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 μm 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
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–CO₂ 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, 2g 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 × 10³ 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 μm obtained after firing for 20 h at 1400°C increased to only 20 μm 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, Q, was obtained by expressing the density as a product Q = Q₀Q₁, where the axial density Q₀ = m⁴/(πd³) and the radial density Q₁ = 4m³/(πD³) were given in terms of the thickness, d, and diameter, D, of the final sintered pellet of mass m, and plotting Q₀ and Q₁ 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 Q₀ and Q₁ 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 Q₀ (and smaller Q₁) 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...