

# Microstructural evolution of Ni-NaCl mixtures during mechanochemical reaction and mechanical milling

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The evolution of microstructure of Ni and NaCl mixtures formed by mechanochemical reaction and mechanical milling has been studied using X-ray diffraction, electron microscopy and magnetic measurements. Separate nano-sized Ni particles were formed by continuous solid-state reaction of  $\text{NiCl}_2 + 2\text{Na}$  during mechanical milling. Further milling resulted in the growth of clustered particles due to inter-particle welding during collision events. On the other hand, milling of micron-sized Ni and NaCl powders resulted in a layered particle morphology and continuous decrease in particle size with increasing milling time. © 1999 Kluwer Academic Publishers

## 1. Introduction

The synthesis of a number of metallic and ceramic ultra-fine powders by mechanochemical processing has been recently reported [1–6]. In this process reactant powders are mechanically milled to form a nanoscale composite microstructure. Displacement reactions, which are either mechanically activated during milling or occur during subsequent low temperature heat treatment, result in the formation of ultrafine metallic or oxide particles embedded in a soluble salt matrix. Providing the volume fraction of the salt phase is sufficiently high, the metallic or oxide particles nucleate and grow as separate particles in the salt matrix. Subsequent removal of the salt phase results in a powder consisting of separable particles 5–20 nm in size. Studies to date have demonstrated the synthesis of ultrafine Fe, Ni, Co and Cu powders as well as  $\text{Al}_2\text{O}_3$  and  $\text{ZrO}_2$ .

An initial investigation [3] of the mechanochemical synthesis of Ni powder via the reaction,  $\text{NiCl}_2 + 2\text{Na} \rightarrow \text{Ni} + 2\text{NaCl}$ , showed that the reaction occurred in an unstable, combustive mode [7, 8] due to the large enthalpy change, resulting in submicron particle sizes. To prevent the occurrence of combustion it was necessary to add NaCl as a diluent phase to the starting mixture. The addition of the diluent phase prevented combustion by decreasing the collision frequency between reactant particles, which had the effect of reducing the reaction rate and the rate of heat generation arising from the reaction. In addition the decreased volume fraction of the Ni formed during milling minimised the coalescence and growth of particles resulting from inter-particle welding associated with collision events. Particle sizes of 10–20 nm were obtained in samples milled to completion of the reaction.

This paper reports the results of a study of the evolution of microstructure and magnetic properties during

the mechanochemical reaction of  $\text{NiCl}_2$  with Na to form Ni. A comparison of particle sizes and magnetic properties obtained via mechanochemical reaction with those obtained by the mechanical milling of equivalent Ni and NaCl mixtures is also reported.

## 2. Experimental

Anhydrous 99.9% pure  $\text{NiCl}_2$  powder ( $\leq 100 \mu\text{m}$ ), Na pieces ( $\leq 5 \text{ mm}$ ), Ni (4, 5  $\mu\text{m}$ ) and NaCl ( $\leq 500 \mu\text{m}$ ) all of 99.9% purity or greater were used as the starting materials. NaCl was added as a diluent to the  $\text{NiCl}_2 + \text{Na}$  starting mixture in order to avoid combustion [3].

The starting materials were loaded and sealed together with 4.8 mm steel balls in a hardened steel vial under high-purity argon atmosphere. The ball to powder mass ratio was 3 : 1. The milling time was varied between 0.5 and 150 h using a Spex 8000 mixer/mill.

The Ni particles were separated from NaCl through a process in which the as-milled powders were washed several times with deionised and deoxygenated water, and finally rinsed with methanol in an ultrasonic bath. The washed powders were dried under vacuum and directly transferred to a high-purity argon filled glove box. All subsequent powder handling was carried out in the glove box.

The structure was studied with a Siemens D5000 X-ray diffractometer with  $\text{CuK}_\alpha$  radiation. The microstructure and particle size were examined by transmission electron microscopy using a Philips 430 TEM equipped with an energy dispersive spectrometer (EDS) for composition analysis and a Gatan Image Filter GIF200 for elemental mapping. The Ni  $\text{M}_{23}$  edge at 68 eV in the electron energy loss spectra was utilised for constructing Ni mapping images with an electron acceleration voltage of 300 keV and energy filter width

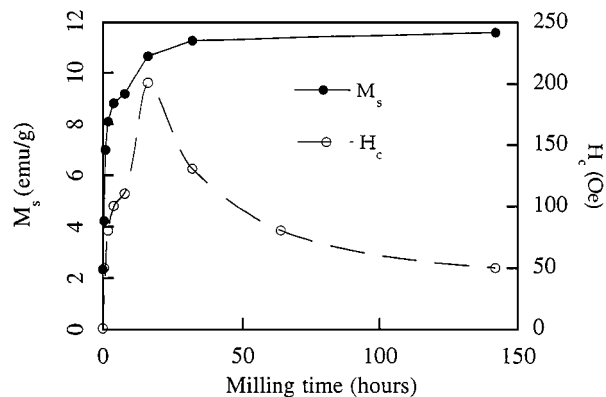


Figure 1 Saturation magnetisation,  $M_s$ , and coercivity,  $H_c$ , as a function of milling time for milling of  $\text{NiCl}_2 + 2\text{Na} + 1.5\text{NaCl}$ .

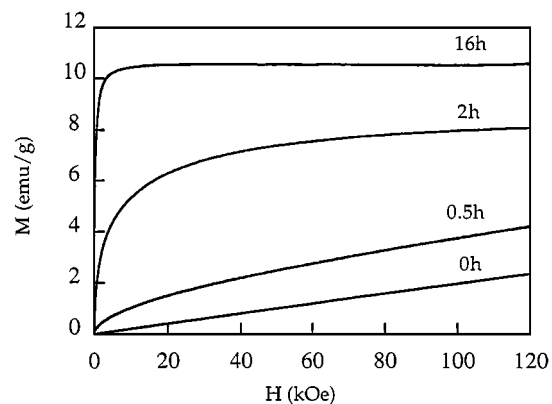


Figure 2 Magnetisation curves of samples milled for different times.

of 12 eV. A Joel 6400 scanning electron microscope (SEM) and a Joel 6300 field-emission scanning electron microscope (FESEM) were used to study of the morphology of the as-milled powders. Magnetic measurements were made at room temperature on cold-pressed cylinder samples using a Vibrating Sample Magnetometer (Oxford 3001 VSM) with a maximum applied field of 120 kOe.

### 3. Results

#### 3.1. Mechanochemical synthesis of Ni

X-ray diffraction measurements confirmed that Ni was formed in a continuous manner during the milling of  $\text{NiCl}_2 + 2\text{Na} + 1.5\text{NaCl}$ . The diffraction peaks for fcc-Ni appeared after milling for 1–2 h and their intensities relative to those of NaCl increased with increasing milling time and approached saturation after milling for ~16 h, in agreement with previous work [3].

Since metallic Ni is the only ferromagnetic phase present, the formation of Ni can be followed by magnetic measurements. Fig. 1 shows measurements of the saturation magnetisation,  $M_s$ , and coercivity,  $H_c$ , as a function of milling time. The  $M_s$  values increased rapidly with increasing milling time for the first 8–10 h and started to level off at milling times  $\geq 16$  h in agreement with the XRD measurements. The values of  $M_s$  were measured to be 10.5 and 12 emu/g for samples milled for 16 and 150 h, respectively. These values are close to the saturation magnetisation,  $M_s = 12.2$  emu/g, expected for the composition of Ni + 3.5NaCl [9], indicating that the solid-state reaction was nearly complete after milling for 15–20 h.

Magnetisation curves corresponding to different milling times are shown in Fig. 2. The starting mixture of  $\text{NiCl}_2 + 2\text{Na} + 1.5\text{NaCl}$  exhibited paramagnetic behaviour as evidenced by the linear dependence of magnetisation on the applied field. The magnetic susceptibility measured from the slope of the M-H curve,  $\chi = 1.96 \times 10^{-4}$  emu/g/Oe, is in good agreement with the value expected for the starting composition [9]. The magnetisation curves of samples milled for between 0.5 and 2 h could be fitted with a combination of a superparamagnetic Langevin function [10, 11] and a linear paramagnetic function. This fitting is consistent with the samples containing a mixture of superparamagnetic

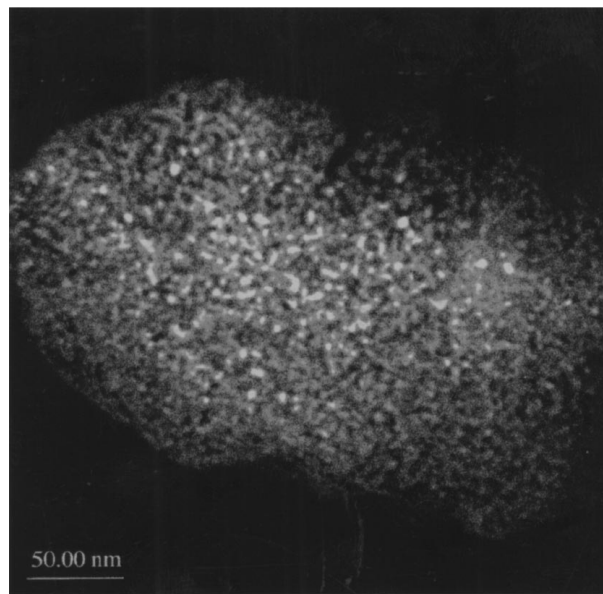


Figure 3 Ni mapped image of as-milled particle, milling time = 2 h.

Ni particles with a particle size of ~10 nm and unreacted paramagnetic  $\text{NiCl}_2$ .

The magnetisation curves of samples milled for 4–8 h could not be fitted with a combination of superparamagnetic Langevin and linear paramagnetic functions. Satisfactory fitting required the addition of a constant magnetisation component, indicating the presence of ferromagnetic Ni. Magnetisation curves typical of a ferromagnet were found in samples milled for 16 h or longer.

A TEM micrograph of an as-milled powder particle is shown in Fig. 3. Using the image filter to map Ni showed that the particle consisted of ~5 nm grains of Ni embedded in a NaCl matrix. The Ni particles obtained after removal of NaCl by the washing process were studied using electron microscopy (TEM and SEM). Samples milled for 1–2 h consisted of separable Ni particles with a particle size of 5–10 nm, as shown in Fig. 4a. The chain structure in Fig. 4a is due to magnetic interactions between single domain particles [12]. For samples milled for 8–16 h, small clusters were found, as shown in Fig. 4b, which consisted of many grains connected by grain boundaries. In samples milled for 32 and 64 h, all particles were multigrain particles with a broad distribution of particle sizes ranging 100–1000 nm. After

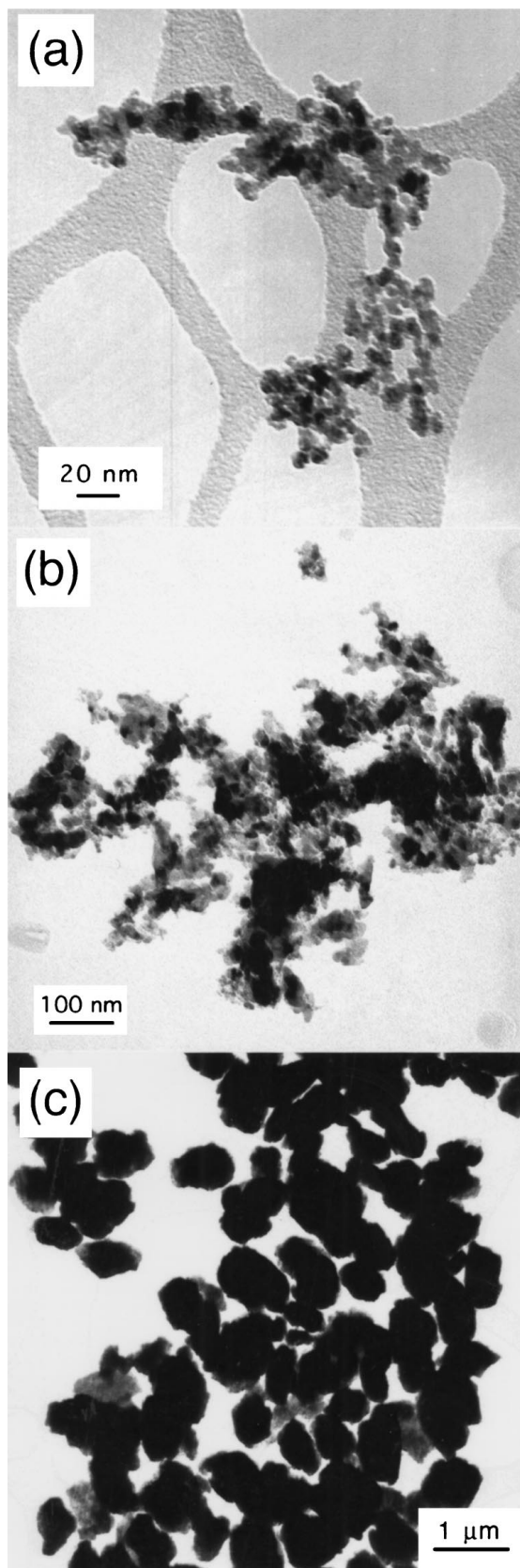


Figure 4 TEM micrographs of washed Ni particles after milling for (a) 2 h, (b) 16 h and (c) 142 h.

milling for 142 h, most particles were in the range of 400–1000 nm, as shown in Fig. 4c.

Washed samples milled for 16 and 142 h respectively were studied with FESEM. As shown in Fig. 5 the particles exhibited a cluster morphology. For the sample milled for 16 h (Fig. 5a), small clustered ~50 nm

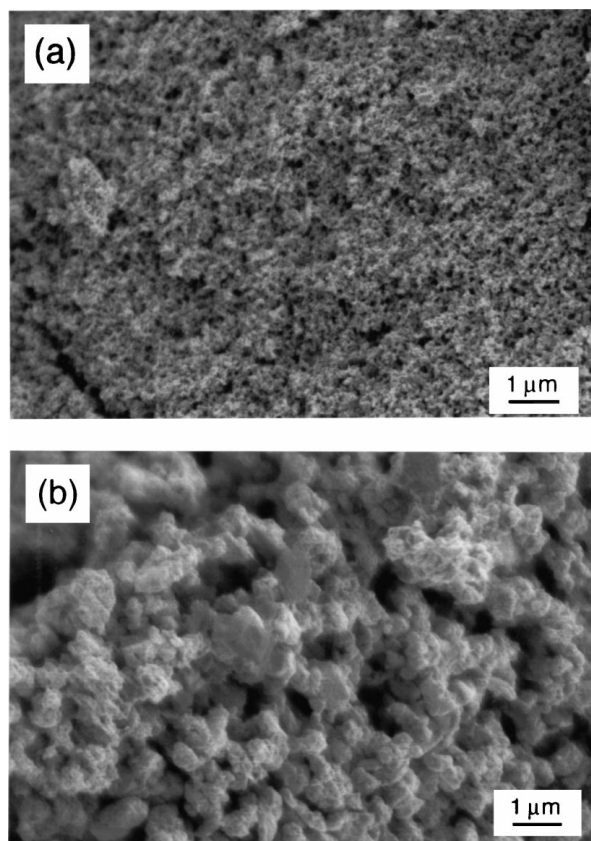


Figure 5 FESEM micrographs of washed sample after milling for (a) 16 h and (b) 142 h.

particles were observed, close to the single domain particle size, as expected from the magnetic measurements. Submicron particles were found in the sample milled for 142 h, as shown in Fig. 5b.

Fig. 6a and b are micrographs of bright-field and dark-field TEM images of a Ni particle in a sample milled for 142 h. The two TEM micrographs clearly show that the Ni particle is a multi-grain particle consisting of Ni grains with a crystallite size of 5–20 nm. Measurements of the effect of milling time on the average grain size determined using the Scherrer method are shown in Fig. 7. The grain size increased only slightly with increasing milling time, within the range 13–16 nm.

### 3.2. Effect of additional diluent

The effect of additional diluent on the  $\text{NiCl}_2/\text{Na}$  reaction was studied by increasing the amount of NaCl in the starting mixture by a factor of two. Fig. 8 shows the magnetic properties as a function of milling time for samples of  $\text{NiCl}_2 + 2\text{Na} + 3\text{NaCl}$ . Comparison of Fig. 8 with Fig. 1 shows that  $M_s$  and  $H_c$  for the samples containing 3NaCl vary with milling time in a similar manner as for the samples containing 1.5NaCl. However, increasing the volume fraction of diluent significantly decreased the reaction kinetics.

The microstructure of  $\text{NiCl}_2 + 2\text{Na} + 3\text{NaCl}$  was also similar to that observed in the milling of  $\text{NiCl}_2 + 2\text{Na} + 1.5\text{NaCl}$ . Separable 5–10 nm Ni crystallites were found after milling for short times. Extended milling resulted in the formation of clustered multi-grain particles

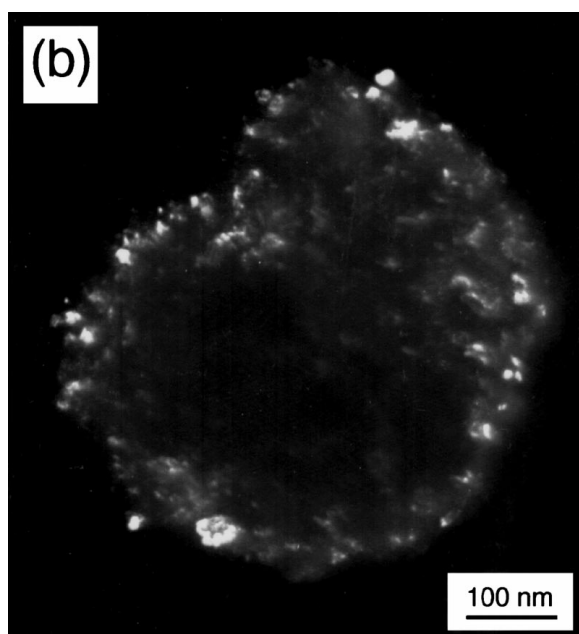
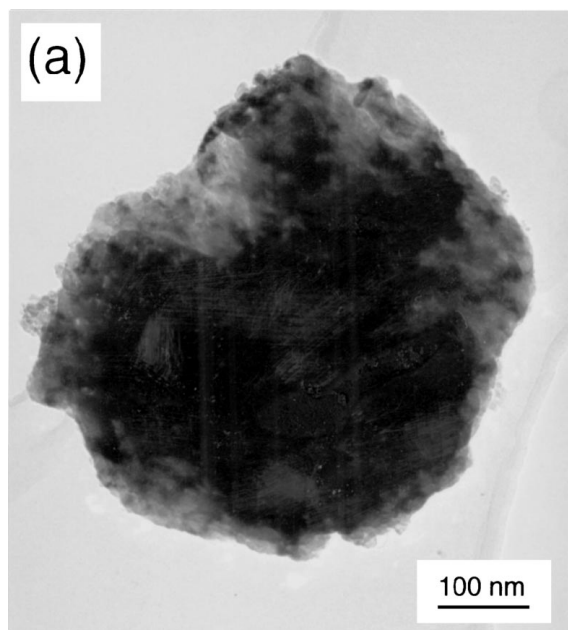


Figure 6 TEM micrograph of Ni particle after milling for 142 h; (a) bright field image, (b) dark field image.

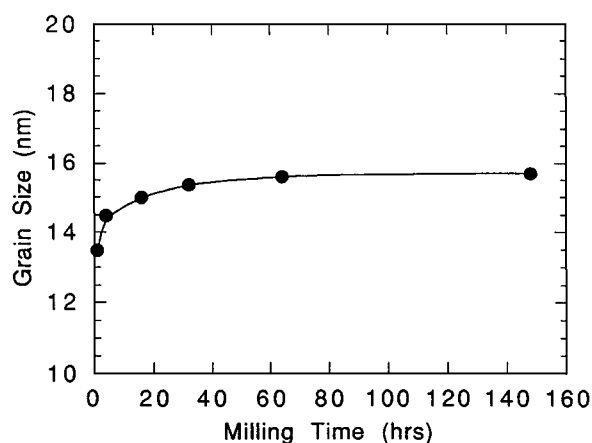


Figure 7 Effect of milling time on grain size.

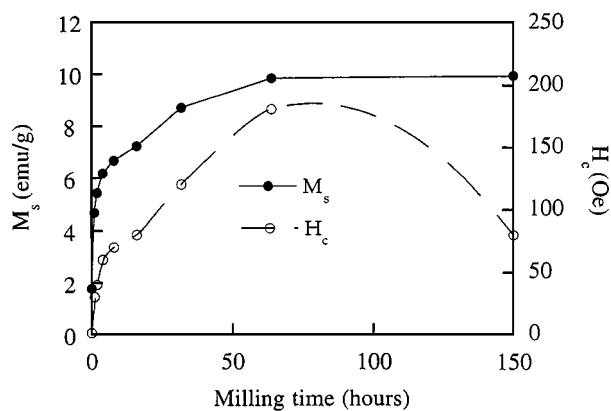


Figure 8 Saturation magnetisation,  $M_s$ , and coercivity,  $H_c$ , as function of the milling time for milling of  $\text{NiCl}_2 + 2\text{Na} + 3\text{NaCl}$ .

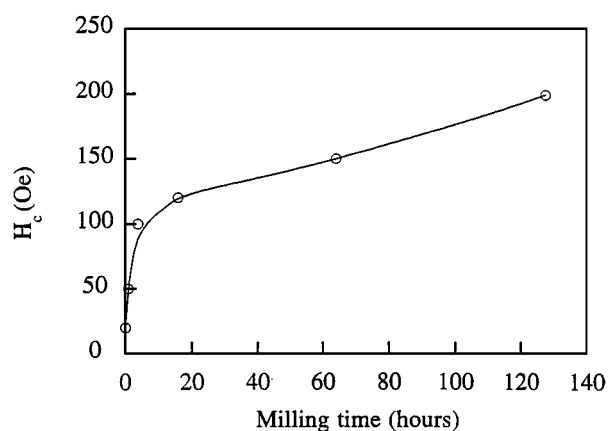


Figure 9 Effect of milling time on coercivity for Ni + 5NaCl mixture.

with sizes of 100–1000 nm resulting from interparticle welding.

### 3.3. Mechanical milling of Ni and NaCl

Mixtures of Ni and NaCl ( $\text{Ni} + 5\text{NaCl}$ ) were milled for times up to 128 h. Measurements of  $H_c$ , as a function of the milling time are shown in Fig. 9.  $H_c$  increased continuously with the milling time reaching 200 Oe in the sample milled for 128 h.

An optical micrograph of a sample milled for 16 h and washed is shown in Fig. 8. The Ni particles were mainly plate shaped, consisting of a deformed, layered morphology. The particle size decreased with increasing milling time and after  $\sim 100$  h was similar to that of the mechanochemically reacted Ni, however, the particles retained the elongated morphology.

## 4. Discussion

### 4.1. Evolution of microstructure

The TEM measurements show that the nucleation and growth of Ni particles occurs in two overlapping stages during milling. In the first stage crystallites of Ni form as individual separated particles. As shown in Figs 3 and 4a, the initial size of the Ni particles is  $\sim 5$  nm or smaller. These particles consist mainly of individual crystallites which form by mechanically activated reaction between

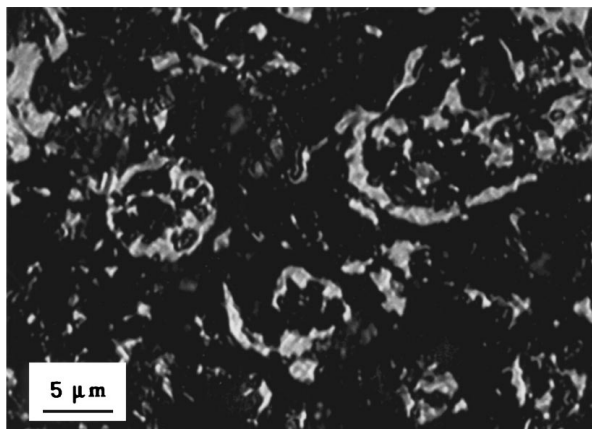


Figure 10 Optical micrograph of Ni + 5NaCl mixture milled for 16 h.

NiCl<sub>2</sub> and Na grains and are separated by the NaCl phase.

With continued milling, the Ni particles agglomerated together as a result of interparticle welding during collision events. As is evident in Figs 4 and 5, the particles evolved into clusters of crystallites which continue to increase in size progressively into micron sized particles with increasing milling time. As shown in Fig. 7, the crystallite size remained nearly constant as the particles grew to  $\sim 1 \mu\text{m}$  with increasing milling time.

In many ductile systems the particle size tends to a steady state value at long milling times, which is determined by the relative rates of welding and fracture. An increase in the particle size of ductile powders during mechanical milling has been reported previously for other systems [13]. In the present study, the role of fracture in limiting the growth of the Ni particles is not clear. As shown in Figs 5 and 6, there is no evidence of particle deformation as normally observed in mechanically milled ductile metal powders. The clustered particle morphology suggests that interparticle welding primarily occurs during collision events, similar to that observed by Harris *et al.* [14].

The addition of the diluent phase enabled Ni to form as separate particles. In addition the diluent has a significant effect on both the kinetics of the NiCl<sub>2</sub>/Na reaction and the subsequent rate of particle growth. The NiCl<sub>2</sub>/Na reaction kinetics are limited by the probability of collisions between the reactant phases during milling. As discussed previously, the addition of the diluent phase decreases the collision frequency between reactant particles, which reduces the reaction rate. With the NiCl<sub>2</sub>/Na reaction, previous studies have shown that the addition of diluents is essential to prevent combustion [3]. Comparison of Figs 1 and 8 shows that decreasing the volume fraction of NaCl from 33 to 49% increased the time required to complete the reaction by a factor of  $\sim 2$ . In addition, the rate of coalescence and growth of Ni particles during milling resulting from inter-particle welding associated with collisions events was also decreased by the presence of the diluent phase.

It is of interest to note that with samples containing 33 vol % NaCl in the starting mixture the milling time (Fig. 1) needed to achieve maximum coercivity was less than that required to complete the reaction, while

with 49 vol % NaCl (Fig. 8) the times coincided. The milling time required to achieve maximum coercivity may be associated with a critical particle size. Thus, the present of the diluent phase has a greater effect on the rate of particle growth than on the rate of the NiCl<sub>2</sub>/Na displacement reaction. Although modelling studies need to be carried out, this behaviour would be expected since the rate of particle growth depends on both the reaction rate and the rate of agglomeration of Ni particles during milling, both of which depend on the amount of diluent present.

## 4.2. Magnetic behaviour

The variation in the magnetic behaviour during milling may be rationalised in terms of the reaction kinetics and particle growth during milling. As discussed in Section 3.1, samples milled for short times (0.5–2 h) exhibited superparamagnetic behaviour due to the small particle size. The particle size estimated from the TEM measurements was in good agreement with values obtained from fitting of the Langevin function to the magnetisation curves in Fig. 2. With longer milling times the samples became increasingly ferromagnetic, and for milling times longer than 8 h it was not possible to distinguish a paramagnetic component of magnetisation. The increase in magnetisation with milling time is thus due to both Ni formation and particle growth. As shown in Fig. 1, the  $M_s$  measurements indicated that approximately 30 h was required to complete the reaction.

For short milling times the decrease in superparamagnetism with growth of the particles also caused the increase in  $H_c$  with increasing milling time. The magnetisation curves in Fig. 2 clearly show that the low coercivity values ( $\sim 50$  Oe) measured for samples milled for 1–2 h, were due to superparamagnetism. With particulate magnetic materials, the highest values of coercivity are expected to be exhibited by particles having the single domain particle size [15], which in Ni is 50–60 nm [11]. The maximum coercivity was exhibited in samples milled for 16 h. As shown in Fig. 4b, TEM examination of samples milled for 16 h showed particles of 30–100 nm, consisting of irregular clusters of grains. The maximum value of  $H_c$  was approximately the same for samples containing 33 and 49 vol % NaCl in the starting mixtures, confirming that the maximum value of  $H_c$  corresponds to a critical particle size. Further milling caused a decrease of coercivity, due to the increase of particle size above the single domain particle size [15].

## 4.3. Evolution of mechanically milled Ni/NaCl microstructure

The present measurements show that the microstructure of the milled Ni + NaCl mixture evolves in a completely different manner from that generated by mechanochemical reaction. During mechanical milling deformation, fracture and welding of the Ni particles occur, resulting in the formation of particles having layered microstructures similar to that observed in mechanically alloyed ductile powders. The particle size and microstructure are progressively refined during milling as compared

with the particle growth that occurs to the Ni particles formed mechanochemically.

It is of interest to note that, while similar particle sizes are obtained with both methods after milling for ~100 h, the coercivity of the mechanical milled Ni particles is significantly higher than that of the mechanochemically formed Ni. The difference in coercivity is due to different morphologies and microstructures of the Ni particles prepared by the two different methods. The high values of coercivity in samples prepared by milling of Ni and NaCl powders is due to the shape anisotropy of elongated structure of Ni particles, while the mechanochemically formed Ni particles have a quasi-spherical structure. It is possible that for significantly longer milling times similar microstructures may evolve for both methods.

## 5. Summary

Mechanical milling of  $\text{NiCl}_2 + 2\text{Na} + 1.5\text{NaCl}$  resulted in formation of nano-sized Ni particles after relatively short milling times. Magnetisation curves could be fitted with superparamagnetic Langevin function, from which the particle size was calculated to be ~10 nm. Longer milling times caused the formation and growth of Ni clusters due to interparticle welding during collision events. The peak in coercivity with increasing milling time was associated with reaching the single domain particle size. Increasing the amount of NaCl diluent present slowed the reaction kinetics.

The milling of micron-sized Ni and NaCl powders was carried out for comparison. A layered structure was observed after milling for a short times and further milling led to structural refinement. The Ni particles had elongated microstructures which resulted in high values of coercivity.

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