

Organometallic Synthesis of β -CoAl Nanoparticles and β -CoAl/Al Nanoparticles and Their Behaviour upon Air Exposure

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Nanocolloids of the intermetallic β -CoAl phase were prepared by a soft organometallic route. They were fully characterized by (HR)TEM, EDX, WAXS, XAS and SQUID magnetometry. Their exposure to air led to an increased saturation magnetization in agreement with Co/Al segregation and the

formation of Co/Al₂O₃ nanocomposite. Furthermore, the β -CoAl nanoparticles could be used as seeds to grow an aluminum overlayer, which passivated the alloyed core against oxidation. These nanoparticles yielded stable colloidal solutions in aromatic solvents.

Introduction

Ferromagnetic metal nanoparticles (NPs) are good candidates for many technological applications such as magnetic tunnel junction, tunneling magnetoresistances, MRAM, read heads and sensors. However, they are highly air-sensitive, and applications require that the NPs be embedded in a passivating material. Most of the studies deal with NPs embedded in alumina,^[1] or magnesia.^[2] These layers protect the NPs against air oxidation and moreover act as dielectric insulators (especially needed for tunnel junctions). Elaboration and characterisation of such embedded magnetic clusters require sophisticated physical techniques. Chemical methods may therefore be a suitable alternative. Indeed, NPs coated with a dielectric layer would be processable by routine, low cost techniques of the microelectronics industry such as spin-coating, and could impact the development of nanotechnologies. Co@Al₂O₃ nanocomposites are ideal systems to test as Co/Al₂O₃ composites have

already been studied as thin films.^[3] Especially, it is well known from surface science studies, that in CoAl alloys, Al selectively oxidises and forms an outer passivating layer of alumina.^[4] It is therefore expected that upon air exposure, CoAl NPs would generate a cobalt core surrounded by an alumina shell, i.e. a Co@Al₂O₃ nanocomposite. Among the various methods developed so far to generate NPs, the organometallic route is one of the best suited to chemically synthesize NPs requiring strictly anhydrous and anaerobic conditions such as Al-based alloys.^[5]

To synthesize the target CoAl nanoparticles we resorted to the organometallic precursors [(AlCp*)₄] (Cp*: pentamethylcyclopentadienyl) and [Co(η^4 -C₈H₁₂)(η^3 -C₈H₁₃)]. Indeed, hydrogenolysis of the aluminum(I) complex [(AlCp*)₄] was reported to yield Al nanoparticles^[6] in high yield, and as such this precursor presents an elegant alternative to the less easily handled alane derivatives. [Co(η^4 -C₈H₁₂)(η^3 -C₈H₁₃)] is also a good and versatile source of Co atoms under H₂ pressure producing cyclooctane as only byproduct.^[7] Furthermore, it does not interact with the Al precursor or Al atoms. Starting from a combination of these two precursors looked thus promising. We report herein the successful synthesis of CoAl NPs, evidences for their alloy character and for the oxidation-induced segregation of aluminum. Furthermore we present, as preliminary results, the formation and oxidation behaviour of CoAl/Al nanoparticles.

Results and Discussion

The synthesis was carried out by hydrogenation of a mixture of the organometallic precursors (in various ratios) under 3 bar of dihydrogen in mesitylene at 150 °C for 48 h

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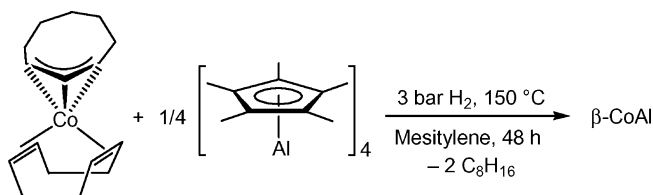
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(Scheme 1). Uncontrolled agglomeration and NPs of large size distribution were observed either for Co-rich or Co-poor compositions. Surprisingly, when an equimolar mixture of the precursors was used, a brown-black homogeneous solution was obtained, even without addition of any capping ligand. Evaporation of the solvent in vacuo led to a black powder, which was characterised by chemical analysis, transmission electron microscopy (TEM), high-resolution TEM (HRTEM), energy-dispersive X-ray spectroscopy (EDX), wide-angle X-ray scattering (WAXS), X-ray absorption spectroscopy (XAS) and SQUID magnetometry. Chemical analysis (43.38% Co, 20.68% Al, i.e. Co/Al = 0.96, close to the expected Co_1Al_1 composition) gives a total metal content of 64 wt.-%, indicative of the presence of residual hydrocarbons in the CoAl material. During the evaporation step, the solvent was trapped and studied by ^1H NMR spectroscopy and GC–MS analysis. The only light by-product that could be evidenced was cyclooctane, which derives from the hydrogenation of cyclooctadiene and cyclooctenyl ligands of the Co precursor. However, the Cp^* moiety of the Al source could not be traced. It is likely that during hydrogenation, a ring opening or polymerisation of the Cp^*H took place, giving a high-molecular-mass hydrocarbon, which may be responsible for the solubility of the particles in mesitylene.



Scheme 1. Organometallic synthesis of colloidal $\beta\text{-CoAl}$ NPs.

Analysis of the TEM images (Figure 1) of a deposit of the colloidal solution of CoAl NPs on a carbon-covered copper grid reveals agglomerates containing particles of very small size (circa 2.5 nm). These NPs are embedded in a shadowy organic material which could correspond to the 36 wt.-% of non-metal content in the sample. Some isolated NPs were also present outside these dense areas, some of them displaying a larger diameter (circa 5 nm). EDX analysis on the agglomerates show a roughly 1:1 (Co/Al) composition in agreement with the chemical analysis. As for the isolated NPs, some were indeed close to the Co_1Al_1 composition, whereas others contained mainly Co (Figure 1 and Supporting Information). HRTEM analysis on these NPs confirmed their very small size. Still, as a consequence of the fast contamination due to the decomposition of the organic matrix under the electron beam, only the structure of the larger NPs (circa 5 nm) could be studied. A representative HRTEM image of the sample is shown in Figure 2. All the NPs observed showed a polycrystalline structure. The 2D fast-Fourier transform of the images systematically evidenced a lattice distance equal to 2.03 \AA , which could be ascribed to the most intense peak in the Co/Al alloy diagram associated to the (110) planes.

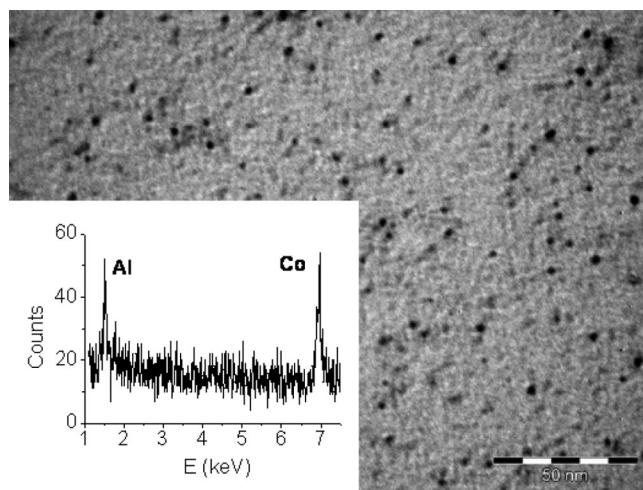


Figure 1. TEM image of $\beta\text{-CoAl}$ NPs and EDX on isolated NPs (Al/Co = 0.85 ± 0.15). Scale bar: 50 nm.

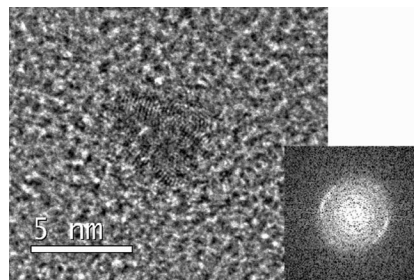


Figure 2. Typical HRTEM image displaying the only lattice distance which could be observed on these systems. Scale bar: 5 nm.

WAXS data were then recorded on the black powder, conditioned in sealed Lindeman capillaries under an inert gas. They clearly evidence that the NPs consist of the intermetallic $\beta\text{-CoAl}$ phase (body-centered cubic, ICSD no. 57596) with a shift of the peaks increasing with θ values indicative of a contraction of the cell parameters. After careful subtraction of the background contribution and FT, the radial distribution function (RDF) was compared to that generated from a model CoAl cluster of β -structure build from 514 atoms, as displayed in Figure 3. The positions of the peaks of the calculated RDF superpose perfectly to that of the experimental one, when the cell parameter is accordingly reduced by 1%. This clearly evidences that the NPs adopt the same structure as the bulk, but with contracted M–M distances as often observed at small size. The coherence length reaches 2.5 nm, so that the crystalline domain extends over the whole NPs for the smaller ones and in further agreement with the polycrystalline character of the larger ones. The shape of the first peak of the RDF is, however, different from that computed from the $\beta\text{-CoAl}$ model cluster and indicates a larger weight of shorter distances in agreement with partial segregation of Co atoms.

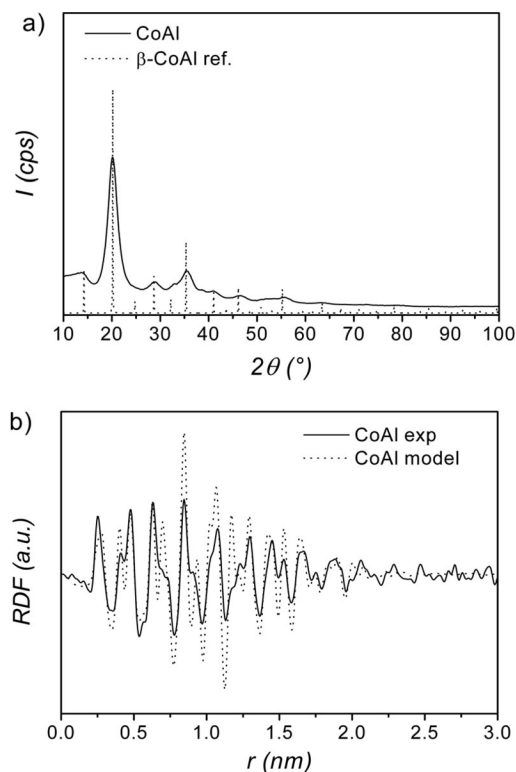


Figure 3. (a) WAXS diagram of CoAl NPs and comparison with tabulated data from the β -CoAl phase; (b) experimental and simulated RDF.

The XAS spectrum was recorded at the Co- K edge to investigate specifically the Co environment (for experimental details see Supporting Information). A typical recording is shown in Figure 4. The shape of the XANES spectrum is different from that of *hcp*-Co taken as a reference. However, the position of the edge is identical (see derivative, inset Figure 4) pointing to non-oxidised Co atoms. The Fourier transform (FT) of the EXAFS data shows a large Co-M peak overlapping the doublet expected for the ordered β -CoAl phase^[8] (Figure 5) in good agreement with the WAXS analysis.

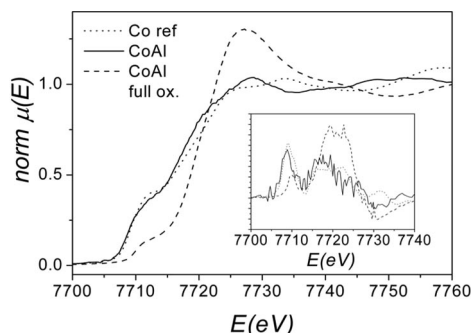


Figure 4. Co- K edge XANES spectra of CoAl NPs. Inset first derivatives of the curves in the pre-edge and edge region (dotted line: Co reference; solid line: CoAl sample).

The magnetic behaviour of the material was investigated by SQUID. Figure 6 displays the hysteresis cycle recorded at 2 K, evidencing a ferromagnetic behaviour, with a coer-

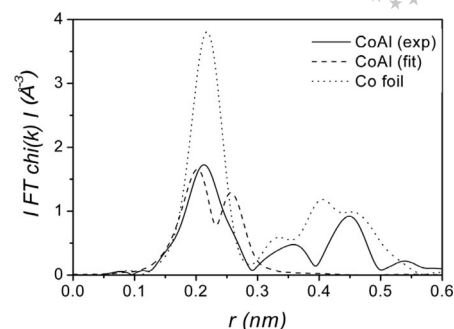


Figure 5. RDF obtained from FT of the EXAFS data at the Co- K edge: CoAl (solid line), Co foil (dotted line) and model RDF for chemically ordered β -CoAl alloy (dashed line).

cive field of 38 mT. The magnetisation is saturated at 5 T at a value corresponding to 32% of that of pure cobalt (horizontal line reported as a reference). At this stage, this magnetisation can be either attributed to the presence of NPs of Co or to NPs of a chemically disordered CoAl alloy, as ferromagnetism in bulk CoAl is related to segregated or out-of-lattice cobalt atoms, such as surface Co antisite atoms^[4b,9] or both. To determine the effect of partial oxidation on the CoAl nanomaterial, the gelatine capsule prepared for the SQUID measurements was deliberately exposed to air for 1 h, and the hysteresis cycle was recorded again (dashed line Figure 6). Surprisingly, the magnetisation measured at 5 T reaches 74% of the value expected for pure cobalt. This effect was reproducibly observed for many batches of CoAl NPs produced according to the same synthetic procedure. To the best of our knowledge it is the first time that air exposure of magnetic metal NPs leads to an enhancement of their saturation magnetisation. This certainly rules out the fact that magnetic properties might be governed by the presence of isolated Co NPs in the sample. Indeed, their oxidation would lead to a dramatic collapse of the magnetisation. On the other hand, this is in agreement with an increased ratio of segregated cobalt atoms in CoAl NPs. Drastic exposure to air leads, however, to a complete collapse of the magnetisation, this time evidencing full oxidation of the sample. This was corroborated by WAXS and XAS experiments: direct exposure of the material to air led to full oxidation of the sample, as seen on the XANES spectrum (Figure 4; see also WAXS data in the Supporting Information).

From the average diameter of the NPs it is possible to estimate the number of metal atoms. Taking into account the composition of the NPs and assuming that the NPs have the same compacity as the bulk, we found out that each NP should contain around 300 Co atoms and 300 Al atoms. In the ideal case, upon air oxidation, Al atoms would completely segregate to the surface and oxidise into an alumina shell. Assuming a spherical core particle with 300 Co atoms ($d \approx 2$ nm), the thickness of the Al_2O_3 shell would be around 0.6 nm (less than two full atomic layers of Al), which is clearly not sufficient to insure the passivation of the cobalt core. To circumvent this problem, we can first

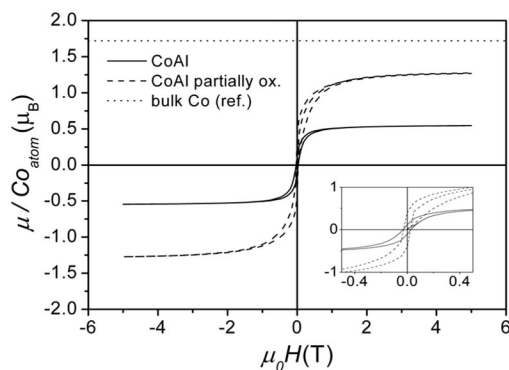


Figure 6. Magnetisation cycles recorded at 2 K on CoAl NPs; inset: enlargement displaying the coercive field (dotted line: partially oxidized CoAl; solid line: CoAl).

think of adapting the synthesis conditions in order to reach NPs of larger size. In this case, as the proportion of surface decreases when increasing the size of the objects, the Al content of each NP would be sufficient to ensure the formation of a thick enough alumina shell upon oxidation to passivate the cobalt core from further air oxidation. Alternatively, producing a cobalt core embedded in an alumina shell at small size requires an increase of the aluminum content in the initial alloy. However, all our attempts at preparing small Al-rich NPs or larger NPs of CoAl (1:1) composition by the simultaneous decomposition of the two precursors were so far unsuccessful.

We thus envisaged a two-step procedure to increase the Al content in the NPs. After the synthesis of the β -CoAl NPs, a second load of the Al precursor (1 equiv.) was added and decomposed under dihydrogen according to the same procedure as before. A black solution was obtained after 48 h from which a black powder could be isolated by evaporation of the solvent. TEM analysis of the NPs evidenced an average size around 2.8 nm (see Supporting Information). To obtain a processable, more stable solution, 0.2 equiv. of stearic acid was added on a redispersion of the NPs in mesitylene. This colloidal solution was stable for days and, after solvent evaporation, afforded a powder, which could be easily handled and redissolved in aromatic solvents (see Supporting Information). SQUID measurements at 2 K evidenced a weak ferromagnetism for the coated NPs, similarly to what was observed for the CoAl seeds. However, in this case, the saturation magnetisation remained almost constant upon air exposure even after 24 h (Figure 7). This is in agreement with the formation of an overlayer of Al at the surface of the first formed CoAl seeds. This CoAl core/Al shell NP would indeed oxidize into a surface-passivated CoAl/Al₂O₃ composite. Magnetisation measurements further suggest that in this case, oxidation does not proceed deep enough to induce any significant Co segregation in the core of the NPs, as the overall magnetisation value remains quite low.

This result is very promising in terms of air stability of the magnetic core. However, a more complete study will be needed to clearly evidence the core-shell structure of the

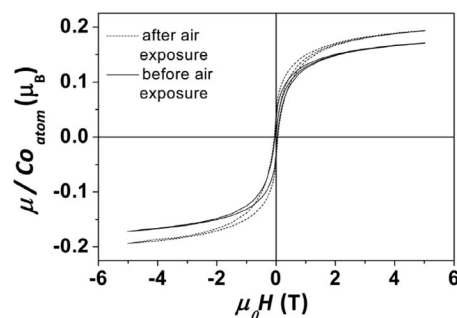


Figure 7. Effect of air exposure (24 h) on the magnetic behaviour of coated CoAl/Al NPs.

composites, which is highly challenging at such a small size, and to fully understand the magnetic behaviour of the nanoparticles before and after oxidation.

Conclusions

This study demonstrates the possibility to form NPs of β -CoAl alloy in organic solution. These NPs are very air-sensitive, giving rise to a fast alumina segregation upon exposure to air. This leads to a strong enhancement of the magnetisation of the NPs as a result of the formation of a cobalt core. However, the resulting alumina is not sufficient for long-term protection of the NPs, and full oxidation is observed upon prolonged exposure to air. We have then shown that a further coverage of the β -CoAl NPs with an Al overlayer improves air stability of the composite and affords magnetic cores embedded in a passivating alumina shell. The preliminary results obtained for the redispersion of the NPs in organic solvents opens a door to the deposition of these nanocomposites by spin-coating.

Experimental Section

General: All manipulations and chemical reactions were conducted by using Schlenk-line and glove-box techniques (argon; H₂O and O₂ content < 1 ppm) and Fischer-Porter vessels. [(AlCp*)₄]^[10] and [Co(η^4 -C₈H₁₂)(η^3 -C₈H₁₃)]^[11] were prepared according to already published procedures.

Synthesis of CoAl Nanoparticles: In a Fischer-Porter bottle, [Co(η^4 -C₈H₁₂)(η^3 -C₈H₁₃)] (0.300 g, 1.084 mmol) and [(AlCp*)₄] (0.176 g, 0.271 mmol) were suspended in mesitylene (20 mL); the mixture was degassed, set to 3 bar H₂ pressure (ca. 10 mmol) and placed into an oil bath of 150 °C. The mixture was stirred for 48 h, whereupon a brown-black solution formed. After removal of the solvent and all other volatile components in vacuo (100 °C, 10⁻³ mbar), a black solid was obtained. Elemental analysis: 28.55 wt.-% Co, 12.48 wt.-% Al (i.e. Co₁/Al₁ composition).

Synthesis of CoAl/Al Nanoparticles: In a Fischer-Porter bottle, [Co(η^4 -C₈H₁₂)(η^3 -C₈H₁₃)] (0.300 g, 1.084 mmol) and (0.271 mmol, 0.176 g) [(AlCp*)₄] were suspended in mesitylene (20 mL); the mixture was degassed, set to 3 bar H₂ pressure (ca. 10 mmol) and placed into an oil bath of 150 °C. The mixture was stirred for 48 h, whereupon a brown-black solution formed. The reactor was cooled to room temperature, and a second load of [(AlCp*)₄] (0.176 g,

0.271 mmol) was added. Thereafter, the reactor was set to 3 bar H_2 . Heating at 150 °C whilst stirring for 48 h afforded a black colloidal solution. The product was isolated as a black powder after evaporation of the solvent. Yield: 65.8 mg (80.3%). Elemental analysis: 34.8 wt.-% Co, 32 wt.-% Al, (i.e. Co_1/Al_2 composition). Before evaporation of the solvent, stearic acid (0.2 mmol, 61.8 mg, Aldrich) can be added to the solution. After 16 h of stirring at room temperature, evaporation of the solvent afforded a black powder, which is highly soluble in aromatic solvents. Yield: 188 mg (100%). Elemental analysis: 22.9 wt.-% Co, 20.7 wt.-% Al (i.e. Co_1/Al_2 composition).

Supporting Information (see footnote on the first page of this article): Full details of the techniques used for the characterisation of the samples. More EDX results on agglomerated or isolated CoAl nanoparticles; WAXS of a fully oxidized sample; TEM image and size distribution of CoAl/Al nanoparticles; TEM image of CoAl/Al NPs coated with stearic acid.

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