Solvent Influence on the Magnetization and Phase of Fe-Ni Alloy Nanoparticles generated by Pulsed Laser Ablation in Liquids

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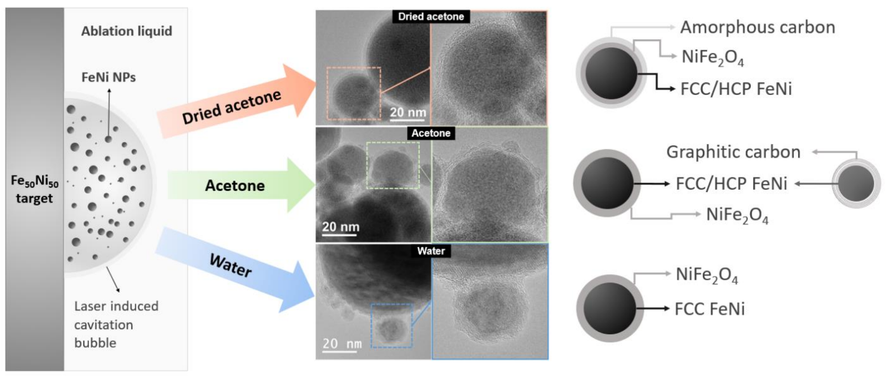
Abstract

$Fe_{50}Ni_{50}$ nanoparticles (NPs) are employed in biomedicine, catalysis, or magnetic actuators due to their soft magnetic response and large magnetization. However, the NPs' properties are determined by the material phase (FCC, HCP, L10), alloy composition, as well as the core-shell structure with a special influence on the C and O content.

Pulsed laser ablation in liquid (PLAL) allows the synthesis of high purity colloidal alloy nanoparticles by ablating a bulk alloy target in the desired solvent. A solvent variation [1] alters the core-shell structure of the generated nanoparticles, and, as a result, provides the opportunity to tune their properties [2]. Organic solvents are usually preferred as a solvent when oxidation is not desired [3]. However, economical laboratory and technical grade solvents typically contain water impurities, a potential oxidation source [4]. Here, we investigated the influence of water impurity in acetone by using molecular sieves (3 Å) to capture water molecules and compared the properties of generated NPs on the ablation of $Fe_{50}Ni_{50}$ alloy in three different ablation liquids, dried acetone (acetone with reduced water impurity after treatment with molecular sieves), untreated acetone, and distilled water.



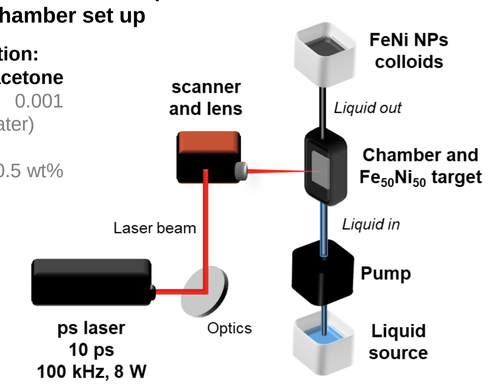
[1] Chem. Rev. (2017), vol. 117, no. 5, pp. 3990–4103
[2] Nanoscale Horizons (2019), vol. 4, no. 6, pp. 1326–1332
[3] Nanomaterials (2020), vol. 10, no. 12, pp. 1–16
[4] ChemPhysChem (2017), vol. 18, no. 9, pp. 1175–1184

Synthesis Method

Pulsed laser ablation in liquid with flow chamber set up

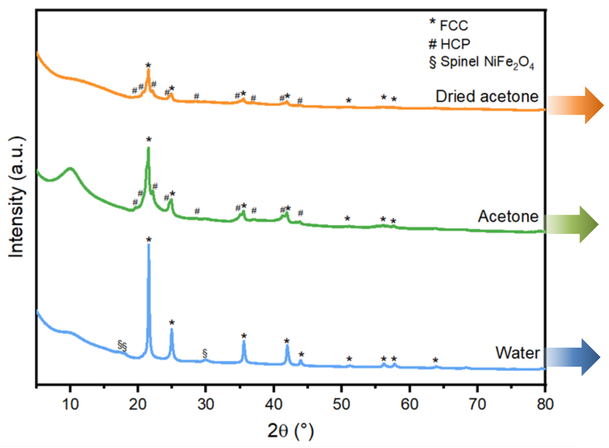
Liquid variation:

- **Dried acetone** (approx. 0.001 wt% of water)
- **Acetone** (approx. 0.5 wt% of water)
- **Water**



Phase Formation and Quantification (Synchrotron XRD)

Synchrotron XRD is performed for FeNi NPs ablated in various liquids to identify the formed NPs phases.



Observed phases

- Dried acetone: FCC FeNi, HCP FeNi, $NiFe_2O_4$
- Acetone: FCC FeNi, HCP FeNi, $NiFe_2O_4$
- Water: FCC FeNi, $NiFe_2O_4$

Ablation Liquid	HCP Content (wt%)*
Dried acetone	35.2 ± 1.0 ~ 41.3 ± 0.9 wt.%
Acetone	38.4 ± 0.2 ~ 47.0 ± 1.3 wt.%
Water	0 wt.%

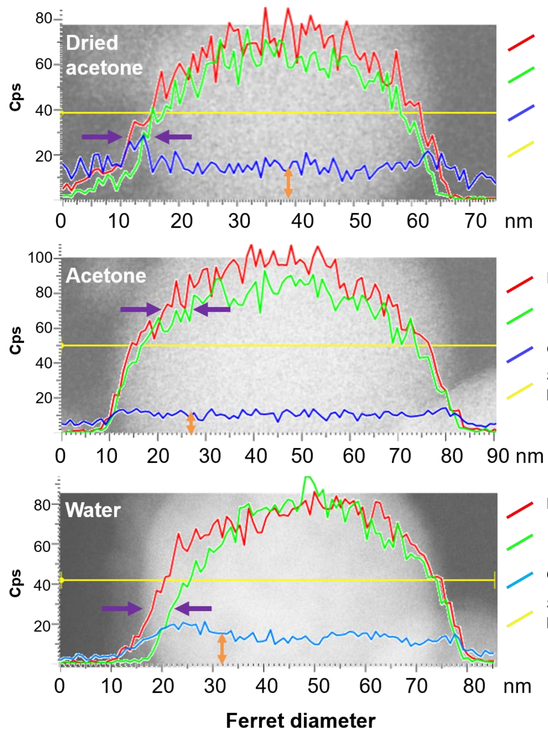
**Measured by Rietveld refinement. The contributions from the $NiFe_2O_4$ phase are excluded due to the low signal in the XRD results.*

The amount of water does not influence HCP phase formation.

- ❖ High-pressure, high-temperature HCP FeNi phase is found in acetone and dried acetone samples, but not in water. Our hypothesis is that different cavitation bubble compositions influence the pressure and temperature conditions.
- ❖ Oxides are still formed even with reduced water impurity in acetone. This may be caused by the molecularly bound oxygen and dissolved oxygen.

Elemental Particle Analysis (EDX-TEM)

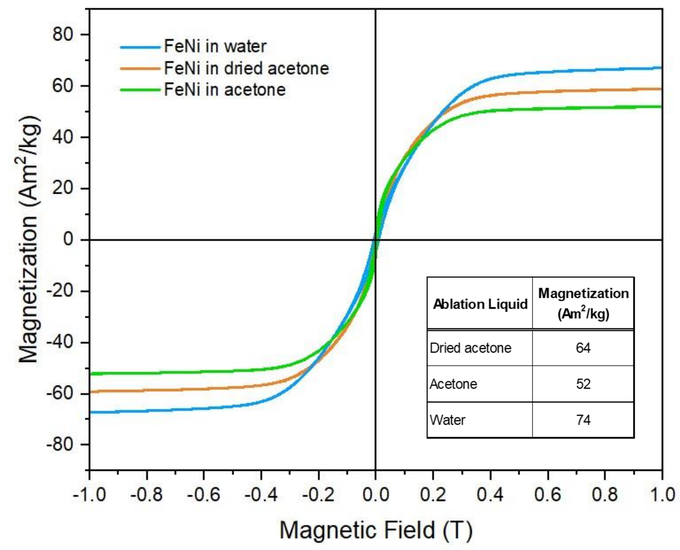
Line scanning of a particle with a diameter of around 50 nm using EDX-TEM to see the elemental distribution within a particle.



- ❖ (purple arrow) Signal differences between Ni and Fe in all samples show the formation of $NiFe_2O_4$ on the NP shell.
- ❖ (orange arrow) Constant signal of O throughout the particle shows that the oxidation only happens on the surface.
- ❖ Fe and Ni signals have similar intensities → the generated NPs retain a 50:50 molar ratio of the target ($Fe_{50}Ni_{50}$).

Magnetization Curves (VSM)

Field-dependent magnetization of the dried powder samples was measured at room temperature (300 K) to compare the influence of water content in the ablation liquid.

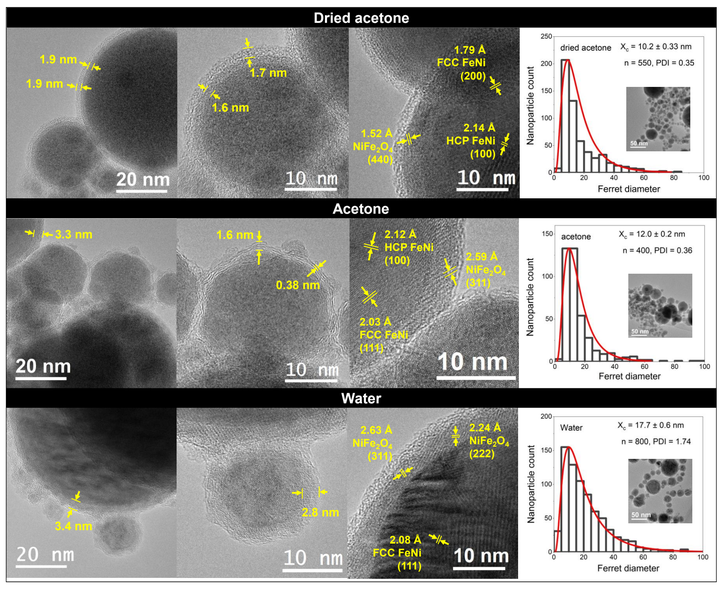


Ablation Liquid	Magnetization (Am^2/kg)
Dried acetone	64
Acetone	52
Water	74

- ❖ FeNi in water showed the highest magnetization (74 Am^2/kg) due to the larger average particle size compared to other samples.
- ❖ FeNi in dried acetone has a larger magnetization (64 Am^2/kg) compared to the FeNi in acetone (52 Am^2/kg) despite their almost similar average particle size, due to the oxide fraction reduction.
- ❖ FeNi in acetone has the lowest magnetization (52 Am^2/kg) due to the small average particle size and the higher oxidation.

Morphology and Size Distribution (HR-TEM)

Analysis of the bright-field (BF) images to identify the phase composition of the core-shell and measure the shell thickness. Particle size distributions show the wide distributions with log-normal fitting.

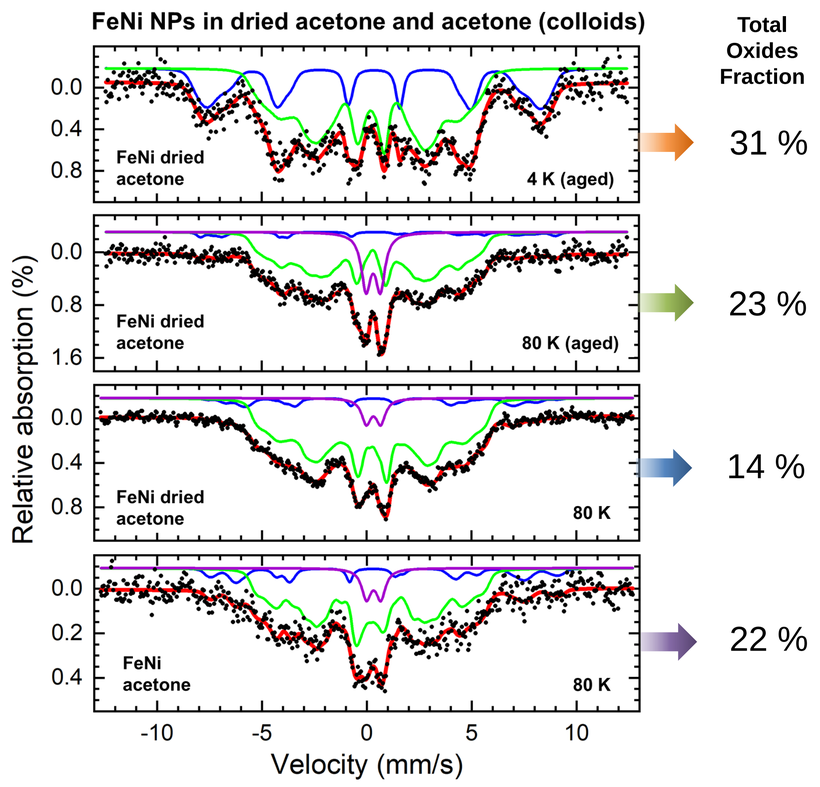


Ablation liquid	Average particle size (X_c, nm)	Core phase	Shell phase	Shell thickness (nm)	
				Average (mean)	Range (min to max)
Dried acetone	10.2 ± 0.3 nm	HCP FeNi	$NiFe_2O_4$	2.4 nm	1.1 - 4.2 nm
		FCC FeNi	Amorphous carbon	1.9 nm	1.5 - 2.9 nm
Acetone	12.0 ± 0.2 nm	HCP FeNi	$NiFe_2O_4$	2.3 nm	1.4 - 3.5 nm
		FCC FeNi	Graphitic carbon	1.2 nm	0.7 - 1.9 nm
Water	17.7 ± 0.6 nm	FCC FeNi	$NiFe_2O_4$	4.9 nm	2.4 - 9.8 nm

- ❖ Diverse core-shell structures, particle sizes, and phases are formed in different ablation liquids. FeNi NPs in water exhibit an average size of 17.7 nm, while the values in acetone and dried acetone are 12 nm and 10.2 nm, respectively.

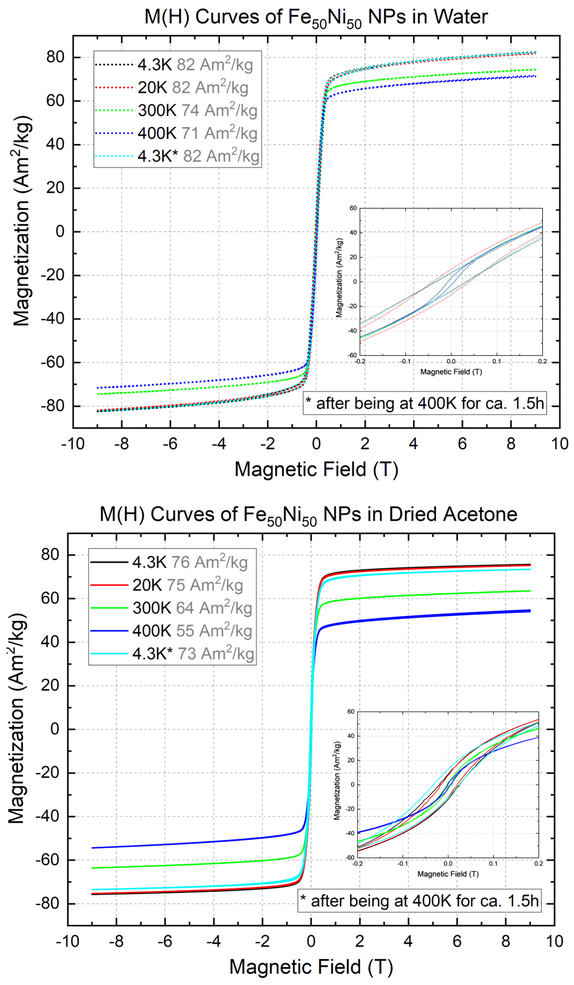
Total Oxide Fractions (Mössbauer Spectroscopy)

Mössbauer spectroscopy of fresh and aged (4-month-old) FeNi NPs colloids to understand the influence of reducing water impurity in acetone and the influence of aging (prolonged storage).



- ❖ Reducing water impurity in acetone suppresses the formation of oxides by 8% in the generated NPs.
- ❖ Aged sample of FeNi NPs in dried acetone shows a 9% increase of total oxides fraction, a similar level as the fresh NPs made in acetone without treatment.

M(H) curves of FeNi in dried acetone and in water at various temperatures



- ❖ FeNi NPs ablated in water have higher thermal stability compared to the FeNi NPs ablated in dried acetone, probably due to the thicker oxide layer which prevents further oxidation.

Conclusion and Outlook

- ❖ Our investigation showed that the magnetization, oxidation level, nanoparticles size, core-shell structure, and the crystallographic phases of $Fe_{50}Ni_{50}$ nanoparticles produced by PLAL are influenced by the water content of the solvent.
- ❖ The high-pressure HCP FeNi phase was found in the sample produced in acetone and dried acetone, but not in water. The reason for HCP phase formation is still being investigated, however, we believe that the different compositions inside the cavitation bubble influence the pressure and temperature conditions.
- ❖ Our observation opens future possibilities for different types of NPs which could be generated just by reducing the amount of water impurity in the organic solvent.

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MATERIALS SCIENCE & ADDITIVE MANUFACTURING

SFB/TRR 270 HoMMage

LESGO

DFG Deutsche Forschungsgemeinschaft German Research Foundation

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