

# CERAMIC MATRIX COMPOSITES FOR SOLAR ENERGY APPLICATIONS; FROM SOLUTION TO PRODUCT

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## Introduction

Ceramic matrix composites consisting of nano-sized metallic nano-inclusions in a ceramic material (NIM:s) have great potential to become the leading materials in a very wide range of applications including; mechanically and thermally durable coatings and compacts for cutting tools and light engines (high-performance ceramics), spectrally selective light absorption for solar thermal devices and signature adaptation in camouflage, heterogeneous catalysis, non-linear optics for photonic switches and frequency converters, transformers, magnetic sensors and memories, colour coatings in halogen lamps and carbon nano-tube growth substrates for cold cathode light emitters.

Despite this remarkable potential for applications there is still limited knowledge concerning how to efficiently tailor the contents and composition the nano-particles and matrix ceramic. In addition, different micro-structures are required for the above mentioned composites; thin films and coatings, highly porous sponges and compacts.

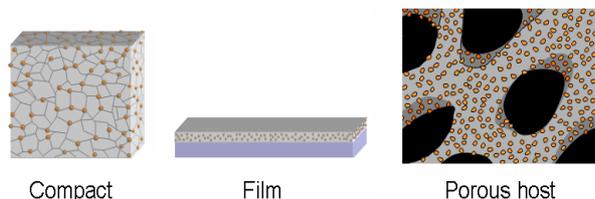


Figure 1. Different forms of nano-inclusion materials.

There are several techniques for preparation of NIM:s having advantages in different areas of application. Although some physical and chemical vapour based techniques (PVD/CVD) are well suited for many industrial applications, they require size limiting and costly high vacuum chambers and control equipment, and do in general not allow for efficient processing of other than low complexity materials on flat substrates.

The solution chemical techniques utilising e.g. dip-, spin-, spray- or roll-coating, on the other hand provide the combination of controlled formation of complex multi-metallic compositions and possibilities of efficient small and large-scale preparation of films and powders. They are also suitable for coating complex shape substrates, and thus allows for a greater flexibility in the production. The main drawback is the rather complex set of solution and solid state reactions leading from the precursor molecules to the target materials. This makes the development of such a process require much chemical and experimental expertise.

Here we report on a novel solution based route that yields homogeneous distributions of Cobalt, Nickel or Copper nano-particles in sizes down to 2-5 nm and metal loadings of up to ca 85-90% (expressed as mol% metal in  $\text{AlO}_{1.5}$ ). Alloyed particles are also possible.

The matrix materials prepared by this process have been investigated on their properties related to; (i) catalysis of the methane reforming reaction producing syngas mixture according to:  $\text{CH}_4 + \text{CO}_2 \rightarrow \text{CO} + \text{H}_2$ ; a gas mixture of importance for

manufacture of industrial chemicals as well as carbon free fuel in the form of H<sub>2</sub> and (ii) spectrally selective solar heat absorbers producing heat for warming private homes and making use of industrial waste heat. Thus both applications are highly relevant for the development of environmentally benign energy production.

## Experimental

We have developed a novel solution based route using simple metal-ion precursors such as nitrates and acetates complex bound by organic molecules being capable to produce extremely small and well distributed cobalt, nickel or copper metal particles within an amorphous alumina matrix. The conversion of the metal-organic complexes dissolved in alcohols goes through evaporation in air and heating under inert atmosphere to 500°C, or higher at heating rates of typically 5-50°C. No or very short annealing times were used. The details of the process will be described elsewhere.

Films were prepared by depositing the solutions mixed to the desired metal-ion ratios (M to Al) on different substrates by spin- or dip coating. After subsequent heat-treatment as described above, dense glossy films were obtained. Films deposited on aluminium being thinner ca 80 nm could be made coloured; gold, purple or blue coloured due to optical interference. A wide range of substrates were successfully tried out for deposition including Si/SiO<sub>2</sub>, aluminium, steel, alumina, quartz and window glass. Up to 200 nm thick layers were deposited although in the normal case films in the range 40-100 were deposited. Multiple depositions with intermittent heating allowed for building thicker films.

High surface area powders were prepared by depositing and evaporating the precursor solution to a concentrated solid or

highly viscous liquid state and subsequently heat-treating the materials to at least 500°C, as described above. The resulting materials were sponge or foam like structures with the M-Al<sub>2</sub>O<sub>3</sub> composites building the ca 50-100 nm thick bubble walls. Such structures yield a very high and accessible surface area when open structures were used. High surface area might also be obtained by adding a thin composite coating on a nano-structured porous material.

The microstructures and elemental composition were obtained with transmission and scanning electron-microscopes; TEM-EDS/ED (Jeol 2000FXII-Link 10000AN) and SEM-EDS (Leo 1550 and 440, and Jeol 820). The crystalline contents were obtained by X-ray diffraction using Guiner-Hägg geometry cameras (K $\alpha$ <sub>1</sub> radiation) or Siemens D5000 diffractometers (K $\alpha$  radiation), the organic and amorphous contents were acquired with IR spectroscopy (Bruker IFS-55) and the decomposition by thermo-gravimetry (TG, Perkin-Elmer TGA7).

## Results and discussion

Composites with metal inclusion sizes down to ~3 nm have been prepared in these systems. With nickel-alumina composites the typical size distributions of the nano-particles were:  $\sigma = 15\%$ , when counting a large population of particles and a number of different samples with different metal loadings. This corresponds to Ni particles of *e.g.* 6.5 +/- 1 nm. Different alloys between the elements Co, Ni and Cu have also been prepared, such as Co-Ni and Cu-Ni. The formation of metal particles within the alumina matrix seems to favour solitary alumina coated metal particles, rather than coalescence of metal particles, which is commonplace in most physical and chemical synthesis routes and loadings above 50%

metal. We obtained unprecedented high particle loadings with up to ca 85-90% Ni without significant coalescence. For loadings above ca 85% and 5-9 nm sized metal particles there is not enough alumina to surround the metal particles. In these cases the particles tend to grow bigger and still to a high degree keep their isolated nature within the matrix. For instance with an Ni loading of 95% the Ni particles grow to three times the size, compared to for a 10 or 75% loading.

Here these materials are presented and their properties with a focus on their solar heat absorption and catalytic properties described.

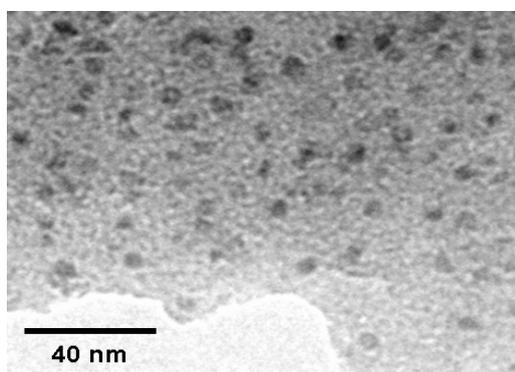


Figure 2. 10% Ni-Al<sub>2</sub>O<sub>3</sub> nano-composite.

*Catalysis; The methane reforming reaction,*  
 $CH_4 + CO_2 \rightarrow 2CO + 2H_2$

A great deal of interest has been devoted to making use of the sometimes surplus and green-house gases CH<sub>4</sub> and CO<sub>2</sub>. One promising answer to this is to convert them to the syn-gas mixture of CO and H<sub>2</sub> that is used as starting point for a large number of useful organic products or as carbon free fuel. In the latter application the CO may be decomposed to CNT for use in light weight materials. Such catalysts are however, not an easy task to accomplish efficiently and it has proved difficult to avoid deactivation of the catalyst due to carbon tube formation [1]. The most studied catalysts for this system are based on Ni nano-particles

supported on a ceramic material such as alumina. It has been found in a number of studies that the Ni particles have to be less than 6-10 nm sized to inhibit growth of carbon filaments on the Ni-particles.

A problem here is the common way of synthesising catalysts; it includes infiltration of a high surface area oxide such as alumina with a salt solution of the metal catalyst and subsequent heat-treatment under reducing conditions to achieve the metal nano-particles. The thereby obtained nano-particles are mobile on the surface at the elevated temperatures used during action and easily grow beyond the size limit for carbon poisoning. Another way to obtain oxide supported Ni-particles is to reduce Ni-containing oxides, such as (Mg,Ni)O or LaNiO<sub>3</sub>. The nickel nano-particles are then obtained when the catalyst is working in presence of methane or through high temperature reduction in H<sub>2</sub> containing atmosphere. In this case the nano-particles may have a better attachment to the surface and be less mobile, but such approaches reduce the synthesis control.

With the present solution route the Ni-nano-particles are formed within the matrix and the nano-particles at the surface will be partially submerged into the matrix and therefore more strongly anchored and stable.

Investigation of 10%Ni-Al<sub>2</sub>O<sub>3</sub> composite catalysts using mass-spectroscopy, and TEM and SEM analysis of the materials after catalytic runs showed that the material was active at temperatures above 500°C. Catalytic cycling studies showed that the composite catalyst deposited on nano-structured alumina in a coorderite monolith is stable and active up to 750°C, while at 800°C the catalyst was unstable.

*Carbon nano-tube (CNT) growth.*  
With films having Ni-particle sizes above 10 nm catalytic growth of carbon nano-tube rugs could be achieved with gaseous carbon sources such as ethene.

*Spectrally selective solar heat collectors.* The films obtained on Al substrates were dense, smooth and loaded with nickel particles in the size range 6-9 nm. Investigation of the optical properties from the IR to the UV range showed that they were suitable as absorber layers in spectrally selective solar heat collectors. Such devices are used for heating liquids including water with solar radiation and are based on a film deposited on metal substrate connected to a pipe in which the heated liquid flows. An optimised absorber consists of a highly heat conducting and reflective metal substrate such as aluminium or copper and a film which should have a very high absorption in the visible range and NIR range and be transparent in the IR range. Such devices thus allows for a high absorption of the energy rich shorter wave-lengths, but avoids being heated up and emit black body radiation in the longer IR wavelengths. In addition highly efficient absorbers also utilise an optical gradient or multilayer design based on refractive index and film thickness.

A highly metal loaded, less than 100 nm thick Ni-Al<sub>2</sub>O<sub>3</sub> film on aluminium containing ca 6-9 nm sized fcc Ni particles showed a solar absorption of 0.83 and emittance of 0.03 at 100°C [2].

Further optimisation based on optic modelling using the measured refractive index and optimising film thicknesses resulted in a three layer structure with an absorption of 97% and an emittance of 5% at 100°C. The structure contains from the bottom: 80% Ni, 40% Ni and a top layer of SiO<sub>2</sub> added through a sol-gel process [2-6]. These figures of merit are as far as we can find in the literature the best reported so far. In addition, the coatings are appealing glossy black and quite durable both chemically and mechanically, which is not typical of the present solar heat absorbers. Thus, these new coatings can be seen as the 4:th generation of solar surfaces with not only the highest level

of optical performance, but also equipped with a durability that present 3:rd generation PVD deposited surfaces lack. This brings the possibility for unprotected applications in visible architecture such as walls of buildings and roofs of private homes.

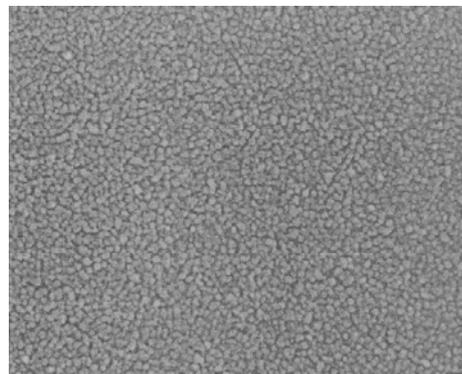


Figure 3. SEM image of 6-9 nm sized Ni particles in Al<sub>2</sub>O<sub>3</sub>.

### Conclusions

Highly nickel nano-particle loaded Ni-Al<sub>2</sub>O<sub>3</sub> composite materials show a wide range of interesting optic and catalytic properties that make them promising candidates for a number of applications, e.g. syn-gas catalysis and solar heat absorbers.

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