedly slow compared to MgO. Recently, the movement of steps was identified as the atomic mechanism of grain boundary migration. According to the equilibrium crystal shape, grain boundaries in NiO are more facetted. The facetted grain boundaries of NiO have fewer steps at the grain boundaries resulting in a relatively lower mobility.

Key words

Grain growth; faceting; disconnections; NiO-MgO; steps

From a mean field perspective, the migration rate V of a grain boundary is the product of the grain boundary mobility m and driving force P:

$$V = m \cdot P \qquad 1$$

If the driving force is assumed to originate from grain boundary curvature, the well-known rate equation for grain growth is obtained:

$$G^2 - G_{t=0}^2 = 2\alpha m\gamma \cdot t = k \cdot t \qquad 2$$

with the grain diameter G, the time t, a geometric constant α, the grain boundary energy γ the grain growth coefficient $k = 2\alpha m\gamma$ [1]. Classically, the grain boundary mobility was related to a diffusion process of atoms jumping across grain boundaries as resembled by the equation

$$m = \frac{D}{k_B \cdot T} \cdot \left(\frac{\Omega}{\delta_{\mathrm{GB}}}\right) \qquad 3$$

with the Boltzmann constant k_B, the temperature T, the molecular volume Ω, the grain boundary thickness δ_{GB} and a diffusion coefficient D.

The understanding of the mechanism of grain boundary motion has evolved considerably due to advances in electron microscopy. Steps and dislocations (‘disconnections’) were identified to be the atomistic element of grain boundary motion in recent work [2-6]. In this framework, a grain grows by attaching atoms from the lattice of the shrinking grain to the lattice of the growing grain. This attachment preferably occurs at steps resulting in the movement of steps along the interface [6]. As such it is apparent that a relationship between the characteristics of steps at the grain boundaries and their migration behavior exists. For example, the number of steps per unit area will change the number of preferable sites for atom attachment and, as such, can dominate the macroscopic migration rate of this interface.

The structure of grain boundaries on the atomic level contains steps to accommodate the lattices of the adjacent crystals and the curvature of the interface. It was reported that the atomistic step planes agree well with the equilibrium crystal shape obtained from macroscopic investigations [3, 4]. However, due to the geometric restrictions this might only apply to one lattice of the grain boundary (the one that is closest to a low energy orientation); the other lattice is forced to form steps of higher index orientations [7]. Still, this infers that the macroscopic equilibrium crystal shape can be used directly to at least partially predict the atomistic structure of steps at grain boundaries as the atomistic stepping follows the same rationale as macroscopic faceting [8, 9].

Determining the impact of step densities and faceting on grain growth requires control of the interfacial anisotropy (i.e. the equilibrium crystal shape). Suitable model experiments are difficult, as a material system is needed where only the interface anisotropy can be changed without changing other properties significantly. Considerable effort was done in perovskite systems, where the atmosphere and doping can be used to tailor the anisotropy of the system [10-13]. In these studies, slower migration of facetted compared to non-facetted interfaces was reported for strontium titanate [12, 15, 27, 28], while the opposite was found for barium titanate [10, 26]. However, in some cases a second phase was present and undergoes a wetting transition with changes in the oxygen partial pressure [14, 15]. Accordingly, the impact of faceting on grain growth could not clearly be isolated in these studies.

The system NiO-MgO is a model system as there is a complete solid solution and Ni^{+2} and Mg^{+2} have similar radii. Thus, there is no electrostatic or strain energy as the stoichiometry varies [16]. The equilibrium crystal shape is fully facetted <111> for NiO and less facetted as the MgO content is increased [17, 18]. Accordingly, the system NiO-MgO is well-suited for model experiments on the impact of faceting on grain growth kinetics.

To produce NiO-MgO solid solution powders, modifications were made to the process developed by Marcilly et al. [19]. Powder mixtures containing $Ni(NO_3)_2 \bullet 6H_2O$ (Sigma Aldrich, No. 244074) and $Mg(NO_3)_2 \bullet 6H_2O$ (Sigma Aldrich, No. 237175) were processed. Citric acid was used as the polyfunctional organic acid with an equal molar concentration to the combined Ni and Mg metallic cations. The powder mixture was melted and dehydrated in a vacuum rotary evaporator (70°C, 0.7 kPa). After dehydration, the melt was cooled, forming a foam structure. A two-step calcination process was developed [16, 20, 21]. The foam was heated (5°C/min) and held at 170°C for 1 hour to complete dehydration and activate the polyfunctional acid. The foam was then heated and held at 500°C for 3h to complete the calcination. Powders were characterized using X-ray diffraction determining homogeneity and crystallite size using Scherrer's equation [22]. Grain growth was measured on large multigrain, multilayer agglomerates at various temperatures and times. The average grain size was measured by SEM using the line intercept method across multiple agglomerates for each sample. At least 100 grains were counted.

XRD analysis of the five base powders showed phase purity and the expected increase of the lattice parameter with increasing Mg concentration as shown (Figure 1). The powder crystallite sizes in Table 1 were calculated using Scherrer's equation and show a slight increase with increasing Ni content. NiO-MgO powders produced by the amorphous citrate method resulted in the formation of hard agglomerates. The primary crystallite size calculated from Scherrer equation ranged from 244-396nm. Hard agglomerates in base powders range from 20-300µm in size, Figure 2a. The hard agglomerates were fully dense and consisted of multiple layers of grains as visible in Figure 2b. Densification of the powder was very poor for conventional sintering, hot pressing and SPS even with additional milling. As such, grain growth studies reported in this paper were carried out on large agglomerates. Agglomerates selected for this study were larger than 50µm in size and more than 1µm thick to ensure multiple grain layers were present initially.

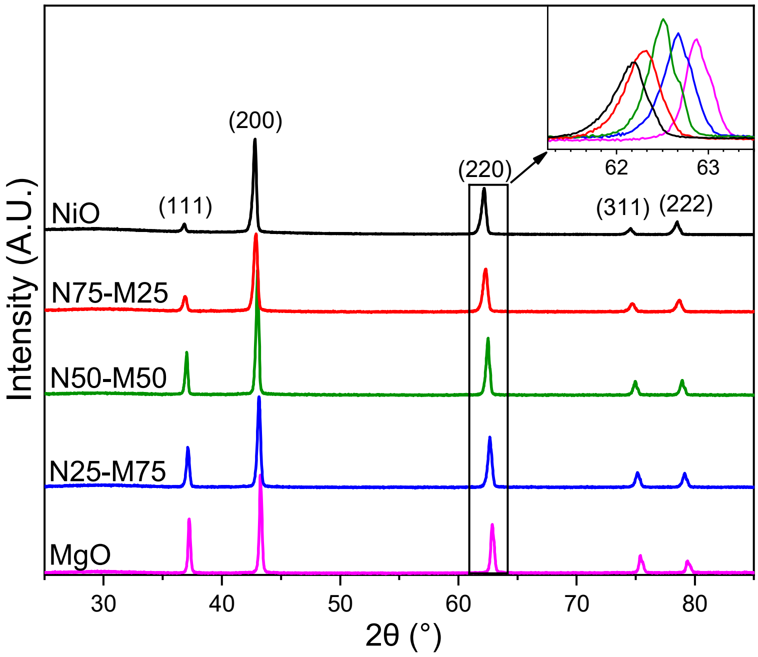

Figure 1 X-ray diffraction patterns of all five compositions of NiO-MgO. The inset shows a magnification of the (220) peak.

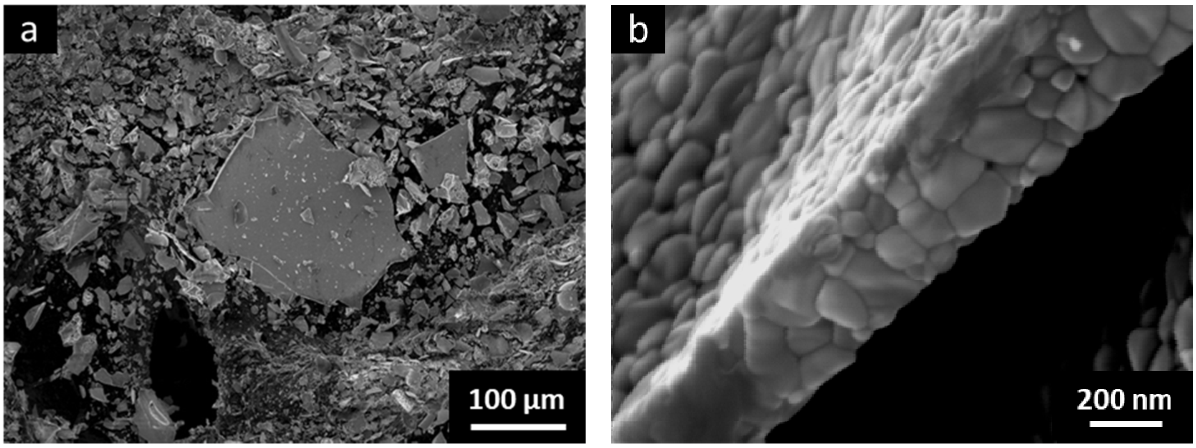

Figure 2 Exemplary SEM micrograph of large agglomerates forming from amorphous citrate process with sizes greater than 100µm for N75:M25 at low (a) and high (b) magnification. The other compositions are comparable.

Average grain size was measured for five compositions after heating to 1000°C, 1250°C, and 1500°C with no hold (Figure 3a). Significant grain growth occurs for all compositions with increasing grain sizes with increasing Ni concentration. Figure 3b shows the grain size evolution during isothermal hold at 1500°C. Parabolic grain growth according to the standard grain growth law (Eqn. 2) occurred. The grain growth coefficients obtained by fitting Eqn. 2 to the mean grain size are shown in Table 1. Representative microstructures at different temperatures are shown in Figure 4. As grain sizes reach several µm and the agglomerate thickness is in the order of 1µm, the agglomerates evolved to a monolayer of grains during grain growth.

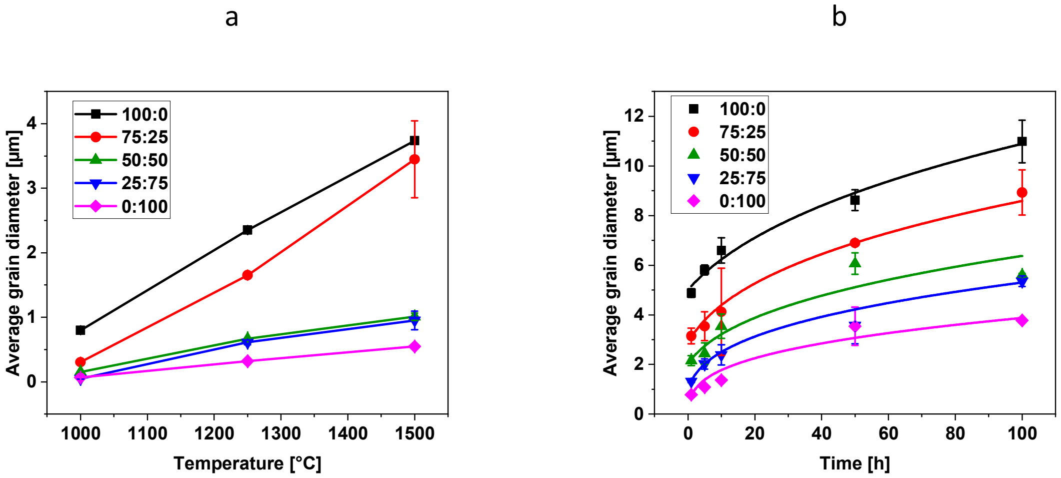

Figure 3 Temperature dependence of average grain size from 1000°C to 1500°C (a) and grain growth kinetics at 1500°C (b).

Table 1 Calculated Scherrer crystallite size and grain growth rates for NiO-MgO solid solutions.

Composition (Ni:Mg)	Crystallite size [nm]	k [µm^2/s]
100:0	396	0.01632
75:25	350	0.01175
50:50	370	0.00448
25:75	280	0.00454
0:100	244	0.00229

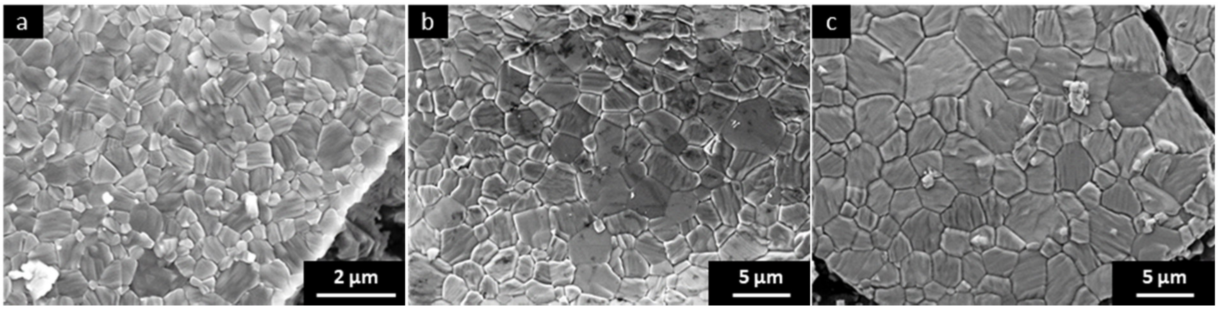

Figure 4 SEM micrographs of 75:25 NiO-MgO samples after heating to 1000°C (a), 1250°C (b) and 1500°C (c).

According to Table 1, the grain growth coefficients of NiO is larger by about 10 compared to MgO. However, these two grain growth coefficients are not directly comparable. In general, the grain growth rates are correlated to a diffusion process. In this regard, the grain growth coefficients need to be interpreted considering the changing diffusion coefficients of these two materials. Certainly, this correlation is not as straight-forward as the classic mean-field modelling suggests, where the diffusion coefficient D is included in the grain boundary mobility as shown in Eqn. 3. The rationale is that grain growth involves atoms jumping across boundaries and a grain boundary diffusion coefficient could be used to predict the migration rate of a grain boundary. However, this relationship does not account for the atomistic mechanism by which interfaces move in solids, i.e. the movement of steps and dislocations along the grain boundary [2-6]. The migration rate of a boundary is probably related to the type and number of steps at the interface. Still, the transition of an atom from one lattice to another can be understood as a diffusion process, where the bond configuration of individual atoms changes by breaking bonds to the shrinking lattice and forming bonds to the growing lattice. This process might include some migration to a suitable lattice site on the growing lattice, i.e. a step. As such, a correlation to a diffusion process still exists. Accordingly, it is assumed that the grain growth rate in NiO and MgO is correlated to atomic diffusion.

To compare the grain growth coefficients reported in this study, suitable diffusion coefficients are needed. Grain boundary diffusion data is not available for NiO and MgO. The best available data are the bulk self-diffusion coefficients, which are 1.5×10^{-9}cm²/sec for NiO and 5.8×10^{-12}cm²/sec at 1500°C [23, 24]. These coefficients are not a good approximation for the diffusion during grain growth, as diffusion processes are much faster at grain boundaries compared to the bulk. However, the ratio of these two diffusion coefficients draws a picture of the expected difference of the grain boundary diffusion: bulk diffusion in NiO is faster by a factor of 250 compared to NiO.

The ratio of grain growth rates for NiO and MgO is 10 (Table 1). This is much less than the ratio of diffusion coefficients of 250. Accordingly, the grain growth coefficients of NiO and MgO are much closer to each other than expected by the respective self-diffusion coefficients, i.e., the grain growth rate in NiO is unexpectedly slow compared to MgO.

The reasons for this behavior are not obvious. First, the experimental setup needs to be considered. Whenever grain growth on surfaces is considered, the occurrence of grain boundary grooves can interfere with grain boundary migration as the grooves might need to diffuse along with the migrating interfaces (or break away from it). In general, it is assumed that grain boundaries are pinned or at least retarded if they intersect the surface [25]. However, the grain size evolution in Fig. 5 does not show any evidence for a complete pinning, and as all experiments were performed with the same setup, it is assumed that if a retarding effect on grain boundary migration occurs, it does not bias the grain growth coefficients presented in Table 1, although they can be lower than those obtained on bulk specimen (notice that it was not possible to obtain bulk specimen as described earlier). In addition, the driving force for grain growth is different if the grain intersects the surface, but again this should not result in a bias as the experimental setup was the same for all compositions. Accordingly, the reason for the unexpected slow grain growth behavior of NiO compared to MgO probably does not relate to the experimental setup.

Potential sources of retarding effects on grain boundary migration are solute drag and Zener pinning. However, the powders used in this study were phase-pure according to the XRD results in Fig. 1 and no evidence for second phase particles were observed by SEM. Accordingly, Zener pinning and particle drag are unlikely to occur. Solute drag by intrinsic point defects is not relevant as Ni and Mg have a very similar size and the same charge and, thus, will have only very weak (if any) tendency to segregate. A segregation of extrinsic defects (i.e. impurities) cannot be excluded. However, as the powders were not mechanically milled, impurity levels are low and arise only from the starting chemicals.

Another potential source is a change of the grain boundary anisotropy and faceting. It is well-known that the equilibrium crystal shape of NiO is fully facetted with <111> facets while MgO is at least partially non-facetted and shows weak <100> faceting [17, 18]. As the grain boundary energy is closely linked to the surface energy, a similar relationship holds for the faceting behavior of grain boundaries, i.e., the grain boundaries in NiO are more facetted than those in MgO.

Recent work in the field of the mechanism of grain boundary migration in ceramics in the absence of grain boundary films and adsorption has underlined the importance of steps and dislocations ('disconnections') at grain boundaries [2, 3, 6]. It is hypothesized that grain boundaries move by the migration of steps and dislocations. As such, the step density will have a crucial impact on grain boundary migration. A facetted grain boundary has a significantly lower step density than a non-facetted one as large atomically flat planes occur on the grain boundary. Based on the disconnection theory, such a grain boundary is expected to have a lower migration rate as it has less steps as potential sinks for the attachment of atoms. This agrees well with the grain growth behavior observed in NiO-MgO.

Overall, the system NiO-MgO represents a promising system for evaluating the relationship between atomistic steps and faceting and grain growth. The unexpectedly slow grain growth rate of NiO seems to be caused by grain boundary faceting and, thereby, by a lower number of steps at the interfaces. To confirm this relationship, a detailed TEM analysis of the stepping properties of grain boundaries with respect to the Ni:Mg ration is needed.

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