8. Summary and Outlook

Synthesis of Cu_{1-x}E_x nano-powder and -colloids

This work presents a novel, clean approach to intermetallic Hume-Rothery Cu_{1-x}Zn_x, Cu_{1-x}Al_x, Ni_{1-x}Al_x and Co_{1-x}Al_x powder materials in organic solution by co-hydrogenolysis of organometallic \textit{all-hydrocarbon} precursor complexes under rigorous oxygen-free conditions. It was shown that the complexes \([(\text{AlCp}^*)_4]\) and \([\text{ZnCp}^*]_2\) readily give Al(0) and Zn(0) upon hydrogenolysis. These compounds were so far unknown as precursors for naked Al and Zn, respectively. In sharp contrast to all synthesis protocols for such classical Hume-Rothery phases in solution existing to date, the decomposition of the precursors quantitatively affords the metals under relatively soft reaction conditions. The organic byproducts are inert, and do not inhibit the alloy formation from the \textit{in situ} released metals. This synthesis method allows a free variation of the Zn- and Al-content, respectively, and thus an access to both \(\alpha\)- and \(\beta\)-phase materials (see below). The synthesis of colloidal alloys, however, depends on the transition metal and does not guarantee a general protocol using one particular surfactant so far. For the synthesis of \((E = \text{Al}, \text{Zn})\) alloy colloids, the polymer PPO was added as steric surfactant. However, the obtained nanoparticles were rather large and polydisperse. Other surfactants could not stabilise the alloy particles. In the case of \(\beta\)-MAI alloys \((M = \text{Co, Ni})\), the particles were stable as metastable colloidal solutions even without any surfactant present. The colloid stability was enhanced by post-synthetic addition of ACA, which however, partially oxidised the Al component. First experiments showed that the co-hydrogenolysis of a metal- and an Al-precursor in presence of an inert hydrocarbon polymer, such as polybutadiene (\textit{vide supra}), gives - at least temporarily - stable colloidal solutions. The subsequent addition of a strongly binding containing capping ligand (e.g. carboxylic acids) is a promising perspective towards a widely applicable transition metal aluminide colloid procedure.

Oxidation of M_{1-x}E_x alloys and core-shell particle formation

The surface oxidation of M_{1-x}E_x alloy particles has been a particular investigation target of this work. The passivation of metal nanoparticles \textit{via} Al oxidation of metal aluminide nanoparticles bears interesting perspectives, aiming at air-stable applied materials, e.g.
magnetic Ni- or Co-nanoparticles. In contrast to other post-synthetic particle coating methods, e.g. by silica coating by sol-gel processes or by noble metals, the in situ formation of an alumina (or ZnO) shell from a M$_{1-x}$E$_{x}$ alloy is based on the high oxophilicity of Al, and Zn, respectively, and thus appears to be a very elegant, non-aqueous method. It was shown that the synthesised M$_{1-x}$Al$_{x}$ nanopowders indeed undergo a phase segregation upon air oxidation, which results in a core of the metal M, which is passivated by an alumina shell. This work offers first perspectives for the generation of air-stable metal nanoparticles from the respective alloys, as well as a study of their magnetic properties. It was shown that the reduction of the Al content in the alloy corresponds to a decrease of the concentration in the bulk core, which adopts the structural type of the pure metal. This is of special importance, since Al (or Zn) is ‘poisoning’ the metal in terms of magnetisation. Hence, this work also concentrated on the determination of the minimum Al content, which is required to form a full oxide shell upon oxidation of a α-phase alloy (Scheme 8.1).

Scheme 8.1. Access to air-stable metal nanoparticles by in situ formation of an alumina shell upon selective Al-oxidation in α-M$_{1-x}$Al$_{x}$ alloy nanoparticles. The cross section of the oxidised particle (right) indicates the full alumina shell.

The investigations of the oxidation behaviour of the synthesised M$_{1-x}$E$_{x}$ nanoparticle powder and colloids have shown that there is so far no general method to produce core-shell type alumina@metal particles. The criteria for the formation of corrosion stable alumina@metal species appear to be the oxophilicity and the diffusion gradient of the transition metal, the particle size, and the oxidation procedure. In the case of Cu-Al alloys, the colloidal particles were rather large (~20 nm) and an interaction of the Cp* ligand with the particle surface was not observed. The oxidation produced a Cu core in an alumina shell, which is unaffected against oxidation down to 17 at.% Al. In contrast, the Ni$_{1-x}$Al$_{x}$ powder particles exhibit a much smaller size of the primary particles (4-8 nm), and have an oxidation resistant Ni core at an even lower Al content than in the case of Cu-Al. In the β-CoAl nanoparticles (~2 nm), both Al and Co oxidise upon air exposure, even with a Al content of 50 at.%.

Although the selective Al-oxidation of β-CoAl nanoparticles in a gelatine capsule does not affect the Co atoms, the observed oxidation sensitivity of the cobalt component in the alloy is a high hurdle...
to overcome towards a simple access to a dense protective layer of alumina@cobalt nanoparticles. A potential perspective might be the chemical oxidation by soft O-donors, such as trimethylamine oxide (Me₃NO) or ortho-chloroperbenzoic acid, which have already been used for the synthesis of core-shell nanoparticles before.[309,310]

The oxidised Ni₁₋ₓAlₓ and β-CoAl nanoparticles show the potential of surface decorated metal nanoparticles, in terms of magnetisation and long-term air resistance, which is necessary for an industrial application of any of the nanoparticles mentioned here and in the introduction. First experiments have shown that Al₂O₃@Co nanoparticles exhibit a significantly higher magnetisation than non-oxidised β-CoAl, confirming the presented concept. A comprehensive investigation of the magnetisation of these materials, in dependence of the Al content and the comparison with bulk M reference data is certainly warranted. As well, the solubilisation of α-MAI alloys as colloids and the control over the particle shape and anisotropy, aiming at a general post-synthetic solubilisation procedure and subsequent oxidation studies represent promising future objects of study.

**Novel perspectives in preparation of nano-alloys**

The obtained results suggest [(AlCp*)₄] as an exotic, but quite interesting precursor to be generally applicable for wet-chemical nanometallurgy of late transition metal aluminides, for example extending the scope of B. Chaudret’s work[90-100] on metal colloids towards classical Hume-Rothery phases that have not been readily available so far. Following the work described above, an investigation of further transition metal aluminate nanoparticles is certainly warranted. Promising precursor candidates are [Pt(cod)₂], [Pd₂(dvds)₃] (dvds = 1,3-divinyl-1,1,3,3-tetramethyldisiloxane), or [Ru(η⁵-cod)(η⁶-cot)], which all are bearing ‘innocent’ olefin ligands, which are supposed to be easily hydrogenated. First experiments have shown, that in the case of the decomposition of equimolar metal amounts of the above mentioned Pd- and Pt-precurors with [(AlCp*)₄], binary α-phases of Pd-Al and Pt-Al, respectively, were obtained. Preliminary work on the synthesis of Ru-Al nanoparticles by hydrogenolysis of [Ru(η⁴-cod)(η⁶-cot)] and [(AlCp*)₄] in mesitylene led to the formation of the complex [(η⁶-mesitylene)Ru(η⁴-cod)], which is quite stable under H₂ pressure, which however, can be overcome by use of high boiling aliphatic solvents, which do not coordinate at the Ru centre.

The synthesis of colloidal M-Al nanoparticles is on the borderline between molecular clusters of the type [Mₐ(AlCp*)ₙ] (a ≥ b) and solid nanoalloys. Previous work has shown that
[Ni(cod)$_2$] and [(AlCp*)$_4$] readily react to the stable complex [Ni(AlCp*)$_4$]. A decrease of the AlCp* concentration certainly leads to the formation of AlCp* stabilised Ni clusters of various sizes. It is reasonable to assume that during the co-hydrogenolysis of [Ni(cod)$_2$] and [(AlCp*)$_4$], such clusters are formed, prior to the decomposition of the AlCp* ligands by H$_2$. Thus, trapping of small clusters and the control over the cluster size is for sure of high interest for understanding the mechanisms of alloy formation by means of hydrogenolysis. Another convenient method to obtain M-E nanoparticles (M = late transition metal d$^8$-d$^{10}$, E = Al, Ga, In) is the decomposition of known bimetallic [M$_d$(EcP*)$_b$] clusters. First experiments have shown that some of these clusters can serve as precursors for a well-defined E-rich phase. For example, the hydrogenolysis of the bimetallic Pt-cluster [Pt($\mu$-GaCp*)$_3$(GaCp*)$_2$] readily gives the intermetallic PtGa$_2$ phase (Figure 6.1). The hydrogenolysis in presence of equimolar amounts of HDA gives a colloidal solution of monodisperse, spherical PtGa$_2$ nanoparticles (diameter: 8 nm).

![Figure 8.1. Synthesis of PtGa$_2$ nanoparticles by hydrogenolysis of [Pt($\mu$-GaCp*)$_3$(GaCp*)$_2$].](image)

Regarding the successful use of [(AlCp*)$_4$] and [ZnCp*$_2$] as straightforward sources for the naked metals, it can be concluded, that the Cp* moiety is an advantageous leaving group being cleanly split off by hydrogenolysis. The question is raising, whether other important alloy components, which are also notoriously difficult to introduce by simple salt reduction, can be accessed from other Cp* complexes of oxophilic metals, such as Jutzi’s [SiCp*$_2$]
The hydrogenation and subsequent cleavage of Cp*H, of course, depends on the nature of the polarity of the M-Cp* bond. Rather ionic bonds, e.g. in [MgCp*₂] are too stable to be hydrogenated. Just to give an inspiring example, the unusual molecular SiAl₁₄ cluster, [(Cp*Al)₆(SiAl₈)] was obtained by employing [SiCp*₂] as Si source.¹⁷⁰

The complex [(quinuclidine)GaH₃] has been introduced as a precursor for the wet chemical synthesis of transition metal gallide nanoparticles. The synthesis of the θ-CuGa₂ phase, which decomposes above 250 °C, nicely demonstrates the potential of the presented synthetic concept, namely the access to metastable alloy phases, which are inaccessible by other, traditional metallurgical routes. Another synthetic targets include the PtGa₅ phase, which is stable up to 180 °C, from [Pt(cod)₂] and [(quinuclidine)GaH₃]. Along these lines, the complex [(pyridine)ZnH₂]³⁰⁸ may also well be a promising candidate for the reaction with the metal complexes used in this work, as well as with the above mentioned noble metal hydrocarbon precursors, to M-Zn nanoparticles, extending the pioneering work of Bogdanović et al. on metal hydrides as precursors for alloys.