NICKEL SHEETS FROM SUSPENSIONS OF THE METALLIC POWDERS IN WATER**

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Materials designs evolving nickel sheets combined with ceramics has applications in either electrical or structural applications. Examples can be taken from the fabrication of high J_c-HTS (high temperature superconductors) tapes[1, 2] or the high temperature SOFCs where the metallic nickel has been used because of good oxidation resistance and good match with the ceramic components (YBCO[3] and YSZ). On the other hand the same properties of nickel can be employed for thermo-mechanical purposes. The joining of alternate metallic and ceramics tapes permits the fabrication of materials with graceful failure and high work of fracture[4-6]. Processing of those laminated materials is a critical point as the final reinforcement depends strongly on the distribution of the layers. Colloidal processing techniques have proved to be an accurate method to develop laminated and graded microstructures in both ceramic-ceramic[7, 8] and metal-ceramic[9] materials by a diverse techniques such as slip casting, tape casting, electrophoretic deposition or screen-printing. For any of those processing techniques,

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the rheology of the slurries is a critical parameter to be controlled in order process suitable samples [10-12].

But the use of metals together to ceramics requires of processing methods to force the microstructural developments or to favor the co-sintering and joining between tapes. In this sense, tape casting has been extensively used to produce substrates and pieces in a wide range of ceramic materials and microstructures [7, 13-15] with precise control of the thickness. Usually the dispersion media has been an organic liquid due to their compatibility with the most common binders and plasticizers[16], but environmental and economical reasons are promoting to the employment of water as the dispersion media[6, 13, 15]. Aqueous slurries for tape casting implies an increment in the solid content of the slurries as a key issue to fabricate handily green tapes[12, 13]. In this sense, previous works employed electrochemical[17] and rheological[11, 18] investigations to optimize slurries of metallic nickel in water up to solid contents of 40 vol%. Dense and porous material has been later fabricated starting with those optimized slurries by colloidal techniques employed in ceramic processing[17-19].

In this paper the fabrication of nickel dense sheets has been faced by the employment of aqueous based tape casting. Previous studies demonstrated that better stability of Ni powders in water was reached when assuring a pH high enough to prevent dissolution (Ni^{2+}) and hydroxylation (through NiO(OH) and $Ni(OH)_2$ species), so that pH must be higher than 9. Furthermore, a maximum zeta potential of about – 50 mV is reached when adding 1 wt % polyelectrolyte at a pH = 10[17]. Well-dispersed suspensions of nickel in water prepared under those conditions were rheologically characterized with different binder contents. The flow curve measured in the CR mode for suspensions prepared to solids loadings of 31 vol % and 40 vol% without binder and after the addition of 5, 10, and 15 wt % of binder are presented in figures 1.a and 1.b

respectively. Obviously, the viscosity significantly increases with the solids loading. It can be seen that suspensions without binder are more viscous than those containing binder for the same solids content, which is explained because of the extra amount of water added with the binder. This effect is more evident in the suspension with high solid content as the drop in viscosity is more significant at high solid contents.

The flow behaviour was characterized by the limit viscosity, η_∞, which refers to the viscosity value extrapolated to infinite shear rate. These values were obtained from CR experiments by fitting the flow curves to the Cross model in the high shear region:

$$\frac{\eta_0 - \eta}{\eta - \eta_\infty} = (k\dot{\gamma})^m \qquad (1)$$

where η_0 is the extrapolation of the viscosity to the zero shear rate and is referred to as zero shear viscosity, η_∞ is the limit viscosity, $\dot{\gamma}$ is the shear rate, k is a constant with dimensions of time and m is a dimensionless constant. The values for the limit viscosities as a function of the volume fraction of solids (ϕ) are plotted in figure 2 for both the suspensions with and without binder. The solid content for the binder containing slurries has been recalculated taking into account the whole amount of water and the nickel powder. These data were fitted to the Krieger-Dougherty model[11],

$$\eta = \eta_s \left(1 - \phi / \phi_m\right)^{-[\eta]\phi_m} \qquad (2)$$

which allows the calculation of the maximum packing fraction (ϕ_m), considered as the volume fraction of solids where the viscosity tends to infinity. In this equation, η_s is the viscosity of the dispersing medium and $[\eta]$ is the intrinsic viscosity, which has a value

of 2.5 for spherical particles and increases as sphericity decreases. It can be seen that all experimental data can be fit very accurately to the model that gives values of ϕ_m= 0.45 and [η]=4.5, indicating the existence of strong interactions between particles. Krieger-Dougherty´s analysis considering the nickel and latex in the solid content and the whole amount of water do not conduct to any result. The absence of correlation when the latex is considered as a solid in the slurry as well as the high intrinsic viscosity indicate that interactions between nickel particles are strong and make insignificant the effect of the latex in the rheological behaviour.

The studied suspensions were tape cast at the conditions described above. It was observed that suspensions with 5 wt % binder led to fragile tapes difficult to handle, whereas those tapes containing 10 or 15 wt % binder were easily handled and had good surface characteristics without cracks demonstrating the feasibility of the process to produce long substrates. The main characteristics of the dry tapes are summarized in Table I. Geometrical green densities are similar for all samples, e.g. 46 % of theoretical density. The thickness of the tape and its final density increases with the solids loading of the suspensions, as expected. It should be noted that thickness of the green tapes exceeds the blades gap of the tape casting process, even after drying. This is due to the high solid content and viscosity of the slurries. Considering that pure Ni is maintained after sintering without no secondary phases, the relative density of the samples treated at 1000ºC/1h in N_2/H_2 is near 99 % of theoretical density, which is a very good value for powder processing and demonstrates the suitability of the tape casting to produce long, flat and dense Ni substrates.

		Green density		Tape thickness (μm)		Sintered density	
	Binder	10%	15%	10%	15%	10%	15%
Ni content vol%	31	46	46	476 ± 45	510 ± 30	98.4	93.3
	40	46	46	570 ± 55	550 ± 60	98.5	98.9

Table II. Characteristics data of the tapes green and sintered tapes processed with binder contents of 10 and 15 wt% (related to nickel powder) and starting solid contents of nickel of 31 and 40 vol%.

In order to select the adequate thermal treatment and to evaluate the weight loss due to binders burning, ATD/TG tests were performed in air up to 800ºC. Figure 3 shows the ATD/TG curves corresponding to a tape prepared with 10 wt % binder. The curve has been divided into three different zones. Zone I corresponds to the removal of water and organic additives and goes from RT to near 400°C. In this zone the DTA curve shows a sharp peak centred near 350ºC and a weight loss of about 4% is recorded in the TG curve. It should be noted that the whole organic content should be slightly higher than 5%, corresponding to the emulsion binder and the dispersant. The remaining organics are removed later but it cannot be detected because a competitive oxidation process starts to occur. From this point, in the zone II, the curve shows an increasing weight gain until 21% which corresponds to the total oxidation of Ni into NiO (which would imply a weight increase of 27%). The differential thermal analysis shows an exothermic peak corresponding to the oxidation process centered at 490°C. Finally, in zone III, it can be seen that above 700°C, the oxidation of the nickel has been completed and no further weight changes are observed. From this curve it can be stated that a

thermal treatment in air at 400ºC is needed for debinding but sintering needs to be done at higher temperature under a reducing atmosphere to reduce the oxide formed during the debinding step. In order to study the sintering conditions to obtain the metallic phase, prevent further oxidation and achieve the densification of the compact a dilatometric test was performed up to 1000°C under reducing atmosphere (figure 4). It can be observed that the total shrinkage is about 17%. This is similar to the sintering behaviour of samples processed by slip casting where no organic matter is present and then no debinding is required. From the derivative the existence of three peaks curve is clearly observed. According to previous papers[17, 18] the first peak at 590°C can be related to the sintering of the fine particles fraction while the other two at 700 and 910°C are related to the sintering of the coarse particles fraction.

Figure 5 shows the SEM micrograph of a sintered tape that has been processed from slurries with 40 vol% of solids and 15 wt% of binder. The sintering cycle included the binder removal in air at 400°C and further sintering at 1000°C for 1 hour under flowing N_2/H_2 atmosphere. The microstructure reveals the high density of the compacts with grains sizes of 15 microns and the presence of remaining porosity inside the grains and located at the triple points.

Summarizing, nickel metallic tapes has been fabricated by tape casting of water based slurries of the metallic powder. Rheological studies show that those slurries has a pseudoplastic behaviour that allows the tape casting process, similar to these stated and employed for ceramic processing. The pure nickel and the binder containing slurries can be included together in Krieger-Dougherty model this indicating that interactions between nickel particles are the most important factor affecting the rheology behaviour with no influence of the binder (up to the 15% studied in this work). Green tapes with a density of 46% th were fabricated. On these tapes the thermogravimetric studies

indicate that before the binder and dispersant are completely removed the oxidation of the nickel starts indicating that a further reduction treatment is required. Further sintering under reductive atmosphere yield the fabrication of dense metallic tapes with a density close to 99 th% and linear sintering shrinkage of 17%. The derivative curve of the shrinkage shows the presence of three peaks at 590, 700 and 910°C. the lower temperature peaks have been associated to the neck formation and sintering of the finer fraction while the higher temperature peak is related to the main sintering of the compact. Electronic microscopy on dense tapes reveals the presence of small porosity intragranular and associated to triple points between grains.

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. According to previous studies[17] concentrated aqueous suspensions of Ni powders were prepared with a polyelectrolyte at basic pH in order to prevent dissolution and to promote the development of NiO-enriched species at the surface. An acrylic-based polyelectrolyte (Duramax D-3005, Rohm & Haas, USA, Mw~2,400) was used as dispersant in a concentration of 1 wt % on a dry solids basis. pH was adjusted to 10 by adding tetramethylammonium hydroxide (TMAH). Suspensions were prepared in deionised water to solids loadings of 31, 35, and 40 vol % (i.e., 80, 82.5, and 85.5 wt %) using an ultrasounds probe (IKA 400S, IKA, Germany) for 1 min and maintained for 24 hours under mechanical stirring.

Tape casting suspensions were prepared by adding to the dispersed slurries a polyacrylic-based emulsion as a binder (Duramax B-1014, Rohm & Haas, USA). This binder is a latex emulsion with a Tg of -26 ºC and 55 wt% of active matter.

Concentrations of 5, 10, and 15 wt % (on a dry solids basis) referred to the as-received binder emulsions (not active matter) were added. This means that some extra amount of water is incorporated with binder addition.

Rheological characterisation was carried out using a rheometer RS50 (Haake, Germany) with a double cone/plate sensor configuration (DC60/2º, Haake, Germany) that requires a sample volume of 5 ml and a testing temperature of 25 ± 0.5 ºC. The flow behaviour was measured by two different testing modes (controlled shear, 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 1000 s^{-1} in 5 min; a plateau at the maximum shear rate (1000 s^{-1}) for 1 min, and decrease to zero shear rate in 5 min. The characterisation at the low shear rate region and the yield point determinations were performed through CS experiment. In these measurements, shear stress is linearly increased until viscous flow occurs. The rheological behaviour of the slurries was fit to regression models having two and four parameters, such as the Ostwald-de Waele and the Casson models, respectively. The influence of the solid fraction on the slurry viscosity was studied considering the Krieger-Dougherty model in order to predict the maximum solid loading to which the slips maintain stable.

To produce the green tapes a self-made tape casting machine was used, which consists in a mobile container and fixed carrier. A Mylar substrate was used as carrier film. The casting parameters were 10 mm/s of casting velocity and 500 µm of gap height between the blades and the carrier film. Considering the blades gap and the velocity it can be assumed that the suspension is subjected to a shear rate of ~20 s^{-1} below the blades.

The thermal behaviour was studied using differential thermal analysis (DTA) and thermogravimetry (TG) with a STA 409 equipment (Netzsch, Germany). The analysis was performed in air until 1400ºC in order to follow the debinding process. The dynamic sintering behaviour of the specimens was studied with a differential dilatometer (Adamel Lhomargy, DI24, France) to 1000ºC/1h under slightly reducing conditions ($95N_2/5\%H_2$ flowing atmosphere).

The densities of the green and sintered compacts were determined by measuring dimensions and weight. Scanning electron microscopy (SEM, Carl Zeiss, DSM-950, Germany) observations were made on polished and chemically etched surfaces. The thickness of the tapes was determined by SEM observations.

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Captions to figures:

Fig. 1. Flow curves measured on CR mode for nickel slurries with starting solid contents of (a) 31 vol% and (b) 40 vol% with different amounts of binder.

Fig. 2. Limit viscosity vs solid content (considering only nickel and water) plot. Solid line corresponds to the fitting curve to the Krieger-Dougherty model with values of ϕ_m= 0.45 and [η]=4.5.

Fig. 3. ATD-TG curve for a green tape fabricated with a 35vol% nickel slurry with 10% of binder in air. Three zones are distinguished corresponding to the organic removal (I) oxidation advance (II) and complete oxidation(III).

Fig. 4. Sintering dilatometric curves recorded for the nickel tapes in reductive atmosphere.

Fig. 5.- SEM micrograph of a nickel tape sintered in reductive atmosphere at 1000º C during 1 hour.

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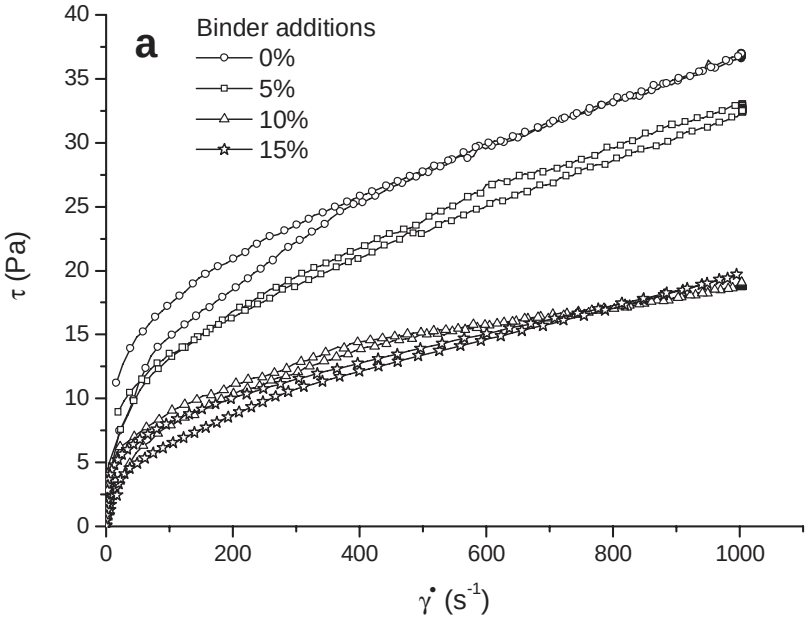

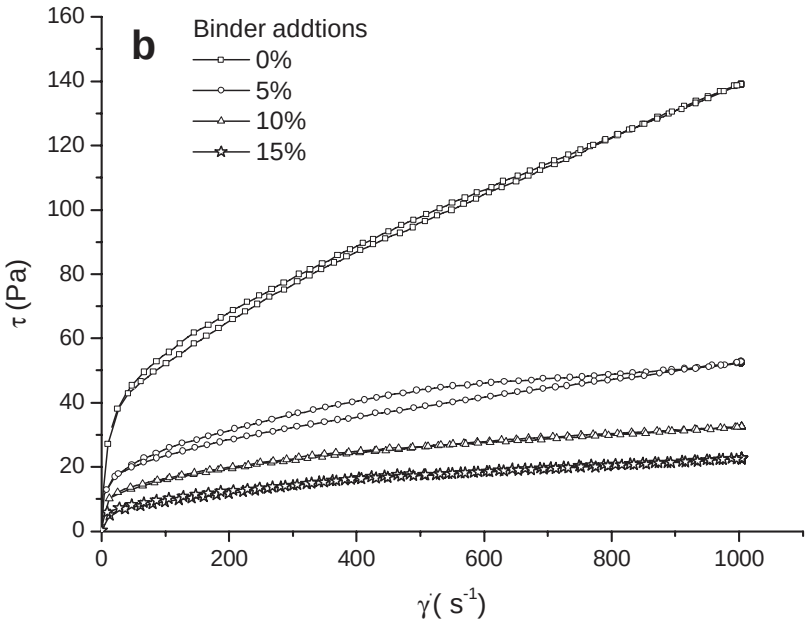

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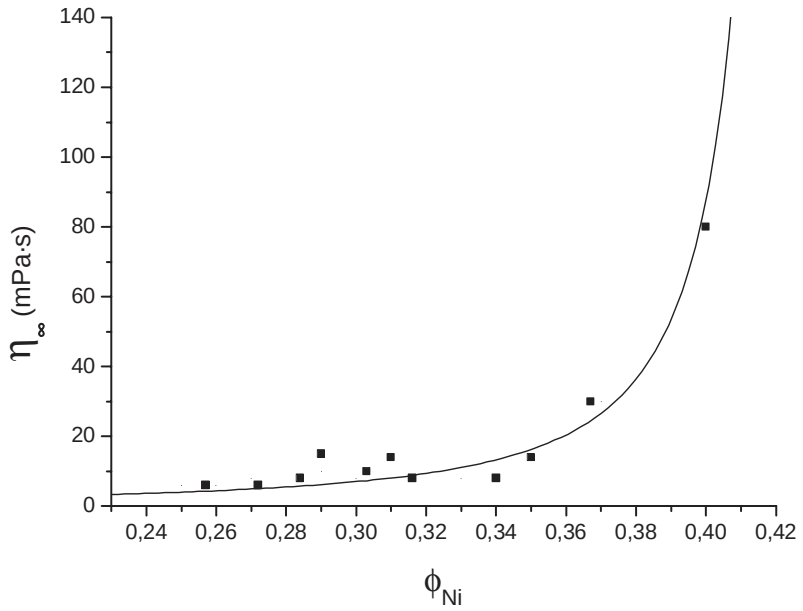

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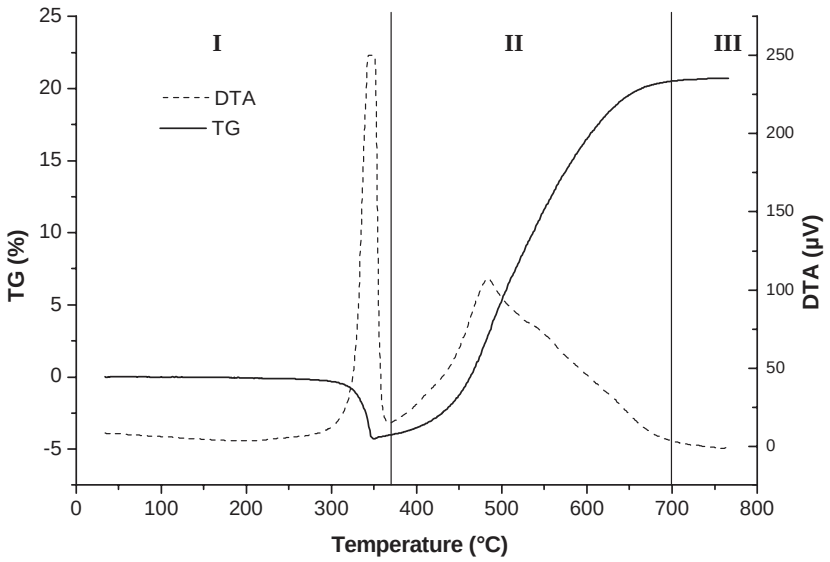

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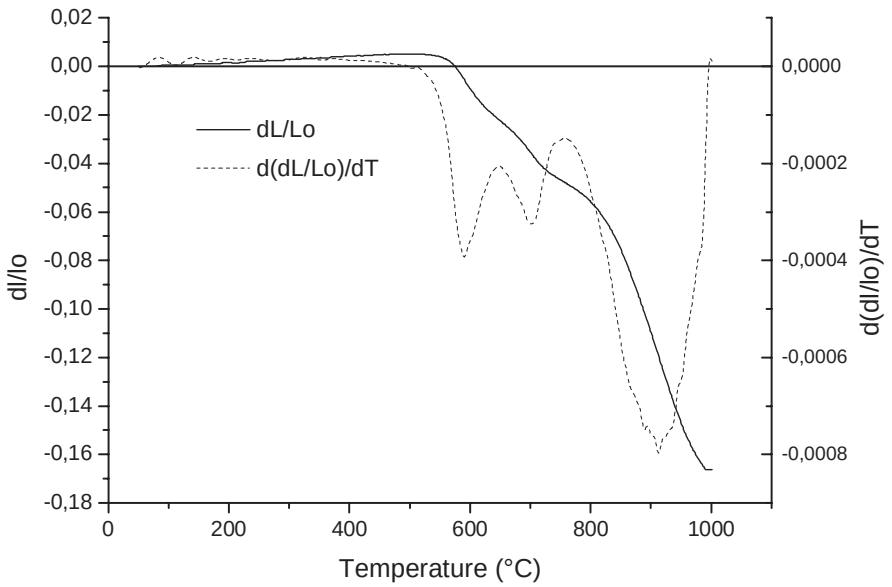

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