

# Reaction of Nickel Atoms with Molten Salts. A New Approach to the Synthesis of Nanoscale Metal, Metal Oxide, and Metal Carbide Particles

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Received February 2, 1993. Revised Manuscript Received May 24, 1993

Ni atoms have been vaporized into a variety of molten salts using a rotary metal vapor synthesis (MVS) reactor. The salts employed in this study were potassium formate, a eutectic mixture of lithium, sodium, and potassium acetates, and a eutectic mixture of sodium and potassium nitrates. The solid Ni products obtained in these reactions are nanocrystalline Ni metal, nanocrystalline Ni<sub>3</sub>C, and nanocrystalline NiO respectively. The products have been characterized by powder X-ray diffraction, infrared spectroscopy, elemental analysis, and BET single-point area analysis.

## Introduction

Metal vapor synthesis (MVS) experiments are almost invariably undertaken at cryogenic temperatures so that the vacuum requirements for efficient metal evaporation can be achieved.<sup>1,2</sup> However, a class of liquids not previously studied in detail, and which have low vapor pressures at relatively high temperatures, are molten salts.<sup>3</sup> These can be defined as melts consisting of ionic entities, e.g., NaCl(l), KCl(l) etc. In principle, a very large number of melts is available for study, but in practice there are certain restrictions. The melting point of the salts must be less than 400 °C so that a Pyrex reaction flask can be used safely under vacuum. Also, the salt should not decompose when molten and should be mobile in the liquid state so that a rotary MVS reactor can be used.

The molten salts chosen for this study satisfy the above criteria. Potassium formate is an example of an organic molten salt. It has a melting point of 167 °C, but rapid decomposition begins about 20 °C above this temperature. The alkali metal acetates all have melting points above 250 °C, but a convenient low-melting ternary eutectic, melting point 180 °C, is formed between lithium, sodium, and potassium acetates, which is stable well above the melting point. The thermal decomposition of potassium acetate has been studied by Ubbelohde and co-workers.<sup>4</sup> The main gaseous decomposition products at 350 °C are, in decreasing amounts: CH<sub>4</sub>, CH<sub>3</sub>COCH<sub>3</sub>, C<sub>4</sub>H<sub>8</sub>, H<sub>2</sub>O. The formation of acetone can be explained by eq 1. The



formation of methane is less easy to explain but is believed to be by reaction of CH<sub>3</sub>COOK with hydroxide or water impurities in the melt or by decomposition of the acetate radical.

The physicochemical properties of molten KNO<sub>3</sub> and NaNO<sub>3</sub> have been much more extensively studied.<sup>5</sup> KNO<sub>3</sub> and NaNO<sub>3</sub> form a stable eutectic, melting point 220 °C, which is ideal for MVS reactions. Apart from the ions K<sup>+</sup>, Na<sup>+</sup>, and NO<sub>3</sub><sup>-</sup>, a host of minor species whose concentration is very temperature dependent, exist, or have been proposed to exist in this melt. With the exception of the work by Brough and Kerridge<sup>6</sup> there has been little reported on the reactions of zerovalent bulk metals with nitrate melts. The more electropositive metals Na, Ca, and Mg react readily at low temperature producing a steady evolution of gas. The less reactive transition metals require much higher temperatures; for example, bulk Ni metal is only surface oxidized at >500 °C in these melts.

MVS is a synthetic technique that has been used extensively for the synthesis of organometallic products, and it is only recently that MVS has been used to produce what are to be considered more classical inorganic materials. The advantage in using MVS is that solid products with very fine particles and hence large surface areas can be made. The interesting properties of nanocrystalline materials are the subject of recent reviews.<sup>7-9</sup> Nanocrystalline oxides are especially useful and are being widely studied as catalysts,<sup>10</sup> as destructive adsorbents,<sup>11</sup> as gas-sensor materials,<sup>12</sup> and as precursors to ceramic materials.<sup>7</sup> The production of nanocrystalline carbide powders is of interest, because in subsequent device fabrication, sintering temperatures<sup>6</sup> are lowered leading to products with higher tensile strengths. Highly dispersed metals are, of course, of interest as potential catalysts.

Earlier work on metal atom-molten salt chemistry<sup>3</sup> has shown a wide variety of chemical reactions can take place. Transition metal oxides are formed by evaporation of first-

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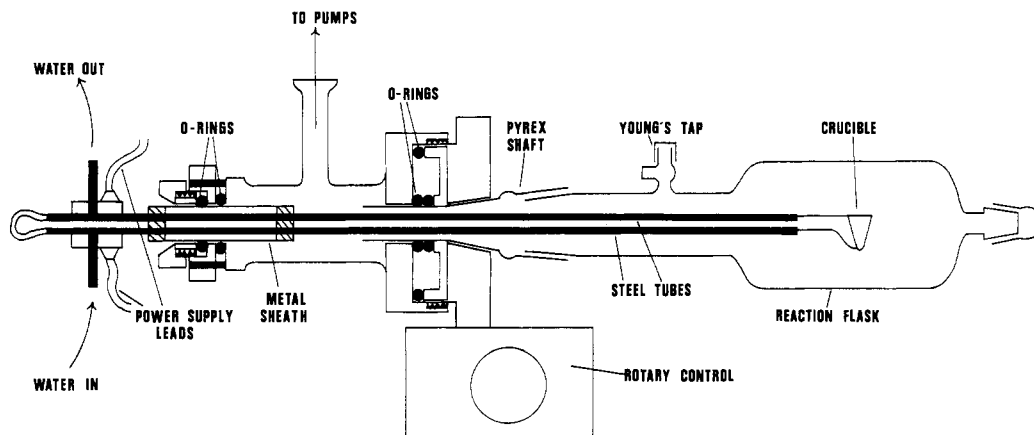


Figure 1. Metal vapor rotary solution reactor used for condensing metal atoms into molten salts (a modification of Timms and Hooker).<sup>3</sup>

row transition metals into molten alkali metal nitrates and nitrites. The more noble metal atoms, e.g., Pd, Ag, and Au, are not oxidized by these melts and form dispersed metal powders. Second-row transition metals, e.g., Ru and Rh, form stable complexes. Reactions of Cr and Mo atoms with  $C_6H_5COONa$ ,  $p-CH_3C_6H_4COONa$ , or  $m-CH_3-C_6H_4COONa$ , dissolved in the acetate eutectic give, among other products, bis(arene) transition-metal complexes. The evaporation of W, Ni, and Pd atoms into molten KSCN gives a mixture of cyano and thiocyanato complexes. Alkali metal halide salts tend to be inert to transition metal atoms, and the bulk metal forms on the surface of these molten salts.

This paper attempts a more in-depth analysis of metal atom reactions with molten salts, by investigation of one metal with a range of molten salts. The aim has been to test this approach for the preparation of nanoscale particles of metals, metal oxides, and metal carbides.

### Experimental Section

The reactions were carried out in a rotary metal vapor synthesis reactor based upon the design of Timms.<sup>1</sup> This reactor consisted of essentially three parts: the rotary section, the reaction vessel, and the vacuum system (Figure 1). The whole apparatus was built around a modified Buchi rotary evaporator. At approximately halfway along its length, a Pyrex shaft was attached to the Buchi rotary section by means of a cone and socket joint. At one end of the shaft, Viton O-rings provided an airtight seal with the reactor casing. At the other end, the shaft had a B-45/50 ground joint where the reaction flask was attached.

The Pyrex reaction flask consisted of a cylindrical bulb of volume 150 cm<sup>3</sup>, attached to a long neck terminating in a B-45/50 ground joint. The bulb shape permitted good wetting of the inner walls of the flask with the minimum amount of molten salt.

The electrode assembly consisted of two water-cooled 6-mm stainless steel tubes held rigidly in a metal sheath by epoxy resin. This assembly could be slid in and out of the reactor on an airtight O-ring "muff-seal" with which the metal sheath was in contact with the reactor casing. The alumina crucible<sup>13</sup> could therefore be kept clear of the salts when they were initially heated and slid into position when the melt was completely wetting the reaction flask.

The vacuum conditions in the reaction flask were achieved by an oil diffusion pump and cold trap, backed by a one-stage rotary pump. When no reaction was taking place, the pressure could be maintained below 10<sup>-3</sup> Torr.

Because of the hygroscopic nature of the materials, all the salts used in the experiments were predried for two days under vacuum at temperatures below their melting points. They were then transferred to an inert-atmosphere box (Vacuum/Atmospheres HE-43 series Dri-Lab) where grinding, mixing, and transfer to the reaction vessel took place. Typically, 10–15 cm<sup>3</sup> of molten salt was used in a reaction.

**General Reaction Procedure.** The salts were heated under vacuum by means of a Bunsen burner. This melted and further dried the salts, giving clear and colorless liquids. The rotary motion of the reaction flask caused the molten salts to wet the inner walls of the flask. At this point, the crucible containing Ni shot (1.0–1.5 g, 99.5%) was slid into position and metal evaporation begun. Once the deposition of Ni was completed (0.2–0.6 g), the molten salts were allowed to cool and solidify. To extract the products, 10 cm<sup>3</sup> of a suitable solvent was admitted under argon into the reaction flask via a syringe. The rotary motion aided dissolution of the alkali metal salts, resulting in a slurry containing the solid product and dissolved salts. The slurry was removed from the flask via a cannula. This process was repeated until all the unreacted salts and products have been obtained. Water used for extraction was deoxygenated by bubbling argon through it for 3 h. Organic solvents used were freshly distilled under argon from suitable drying agents prior to use. All subsequent manipulations involving solvents or solutions were undertaken using a Schlenk line, an argon gas supply, and standard vacuum/inert atmosphere techniques where necessary. Manipulation of air-sensitive solids was done in the inert atmosphere box.

Powder X-ray diffraction patterns were obtained using a Scintag XDS 2000 scanning diffractometer over the range 20–100° at a rate of 2°/min. Air-sensitive samples were pacified prior to measurement by allowing slow contact with air. The sample crystallite size was calculated using the Scherrer equation with reference to KCl. Phase identification was done by comparison to the JCPDS powder diffraction file.<sup>14</sup>

The BET surface area values for the samples were obtained with a Micrometrics Flowsorb II 3000 apparatus. Infrared spectra were measured using a KBr pellet technique and a Perkin-Elmer 1330 spectrophotometer. <sup>1</sup>H NMR data were obtained using a WM 400-MHz instrument. Mass spectra were recorded on a Finnegan MAT CH5 instrument. Carbon and hydrogen analyses were obtained from Galbraith laboratories. Metal analyses were determined by a gravimetric procedure.<sup>15</sup> Nitrite and carbonate anions were determined using titrimetric procedures.<sup>15</sup>

### Results

**Nickel Atoms and KNO<sub>3</sub>/NaNO<sub>3</sub>.** Evaporation of Ni atoms into the nitrate melt produced a finely divided,

(14) Powder Diffraction File: Inorganic Phases; JCPDS, International Center for Diffraction Data, 1985.

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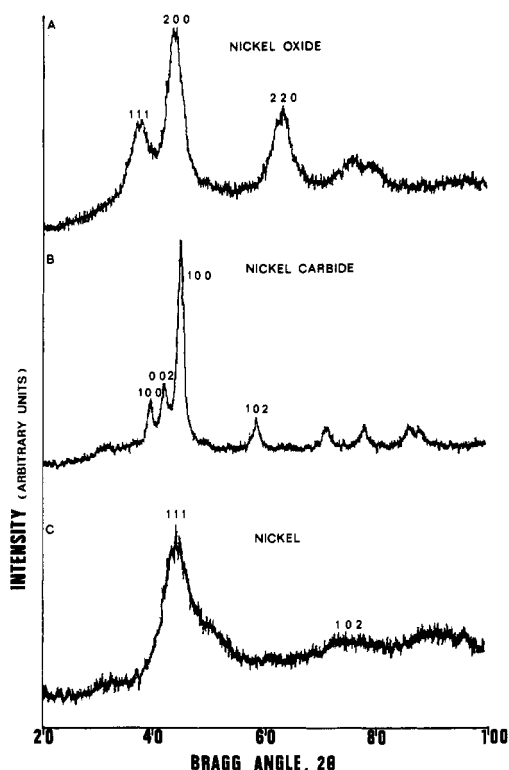


Figure 2. (A) XRD pattern of NiO from  $\text{NaNO}_3/\text{KNO}_3$  melt. (B) XRD pattern of  $\text{Ni}_3\text{C}$  from  $\text{LiOAc}/\text{NaOAc}/\text{KOAc}$  melt. (C) XRD pattern of Ni metal from  $\text{KOOCH}$  melt.

suspended, black solid. Extraction of the cooled solidified melt with water yielded an insoluble black powder. This was removed from the aqueous solution of nitrates and soluble products by filtration.

The black product, A, was identified as nanocrystalline NiO on the basis of its X-ray diffraction pattern (Figure 2). The analytical data obtained for A, a typical sample, are contained in Table I. These values were consistently reproducible for several samples. The yield of NiO products, calculated from the amount of Ni evaporated, ranged between 80 and 87%. These values are large compared to conventional MVS reactions undertaken at cryogenic temperatures, where yields of organometallic products rarely exceed 30%.

The NiO particle size (calculated from the BET surface area) is only slightly larger than the crystallite thickness (calculated from the broadening of the X-ray diffraction lines). This implies that the particles are comprised of individual crystallites, with little agglomeration. The IR spectrum of A showed a broad absorption between 3600 and 3000  $\text{cm}^{-1}$ , indicative of  $\text{H}_2\text{O}$  adsorbed onto the NiO particles. However, no IR absorptions due to  $\text{NO}_3^-$  anions were detected.

Heating A at various temperatures progressively removed the adsorbed water but caused the NiO particles to sinter. This was evidenced by sharper peaks in the X-ray diffraction pattern and with a marked decrease in surface area. After heat treatment at 500  $^\circ\text{C}$  for 5 h, the  $\text{H}_2\text{O}$  was completely removed, and the sample did not absorb significant amounts of water from the atmosphere. It was not possible to remove  $\text{H}_2\text{O}$  under vacuum at ambient temperature and hence prevent sintering of the small NiO crystallites. For an unheated sample with water present, the amount of Ni was analyzed to be 71 wt %. However, when dry, the amount of Ni for the same sample

approached that of NiO, 78.6 wt %, much more closely (Table I).

Analysis for  $\text{NO}_2^-$ , nitrite anions, was carried out on the aqueous solution containing the dissolved  $\text{KNO}_3$  and  $\text{NaNO}_3$  after the reaction with Ni atoms. The ratio of Ni evaporated: $\text{NO}_2^-$  produced was found to be 1:1 for all the experiments.

**Nickel Atoms and  $\text{Li}^+/\text{Na}^+/\text{K}^+$  Acetate.** Evaporation of Ni atoms into the molten acetate eutectic produced a black solid suspended in the melt and the evolution of gas. The rate of gas evolution was directly proportional to the rate of metal evaporation and also to the melt temperature. The rate also increased continuously throughout the course of the experiment. When gas evolution became too fast, the reaction had to be halted as the increase in pressure prevented efficient Ni evaporation. Typically, 0.2 g of Ni could be evaporated before this stage was reached. The gas could not be trapped at 77 K and only very small amounts could be collected by isolating the reaction flask from the dynamic pumping system, before Ni evaporation ceased, and gas production stopped. Analysis of the gas sample by mass spectroscopy gave no peaks above 10 amu, and hence it was tentatively identified as  $\text{H}_2$ .

To extract the solid black product, the alkali metal acetates were dissolved in MeOH. The resulting suspension was filtered yielding black powder and an orange solution. The black powder was divided into samples. One sample, B, was washed with MeOH, and the other sample, C, was washed with  $\text{H}_2\text{O}$ . Both B and C, when dry, were invariably pyrophoric when exposed to air rapidly, a property associated with highly dispersed materials. The amount of alkali metal acetate remaining with the solid samples varied as to the washing procedure used. If only MeOH was used, sample B, a significant amount of acetate impurity was present, as evidenced by the IR spectrum and elemental analysis (Table I). However, the BET surface area remained high. If portions of  $\text{H}_2\text{O}$  were used to wash the solid (in which alkali metal acetates are very soluble), the acetates were removed beyond detection limits. However, the surface area decreased. It should be noted that if water was used for the extraction of the sample, the surface area was reduced to near zero! (The crystallites remained small, but presumably agglomerated to relatively large particles.) Thus, extraction in methanol followed by washing with  $\text{H}_2\text{O}$  provided a compromise between obtaining pure samples, while retaining a high surface area. The X-ray diffraction pattern for both B and C showed  $\text{Ni}_3\text{C}$  as the only crystalline phase present.

**Nickel Atoms and  $\text{K}^+$  Formate.** Evaporation of Ni atoms into  $\text{K}^+$  formate produced a black solid suspended in the melt and gas evolution. The rate of gas evolution was not proportional to the rate of metal evaporation but was very sensitive to melt temperature. This implies that unlike the Ni atom/alkali metal acetate reaction, the gas evolution was due to  $\text{K}^+$  formate thermal decomposition and not to Ni atom reaction with the melt although the presence of the Ni did lower the decomposition temperature somewhat.

After the reaction, the black solid was obtained by dissolving the  $\text{K}^+$  formate in MeOH and filtering the slurry. Unlike the  $\text{Ni}_3\text{C}$  from the Ni/acetate reaction, the solid from this reaction could not be purified by washing with MeOH or  $\text{H}_2\text{O}$  to remove adsorbed  $\text{K}^+$  formate. The composition of the products obtained from different reactions was variable. Elemental analysis showed a

Table I

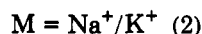
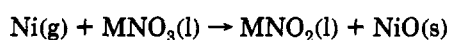
sample	melt	extraction solvent	washing solvent	species I.D. by XRD	crystallite size (nm)	BET S.A. (m <sup>2</sup> g <sup>-1</sup> )	particle <sup>a</sup> size	elemental anal. (wt %)		
								Ni	C	H
A	KNO <sub>3</sub> /NaNO <sub>3</sub>	H <sub>2</sub> O	H <sub>2</sub> O	NiO	(2.6–3.1)	230	36	77.0 <sup>c</sup>		
B	Li/Na/K acetate	MeOH	MeOH	Ni <sub>3</sub> C	(9.0–12)	89		78.2	15.8	0.81
C	Li/Na/K acetate	MeOH	H <sub>2</sub> O	Ni <sub>3</sub> C	(8.5–11)	40	94	89.1	10.6	<0.5
D	K <sup>+</sup> formate	MeOH	MeOH	Ni	<i>b</i>	16		71.4	8.52	<0.5
E	K <sup>+</sup> formate	MeOH	H <sub>2</sub> O	Ni		13		77.0	7.01	<0.5

<sup>a</sup> Particle size values given only where sample consists of initially one phase. <sup>b</sup> Crystallite sizes not measurable from XRD, as peaks were too broad and overlap each other. <sup>c</sup> % Ni obtained from sample heated to 500 °C to eliminate H<sub>2</sub>O.

substantial amount of carbon present (Table I). However, the X-ray diffraction implied the product consisted of a very small Ni crystallites with some NiO. This implied the presence of carbon was due to the adsorbed K<sup>+</sup> formate and not Ni<sub>3</sub>C. This was confirmed by IR analysis. The BET surface areas were only moderate.

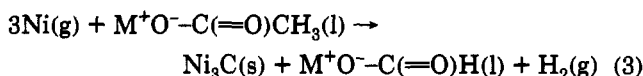
### Discussion

All the evidence suggests that the reaction of Ni atoms with the nitrate melt can be represented by the following equation:



The heat of reaction for eq 2 is calculated in Table II (at standard temperature and pressure) for both bulk Ni metal and Ni metal atoms (reactions 1 and 2). The values indicate that the formation of NiO is thermodynamically favorable in both cases, but is more exothermic when Ni atoms are used, as expected. The NiO obtained is XRD phase pure, the only measurable impurity being adsorbed H<sub>2</sub>O which cannot easily be removed, and perhaps this is to be expected with such high surface area oxides. The high yields obtained imply metal atom reactions at elevated temperatures are efficient reactions with no zerovalent metal particles as a side product. Also, the complete oxidation of the Ni atoms shows that under the appropriate conditions, transition metals can react quantitatively with nitrate melts.

In contrast to the Ni atom/nitrate melt reaction, Ni atom/organic melt reactions are much more complex, and simple, stoichiometric equations are written with less confidence. However, eq 3 describes our findings. On



first inspection, one might expect the Ni atoms to react with acetate to form NiO rather than Ni<sub>3</sub>C, as formation of NiO appears to be much more thermodynamically favorable.  $\Delta H_f^\circ$  NiO = -238 kJ mol<sup>-1</sup>  $\Delta H_f^\circ$  Ni<sub>3</sub>C = 67.1 kJ mol<sup>-1</sup>.<sup>16</sup> However, this reaction pathway seems to be disfavored. Calculation of values for the heats of reaction for selected pathways (at standard pressure and temperature) gives insight into the thermodynamics of possible processes (Table II). The difference in values for reactions 3 and 4 clearly illustrates the thermodynamic advantage of using Ni metal atoms over bulk Ni metal. With Ni

Table II

reaction no.	reaction	$\Delta H_f^\circ$ , heat of reaction <sup>a</sup> (kJ mol <sup>-1</sup> )
1	Ni(s) + NaNO <sub>3</sub> (s) → NiO(s) + NaNO <sub>2</sub> (s)	- 129
2	Ni(g) + NaNO <sub>3</sub> (s) → NiO(s) + NaNO <sub>2</sub> (s)	- 555
3	3Ni(s) + CH <sub>3</sub> COONa(s) → Ni <sub>3</sub> C(s) + HCOONa(s) + H <sub>2</sub> (g)	+109
4	3Ni(g) + CH <sub>3</sub> COONa(s) → Ni <sub>3</sub> C(s) + HCOONa(s) + H <sub>2</sub> (g)	- 1170
5	Ni(s) + CH <sub>3</sub> COONa(s) → NiO(s) + CO(g) + CH <sub>3</sub> Na(s) <sup>b</sup>	+382
6	Ni(g) + CH <sub>3</sub> COONa(s) → NiO(s) + CO(g) + CH <sub>3</sub> Na(s) <sup>b</sup>	- 43.6

<sup>a</sup> From ref 16. <sup>b</sup> Heat of formation of CH<sub>3</sub>Na estimated from heat of formation of CH<sub>3</sub>Li (from ref 17).

metal atoms, the process to form Ni<sub>3</sub>C is highly exothermic, as opposed to endothermic with bulk Ni (reactions 5 and 6).

The evidence implies that Ni atoms cleave the carbon-carbon bond in the acetate moiety, with the methyl carbon atom becoming the carbidic carbon in the Ni<sub>3</sub>C product. When there are no methyl carbon atoms present, no Ni<sub>3</sub>C is formed, as is observed in the Ni atom/potassium formate reaction.

Earlier studies have shown that Ni atoms, or rather Ni clusters, will cleave carbon-carbon bonds in "inert" solvents such as alkanes even at very low temperatures.<sup>18</sup> The Ni powders obtained consist of nanocrystalline Ni metal and species such as Ni-CH, Ni-CH<sub>2</sub>, and Ni-CH<sub>3</sub>. Simply heating these powders under an argon atmosphere at 181 °C produces Ni<sub>3</sub>C.<sup>19</sup>

In an acetate melt environment it is likely that a similar mechanism is in operation. The Ni atoms aggregate to form clusters (either on the molten salt surface or while migrating through the salt) which then cleave the carbon-carbon bond to give Ni<sub>cluster</sub>-CH<sub>x</sub> species. At 180 °C, the melt temperature, these Ni species would be expected to lose H<sub>2</sub>(g) and hence form Ni<sub>3</sub>C. (In the present work and earlier studies there is a propensity for small Ni clusters to form Ni<sub>3</sub>C when heated in contact with organic reagents, even when oxygen is present in the organic reagents. Single Ni atoms might not cleave C-C bonds, because it takes a cluster of at least three Ni atoms to form one "molecule" of Ni<sub>3</sub>C.) The remainder of the cleaved acetate ion may form formate ions as an intermediate before further decomposition to carbonate ions. It can be estimated that the ratio of acetate:formate would be 200–500:1 after a typical reaction, assuming no formate decomposition. This ratio prohibits detection of formate by <sup>1</sup>H NMR.

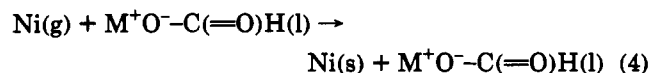
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Equation 4 describes the results of Ni atom deposition into formate melts; simple Ni atom agglomeration took place, the formate ions were essentially inert. In this case as well, very small crystallites of material were produced.



It is perhaps a surprising result that from all three of these products, NiO, Ni<sub>3</sub>C, and Ni produced in molten salts remain nanoscale in dimension and are indeed smaller than comparable samples formed in cryogenic MVS reactions. It is intuitively expected that compound formation in high-temperature melts would cause sintering of the products to coarse-grained, low surface area materials. However, it appears to be an intrinsic property of ionic liquids to prevent this sintering.<sup>20</sup> Adsorption of the melt cations and anions helps the Ni products be

compatible with the molten salt system. Once the NiO or Ni<sub>3</sub>C crystallites reach a certain size, it becomes much less thermodynamically favorable to sinter the particles, as the charged surface species have to rearrange themselves through the quasi-crystalline melt lattice. The adsorbed ions therefore act as a barrier to sintering, and the crystallites remain small. This is true only as long as products are insoluble in the melt.

The strongly adsorbed ions are difficult to remove, unless a solvent which has a high affinity for such ions is used, e.g., H<sub>2</sub>O in these cases. The dissolution of adsorbed surface ions does not noticeably affect the crystallite size, but has a major influence on the particle size and surface area.

**Acknowledgment.** The support of the National Science Foundation is acknowledged with gratitude.

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