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# Preparation of polycrystalline nickel oxide for diffusion studies

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Grain-boundary diffusion experiments in doped NiO specimens require fully dense, fine-grained specimens free from unknown residual impurities, but the preparation of such specimens encounters problems in reducing porosity to sufficiently low levels and in ensuring good bonding and freedom from contamination at the boundaries. Ceramic processing techniques have been investigated experimentally in relation to these factors and it is concluded that suitable high density may be obtained using careful control of processing parameters and of factors such as powder particle size, but that the resultant specimens will not be much use unless particular effort is directed to elimination of the minute traces of insoluble impurity that clog up the boundaries and control their character. Preparation of pure boundaries that exhibit intrinsic behaviour is highlighted as a major materials problem in grain-boundary studies.

## 1. Introduction

Low-temperature oxidation of a metal surface proceeds by transport of reactants through the oxide layer that otherwise protects that surface. It occurs in many metals, but detailed explanation of the changes that take place has been largely based on observations of the nickel–nickel oxide system, in which it has been found that oxidation rates below about half the absolute melting temperature of the oxide are controlled by grain-boundary diffusion [1]. In order to limit the ravages of oxidation, therefore, it is necessary to slow down this diffusion, and the most direct way of finding how to do this is to extend measurements of grain-boundary diffusion in pure nickel oxide [2] to specimens containing impurities that can block such diffusion. An immediate problem, however, is that the technique used to prepare specimens of pure nickel oxide, oxidation of nickel foil [2], is not readily adapted to preparation of specimens that incorporate impurities, while alternative fabrication methods appear unable to produce the type of specimen needed in a diffusion experiment.

The need for specimens, coupled with uncertainty as to why fabrication has proved difficult, provided impetus for a survey of appropriate ceramic processing techniques. The present work, therefore, consists of experimental observations on the application of such techniques to the preparation of polycrystalline nickel oxide diffusion specimens, plus a report of progress that has allowed autoradiography experiments to be carried out. A difference in grain-boundary diffusion was observed between ceramic and oxidized foil specimens, but it could not be directly linked to any readily measurable property of the specimens.

## 2. Specification of specimens

Grain-boundary diffusion can be observed in either polycrystal or bicrystal specimens, but since boundaries in NiO bicrystals are atypical, owing to excess contamination by residual impurity [3], only polycrystalline specimens will be considered here. A sectioning experiment requires a grain size that is sufficiently small to allow the tracer that enters the boundaries to be readily detected, but not so small that diffusion across many grains smears out all evidence of the boundaries as separate entities. A grain size of about 10 $\mu$m is appropriate [2]. A sectioning experiment also requires the specimen to be free from porosity, since residual pores connected to the surface collect spurious tracer that overwhelms the distribution of tracer in the boundaries. The specimen, therefore, needs to be fully dense.

Because the influence of a specific impurity can be investigated only when other impurities are absent, a primary objective is the preparation of clean grain boundaries free from unwanted impurities. A doped specimen may be obtained subsequently by adding a small quantity of known impurity to clean matrix material. To ensure homogeneity of doping, however, the initial oxide powder should have the same composition as the intended final specimen, a condition achieved in practice by freeze drying a starting solution of appropriate composition [4]. Since freeze drying operates most conveniently with aqueous solutions, the starting nickel salts for preparation of oxide need to be water soluble.

## 3. Materials processing

### 3.1. General details

The three processing stages needed to convert ceramic powder to dense solid – powder preparation, compacting and firing – are closely interrelated in that choice of processing treatment for one stage affects behaviour in the others. Since optimum results can be

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obtained only by a careful balance between competing mechanisms [5], the observations presented here are necessarily heuristic.

Firing the ceramic not only results in densification but also in grain growth, and this must be held in check when small grain size is required. Additives to check grain growth at high temperature cannot be used when specimens need to be free of unwanted impurity, and it is thus necessary to fire at temperatures below those that cause rapid grain growth. For this reason the technique of hot pressing, which subjects specimens to lower temperatures for shorter times than normal firing, needs particular attention.

### 3.2. Hot pressing

Dies and rams of graphite reduced nickel oxide to metallic nickel, and it was therefore necessary to use alumina, which is more expensive and more prone to failure. A reaction between alumina die and pellet was an early cause of die failure, but this was overcome by embedding the pellet in protective powder, though it was necessary to choose a powder that was both physically and chemically inert. Boron nitride, for example, chosen for its self-lubrication properties and resistance to sintering, was found not only to reduce nickel oxide to nickel but also, on account of low thermal expansion, to prevent removal of the pellet after cooling. Best protection was provided by alumina powder, since the reaction with nickel oxide could then be prevented from reaching the die, while the reacted surface of the pellet could be removed by grinding.

Gas entrapment was encountered in cylindrical pellets hot pressed at temperatures up to 1200° C. Reduction of the oxide cause high-pressure $CO$–$CO_2$ gas to be produced in internal pores, leading to bloating of the pellet during subsequent heat treatment, but even when reduction was absent the grain boundaries were sufficiently weak for grain pull-out to be prevalent during subsequent surface polishing. Incomplete grain bonding has been noted as characteristic of pressure densification in both hot-pressed [6] and hot-isostatically pressed [7] nickel oxide. Hot pressing at 25 MPa left a large pore content, but even at much higher pressures [6] hot pressing has failed to eliminate either residual porosity or weakness of boundaries. It was concluded that specimens plastically squeezed by external force were likely to be imperfectly aggregated and that it was necessary to investigate the greater surface activity obtainable at the higher temperatures used in sintering.

## 4. Sintering

### 4.1. Material for powder preparation

The water-soluble salts, nickel nitrate hexahydrate and nickel sulphate heptahydrate, were used to prepare oxide powder. Nickel nitrate decomposes to nickel oxide at much lower temperature (340° C) than nickel sulphate (848° C), and since sintered density is usually improved by calcining at a low rather than a high temperature [8, 9], it might be expected that nickel nitrate would provide the better material. Experiment showed otherwise. Densities with nitrate-derived powder were consistently some 10% below those with oxide derived from sulphate. This poor performance was attributed to melting of the nitrate salt, followed by evaporation below decomposition temperature to a cemented mass that converted to poor sintering stock.

Densities from oxide derived from nickel oxalate were similar to those from sulphate, while densities with powder from nickel hydroxide were somewhat lower, but since neither of these two starting salts were soluble in water, investigation was concentrated on powder from sulphate.

### 4.2. Procedure

Oxide from sulphate was compacted by uniaxial cold pressing to cylindrical pellets, 2 g mass and 15 mm diameter, that were sintered under oxygen. Specimen densities, determined by measurement of weight and dimensions, were obtained as a percentage of theoretical density, taken to be $6.8 \times 10^3\,\mathrm{kg\,m^{-3}}$. Preparation treatment was varied in order to seek maximum density, a successful sinter being one that gave suitable grain size and high density. Grain size was not, in fact, a problem, since the mean size of 15 $\mu$m obtained after firing for 20 h at 1400° C increased to only 20 $\mu$m at 1500° C, both sizes being acceptable. Although grain growth has been reported as rapid at 1500° C [10], no evidence was found of pores stranded within grains as a result of boundary migration.

Raising the firing temperature from 1400 to 1450° C increased density by more than 1%, but a further raise in temperature to 1500° C added little extra to density. In principle, maximum density is obtained by sintering a powder of fine equi-sized particles that has been compacted to uniform green density [11], but in practice only a crude approximation to this condition is reached, an approximation obtained only by experimental investigation of all the factors involved.

### 4.3. Compacting

The effect of compacting pressure, $P$, on specimen density, $\varrho$, was obtained by expressing the density as a product $\varrho = \varrho_d \varrho_A$, where the axial density $\varrho_d = m^{1/3}/d$ and the radial density $\varrho_A = 4m^{2/3}/\pi D^2$ were given in terms of the thickness, $d$, and diameter, $D$, of the final sintered pellet of mass $m$, and plotting $\varrho_d$ and $\varrho_A$ against $P$ to show the relative changes in axial and radial shrinkage. Such plots, of which Fig. 1 is an example, showed that maximum density occurred at intermediate values of $\varrho_d$ and $\varrho_A$ that corresponded to optimum compaction. The optimum value of $P$ varied with the state of the powder, being lower for a fine powder than for a granular overcalcined one. An additional observation was that when powders were subjected to the same compacting pressure, $P$, larger values of $\varrho_d$ (and smaller $\varrho_A$) were associated with finer powder.

It was necessary to avoid very fine powder since the large displacement of the ram needed for compaction produced concave pellets containing cracks near the rim as a consequence of non-uniform compaction [5]. Such defects could be mitigated by incorporation of binder, but only at the expense of a distribution of fine

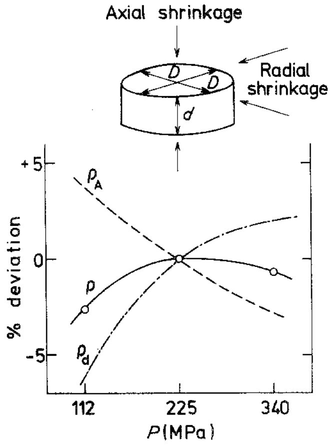

*Figure 1* Variation of the axial ($\varrho_d$) and radial ($\varrho_A$) contributions to density, $\varrho$, as a function of compacting pressure, $P$, for nickel sulphate calcined for 20 h at 925° C and sintered for 20 h at 1400° C. Curves give percentage deviation from value at $P$ = 225 MPa.

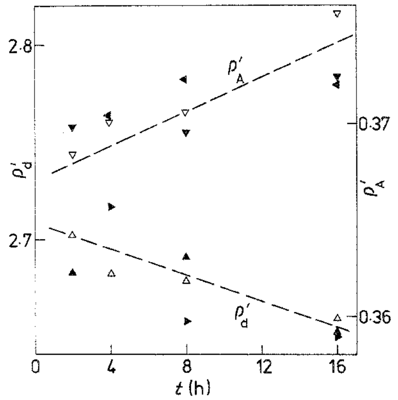

*Figure 3* Variation in axial and radial shrinkage with calcining time, $t$, indicating deterioration in calcined powder quality. Calcining temperature: (△, ▲, ▽, ▼) 920° C, (◀, ▶) 890° C. Sintering temperature: (△, ▽) 1400° C, (▲, ▼, ◀, ▶) 1450° C. Compacting pressure: 225 MPa.

blowholes, developed during burning off of the binder, that could not be eliminated. An attempt to obtain more uniform compaction by use of cold-isostatic pressing gave little improvement in density, and hence most investigation continued to use uniaxial compaction.

A plot entirely similar to Fig. 1 was obtained when oxide was calcined from nickel oxalate, though with slightly different values of $\varrho_d$ and $\varrho_A$ that attested to the different physical character of the presintered powder.

### 4.4. Calcining

Changes produced by calcining treatment were examined by use of normalized values of axial and radial shrinkage, $\varrho'_d = \varrho_d/\varrho^{1/3}$ and $\varrho'_A = \varrho_A/\varrho^{2/3}$, where $\varrho'_d\varrho'_A = 1$, since this allowed results at different sintering temperatures to be incorporated on the same plot. Fig. 2 shows that optimum calcining temperature was near 925° C and that values of $\varrho'_d$ and $\varrho'_A$ diverge at higher temperatures.

The usual procedure for obtaining active powder free of aggregates is to calcine not too far above decomposition temperature [9, 11], though the overactive powder obtained when too close to decomposition is of poor quality [5], as witness the downturn in density below 920° C in Fig. 2. An attempt to improve quality at low temperatures by increasing calcining time appeared at first to make things worse, since density was observed to decrease, accompanied by the divergence in axial and radial shrinkage shown in Fig. 3, which indicated that conditions were moving away from the optimum. Improvement in density required an increase in calcining time to at least 20 h. The deterioration in density was obtained when powder colour was grey or grey speckled with green and when sintered pellets were a mottled grey–green, whereas well-calcined powders were light olive green and sintered under oxygen to uniform blackness. The deterioration thus appears to be due to inhomogeneous stoichiometry produced by the calcining. Calcining for 20 h at 925° C ultimately yielded a density of 96%.

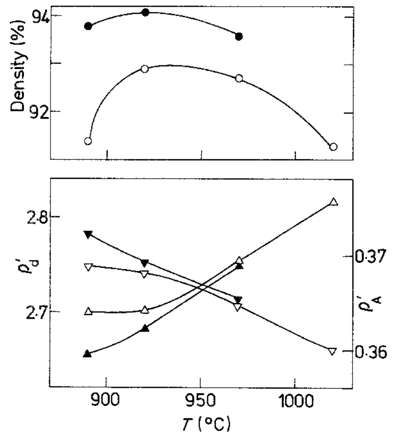

*Figure 2* Variation of density, $\varrho$ (○, ●), radial component $\varrho'_A$ (△, ▲), and axial component $\varrho'_d$ (▽, ▼) with calcining temperature $T$ for nickel sulphate calcined 2 h at each temperature and compacted at 225 MPa. Sintering temperature: (○, △, ▽) 1400° C, (●, ▲, ▼) 1450° C.

### 4.5. Freeze drying

Sintering was easier with freeze-dried powders obtained from aqueous nickel sulphate solution. Small frozen spheres, obtained by spraying a fine jet of the solution into a chilled liquid immiscible with water, were collected and sublimed under a vacuum kept below the cryohydric point [4]. For rapid freezing, a liquid such as hexane, with a density below that of the solution, was needed. During sublimation, which lasted many hours and required application of heat during later stages, the spheres of green ice transformed to friable yellow balls of almost anhydrous powder as the molecular content of the sulphate was reduced from $7H_2O$ to about $0.15H_2O$. These yellow balls readily converted to free-flowing spheres of oxide.

Freeze-dried powder calcined for 10 h at 925° C and cold pressed at 225 MPa sintered to a density, $\varrho$, of 97%, with a low value of 2.67 for $\varrho'_d$ which indicated that compaction had not been optimized and that higher ultimate density was possible.

## 5. Assessment

### 5.1. Particle size

An ideal powder for sintering consists of equi-sized particles separated by equi-sized pores that all shrink

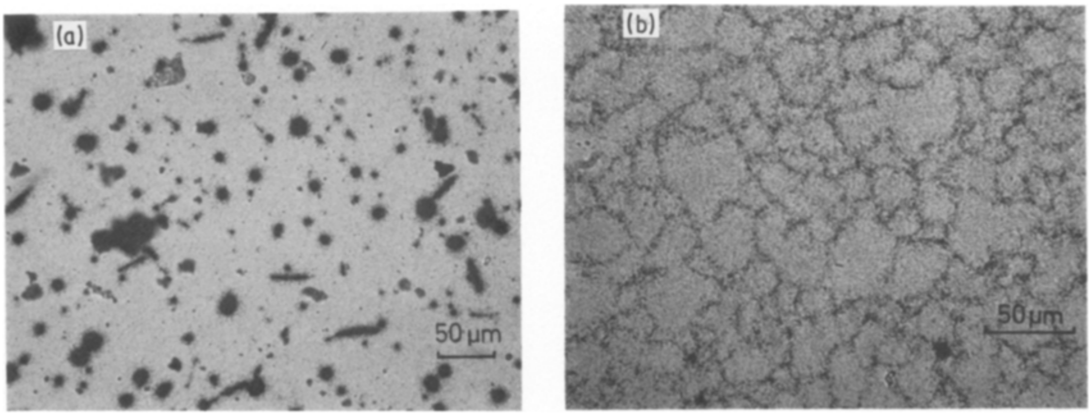

*Figure 4* Autoradiographs after diffusion for 2 h at 700° C. (a) Ceramic specimen of 97% theoretical density, (b) oxidized foil specimen.

at the same rate to a completely dense specimen. The smaller the particles the faster the sintering rate [11], but since fine particles have poor pressing characteristics [5] it is advisable to calcine some crispness into the powder, even though this is likely to introduce agglomerates that are the prime source of voids in a sintered pellet [8]. To determine the extent to which this occurred in nickel oxide a particle-size analysis was carried out on powder calcined at 925° C to yield maximum density.

The analysed powder consisted of clumps of average size 0.3 $\mu$m made up of smaller particles approximately 0.02 $\mu$m in size, as determined by X-ray line broadening, with some additional large agglomerates 3 to 5 $\mu$m in size. Consolidation was, therefore, mainly a two-stage process within and between clumps, but with some disruption to densification arising from differential shrinkage between the large agglomerates and the remainder of the powder. Some preliminary ball-milling experiments to break up these agglomerates were largely ineffective, leading to an improvement in density over unmilled powder of only $\sim 0.2\%$.

### 5.2. Porosity

The microstructure observed after sintering at 1450° C contained some irregularity in grain size, the variation extending from regions containing predominantly small grains 3 to 5 $\mu$m in size to regions made up almost entirely of grains 30 $\mu$m in size. Pores were observed on some grain boundaries, mostly at triple points, and mostly in small grain regions. Post-sintering anneals at 100° C above sintering temperature for at least 16 h made little change in either pore distribution or grain size, but some surface filling [12] was observed. Measurements on pellets thinned by grinding showed that surface density was usually higher than in the bulk.

Apart from the occasional crack, the observed microstructure was in accordance with that expected from the observed distribution of particle sizes. In particular, the concentration of pores around small grains 3 to 5 $\mu$m in size may be attributed to agglomerates that sintered with very little grain growth. This is an indication of boundary stability, a characteristic also evident in the absence of grain growth during post-sintering anneals, and points to the presence of some factor inhibiting boundary motion.

### 5.3. Autoradiography

A density of 97% was considered sufficient for assessment of grain-boundary diffusion by high-resolution autoradiography, using low-energy beta radiation from $^{63}$Ni tracer. Surfaces for autoradiography were cleaned and flattened by surface sputtering, preannealed in oxygen at 700° C to establish specimen equilibrium, given a thin coating of $^{63}$Ni evaporated from dried nickel salt solution, and then subjected to a 2 h diffusion annealed at 700° C. In oxidized foil at this temperature grain-boundary diffusion was dominant at a penetration depth of 1 $\mu$m [2], and hence a layer this thick was removed from the ceramic specimen by sputtering before the surface was placed in contact with Kodak AR10 emulsion and left for two weeks.

The result, compared in Fig. 4 with an autoradiograph at the same depth in an oxidized foil specimen after an identical diffusion anneal, shows an almost complete absence of grain-boundary diffusion and negligible other tracer structure. By contrast with the foil specimen, in which the few small holes have an irregular fissured shape caused by boundary degradation [13], the circularly shaped pores in the ceramic specimen appear quite unrelated to substructure, even though they are known to be sited on boundaries and at triple points. Some of the long thin pores resemble boundaries, though of a different kind from the irregularly shaped boundaries in Fig. 4b, but tracer is present inside these pores only because it has been evaporated between separated surfaces. Tracer was never observed within bonded surfaces, and hence boundaries formed by sintering of oxide powder behave differently from those formed in oxidized polycrystalline metal.

### 5.4. Boundary impurity

Since segregated impurity might account for the lack of both diffusion and mobility in ceramic boundaries [3], mass spectroscopy was carried out on both the nickel sulphate starting salt and the calcined NiO powder, but the results served mainly to demonstrate high purity, since the only detected trace impurities common to both materials were manganese and silicon. X-ray photoelectron spectroscopy (XPS) of the fracture surface of a sintered pellet, ruptured approximately along a diametral plane, confirmed the presence of silicon, at the low fractional concentration of $10^{-4}$

in a surface layer 3 mm thick, and also revealed the presence of tin, but failed to detect other impurities. Silicon is a suspect impurity because its lack of solubility in the nickel oxide lattice causes it to collect on particle surfaces and to remain on grain boundaries in the final sintered specimen.

## 6. Discussion

Diffusion along a grain boundary at 700° C in oxidized nickel foil takes place by movement of nickel vacancies within a narrow width of 0.7 nm [2]. Such a mechanism fails to operate in ceramic specimens, and in order to provide guidance for further investigation it is helpful to put forward suggestions as to why this should be so. The most plausible is that diffusion along a narrow boundary pathway that is little bigger than the lattice spacing may easily be blocked by insoluble impurity that is unable to disperse into the adjacent lattice.

Active powders that sinter well also attract impurity [14], and adsorbed impurity tends to stabilize surface structure, as has been directly demonstrated for sodium chloride surfaces exposed to air and heated to 0.6 absolute melting temperature [15]. Stability arises because impurity is adsorbed at kink and step sites, which are thereby immobilized, and an inevitable consequence of an immobile surface is an absence of surface diffusion, which normally proceeds along step sites. Sintering of such surfaces embeds these impurities in defect sites on the boundary, where they impede boundary diffusion. Thus, a boundary of $n^2$ cation sites may, to first approximation, be effectively blocked by no more than $n$ impurity ions. A monolayer of impurity on all boundaries between $10\,\mu$m grains would be undetectable by bulk analysis, and the smaller concentrations effective in clogging boundaries would be even more elusive. Low values of boundary impurity are also suggested by the measurements made of silicon by XPS, which indicate that surface concentrations encountered in practice may be no more than 1 impurity ion per 25 cation boundary sites.

Soluble impurities which are mobile within the specimen do not cause problems and, when used as additives, are capable of assisting the sintering process. Insoluble impurities, by contrast, are trapped within the boundary and contribute to boundary weakness through impaired bonding, while at the same time acting as obstacles to boundary migration. A meagre amount of contaminant may thus account for the behaviour of ceramic grain boundaries.

The one possible contaminant that has been identified is silicon, which is presumably attracted during processing by the negative charge on NiO surfaces containing excess oxygen ions [16] to form $SiO_2$ precursors. There is evidence that contamination by calcium and silicon oxides, observed directly as second-phase precipitates, severely inhibit grain-boundary diffusion in NiO [3]. One consequence of a high-level anneal may be the precipitation of aggregated impurity at boundary defects such as facets, where the disorder associated with incoherent boundaries between second-phase particles and matrix crystal may allow limited diffusion along discrete grain-boundary pipelines, as observed in alkali halides [17]. Some of the black spots in Fig. 4a may represent such pipelines and thus give an inchoate indication of where boundaries are located.

The deficiencies caused by insoluble impurities in ceramic specimens are absent in oxidized nickel foil. Conversion to oxide is effected by self-diffusion of the oxide components, and hence subsequent diffusion in the converted grain boundaries is merely a continuation of a similar process. Furthermore, the oxidation process itself leads to a redistribution of impurities which tends to denude the outer part of the oxide of impurities having lower diffusivity than nitrogen. Thus it was possible [2] to grow a fine-grained polycrystalline oxide by oxidation at a temperature (1100° C) where there was sufficient boundary diffusion to grow a reasonable film thickness but low enough boundary mobility to limit grain growth even in the absence of impurity pinning of the boundaries.

## 7. Conclusions

The density of specimens prepared by ceramic processing techniques needs to be improved further before quantitative sectioning experiments on grain-boundary diffusion are possible. An improvement to near theoretical density appears possible by control of calcining and pressing conditions, and by investigation of particle size in order to eliminate agglomerates from the presintered powder. Unless, however, precautions are taken to eliminate adsorption of deleterious impurities on to powder surfaces during processing, the dense specimens may still be unsuitable for informative experiments owing to blocking of boundaries by trace contamination. The preparation of intrinsic grain boundaries remains a major materials problem in the study of grain-boundary behaviour.

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