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Preparation of porous nickel electrodes for molten carbonate fuel cells by non-aqueous tape casting

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The casting behaviour, ultimate tensile strength and the sintering process of tapes consisting of nickel powder, ethanol, polyvinylbutyral as the binder, polyethylene glycol (molecular weight 200, PEG2) or dibutyl phthalate (DBP) as the plasticizer, and glycerol trioleate as the dispersant agent, were studied. On increasing powder content in the slurry the packing factor of nickel in the green increased, but the ultimate tensile stress and strain to failure decreased. Increasing binder to total binder ratio caused the green density and strain to failure to decrease, but the ultimate tensile stress increased for both PEG2 and DBP. The maximum strain to failure (about 35% for both PEG2 and DBP) in the case of DBP was obtained with an amount of plasticizer lower than that of PEG2. When tapes having different composition were sintered at various temperatures, a linear relation was found between packing factor and fired density, independently of the kind of binder and plasticizer used.

1. Introduction

Molten carbonate fuel cells (MCFCs) are presently under development for electric utility power generation [1, 2]. Nickel porous structures are used as anodes and cathodes for MCFCs [3]. Porous nickel plaque (50%–70% total porosity), stabilized by chromium, provides a sintering-resistant anode structure. However, porous nickel plaque (70%–80% total porosity), *in situ* oxidized and lithiated to $Li_xNi_{1-x}O$ solid solution, provides a cathode structure. The preparation technique of these structures is based tape casting of bindered metal slurries on a suitable support material followed by controlled drying. This process requires subsequent thermal treatment of the green structure in a reducing atmosphere to eliminate orgainic compounds and to sinter the nickel plaque. The final microstructure and porosity of the plaque depends on green composition, sintering process and type of nickel powder [3, 4]. Aqueous tape casting with polyvinyl alcohol or methyl cellulose as the binder, is generally used to obtain nickel green structures [3, 5]. The use of a continuous casting machine requires a fast evaporation of the solvent, so aqueous tape casting is not indicated. To overcome this problem, the present work investigated the preparation of green structures by non-aqueous tape casting, evaluating the effect of the composition of the slurry on the density and tensile strength of the green structure and on the density and microstructure of the electrode, following thermal treatment. Green tensile strength is a good indicator of green tape homogeneity [6], which will also affect the sintering behaviour. The ultimate tensile stress is important for hándling. High strain to failure in the tape is necessary for successful removal of tapes from the carrier substrate and subsequent handling.

2. Experimental procedure

The process of tape casting was performed on two kinds of nickel powder, Ni INCO 255 and 287: Table I shows the characteristics of these powders.

As shown in Table II, the milling is done in two stages, with and without binder and plasticizer [7]. First, the dispersant (glycerol trioleate) was added to the solvent (ethanol) followed by nickel powder. This slurry was ball milled for 5 h in order to separate nickel particles and to break up weak agglomerates. Then binder and plasticizer were added to the above suspension and the resulting slurry was milled for 24 h. The slurry was then cast onto two different substrates, beeswax-coated glass surface and mylar. The drying was performed slowly in a controlled ethanol atmosphere.

The resulting green tape was thermally treated under flowing hydrogen as follows:

(i) heating rate from room temperature to 500 °C, 1 °C min^{-1};

(ii) soak at 500 °C for 3 h (debinding);

(iii) heating rate from 500 °C to maximum temperature, 1 °C min^{-1};

(iv) soak at maximum temperature (700 and 850 °C) for 3 h (sintering);

TABLE I Physical characteristics of Ni INCO 255 and 287 powders

	INCO 255	INCO 287
Average particle size (μm) (Fisher sub-sieve sizer)	2.2–3.0	2.6–3.3
Apparent density ($g cm^{-3}$)	0.5–0.65	0.75–0.95
Specific surface area ($m^2 g^{-1}$)	0.68	0.58

TABLE II Materials and milling procedure

Process step	Material	Function
Mill for 5 h first stage	Nickel powder	Substrate material
	Glycerol trioleate	Dispersant agent
	Ethanol	Solvent
Add to above and mill for 24 h, second stage	Polyvinylbutyral	Binder
	Polyethylene glycol MW200	Plasticizer
	Dibutyl phthalate	Plasticizer

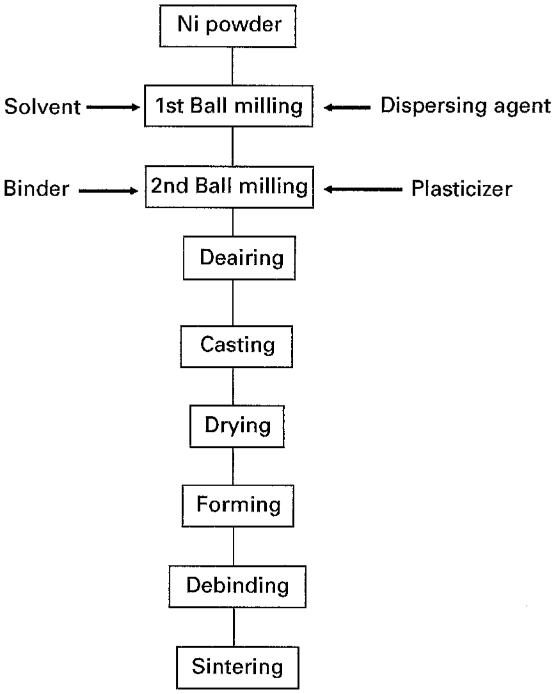


Figure 1 The fabrication process for nickel electrodes for MCFC by non-aqueous tape casting.

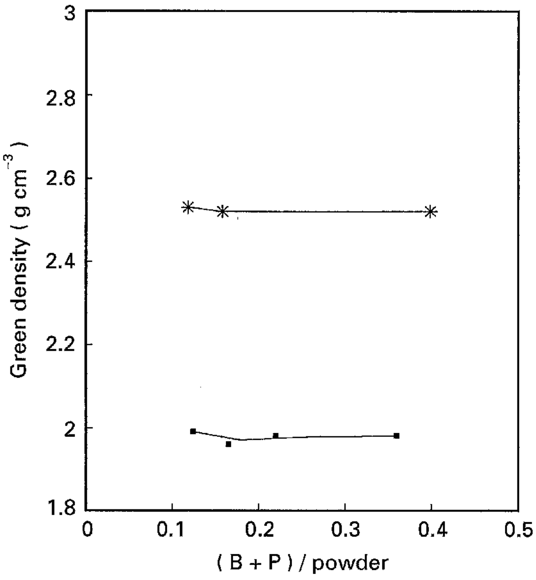


Figure 2 Variation of green density with total binder for nickel INCO (■) 255 and (∗) 287.

(v) cooling rate from maximum temperature to room temperature, 2 °C min^{-1}.

Density values were obtained from mass and volume measurements. Tensile strength measurements were taken using an Instron 5565 dynamometer, at a loading rate of 0.033 mm s^{-1}. Scanning electron micrographs were collected using a Leica Stereoscan 440 scanning electron microscope.

3. Results and discussion

The flow chart in Fig. 1 shows the different stages of the process for obtaining porous nickel plaques. The first part of this work deals with the obtention of a homogeneous and crack-free green tape. This depends on the good choice of the constitutents of the slurry and on their quantitative optimization. The second part of the present paper discusses the effects of thermal treatment on the compaction process and the resulting microstructure.

3.1. Effect of total binder (binder + plasticizer)

The quantitative optimization of binder was researched. Suspensions with decreasing binder rates (25–3 wt % powder content) were prepared (the proportions of the other constitutents were not varied). The total binder (binder + plasticizer) to nickel powder ratio was varied keeping the organic composition constant (binder to total binder ratio = 0.55, using polyethylene glycol as the plasticizer) but varying the amount of powder added to the slip. For binder rates lower than 6.5 wt%, cracks were noticed during drying and significant fissuring occurred when tapes were handled. A slurry composition with 6.5 wt % polyvinyl butyral (PVB) resin was retained as the minimal rate for subsequent study.

As shown in Fig. 2, where green density is plotted as a function of total binder, for both nickel INCO 255 and INCO 287, green density was independent of the total binder to powder ratio. From the values of green density, the packing factor, PF, of nickel particles was calculated as

$$PF = W_{Ni} d_g / d_{thNi} \qquad (1)$$

where d_g is the green density, d_{thNi} the theoretical nickel density and w_{Ni} the nickel weight fraction in the green tape.

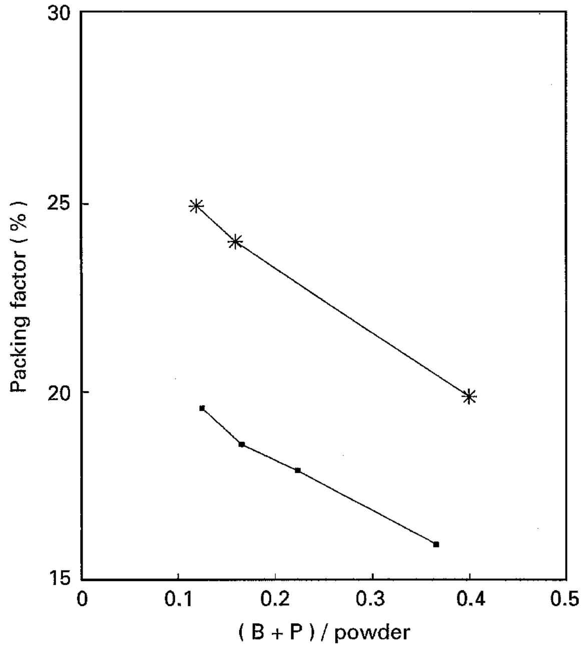


Figure 3 Variation of packing factor with total binder for nickel INCO (■) 255 and (*) 287.

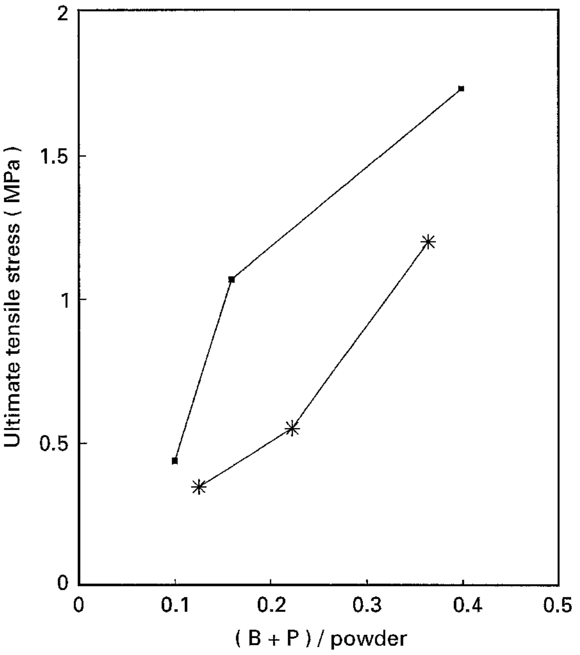


Figure 4 Variation of ultimate tensile stress of green tapes with total binder for nickel INCO (■) 255 and (*) 287.

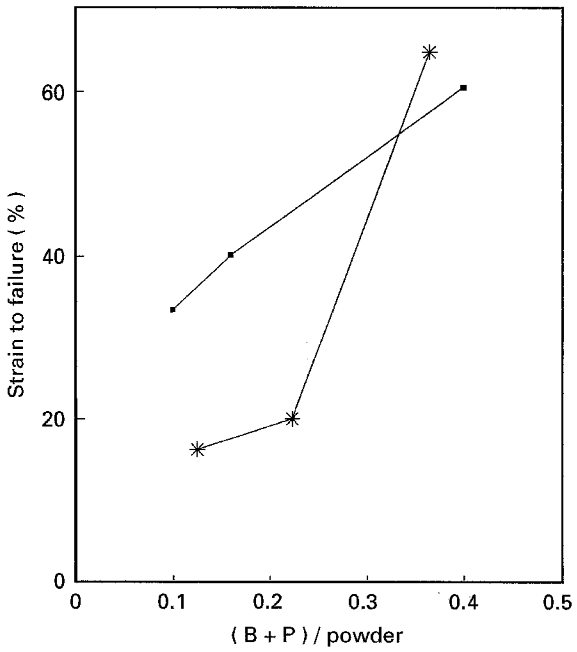


Figure 5 Variation of strain to failure of green tapes with total binder for nickel INCO (■) 255 and (*) 287.

Fig. 3 shows the PF as a function of total binder: as expected [8], for both nickel INCO 255 and INCO 287, PF decreased with increasing total binder owing to increase in the interparticle distance.

Figs 4 and 5 show ultimate tensile stress and strain to failure of the green tape, respectively: in this case, both ultimate tensile stress and strain to failure increased with increasing total binder content.

3.2. Effect of binder to total binder ratio

Plasticizers are added to the slip to confer sufficient flexibility to the green tape for easy handling and storage. The most important effect of the plasticizer is to reduce the glass transition temperature of the binder, T_g, to room temperature or less [9]. The resistance to movement of the binder must be reduced and this is possible by adding a plasticizer, which has a lower molecular weight and provides higher flexibility. Nevertheless, plasticizer additions are accompanied by a significant decrease in the strength of the tape [10]. The plasticizer is necessary as a release agent, because without it the tape is difficult to remove from the glass substrate without tearing. The qualitative and quantitative optimization of the plasticizer for polyvinyl butyral was therefore researched. This resin is generally plasticized by derivative glycol and phthalates: two kinds of plasticizer were tested, polyethylene glycol (molecular weight 200, PEG2) and dibutyl phthalate (DBP). In this case the binder to total binder ratio B/(B + P) was varied, keeping the total binder to powder ratio constant at 0.223.

The green tape containing no plasticizer was fragile and stuck to the glass plate, while the presence of plasticizer prevented the sticking of the green tape.

As shown in Fig. 6, for both PEG2 and DBP, green density increased with increasing amount of plasticizer, as indicated by the results of DiMilia and Reed [11] and Nies and Messing [12]. The increase in green density with plasticizer content was higher for DBP.

Figs 7 and 8 show the ultimate tensile stress and the strain to failure of the green tape as a function of binder to total binder ratio, respectively. For both PEG2 and DBP, the ultimate tensile stress increased in the same way with increasing binder to total binder ratio, while strain to failure decreased with increasing B/(B + P). Moreover, in the case of DBP as the plasticizer, the maximum strain to failure (about 35% for both PEG2 and DBP) was obtained at lower additions of plasticizer.

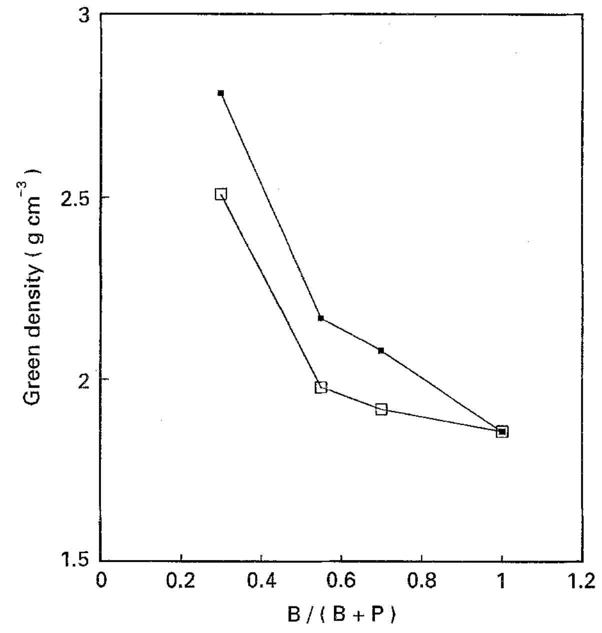


Figure 6 Effect of binder to total binder ratio, B/(B + P), on green density. (■) DBP, (□) PEG 2.

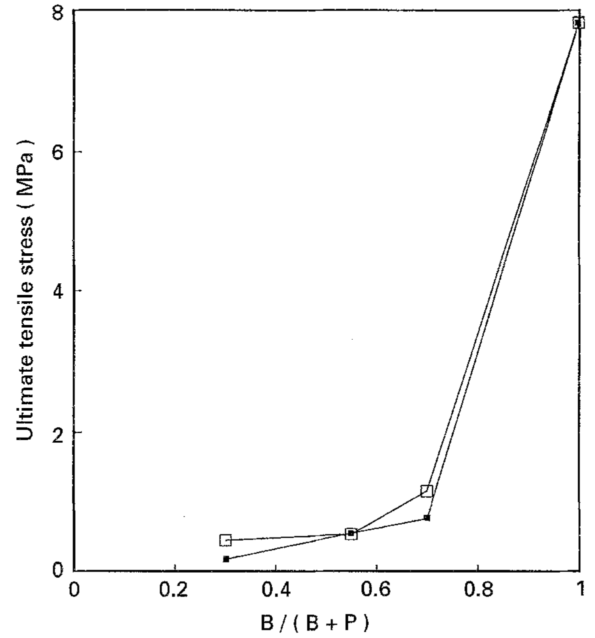


Figure 7 Effect of binder to total binder ratio, B/(B + P), on ultimate tensile stress of green tapes. (■) DBP, (□) PEG 2.

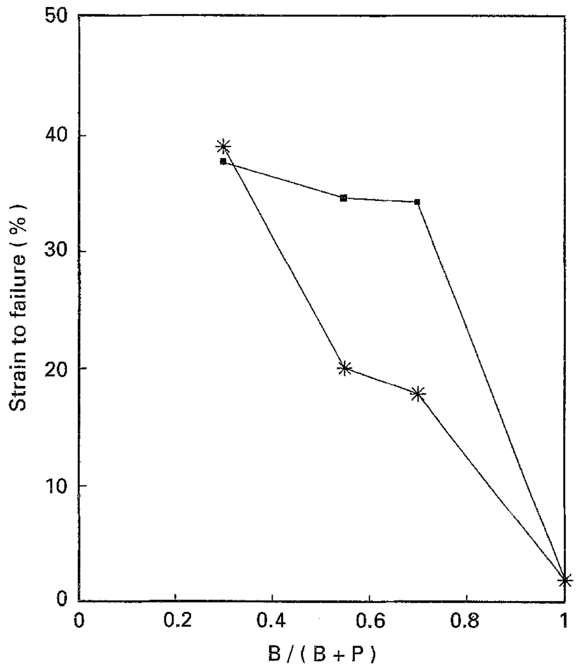


Figure 8 Effect of binder to total binder ratio, B/(B + P), on strain to failure of green tapes. (■) DBP, (∗) PEG 2.

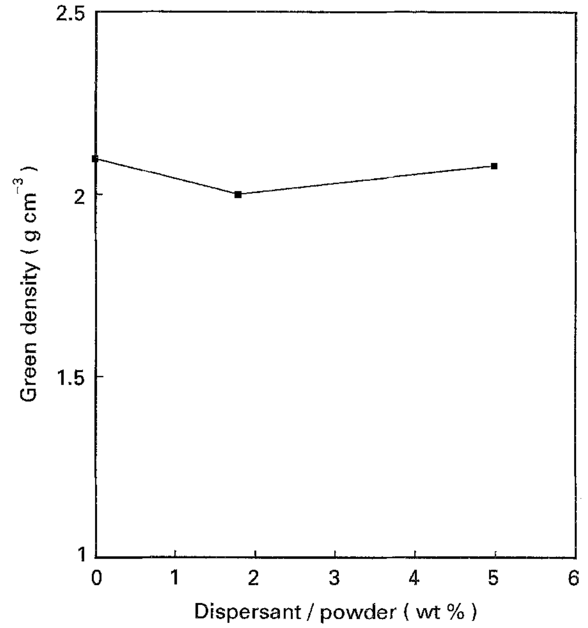


Figure 9 Dependence of green density on dispersant content.

3.3. Effect of dispersant

Fig. 9 shows the dependence of green density on the content of dispersant (glycerol trioleate): it can be seen that the effect of dispersant on green density was negligible.

3.4. Thermal treatment

The organics introduced into the slurry and still present in the green tape must be eliminated before sintering by a thermal treatment: this is debinding. Debinding was performed at 500 °C: the weight change of the sample following thermal treatment at 500° C for 3 h indicated that all organics were eliminated; above 500 °C, a sintering process takes place.

Fig. 10 shows nickel INCO 255 relative density as a function of thermal treatment temperature for the samples with a total binder to powder ratio of 0.223 and binder to total binder ratio of 0.55. The slight densification at 500 °C is related to the rearrangement of nickel particles following organic compounds burnout, while for temperatures higher than 500 °C, the density increase is due to the sintering process of the nickel plaque.

SEM analysis (Fig. 11) confirmed the results of density measurements. It can be seen that sintering of the plaque thermally treated at 500 °C did not occur, while the samples thermally treated at 700 and 850 °C were characterized by a smoothing of the particle surface, elimination of very fine pores, and the formation of larger pores between particles; moreover, necks form between the particles, drawing the particles closer together, and resulting in shrinkage in all three dimensions. No residual impurities from the organics burn-out were visible.

Fig. 12 shows the dependence of the relative density of sintered plaques versus nickel packing factor: when tapes with different compositions were sintered at various temperatures (700 and 850 °C), a linear relation was found between packing factor and fired density, independently of the kind of plasticizer and of the use of methylcellulose as the binder (aqueous tape casting).

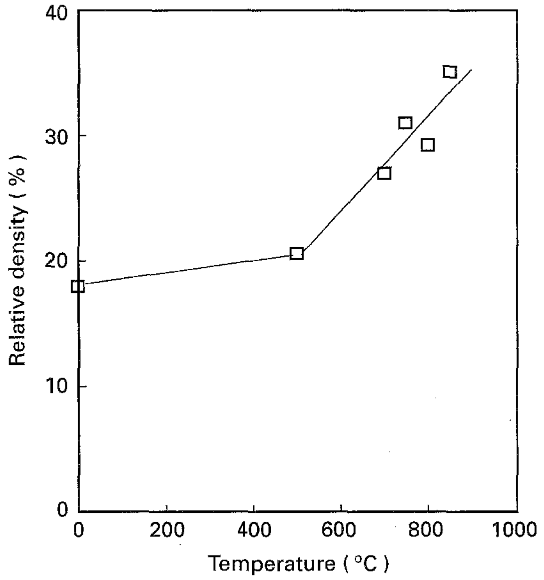
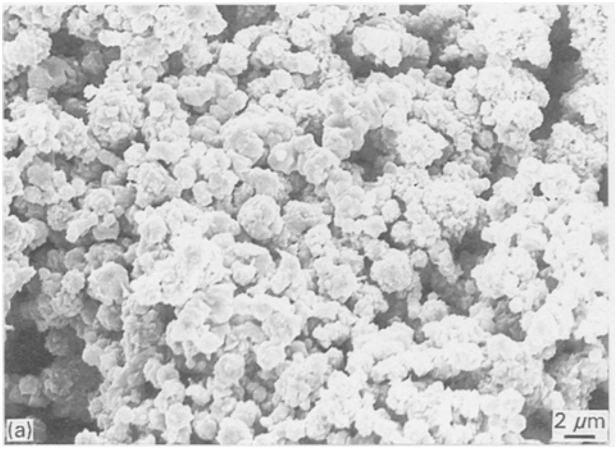
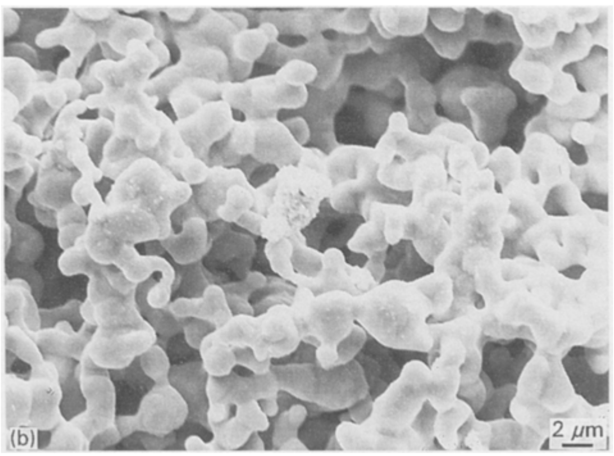


Figure 10 Dependence of nickel INCO 255 relative density on thermal treatment temperature.





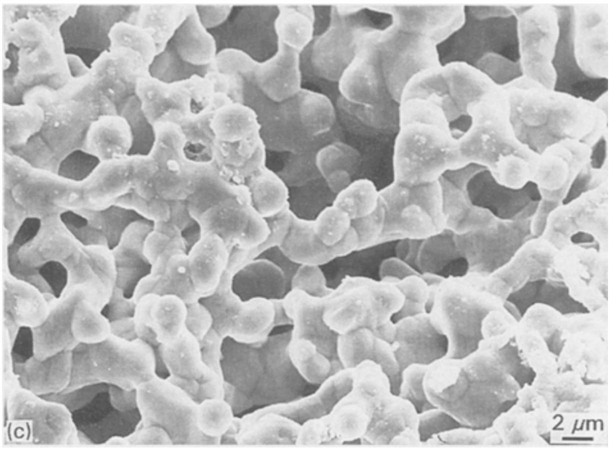


Figure 11 SEM analysis of nickel INCO 255 plaques thermally treated at (a) 500 °C, (b) 700 °C and (c) 850 °C.

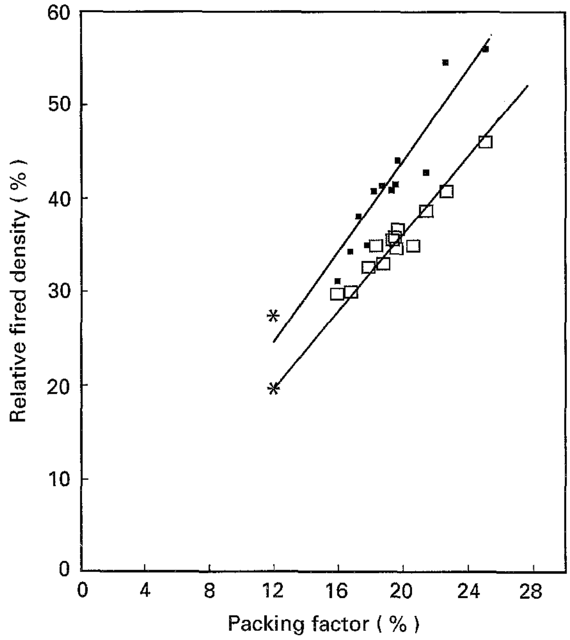


Figure 12 Relative fired density versus packing factor at (■) 850 °C and (□) 700 °C. (*) The composition with methylcellulose as the binder (aqueous tape casting).

4. Conclusions

Slurry formulations for non-aqueous tape casting of nickel powder were studied. On decreasing the powder content, the packing factor of nickel in the green state decreased, but ultimate tensile stress and strain to failure increased. As the percentage of binder is increased at the expense of the plasticizer, ultimate tensile stress increased, but green density and strain to failure decreased. DBP was the best plasticizer agent, because the same strain to failure of PEG2 was obtained with a lower amount of material.

To obtain plaques with high porosity (about 70%), it is necessary to sinter the green tape at a temperature around 700 °C using green compositions with a high organic compound content.

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