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**PREPARATION OF COLLOIDAL METALS  
OF IRON GROUP WITH UNCAPPED SURFACE IN POLAR APROTIC MEDIUM**

A novel method of preparation of the nanoscale Fe, Co and Ni metals in colloidal form and as nanopowders is based on reduction of metal halides with sodium naphthalide in solutions of N-methyl pyrrolidone (NMPO). Room temperature reactions followed by solution annealing at 170–200 °C result in formation of uncapped nanoparticles of iron and cobalt metals and nickel carbide Ni<sub>3</sub>C. Colloidal metallic nickel was obtained in reaction of colloidal iron with NiCl<sub>2</sub> in NMPO solutions. The surface of the obtained metallic nanoparticles is capable of chemical derivatization; their post-synthesis reaction with oleic acid resulted in hydrocarbon-soluble products.

Searching for convenient methods of preparation of colloidal metals represents chemist's efforts with a long history. One of the older tasks relates to catalysis with the emphasis on heavy transition metals. Most of the developed methods for preparation of their colloids are based on the facile reduction of metal cations possessing high reduction potentials, which could be easily done in aqueous solutions. Nowadays, a broader range of applications determined the demand for more electropositive metals in colloidal state. New tasks appear to be more challenging as they require protection from oxygen and using stronger reducing agents. Water as a solvent becomes less suitable, especially for more reactive metals. The highest reducing power has been approached in the systems utilizing lithium [1–3] or sodium [4, 5] naphthalides, and alkali and electride anions [6–9]. Reduction of metal cations is typically performed in solvents with low polarity, hydrocarbons or ethers such as THF, glyme, diglyme, dimethyl ether, etc. Such active metals as alkaline earths (Mg, Ca), lanthanides and actinides have been obtained by these methods as fine powders.

In this paper we report a new facile method for preparation of the nanoscale metals in colloidal form and as nanopowders. The new method is applicable to relatively active metals and, importantly, allows the post-synthesis surface chemistry. We performed reduction of anhydrous metal chlorides and bromides with sodium naphthalide using one of the "supersolvents", N-methyl pyrrolidone (NMPO), as a reaction and colloid-forming medium. Capping ligands or surfactants are not necessary in this method since the solvent and ionic by-products provide a sufficient colloid stabilization. As we have demonstrated, the nanoparticles of metals isolated from these colloids possess active surface allowing its derivatization with the desired capping ligands. The pro-

posed method will be useful for the development of new catalysts, as well as functional materials for microelectronics, information storage and for biology and medicine.

The reagents and solvents were purchased: anhydrous iron (II) chloride, cobalt (II) bromide and nickel (II) chloride from Alfa Aesar, naphthalene, anhydrous 1-methyl pyrrolidinone, tetrahydronaphthalene and decahydronaphthalene from Aldrich, sodium from Fisher Scientific. All manipulations were performed in the atmosphere of ultrapure nitrogen in a glovebox of the Vacuum Atmospheres Company (VAC). Dynamic Light Scattering (DLS) experiments were performed on Malvern Zetasizer Nano instrument. Powder X-ray diffraction studies were performed on Scintag, XDS 2000 diffractometer (CuK<sub>α</sub> radiation). Transmission Electron Microscopy studies were performed on JEOL 2011 TEM instrument.

In a typical preparation, 5 mmol of anhydrous metal chloride (or bromide) dissolved in 50 mL of N-methyl pyrrolidone (NMPO); 10 mmol of flattened sodium metal and 15 mmol of naphthalene dissolved in 50 mL of NMPO (usually dissolution at room temperature is completed in 1.5–2 h). Both solutions are centrifuged prior to mixing in order to separate possible contaminants. The second solution is rapidly added to the first one at room temperature under intensive stirring. After several hours, the solution is centrifuged in order to separate precipitated sodium chloride and possible agglomerated metal. Thermal treatment is done in Kjeldahl flasks heated with heating mantle at high voltage output to maintain ~10 deg/min rate. Intensive stirring is maintained during the experiment. After cooling, the precipitation is initiated by adding tetralin and decalin to NMPO colloids; the precipitates are washed with tetralin and decalin and dried in vacuum. Sur-

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face derivatization is done by treatment of the original NMPO colloid or freshly precipitated powders with excess of the desired capping ligand.

Formation of colloidal metals by reduction of metal ions in solutions of N-methyl pyrrolidone was studied at room temperature followed by elevated temperature treatment. The reduction reaction takes place instantly upon addition of sodium naphthalide solution to a metal salt solution, resulting in formation of brown-black fluids with no visible light scattering properties. The obtained liquids contained 0.05 mol/L of metals; growth of colloidal particles in these solutions was monitored by the Dynamic Light Scattering method. Initial measurements were performed within 30 min after mixing of the reagents, indicating the presence of 2–3 nm particles in solutions. The dynamic nature of these solutions was evidenced by enlargement of these particles in time; the 24-hour-old solutions contained 3–4 nm particles. In the next step, the obtained solutions were thermally treated to promote the nanocrystal growth. In all experiments the temperature was raised with a high rate of ~10 deg/min, ending at 200 °C, which

is close to the boiling point of NMPO (202 °C) at atmospheric pressure. Iron colloids remained transparent (in thin layer) throughout 20–30-min experiments; the DLS studies showed the presence of 4.5–5 nm particles (fig. 1).

Cobalt colloids exhibited some light scattering at 190–200 °C within 1–2 min (fig. 2); however nickel colloids showed a sign of decomposition sooner than others producing suspensions of black solid at as low temperature as 180–190 °C.

In order to identify the products of the reactions, the colloids were heated at 200–202 °C for 30 min followed by cooling to room temperature and isolation of the solids. Iron colloids appeared to be more stable than others again; in order to facilitate precipitation, it was necessary to add a non-polar solvent tetralin. The obtained precipitates were strongly magnetic (this property was used for their separation from solutions) and air-sensitive. Cobalt-containing colloids did not require any precipitation assistance and produced solids with pronounced magnetic properties with no tetralin added. The solids obtained from colloids of nickel surprisingly appeared to be non-magnetic.

The X-ray diffractometry studies of the obtained solids (the samples were protected from oxidation with polymeric film) showed that nickel-containing product is actually hcp-structured nickel carbide  $\text{Ni}_3\text{C}$  mixed with NaCl (fig. 3).

Powders obtained from cobalt colloids showed only weak diffraction, presumably attributed to metallic cobalt. Iron-containing powders in our experiments appeared to be amorphous. Attempts to examine these powders under open air (to eliminate sensitivity loss due to protecting film) resulted in immediate exothermic oxidation. In order to obtain stronger evidence of the metallic nature of the iron and cobalt products, both solids were annealed at 600 °C in vacuum. Both products showed sharp peaks in their X-ray diffractograms, corresponding to cubic iron and cobalt metals (figs. 4, 5).

Since metallic nickel did not form in our reaction sys-

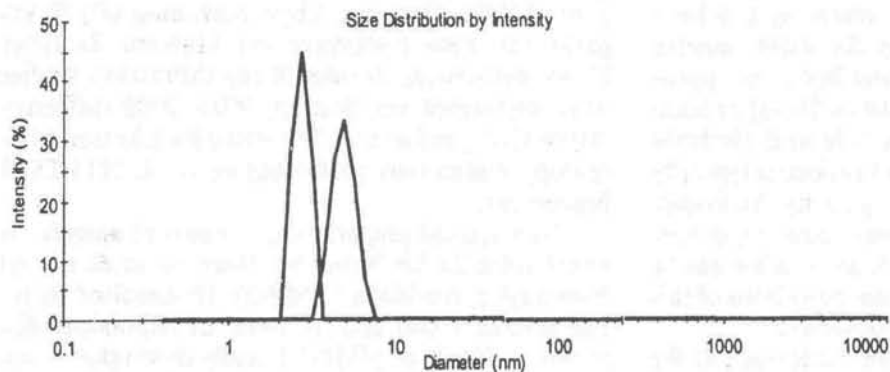


Fig. 1. Dynamic Light Scattering spectra of iron colloids: 2.71 nm — room-temperature product; 4.84 nm — colloid after heating at 200 °C.

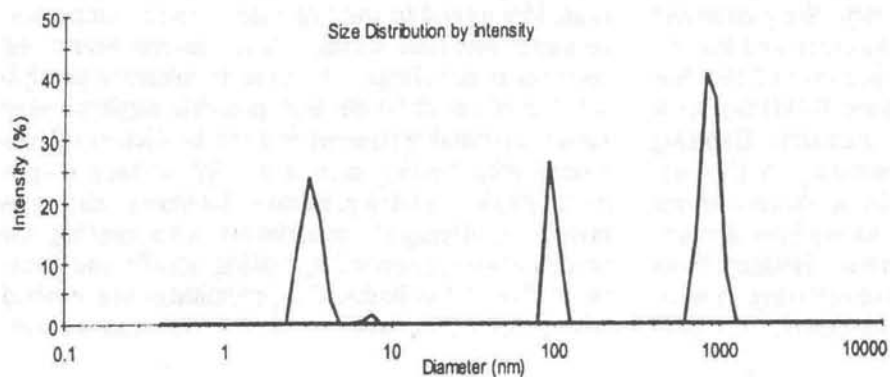


Fig. 2. Dynamic Light Scattering spectra of cobalt colloids: 3.25 and 96 nm — room-temperature product; 880 nm — colloid after heating at 170 °C.

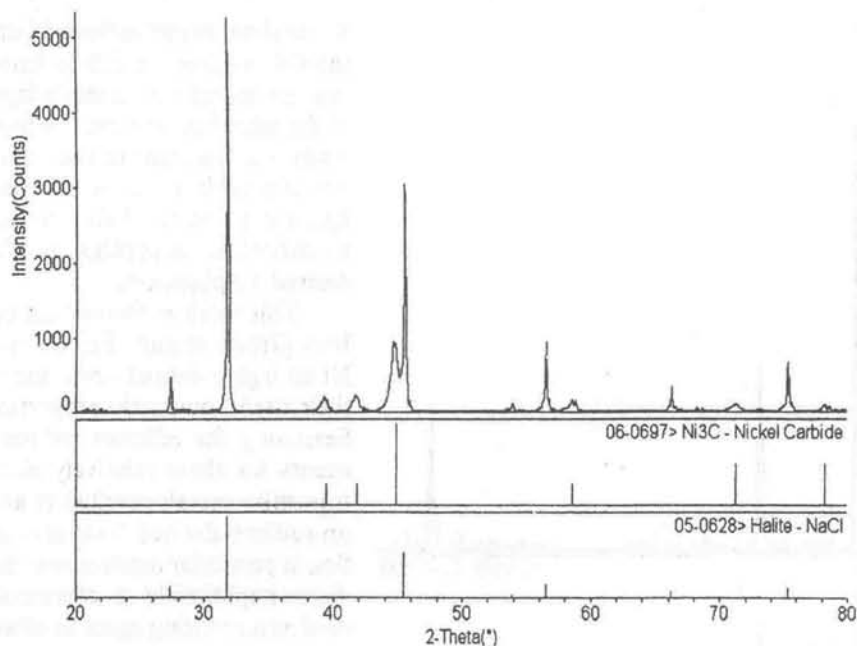


Fig. 3. X-ray diffractogram of the powders obtained from nickel precursors.

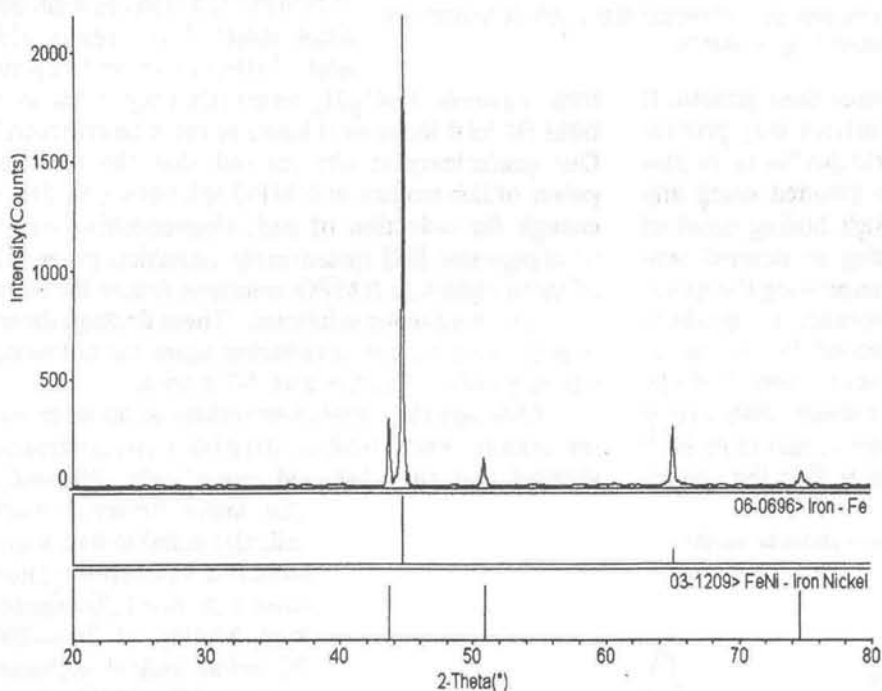


Fig. 4. X-ray diffractogram of the powders obtained from iron precursors after annealing at 600 °C. Additional low-intensity pattern is attributed to Ni added in order to passivate the surface of iron.

tem, we attempted to obtain it by reacting the iron colloid with  $\text{NiCl}_2$  in NMPO solution. Monitoring the reaction by Dynamic Light Scattering revealed that the original 5 nm particles were consumed

capability to solvate ions ( $DN=27.3$ ), which enables it to dissolve simple metal salts and to promote their dissociation. We presumed that NMPO as a strong donor may link to the surface of the growing

and that the newly formed scattering species had a size of 120 nm (fig. 6). The precipitates obtained from these colloids by heating at 200–202 °C for 30 min, were magnetic and showed X-ray diffraction peaks of fcc-structured metallic nickel (fig. 7).

In order to examine the surface reactivity of the obtained nanocrystalline iron and cobalt, we performed their reaction with oleic acid at ambient conditions. The products were insoluble in NMPO, but readily soluble in hydrocarbons, which could be expected based on solvent polarity considerations. These surface-derivatized products did not lose their capping ligand upon treatment with NMPO, despite the fact that oleic acid is soluble in this solvent.

Iron and cobalt were characterized by Transmission Electron Microscopy (TEM). Hydrocarbon (tetralin) colloids of both metals (capped with oleic acid) were used for depositing monolayers of nanoparticles on the TEM grid. Iron formed ordered assemblies of 5 nm uniform particles (fig. 8); cobalt formed nanoparticles with broad size distribution. These results correlate with the Dynamic Light Scattering results obtained on the original thermally treated NMPO colloids (fig. 1).

This paper reports details of a new technique for the synthesis of colloidal metals, which is applicable to relatively electropositive metals. The room-temperature reduction of anhydrous metal halides is performed in solutions of polar aprotic solvent N-methyl pyrrolidone (NMPO), which plays vital role in this method. This solvent has a high dielectric constant  $\epsilon=32.6$  and

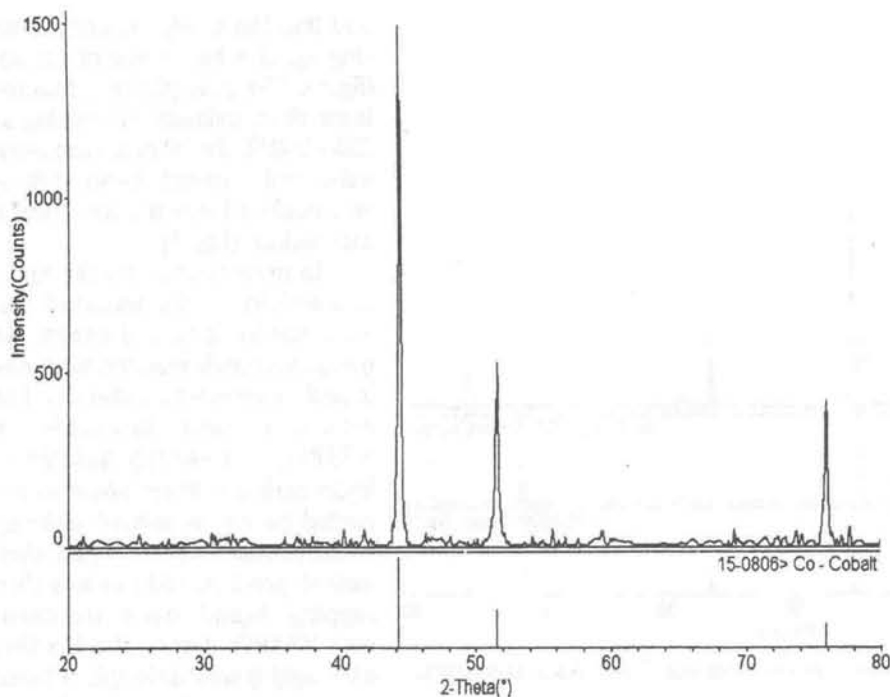


Fig. 5. X-ray diffractogram of the powders obtained from cobalt precursors after annealing at 600 °C.

nanocrystals and therefore influence their growth. It was also supposed that this polar solvent may promote colloid stabilization via electric double-layer mechanism. For these reasons we avoided using any surfactants or capping ligands. High boiling point of NMPO (202 °C) allows processing at elevated temperature, which is beneficial for improving the quality of the nanocrystals. This approach to synthesis of colloidal inorganics was proposed in our earlier work on nanocrystalline metal oxides, where diethylene glycol was used as a polar medium with strong solvating properties [10, 11]. A common feature of both metal and metal oxide syntheses is that the as-syn-

thesized nanocrystals have an uncapped surface, which is however protected with a labile layer of the adsorbed solvent. A post-synthesis treatment of the nanocrystals with various capping ligands permits their surface modification according to the desired application.

This work is focused on the Iron Group metals, Fe, Co and Ni as highly desired ones due to their useful magnetic properties. Searching for efficient reducing agents for these relatively electropositive metals resulted in anion-radicals derived from aromatics, in particular naphthalene. Sodium naphthalide is commonly used as a reducing agent in ether-type solvents, however we found that it may be prepared and used in NMPO solutions as well. Sodium metal slowly reacts with neat NMPO at room tempera-

ture, however  $\text{NaC}_{10}\text{H}_8$  forms relatively stable solutions (at least for several hours at room temperature). Our preliminary results showed that the reducing power of this reagent in NMPO solutions is sufficient enough for reduction of such electropositive metals as manganese [12] (presumably reduction potentials of these metals in NMPO solutions follow the same trends as in aqueous solutions). These findings determined our choice of a reducing agent for obtaining nanocrystalline Fe, Co and Ni metals.

Although the initial observations in all three metal systems were similar, detailed characterization showed that they behaved remarkably differently.

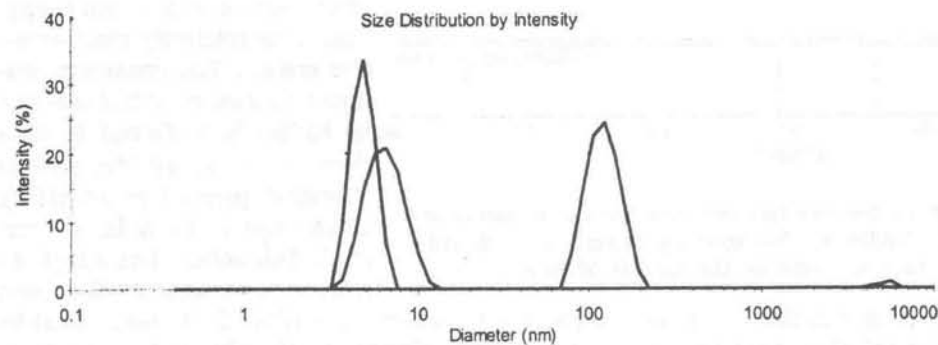


Fig. 6. Dynamic Light Scattering spectra of iron colloid (4.84 nm); iron colloid exposed to air for 2 min (6.53 nm); nickel colloid obtained from iron colloid (122 nm).

The initial brownish-black colloids reacted to heat treatment in a different way: iron colloid survived 30-minute-long heating at 200–202 °C; cobalt colloid agglomerated at 190–200 °C, however nickel-based fluids quickly decomposed at 180–190 °C. The precipitates obtained from iron and cobalt colloids (in order to protect Fe nanoparticles from oxidation, 10 mol. % of  $\text{NiCl}_2$  was added to the colloids



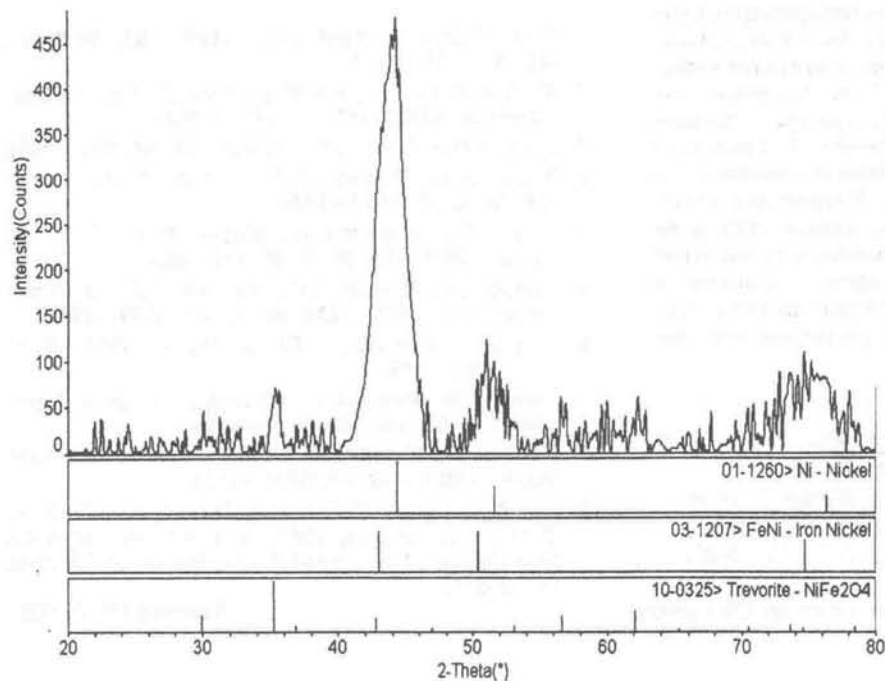
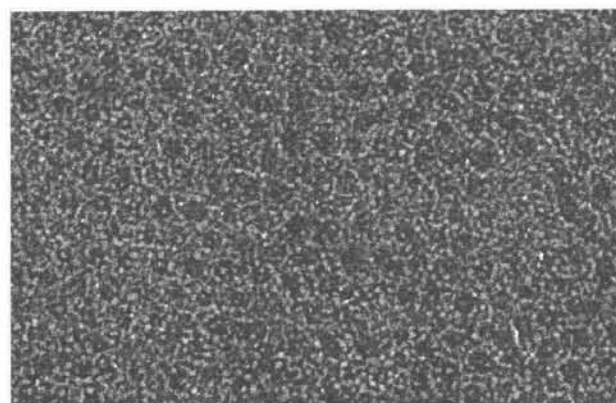


Fig. 7. X-ray diffractogram of the powders obtained from nickel colloids.



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Fig. 8. TEM image for iron nanoparticles (annealed at 200 °C and then oleate-capped).

one day prior to isolation) were strongly magnetic, however the one obtained from nickel system was non-magnetic. Based on X-ray diffractometry results, iron appeared practically amorphous, cobalt showed weak diffraction of the metal, but nickel appeared as a mixture of nickel carbide  $\text{Ni}_3\text{C}$  (hcp-structure) and sodium chloride. Annealing the iron and cobalt precipitates at 600 °C in vacuum and

further examination by XRD proved the metallic nature of both products with cubic lattice.

As our attempts to obtain colloidal nickel by the direct reduction of  $\text{Ni}^{2+}$  with naphthalide anionradical resulted in nickel carbide formation, we attempted to obtain it in reaction of its salt with colloidal iron:



The pre-synthesized iron colloid was used as a reducing agent for nicked chloride dissolved in NMPO. As evidenced by the DLS, the original 5 nm nanoparticles were consumed and new 120 nm large objects appeared within 1 h. Heating of these solutions at 200 °C for 30 min followed by cooling resulted in precipitation of the magnetic solids, which according to X-ray dif-

fraction studies were identical to nickel metal with cubic structure.

The observed phenomenon with nickel raised two questions: what is the donor of carbon for nickel carbide formation, and why nickel behaves differently from iron and cobalt. It seems to be clear that naphthalide ion must act as a source of carbon, since in the alternative system, containing the same solvent and naphthalene (remaining after iron colloid synthesis), nickel metal is produced. This conclusion correlates with the observation that  $\text{Ni}_3\text{C}$  appears as a minor component in a mixture with Ni metal when  $\text{NiBr}_2$  is reduced by Li metal suspended in toluene, in the presence of 2 eq. of tetramethyl ethylenediamine and 0.2 eq. of naphthalene [1]. The second question appears to be more challenging, however, it is likely that pronounced catalytic activity of this metal might be the answer.

In conclusion, we report a novel method for the preparation of colloidal metals with uncapped nanoparticle surface in polar aprotic solvent N-methyl pyrrolidone. In post-synthesis steps, the nanoparticles can be functionalized with various capping ligands, depending on desired application.

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**РЕЗЮМЕ.** Новый метод синтеза наноразмерных металлов Fe, Co и Ni в коллоидной форме и в виде нанопорошков основан на восстановлении галогенидов металлов нафталидом натрия в растворах N-метилпирролидона (НМП). Реакции при комнатной температуре сопровождаются нагреванием раствора до 170–200 °С в результате образования наночастиц металлического железа и кобальта, а также карбида никеля Ni<sub>3</sub>C. Коллоидный металлический никель получен по реакции коллоидного железа с NiCl<sub>2</sub> в растворах НМП. Поверхность металлических наночастиц восприимчива к химическому замещению; в результате постсинтетических реакций этих частиц с олеиновой кислотой получены продукты, растворимые в углеводородах.

1. Leslie-Pelecky D.L., Zhang X.Q., Kim S.H. et al. // Chem. Mater. -1998. -10, № 1. -P. 164–171.
2. Leslie-Pelecky D.L., Bonder M., Martin T. et al. // Ibid. -1998. -10, № 11. -P. 3732–3736.
3. Kirkpatrick E.M., Leslie-Pelecky D.L., Kim S.H.,

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- Rieke R.D. // J. Appl. Phys. -1999. -85, № 8. -Pt. 2B. -P. 5375–5377.
4. Baldwin R.K., Pettigrew K.A., Ratai E. et al. // Chem. Commun. -2002. -17. -P. 1822–1823.
  5. Hope-Weeks L.J. // Ibid. -2003. -24. -P. 2980, 2981.
  6. Nelson J.A., Wagner M.J. // Chem. Mater. -2002. -14, № 4. -P. 1639–1642.
  7. Nelson J.A., Bennett L.H., Wagner M.J. // J. Mater. Chem. -2003. -13, № 4. -P. 857–860.
  8. Nelson J.A., Bennett L.H., Wagner M.J. // J. Amer. Chem. Soc. -2002. -124, № 12. -P. 2979–2983.
  9. Tsai K.L., Dye J.L. // Chem. Mater. -1993. -5, № 4. -P. 540–546.
  10. Caruntu D., Remond Y., Chou N.H. et al. // Inorg. Chem. -2002. -41. -P. 6137–6146.
  11. Caruntu D., Caruntu G., Chen Y. et al. // Chem. Mater. -2004. -16. -P. 5527–5534.
  12. Ban Z., O'Connor C.J., Goloverda G., Kolesnichenko V. // Abstr. of Papers, 225th ACS National Meeting, New Orleans, LA, United States, March 23–27, 2003, INOR-246.

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## FTIR-SPECTROSCOPIC STUDIES OF TANTALUM (V) SPECIES FORMED IN 1-BUTYL-1-METHYL-PYRROLIDINIUM CHLORIDE—TaCl<sub>5</sub> IONIC LIQUID WITH ADDITIVES OF ALKALI HALIDES

Ionic liquid 1-butyl-1-methyl-1-pyrrolidinium chloride—TaCl<sub>5</sub> (molar ratio 65:35) was synthesized with the aim of electrochemical deposition of tantalum coatings at ambient temperature. To elucidate the mechanism of the deposition process, FTIR spectroscopic studies were performed. A detailed analysis indicates the formation of TaCl<sub>6</sub><sup>-</sup> complexes and some oxochloride complexes of tantalum (V) with bridge oxygen bonds Ta—O—Ta. Addition of alkali chlorides has no effect on the vibrational features of tantalum (V), whereas LiF leads to the formation of mixed complexes TaCl<sub>6-n</sub>F<sub>n</sub><sup>-</sup> with simultaneously decreasing amount of the tantalum (V) species with Ta—O—Ta bridge bonds.

Low-temperature molten salts (LTMS), or ionic liquids, which are a combination of organic and inorganic compounds, are very attractive and promising media for electrochemical deposition of highly reactive metals, such as refractory metals that cannot be obtained from aqueous solutions or only out of high-temperature molten salts. One of the important advantages of the deposition from ionic liquids is that the properties of the substrates are not changed during electrochemical treatment as in the case of high-temperature molten salts.

A few studies concerning attempts of electrodeposition of tantalum (V) from ionic liquids were published: the electrodeposition of tantalum from EMIC—AlCl<sub>3</sub> was studied by Barnard and Hussey [1], from EMIC — by Matsunaga [2]. Only the first steps corresponding to Ta<sup>5+</sup>/Ta<sup>2+</sup> reactions were discussed. The electrodeposition of tantalum metal was not achieved. The addition of LiF to EMIC—TaCl<sub>5</sub> leads to the electrodeposition of tantalum, which was reported by Morimitsu and Matsunaga [3].

The influence of alkali metal cations on the elect-

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