Core-shell Ti(C,N)-Ni structures fabricated by chemical precipitation of Ni-based nanoparticles on TiCN suspensions and its implication in the processing of FeNi-based cermets

colloidal processing

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Objectives:

Core-Shell structures have been designed by the chemical precipitation of Ni nanoparticles (NP's) onto the surface of Ti(C,N) micronic particles previously stabilized in an aqueous suspension. Synthesis of Ni NP's have been obtained by the reduction of Ni^{2+} by hydrazine in water solution in the presence of ultrasound. To optimize the coverage of Ti(C,N) surface by the Ni NP's, the main synthesis parameters were studied. The final objective is the interphase tailoring between the ceramic reinforcement (Ti(C,N)) and the ferrous metal matrix (FeNi) for Hard Metals.

Experimental Conditions

Parameter	Molar ratio ($Ni^{2+}/KOH/N_2H_4$)	Ni^{2+} (M)	T (ºC)	Time (Min)	P [W] (%)	R (W/mol·s)
$[Ni^{2+}]$	1/10/60	0.1	40	60	100	0.175
	1/10/60	0.075	40	60	100	0.233
	1/10/60	0.05	40	60	100	0.350
	1/10/60	0.02	40	60	100	0.875
$[N_2H_4/Ni^{2+}]$	1/10/60	0.05	40	60	100	0.350
	1/10/20	0.05	40	60	100	0.350
	1/10/6	0.05	40	60	100	0.350
Temperature	1/10/60	0.01	40	60	100	0.175
	1/10/60	0.1	50	60	100	0.176
US	1/10/60	0.1	50	5	100	25.432
	1/10/60	0.1	50	5	50	1.282
	1/10/60	0.1	50	60	100	0.176
	1/10/60	0.1	50	5	100	25.432

Synthesis of Ni NP´s

Solution A: $H_2O + Ni(NO_3)_2{\cdot}6H_2O$
Solution B: $H_2O + KOH + N_2H_4{\cdot}H_2O$

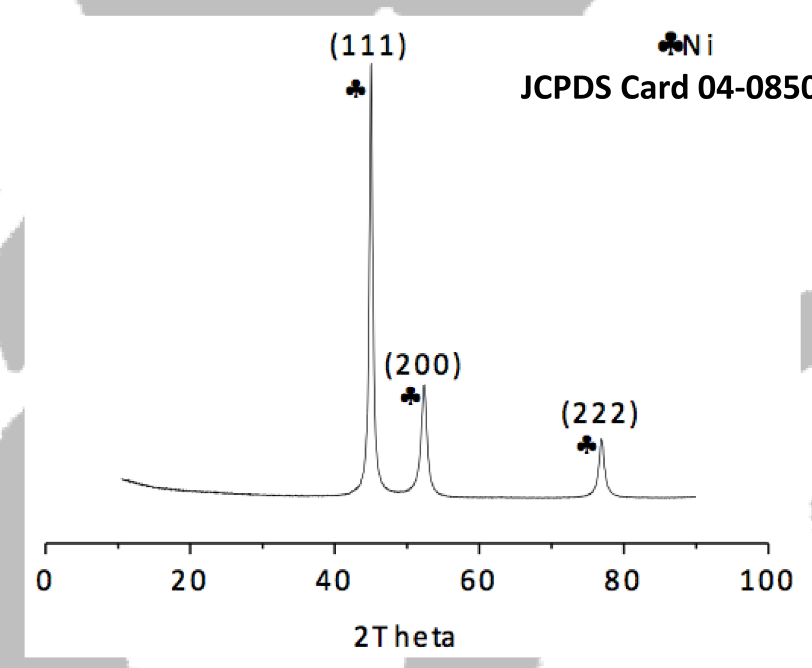
A + B —US→ Ni

One-Pot Synthesis Ti(C,N)-Ni

Suspension A: H_2O + **Ti(C,N)** + $Ni(NO_3)_2{\cdot}6H_2O$
Solution B: $H_2O + KOH + N_2H_4{\cdot}H_2O$

A + B —US→ Ti(C,N)-Ni

Identification of Ni NP's

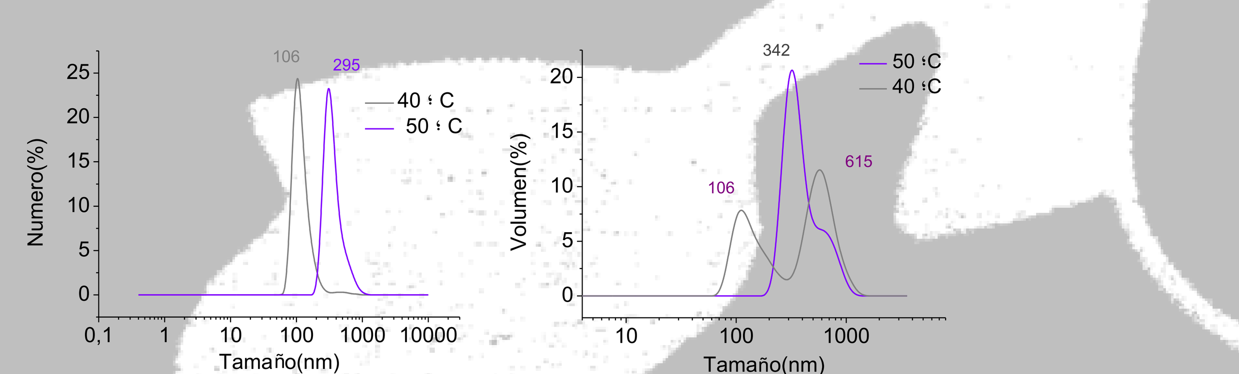


XRD of NP´s showing pure metallic Ni

All NP's exhibit the same characteristic pattern of **FCC Ni** according to the **JCPDS card nº 04-0850**

The **synthesis yield** maintained **constant** settling around **80-85%**

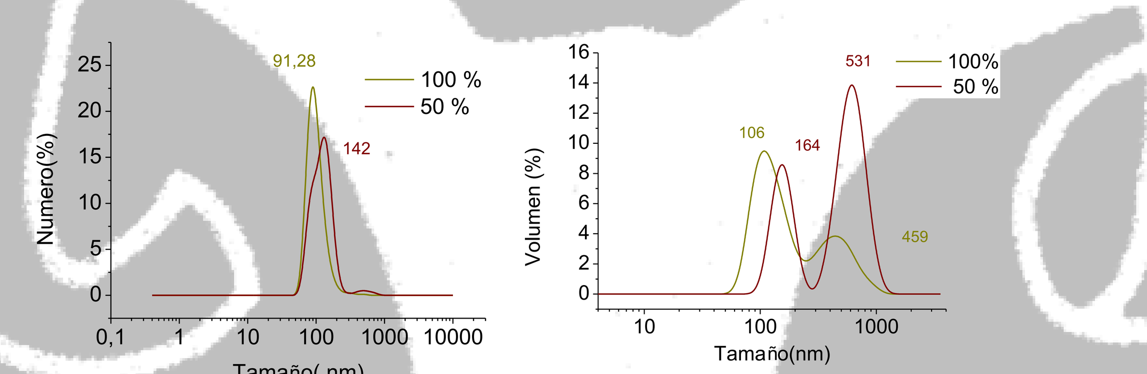
Temperature effect



The higher is the temperature the wider is the population of Ni aggregates.

- In both synthesis the solution turns to black color during the ultrasound application
- Thermal energy speed up the Ni nuclei evolution to aggregates

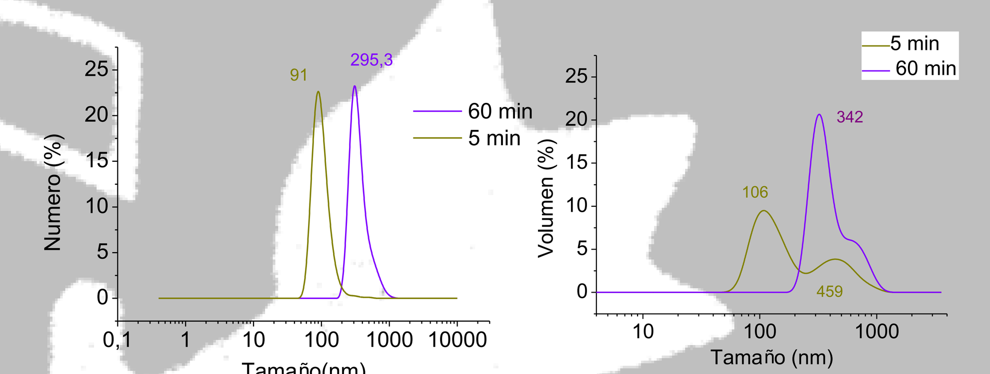
US Power effect



The higher is US power the smaller are the Ni NP's.

- Stronger ultrasound implies a better dispersion of the NP's since energetic shock waves produced by the probe reduces the size and the agglomeration state of the Ni NP´s.

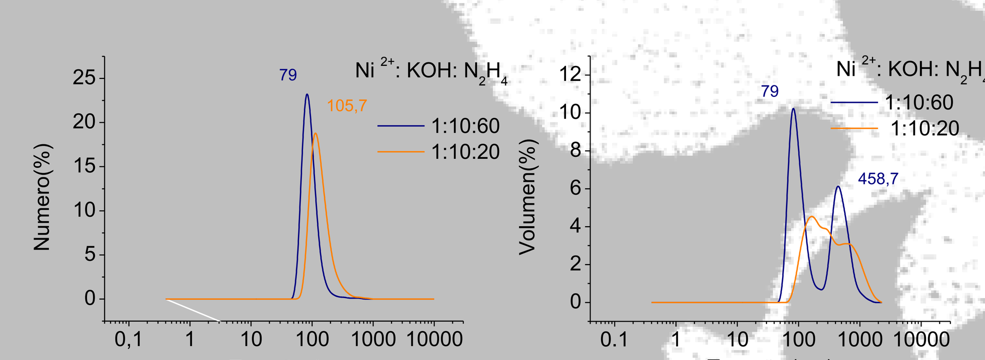
US Time effect



The lower is US time the smaller are the Ni NP's.

- The complete reduction of the Ni NP's occurs after the first five minutes of US.
- Larger US times promote the formation of the Ni aggregates.

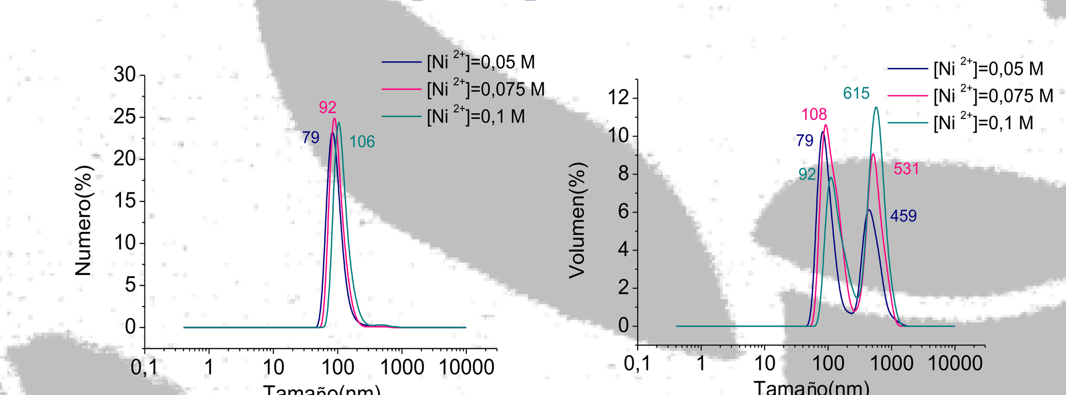
$[N_2H_4/Ni^{2+}]$ ratio effect



The higher is the $[N_2H_4/Ni^{2+}]$ ratio the smaller are the Ni NP's.

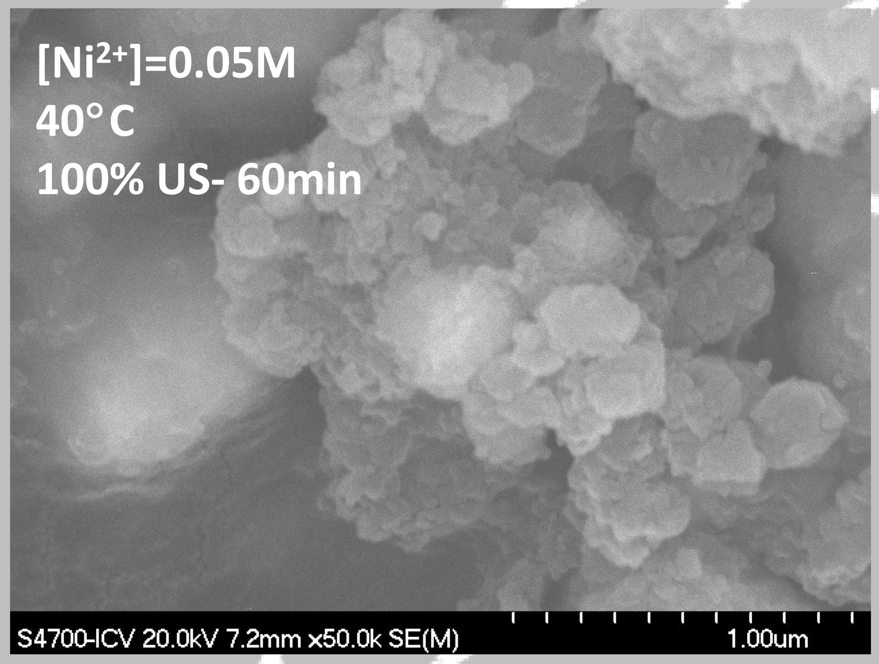
- The reduction rate of the Ni^{2+} was slowed as the amount of hydrazine decreases. Only few nuclei were formed in the early stage of the reduction reaction, which growth during the later synthesis steps.
- The addition of hydrazine in excess contributes to the formation of Ni NP´s, evidencing it significant role as a synthesis modifier.

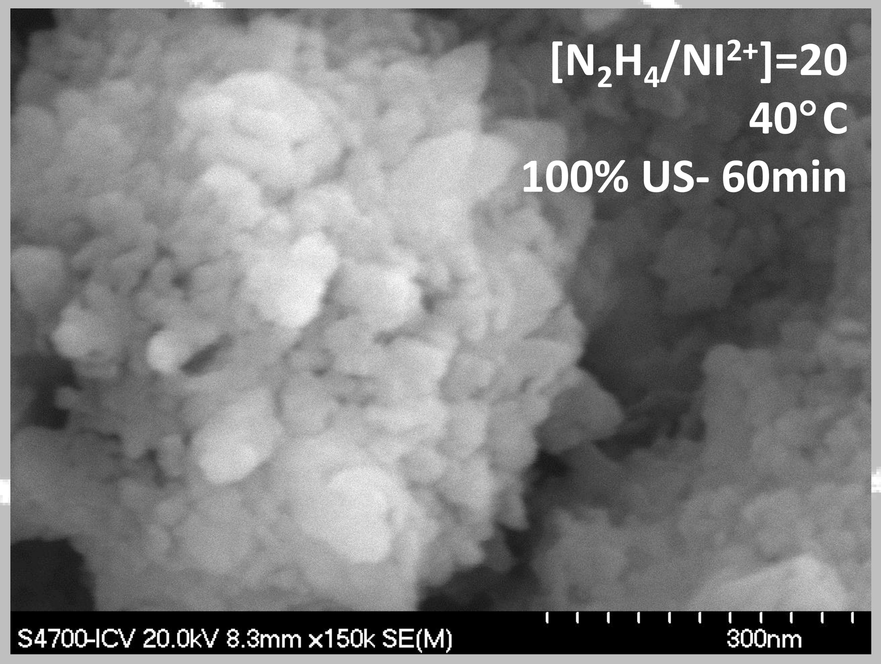
$[Ni^{2+}]$ effect



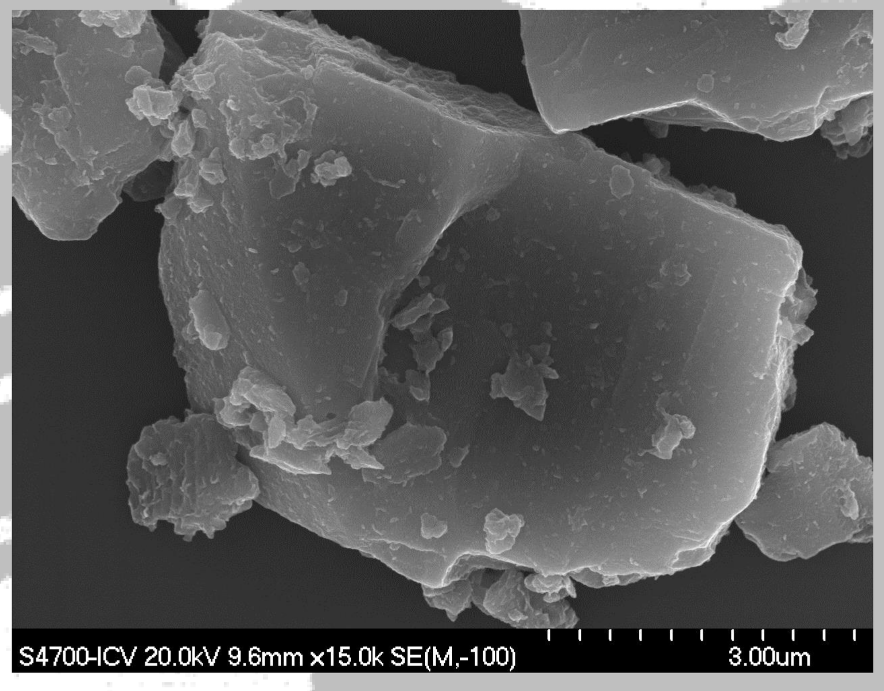
The lower is the Ni^{2+} concentration the smaller are Ni NP's.

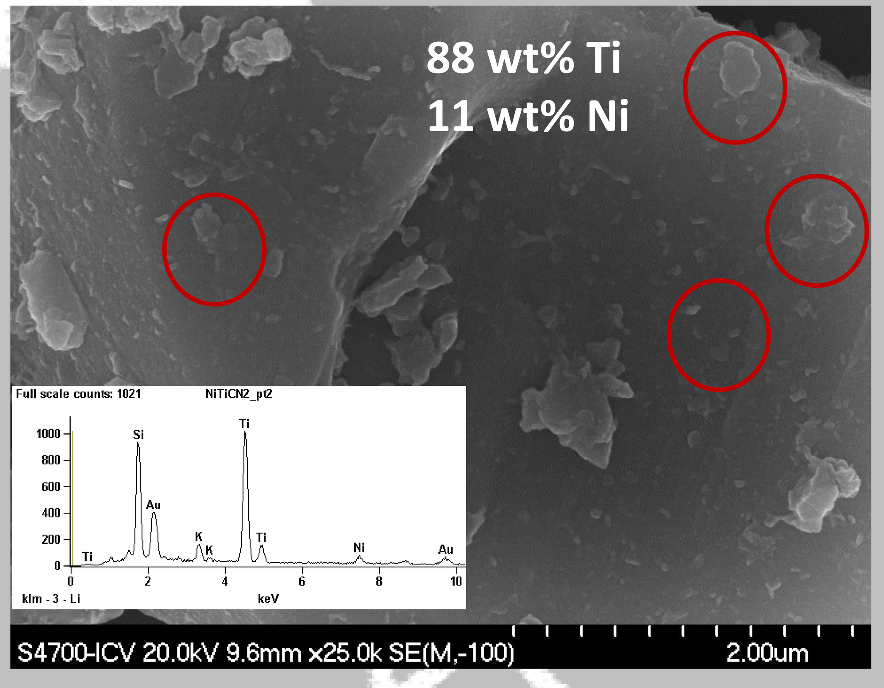
- Ni NP's **80 nm** in diameter were obtained from the 0.05M Ni^{2+} precursor bath.
- In a first step, nuclei were formed and an increase of the precursor concentration speeds up its Oswalt Ripening growth to 90-105 nm.
- The particle surface potential can't avoid the formation of aggregates, and primary particles arrange forming agglomerates with a main size of **460 nm**.





One-Pot Core-Shell Ti(C,N)-Ni





The optimal route to obtain the most suitable Ni NP´s was used. Ni NP´s on the surface of Ti (C, N) were identified

Conclusions:

- The synthesis of Ni NP´s by a reduction method using hydrazine as reductor agent in aqueous medium has been succesfully achieved. Although the amount of hydrazine for the synthesis of Ni NP's is considerably higher than other previously reported (R=60), the synthesis of pure Ni NP´s, 80 nm in diameter, was carried out in shorter times (up to 5 min).
- **Ti(C,N)-Ni Core-Shells were obtained providing a route for the bottom up design of FeNi-Ti(C,N) interphases in CERMETS.**

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