Forming of nickel compacts by a colloidal filtration route

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Abstract

Concentrated suspensions of metal Ni powders have been prepared in water by dispersing with a polyelectrolyte and tetramethylammonium hydroxide at alkaline pH. Optimisation of the suspensions was studied by measuring the rheological behaviour as a function of pH and volume fraction of solids. The maximum packing fraction has been calculated with the Krieger–Dougherty model and the fractal dimension from the yield stress values determined from flow curves. The shear thinning behaviour and the fractal dimension demonstrate that suspensions form a structure at rest that retards sedimentation and easily flows on shearing. Optimised suspensions were slip cast in plaster moulds leading to green densities above 50% of theoretical. The good stability and homogeneous packing during consolidation also allows a reduction in the sintering temperature to obtain dense compacts. A relative density above 97% of theoretical has been attained after heating at 900 °C/1 h in flowing argon.

Keywords: Powder processing; Powder consolidation; Nickel; Slurry filtration

1. Introduction

Nickel (Ni) and Ni–matrix composites are widely used for many structural and functional applications, such as thermal barrier coatings, electrodes for fuel cells, and semiconductor gas-sensor devices. Most of these applications require the use of complex structures such as laminates or dispersed second phases [1,2]. Pure Ni and its alloys and mixtures with other metals can be produced by deformation methods, but Ni–ceramic composites must be shaped by using powder processing techniques, the focus being on reaching a high dispersion level between the phases. In this sense Ni-based materials are commonly manufactured by pressing, extrusion, injection moulding, etc. Powder processing techniques are also useful to tailor complex microarchitectures [3] and to produce bodies with controlled porosity [4].

Many of the applications involving such structures could be faced with the dispersion of Ni powders into a liquid medium and further consolidation into complex-shaped bulk bodies, thick films or coatings. The basic requirement for slurry consolidation methods is to maintain a high dispersion at each different processing stage in order to obtain a defect-free sintered material. Colloidal processing of ceramics has received great attention in the last two decades, because it allows the fabrication of green bodies with larger densities and more homogeneous microstructures [5]. The colloidal approach implies the preparation of stable suspensions with dominating repulsive forces among particles capable of maintaining the dispersion even during consolidation. Studies dealing with colloidal behaviour of metal powders usually describe the electrophoretic and surface behaviour of the dispersions [6,7], but studies concerning the rheological properties of concentrated Ni suspensions are scarce.
The preparation of non-aqueous Ni suspensions and various forming methods have been reported elsewhere [7,8], but the characterisation of the rheological properties has not received due attention. Tseng et al. [9–11] have recently studied the rheological behaviour of non-aqueous Ni suspensions dispersed with polymeric surfactants. The suspensions exhibit a shear thinning behaviour that suggests the formation of a flocculated structure that breaks down on shearing. The aggregation state is characterized by a fractal dimension ($D_f$), which is estimated from the measured values of the yield stress [11,12].

The use of water is preferred because of environmental, health and cost benefits. However, aqueous suspensions of nickel powders have a complex surface behaviour which is highly dependent on pH history. Previous work [13] reported that the isoelectric point (IEP) of the same nickel powders used in this work occurs at pH 3.5–4. Below the IEP there is surface dissolution of Ni$^{2+}$. Above the IEP a plateau zeta potential region was observed with predominant NiO(OH) and Ni(OH)$_2$ species, and at higher pH (>9) NiO-enriched species developed at the surface. According to these studies, aqueous suspensions of nickel should be prepared at basic pH in order to avoid dissolution and/or hydroxylation. However, when the volume fraction of particles increases, overlapping among electrical double layers surrounding the particles increases, which can lead to flocculation. In addition, nickel powders have a high density, so that electrostatic repulsion is not sufficient itself to overcome the tendency to settle. For this reason, the addition of polyelectrolyte helps to prevent flocculation. Previous work [14] reported the aqueous gelcasting of Ni suspensions dispersed with a polyacrylic-based dispersant, but pH was maintained at the natural value (pH < 9), which was later demonstrated to be insufficient to prevent the enrichment of surface NiO(OH) species. The moderate maximum solids loading (27 vol%) and the extreme shear thinning behaviour of those suspensions led to low green densities (<42% of theoretical).

In this work, concentrated aqueous suspensions of nickel powders in water are prepared at basic pH using polyelectrolyte. The stability of suspensions with solids loading up to 40 vol% is studied by means of rheological measurements at controlled shear and controlled stress conditions. The evolution of viscosity with volume fraction of particles is used to predict the maximum packing fraction, while the corresponding yield values are used to estimate the colloidal aggregation state. Nickel compacts are prepared by a slip casting route, the green densities being up to 53% of theoretical. The efficient dispersion of powders allows for a reduction in the sintering temperature with regard to a sintering schedule used in previous work.

2. Experimental

A commercial nickel powder (INCO T-110, Canada) with a mean particle size of 2.5 µm, a surface area of 1 m$^2$/g and a density of 8.82 g/cm$^3$, was used. Suspensions were prepared in deionised water for solids loadings ranging from 15 to 40 vol% using an ultrasound probe (IKA 400S, IKA, Germany) for 1 min and maintained for 24 h under mechanical stirring. An acrylic-based polyelectrolyte (Duramax D-3005, Rohm & Haas, USA) was used as dispersant in a concentration of 1 wt% on a dry solids basis. pH adjustments were made by adding tetramethylammonium hydroxide (TMAH) up to pH values of 9–11.

Zeta potential measurements were performed using the microelectrophoresis technique (Zeta-meter 3.0$, Zetameter, USA). Ionic strength was fixed with $10^{-3}$ M KCl.

Rheological characterisation was carried out using a rheometer RS50 (Haake, Germany) with a double cone/plate sensor configuration (DC60/2°, Haake, Germany) that requires a sample volume of 5 ml and a testing temperature of 25 ± 0.5 °C. The flow behaviour was measured by two different testing modes (controlled rate, CR, and controlled stress, CS). To obtain the high shear flow behaviour CR experiments were carried out employing a measuring program in three stages; first a linear increase of shear rate from 0 to 1500 s$^{-1}$ in 7.5 min; a plateau at the maximum shear rate (1500 s$^{-1}$) for 1 min, and a decrease to zero shear rate in 7.5 min. The characterisation at the low shear rate region and the yield point determinations were performed through CS experiments. In these measurements, shear stress is linearly increased until viscous flow occurs. The rheological behaviour of each slurry was fitted to regression models having two and four parameters. The influence of the solids fraction on the slurry viscosity was studied using the Krieger–Dougherty model in order to predict the maximum solid loadings for which the slips maintain stability. Optimised suspensions were slip cast in plaster of Paris moulds to obtain solid disks and plates. The cast bodies were carefully removed from the moulds and dried in air at room temperature for at least 24 h.

The dynamic sintering behaviour of the specimens was studied with a differential dilatometer (Adamel Lhomargy, D124, France) to 1550 °C. Cast bodies were sintered in Ar atmosphere at 900 °C/1 h. The densities of the green and sintered compacts were determined by the Archimedes method, using mercury and water, respectively.

Scanning electron microscopy (SEM, Carl Zeiss, DSM-950, Germany) observations were made on polished and chemically etched surfaces.
3. Results and discussion

Fig. 1 shows the variation of zeta potential with polyelectrolyte concentration for nickel suspensions prepared at fixed pH values of 8.5 (natural pH), 10, and 11. For any fixed pH, the magnitude of the zeta potential tends to increase with polyelectrolyte addition, until a maximum zeta potential of about −50 mV is reached for 1 wt% polyelectrolyte. This is probably related to the fact that the addition of an anionic polymer shifts down the isoelectric pH and increases the magnitude of the zeta potential as more dispersant adsorbs on the particles surface. However, considering the experimental errors in zeta potential determinations, it is not possible to establish clear differences depending on pH. These possible differences may become more evident for concentrated suspensions, where the polyelectrolyte has a remarkable role in the stability.

The dispersing conditions of nickel suspensions were studied first at a volume fraction of particles of 0.31 (80 wt%). Fig. 2 compares the flow curves of suspensions dispersed at the following conditions: (1) adding only a base (TMAH) up to pH 10; (2) adding only polyelectrolyte to a concentration of 1 wt%, the resulting pH being ∼9; and (3) adding both the polyelectrolyte (1 wt%) and the strong base up to pH 10. The suspensions with only TMAH have the highest viscosity and significant thixotropy, while those with polyelectrolyte have a very small thixotropy and intermediate viscosity, the best dispersing conditions being reached when both additives are used together. All suspensions have a shear-thinning behaviour (i.e. viscosity decreases as shear rate increases), but the apparent yield stress is lower for suspension 3.

Further experiments were made with suspensions dispersed with 1 wt% polyelectrolyte and TMAH additions at pH values of 9–11. Suspensions were prepared to volume fractions ranging from 0.15 to 0.40 (60–85.2 wt%). For low solids loadings, the viscosity is very similar for suspensions prepared at pH 9 and 10, and increases for that prepared at pH 11. Suspensions with low solids loadings show slight pseudoplasticity, as well as a small thixotropy. As solids loading increases the differences in viscosity also increase, the largest viscosity being always obtained at pH 11 and the lowest at pH 10. The flow curves of suspensions with a volume fraction of 0.35 (82.5 wt%) are shown in Fig. 3. The pH dependence may be explained considering that pH 9 is near the equilibrium pH and there is still a significant amount of hydroxylated species. When solids loading increases a higher electrostatic repulsion is needed to avoid particle interactions. However, an excess of charge leads to a double layer thinning, as in the case of pH 11.
suspensions, where a large concentration of base is necessary to achieve that pH.

More detailed analysis of the effect of volume fraction of particles was made by measuring the flow behavior of the different suspensions under both controlled rate (CR) and controlled stress (CS) conditions.

For a useful prediction of the general shape of a flow (or viscosity) curve, a regression model that differentiates the extreme shear regions must be used. One such model is the Cross model

\[ \frac{\eta_0 - \eta}{\eta - \eta_\infty} = (k\gamma)^m. \]  

(1)

In this equation, \( \eta_0 \) is the extrapolation of the viscosity to the zero shear rate and is referred to as zero shear viscosity, \( \eta_\infty \) is the limit viscosity, which refers to that extrapolated to infinite shear rate, \( \gamma \) is the shear rate, \( k \) is a constant with dimensions of time and \( m \) is a dimensionless constant. In this work, \( \eta_0 \) was obtained by extrapolating to zero shear the values measured in CS mode, while CR curves were used to obtain \( \eta_\infty \) values. It was observed that \( \eta_0 \) values are several orders of magnitude higher than the corresponding \( \eta_\infty \) values. That is, there are strong differences between the flow behavior at very low shear rates and that at very high shear rates. Suspensions behave as shear-thinning fluids, but there is a critical minimum stress (yield stress) before flow takes place. This strong shear thinning behavior leads to very large errors in \( \eta_0 \), so that fitting to the Cross model was performed for \( \eta_\infty \) values obtained from the CR curves.

Fig. 4 shows the variation of \( \eta_\infty \) with the volume fraction of particles (\( \phi \)). It can be observed that the viscosity increases with solids content, but there is a maximum concentration of particles for which the viscosity tends to infinity, indicating that a compact structural network has been formed. It is clearly observed that the slurry at pH 10 allows for higher concentrations than the two others. This concentration defines the maximum packing fraction (\( \phi_m \)). For concentrated suspensions, the Krieger–Dougherty model (Eq. (2)) is frequently used to describe the dependence of viscosity with volume fraction. This model introduces the intrinsic viscosity [\( \eta_i \)] that has a value of 2.5 for suspensions of spherical particles,

\[ \eta = \eta_i (1 - \phi/\phi_m)^{-(n)/m}. \]

(2)

where \( \eta_i \) is the viscosity of the dispersing media. For concentrated suspensions of non-spherical particles the exponent factor \( \eta_i\phi_m \) is commonly replaced by an exponent \( n \), this model being referred to as the modified Krieger–Dougherty model, which fits a broad variety of suspensions of different materials. Maximum packing fractions of suspensions at pH 9–11, were evaluated from the experimental results of \( \eta_\infty \) plotted in Fig. 4 (Table 1). Values for \( \eta_0 \) are not reported as the strong structure of the suspensions impedes a reliable determination. All \( \phi_m \) values are lower than the random close packing (\( \phi = 0.68 \)), but those determined from high shear conditions are considerably larger than those obtained at low shear. This suggests that suspensions have a particle structure which rearranges on shearing. Some information can be obtained by means of the analysis of yield values.

The apparent yield stress (\( \sigma_0 \)) was calculated from the log–log plot of stress vs. strain using the curves measured at CS conditions. The values obtained for the different suspensions are shown in Table 2. The lowest yield values are those corresponding to suspensions prepared at pH 10, whereas those prepared at pH 11 have the largest. The yield stress values were also calculated by fitting the flow curves measured in CS mode with common regression models for shear-thinning fluids. In Table 2, the yield values obtained with Casson and Bingham models are also shown. Fitting to the Casson model leads to much higher yield values. The same occurs for the Bingham model, where the yield values are even higher since that model does not account for the very low shear region.

Tseng et al. [10,11] have reported that concentrated Ni suspensions showed shear-thinning over much of the shear rate range they examined, which is explained in terms of particle aggregation for two limiting regimes of irreversible colloid formation that can be characterized using fractals [12]: (1) a diffusion-limited colloid

**Table 1**

<table>
<thead>
<tr>
<th>pH</th>
<th>( \phi_{\text{max}} )</th>
<th>( n )</th>
</tr>
</thead>
<tbody>
<tr>
<td>9</td>
<td>0.42</td>
<td>2.3</td>
</tr>
<tr>
<td>10</td>
<td>0.60</td>
<td>4.5</td>
</tr>
<tr>
<td>11</td>
<td>0.50</td>
<td>4</td>
</tr>
</tbody>
</table>

Fig. 4. \( \eta_\infty \) vs. volume fraction of solids (\( \phi \)) at three different pHs. The values have been estimated using the Cross model for curves recorded in the CR mode.
aggregation (DLCA) characterized in the scale-invariant fractal dimension $D_{f}$ and (2) a reaction-limited colloid aggregation (RLCA), with $D_{f} \sim 2.1$. Those authors make use of a model proposed by Shih et al. [15] to estimate $D_{f}$ from the relation of yield stress with volume fraction of solids, in the form:

$$r_{0} \propto \phi^{m},$$

where

$$m = \frac{d + X}{d - D_{f}},$$

$D_{f}$ and $X$ are the fractal dimensions of the clusters and the backbone of the clusters, respectively. The Euclidean dimension ($d$) equals 3 for the fractal geometry in three dimensions, and it may be assumed that $X = 1$. To determine the value of $D_{f}$ the value of $m$ is needed. Fig. 5 shows the variation with volume fraction of $r_{0}$ values calculated from the log–log plot. Similar curves were plotted using the $r_{0}$ values obtained after fitting the flow curves to Bingham and Casson models (Table 2). The regression parameters $a$, $m$ as well as the $D_{f}$ values obtained for each pH and rheological model are summarized in Table 3. Suspensions prepared to pH 10 show a worse fit to a linear model because at this pH the suspensions show lower yield points thus increasing the uncertainty of measurements. The values of $D_{f}$ range from 1.9 to 2.4 for yield values calculated with any of the selected models. With the log–log and Casson fittings the values range from 2.1 for pH 10 and 11 to 2.4 for pH 9. The exception is for the Bingham yield stress at pH 10, where $D_{f}$ is lower (1.9), but this may be due to the poorer regression index. In all the cases the $D_{f}$ values are lower for pH 10 and higher for pH 9 independently of the model used. The obtained $D_{f}$ values indicate that suspensions form a RLCA type structure in which particles rearrange during shearing, and this explains why the maximum packing fraction is much higher in the high shear region. These results are in good agreement with those of Tseng et al. [11], who observed that surfactant addition decreased viscosity but did not alter the suspension structure. In our study all suspensions have the same content of deflocculant relative to solids content and pH variations. Although

Table 2
Apparent yield stress values of the slurries at different solid contents and pH

<table>
<thead>
<tr>
<th>$\phi$</th>
<th>$\sigma_{0}$ (Log–log plot)</th>
<th>$\sigma_{0}$ (Casson)</th>
<th>$\sigma_{0}$ (Bingham)</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>pH</td>
<td>pH</td>
<td>pH</td>
</tr>
<tr>
<td>9</td>
<td>0.15 0.17</td>
<td>0.12 0.38</td>
<td>0.77 1.31</td>
</tr>
<tr>
<td></td>
<td>0.21 0.46</td>
<td>2.71 3.76</td>
<td>5.11 6.81</td>
</tr>
<tr>
<td></td>
<td>0.31 2.54</td>
<td>23.17 10.22</td>
<td>33.46 16.67</td>
</tr>
<tr>
<td></td>
<td>0.35 5.57</td>
<td>47.88 18.77</td>
<td>67.13 32.05</td>
</tr>
<tr>
<td></td>
<td>0.40 30</td>
<td>93.77 46.51</td>
<td>134.6 73.76</td>
</tr>
</tbody>
</table>

The values have been obtained from the log–log plot of stress vs. strain and by fitting the flow curves to the Bingham and Casson models.

Table 3
Linear fitting values and fractal dimensions calculated from the plots similar to those shown in Fig. 5

<table>
<thead>
<tr>
<th>pH</th>
<th>Log–log plot</th>
<th>Casson</th>
<th>Bingham</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>$a$</td>
<td>$m$</td>
<td>$R^{2}$</td>
</tr>
<tr>
<td>9</td>
<td>4.80</td>
<td>4.69</td>
<td>0.989</td>
</tr>
<tr>
<td>10</td>
<td>3.20</td>
<td>4.49</td>
<td>0.965</td>
</tr>
<tr>
<td>11</td>
<td>4.12</td>
<td>4.29</td>
<td>0.999</td>
</tr>
<tr>
<td>9</td>
<td>4.69</td>
<td>0.986</td>
<td>0.980</td>
</tr>
<tr>
<td>10</td>
<td>3.39</td>
<td>0.968</td>
<td>0.980</td>
</tr>
<tr>
<td>11</td>
<td>3.64</td>
<td>0.968</td>
<td>0.980</td>
</tr>
<tr>
<td>9</td>
<td>4.20</td>
<td>0.999</td>
<td>0.999</td>
</tr>
<tr>
<td>10</td>
<td>3.28</td>
<td>0.975</td>
<td>0.990</td>
</tr>
<tr>
<td>11</td>
<td>3.68</td>
<td>0.975</td>
<td>0.990</td>
</tr>
</tbody>
</table>
pH influences the viscosity it has no clear effect on the $D_f$ value.

Fresh suspensions were slip cast on plaster moulds to obtain discs and plates. The variation of green densities with volume fraction is plotted in Fig. 6. The density tends to increase with volume fraction for a given pH, except for pH 10, where a constant density of ~50% of theoretical is reached at any volume fraction. These densities are considerably higher than those reported previously (<42%). For the same volume fraction, the green density increases as the suspension viscosity decreases. Green densities above 50% of theoretical are only obtained at pH 11 for solids loadings ≥35%, but the viscosity is too high for easy handling. These results demonstrate the high degree of dispersion reached with the combined action of a polyelectrolyte and a strong base.

Slip cast samples were sintered in an Ar flowing atmosphere. Fig. 7 shows the shrinkage level (a) and the sintering rate (b) resulting from the dynamic sintering studies for samples obtained in this work in comparison to those obtained by gelcasting using non-optimised slurries [14]. The final shrinkage to achieve a complete densification is lower in the sample obtained with the optimised slurries as a result of the higher packing density. In the derivative curves two different peaks are observed. The first one is related to the sintering between the finer particles and is centred at the same temperature for the two samples described, but the beginning of the neck formation starts 100 °C before for the samples obtained in this work. The second peak is assigned to the sintering of larger particles. The maximum sintering rate of samples obtained in this work occurs at about 150 °C lower than for the gelcast samples. In fact at this temperature the shrinkage is close to the final value indicating that the fraction of large particles (and/or agglomerates) is very low.

![Fig. 6. Green density of slip cast pieces obtained with slurries at different solid content and pH.](image)

![Fig. 7. (a) Sintering curves for the samples obtained in this work and in a previous work with non-optimized curves [14]. (b) Derivative of the shrinkage curves.](image)

![Fig. 8. SEM micrograph of a chemically etched sample obtained by slip casting with an optimized slurry and sintered at 900 °C in a flowing argon atmosphere.](image)
Fig. 8 shows the SEM microstructure of a polished and etched Ni sample sintered at 900°C/1 h. Ni has grain sizes ranging from 3 to 30 µm, the average size being ~5 µm. Most of the porosity is intragranular, although remaining porosity can be observed at the triple points or located at the grain boundaries. Final densities above 97% of theoretical, and homogeneous microstructures without large defects and with controlled grain size are reached, thus demonstrating that the suspensions had a good dispersion level.

4. Conclusions

Concentrated aqueous suspensions of Ni powders have been prepared by combining a polyelectrolyte and a strong base. Stable suspensions have been prepared to solids loadings up to 40 vol% (82.5 wt%). Optimisation of the rheological behaviour has been performed on the basis of rheological models of two and four parameters, by combining measurements performed at controlled shear rate and controlled shear stress. The maximum packing fraction of the suspensions was calculated to be near 0.60, slightly higher than the obtained green densities. The estimation of the yield stress values demonstrates that the suspensions have a strong structure at rest, which is destroyed on shearing, in agreement with the shear thinning behaviour observed from the flow curves.

Slip casting of optimised suspensions has led to higher green densities (up to 53% of theoretical). As a consequence, sintering starts earlier than previously reported [14] and dense, homogeneous materials have been obtained after a thermal treatment at 900 °C/1 h.

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References