



# **Rivestimenti galvanici innovativi per applicazioni anti - usura**

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# TIPI DI RIVESTIMENTI GALVANICI

## ➡ Rivestimenti decorativi



## ➡ Rivestimenti funzionali



- ➡ Spessori «elevati»
- ➡ Durezza
- ➡ Resistenza ad usura
- ➡ Resistenza a corrosione
- ➡ Proprietà magnetiche
- ➡ Rivestimenti singoli o multilayer

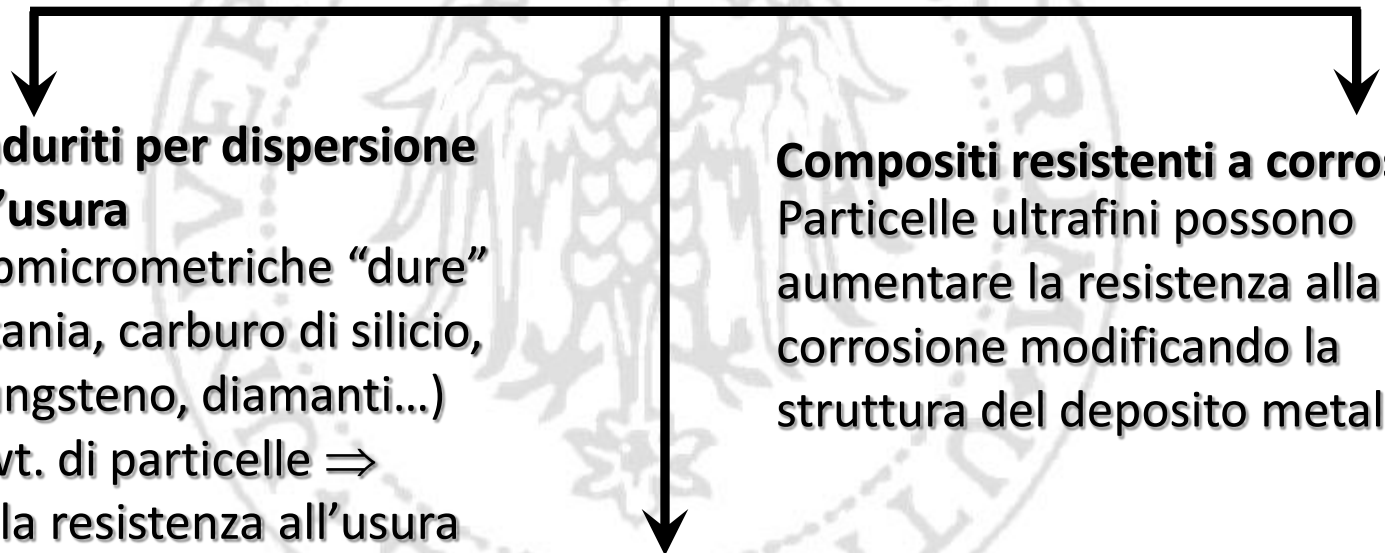


- Cr duro
- Ni
- Leghe di Ni (Ni/Co, Ni/P, Ni/Zn, NiW, Ni/B...)
- Rame e leghe di rame (Cu/Zn, Cu/Sn, Cu/Zn/Sn)
- Cobalto e leghe di cobalto
- Rivestimenti compositi



- ➡ **Rivestimenti compositi di matrice metallica:**
- ➡ **Metallo o lega**
- ➡ **+ particelle di:**
  - **Ossidi ( $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{Cr}_2\text{O}_3$ )**
  - **Carburi ( $\text{SiC}$ ,  $\text{WC}$ ,  $\text{TiC}$ ,  $\text{Cr}_3\text{C}_2$ )**
  - **Nitruri ( $\text{TiN}$ ,  $\text{CrN}$ )**
  - **Grafite**
  - **Diamante**
  - **Polimeri ( $\text{PS}$ ,  $\text{PTFE}$ )**

➡ La dispersione omogenea di una seconda fase in un metallo o in una lega crea uno strato superficiale con proprietà migliorate o completamente diverse



## **Compositi induriti per dispersione resistenti all'usura**

Particelle submicrometriche "dure" (allumina, titania, carburo di silicio, carburo di tungsteno, diamanti...)

Fino a 2-4%wt. di particelle ⇒ aumento della resistenza all'usura

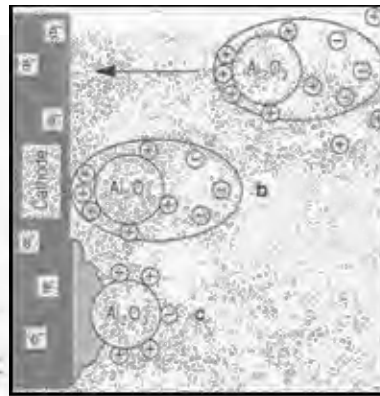
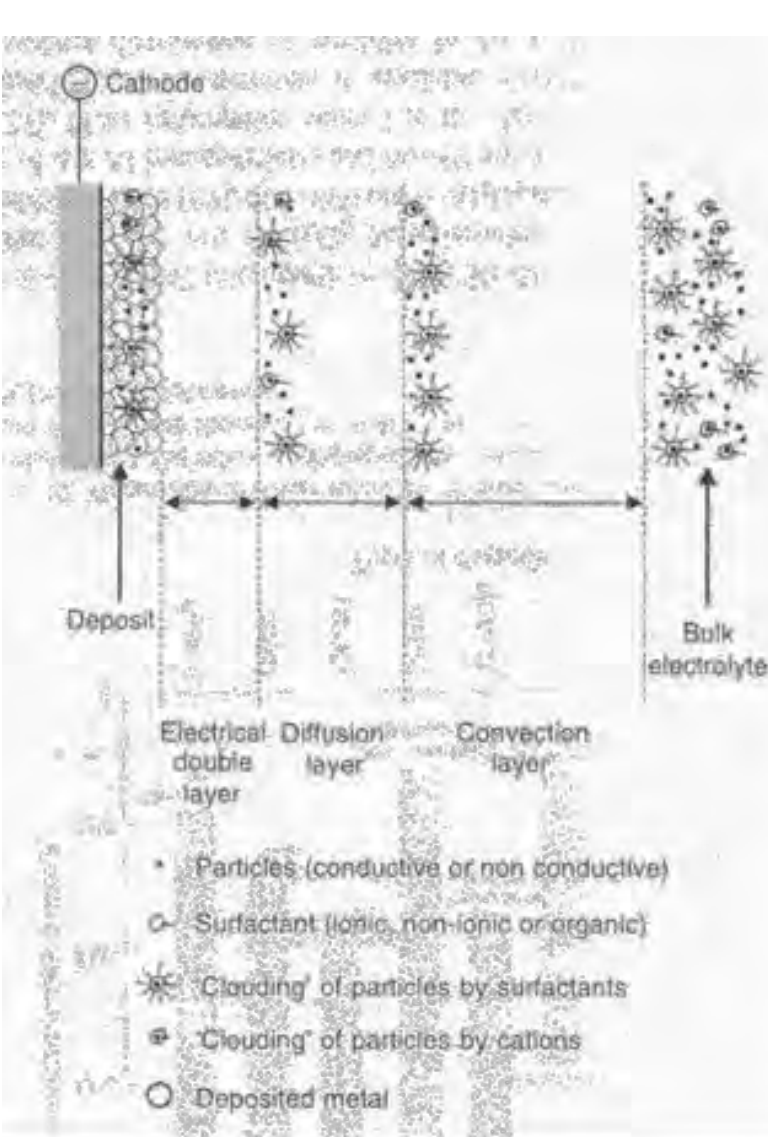
## **Compositi resistenti a corrosione**

Particelle ultrafini possono aumentare la resistenza alla corrosione modificando la struttura del deposito metallico

## **Compositi auto-lubrificanti**

L'introduzione di un lubrificante solido (grafite, bisolfuro di molibdeno, PTFE) abbassa il coefficiente di usura soprattutto sotto alti carichi.

# MODELLO CELIS et alii 1987



- 1°: Le particelle dopo la loro aggiunta nel bagno si circondano di una nuvola ionica
- 2°: Si trasferiscono al bordo dello strato di diffusione spinte dall'agitazione del bagno
- 3°: Diffondono verso il catodo attraversando lo strato di diffusione
- 4°: Si assorbono sulla superficie del catodo
- 5°: Le particelle assorbite sul catodo vengono inglobate all'interno solo se una certa frazione degli ioni si riduce sul catodo

## ➡ Ni/SiC – Ni/Al<sub>2</sub>O<sub>3</sub>:

- effetto del bagno galvanico
- effetto del rinforzante
- effetto del tipo di corrente utilizzata (DC o PC)
- effetto degli US

- microstruttura
- proprietà meccaniche
- proprietà tribologiche
- anticorrosione

## ➡ Cu/SiC:

- effetto del bagno galvanico
- effetto del rinforzante
- effetto del tipo di corrente utilizzata (DC o PC)

- microstruttura
- proprietà meccaniche
- proprietà tribologiche
- anticorrosione

## ➡ Ni/Al

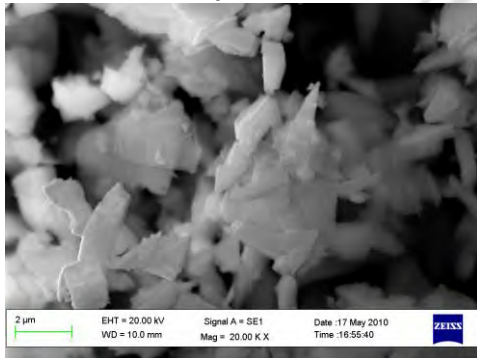
## ➡ Scaling-up – industrializzazione

# PRODUZIONE RIVESTIMENTI

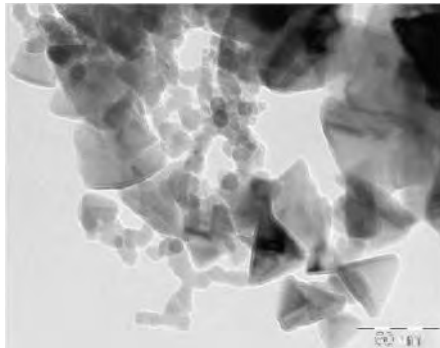
## ***Pretrattamenti superficiali***

- ✓ Sgrassaggio ultrasuoni
- ✓ Sgrassaggio elettrolitico
- ✓ Decapaggio acido

## ***SiC Micro-particles***

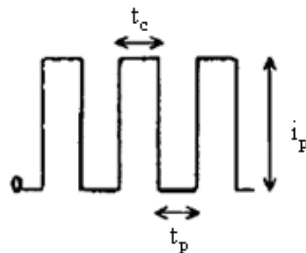


## ***SiC Nano-particles***



## ***Corrente applicata: continua e pulsata***

$$T = \frac{t_c}{t_c + t_p} = 50\%$$

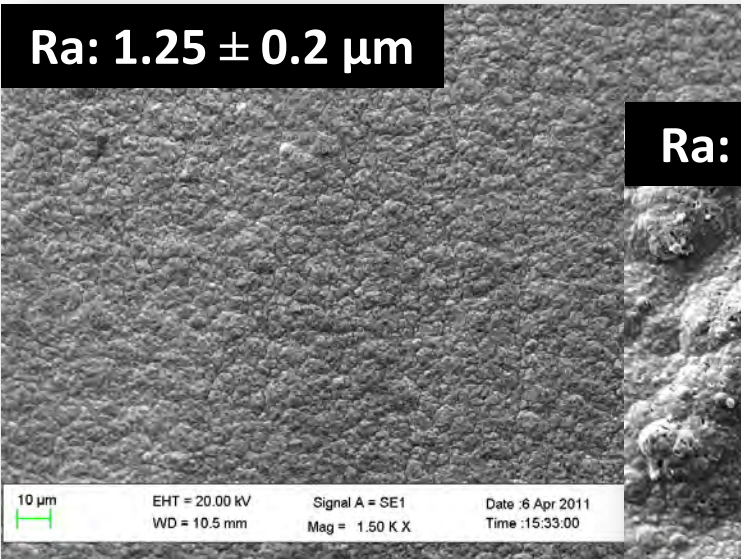


***Ultrasuoni***  
**200W**  
**24kHz**

# Ni/SiC - MICROSTRUTTURA

*Pianta*

**Ra:  $1.25 \pm 0.2 \mu\text{m}$**

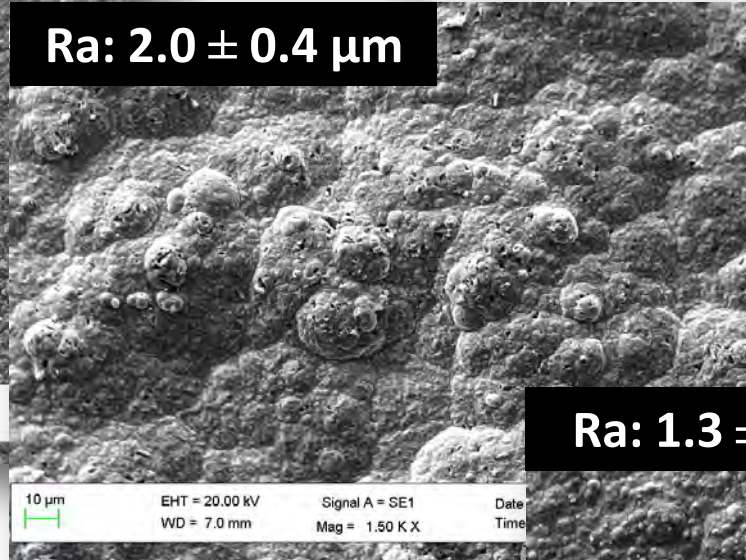


***Ni puro DC***

***Plating bath – Nickel  
sulfamate high speed***

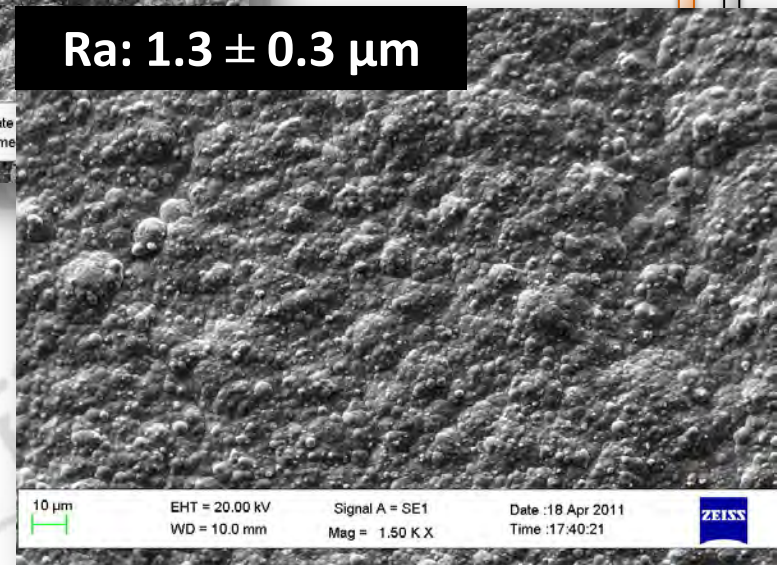
- ✓ 500 g/l  $\text{Ni}(\text{SO}_3\text{NH}_2)_2 \cdot 4\text{H}_2\text{O}$
- ✓ 20 g/l  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$
- ✓ 25 g/l  $\text{H}_3\text{BO}_3$
- ✓ 1 ml/l surfactant
- ✓  $4\text{A}/\text{dm}^2$
- ✓ 20g/L of  $\mu\text{SiC}$  or  $n\text{SiC}$

**Ra:  $2.0 \pm 0.4 \mu\text{m}$**



***Ni+ $\mu\text{SiC}$  DC***

**Ra:  $1.3 \pm 0.3 \mu\text{m}$**



***Ni+nSiC DC***

M. Lekka, A. Lanzutti, A. Casagrande, C. de Leitenburg, P.L. Bonora, L. Fedrizzi, Surface & Coatings Technology (2012), doi: 10.1016/j.surfcoat.2012.03.016

# Ni/SiC - MICROSTRUTTURA

*Ni*

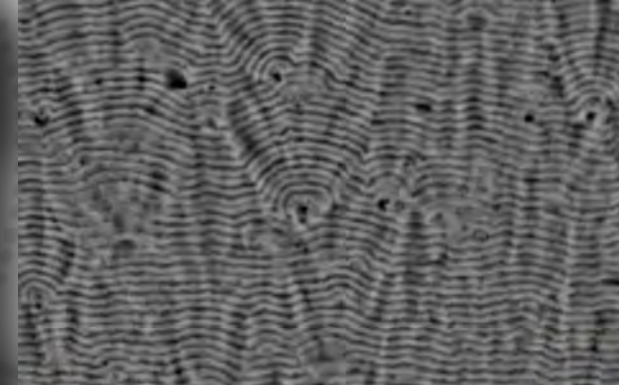
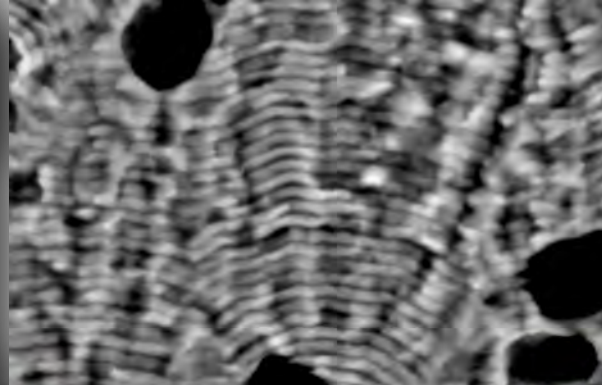
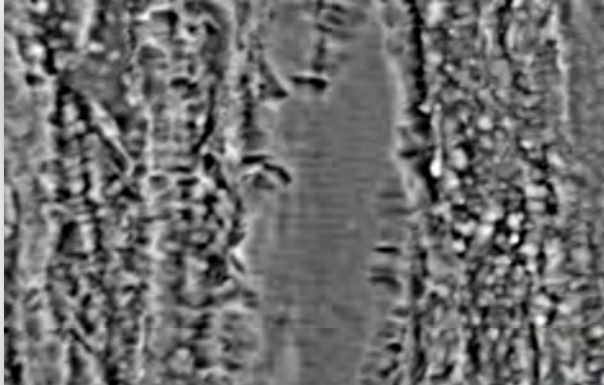
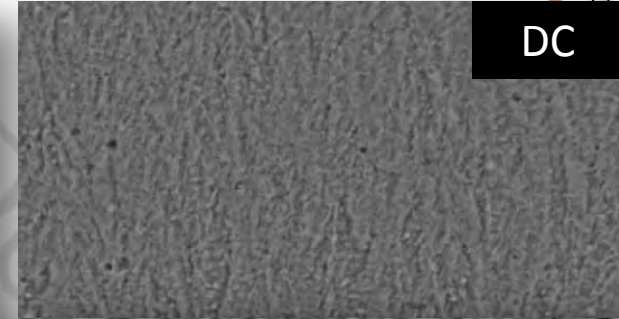
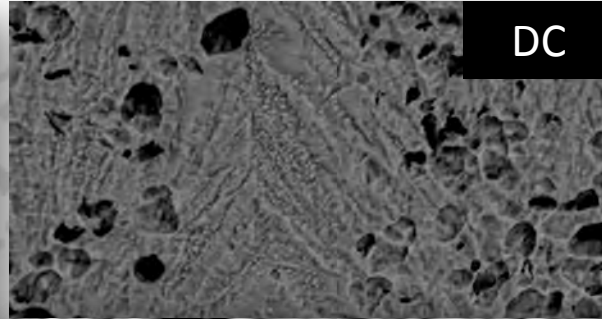
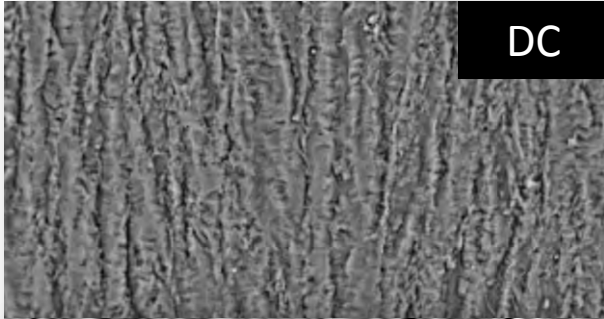
*Ni/  $\mu$ SiC*

*Ni/  $n$ SiC*

DC

DC

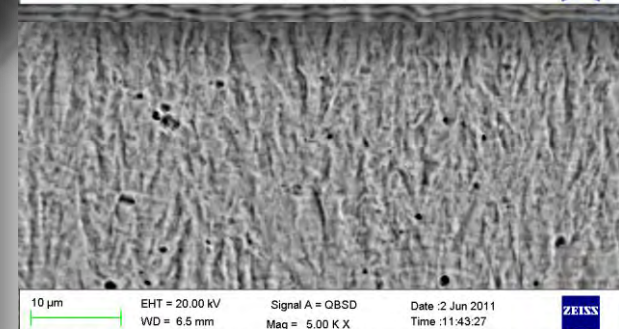
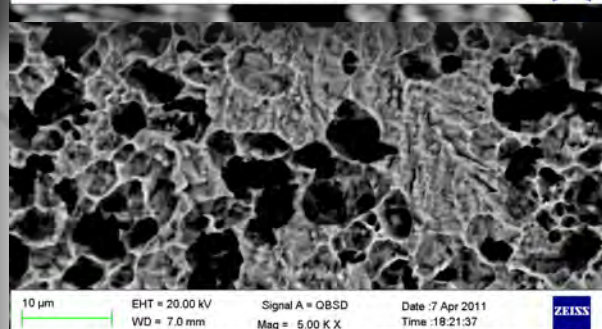
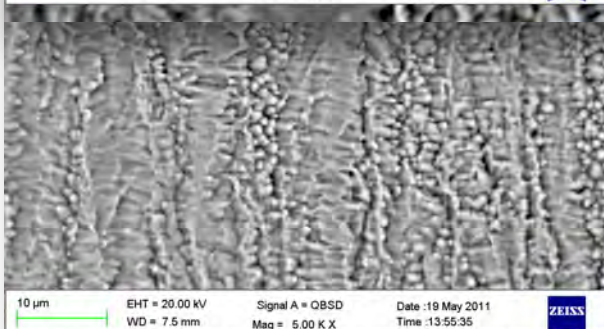
DC



2  $\mu$ m EHT = 20.00 kV Signal A = QBSD Date :20 May 2011  
WD = 5.0 mm Mag = 10.00 K X Time :9:34:07

1  $\mu$ m EHT = 20.00 kV Signal A = QBSD Date :7 Apr 2011  
WD = 6.0 mm Mag = 20.00 K X Time :17:00:11

2  $\mu$ m EHT = 20.00 kV Signal A = QBSD Date :2 Jun 2011  
WD = 8.0 mm Mag = 10.00 K X Time :10:25:57

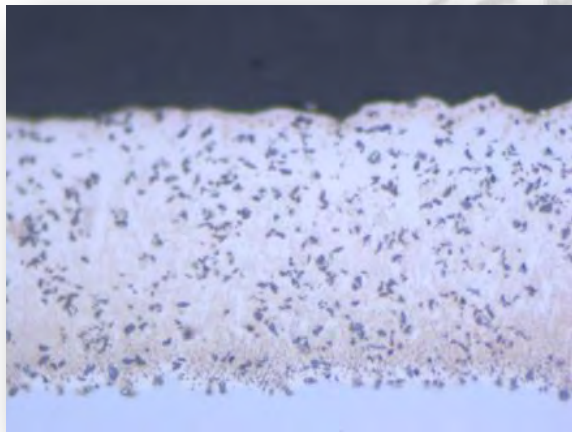


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WD = 7.5 mm Mag = 5.00 K X Time :13:55:35

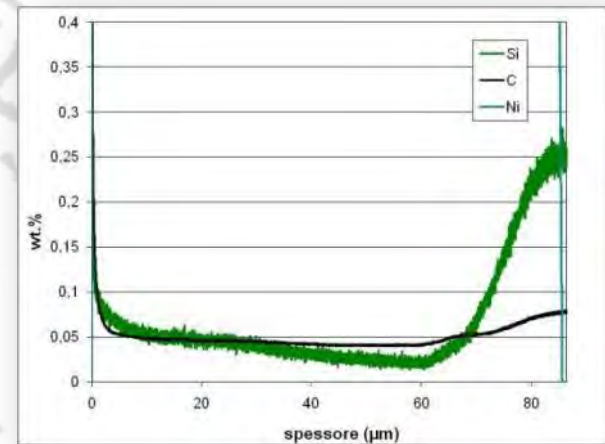
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10  $\mu$ m EHT = 20.00 kV Signal A = QBSD Date :2 Jun 2011  
WD = 6.5 mm Mag = 5.00 K X Time :11:43:27

*Ni/ $\mu$ SiC*



*Ni/nSiC*



**Frequency [Hz]**

**% SiC wt.**

**DC**

$0.8 \pm 0.2$

**0.01**

$2.9 \pm 0.2$

**0.1**

$3.1 \pm 0.3$

**1**

$3.7 \pm 0.5$

**10**

$2.3 \pm 0.2$

**Frequency [Hz]**

**% SiC wt.**

**DC**

$0.06 \pm 0.002$

**0.01**

$0.04 \pm 0.005$

**0.1**

$0.04 \pm 0.006$

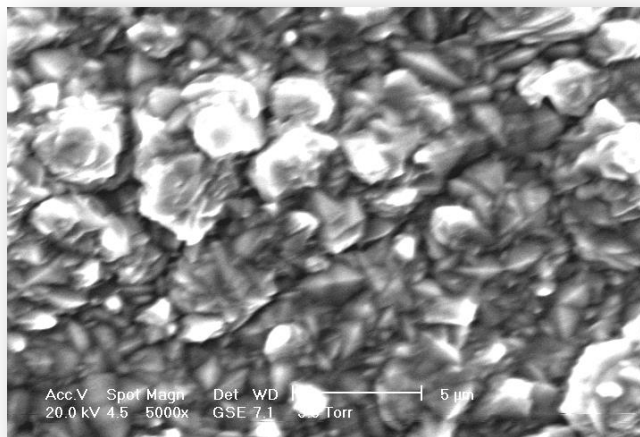
**1**

$0.04 \pm 0.001$

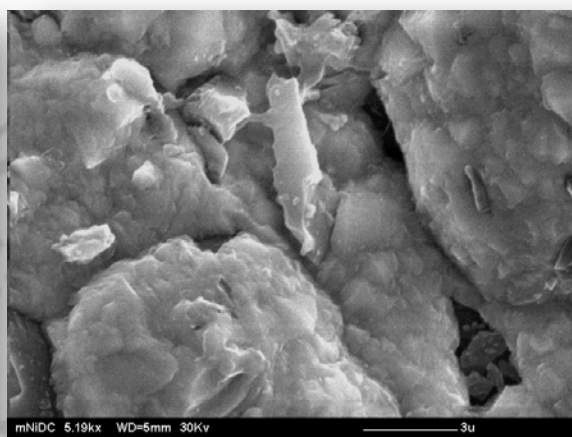
**10**

$0.03 \pm 0.001$

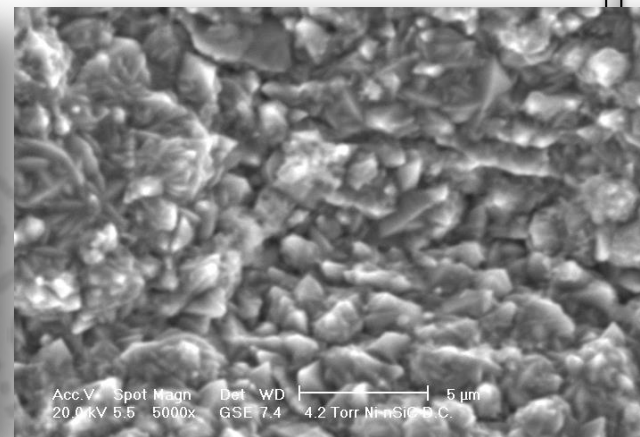
# Ni/SiC - MICROSTRUTTURA



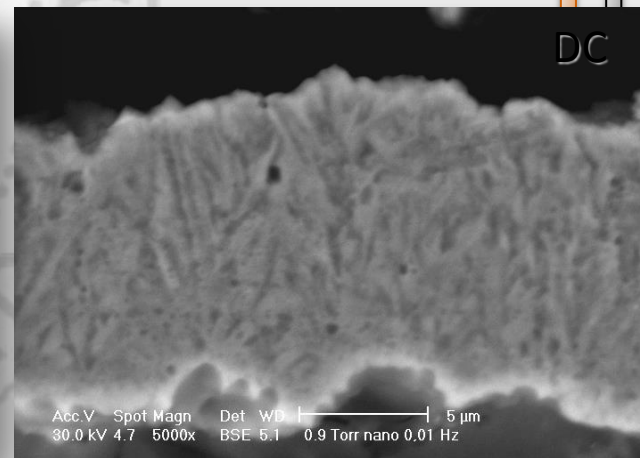
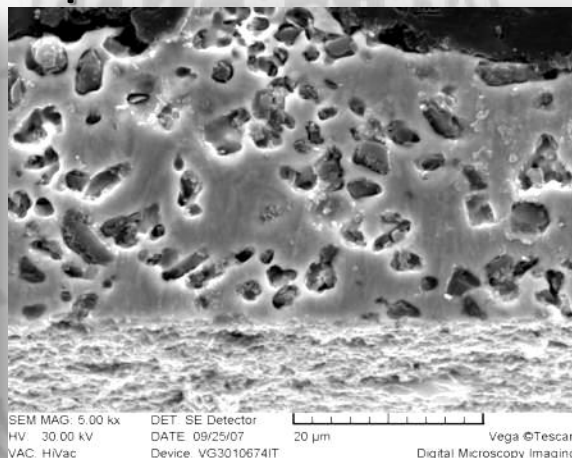
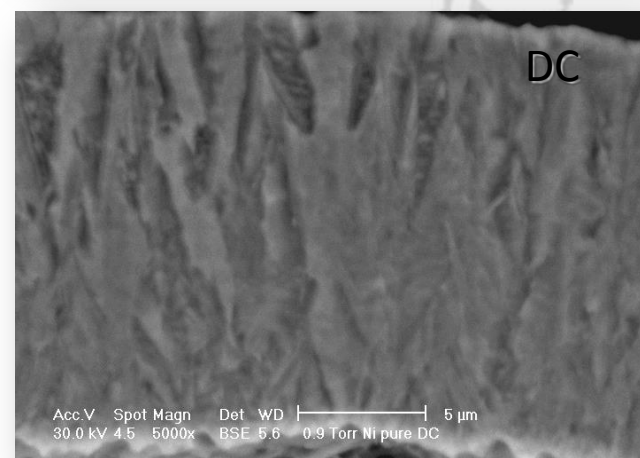
**Ni-DC**



**Ni+µSiC-DC**



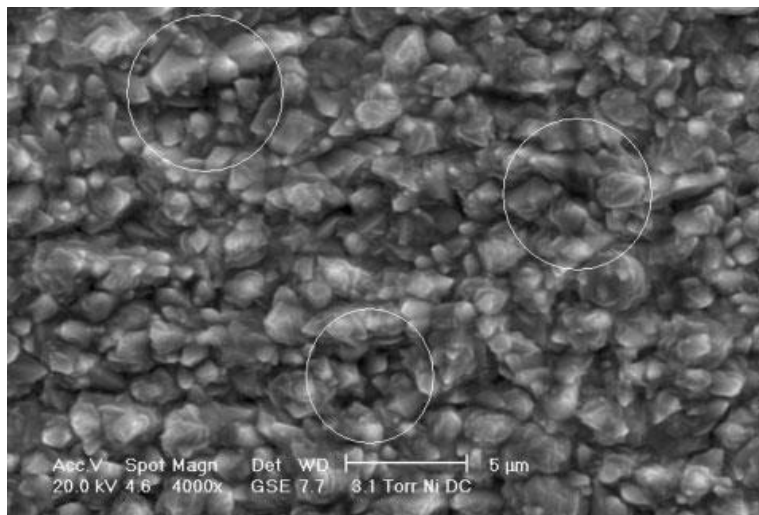
**Ni+nSiC-DC**



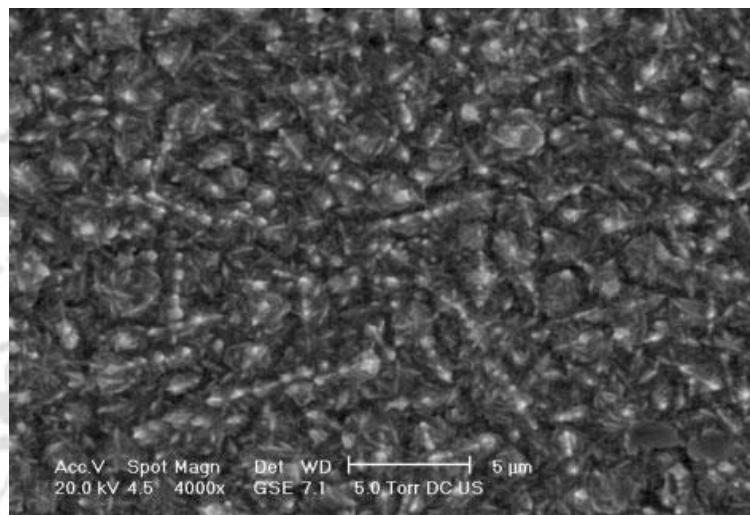
## **Plating bath – Watt's type**

240g/L NiSO<sub>4</sub> - 45g/L NiCl<sub>2</sub> - 30g/L H<sub>3</sub>BO<sub>4</sub> - 2.5g/L CH<sub>3</sub>(CH)<sub>11</sub>OSO<sub>3</sub>Na

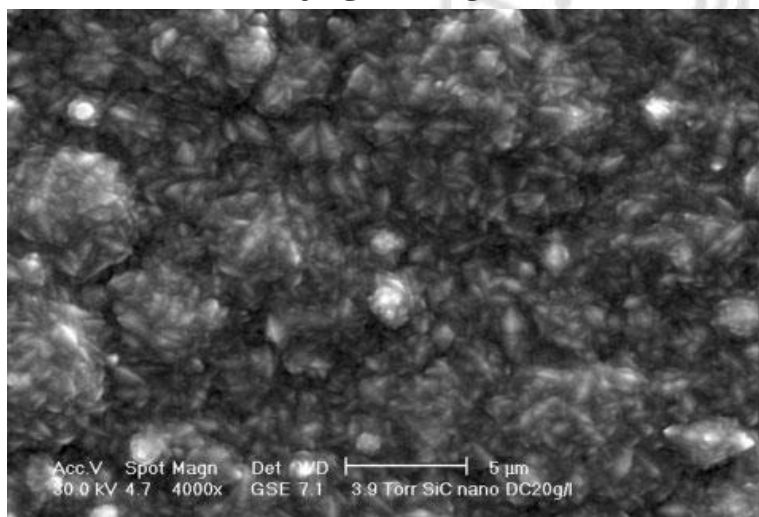
**2A/dm<sup>2</sup> 20g/L of µSiC or nSiC**



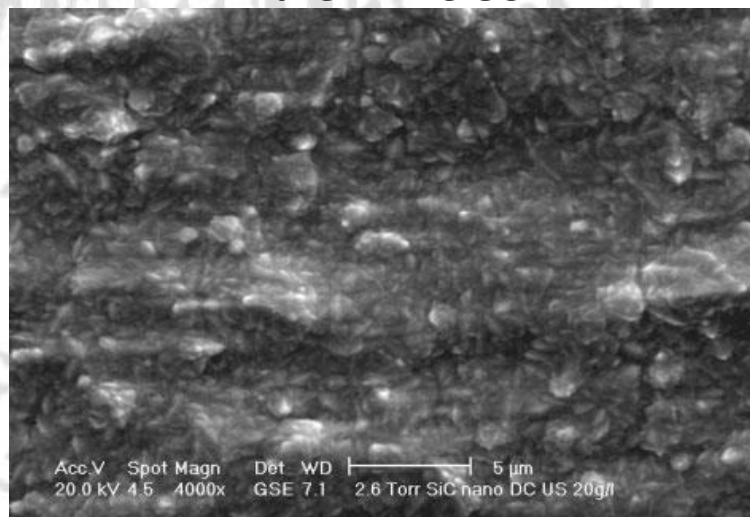
**Pure Ni DC**



**Pure Ni DC US**



**Ni+nSiC DC**



**Ni+nSiC DC US**

**Plating bath –  
Watt's type**

240g/L NiSO<sub>4</sub>

45g/L NiCl<sub>2</sub>

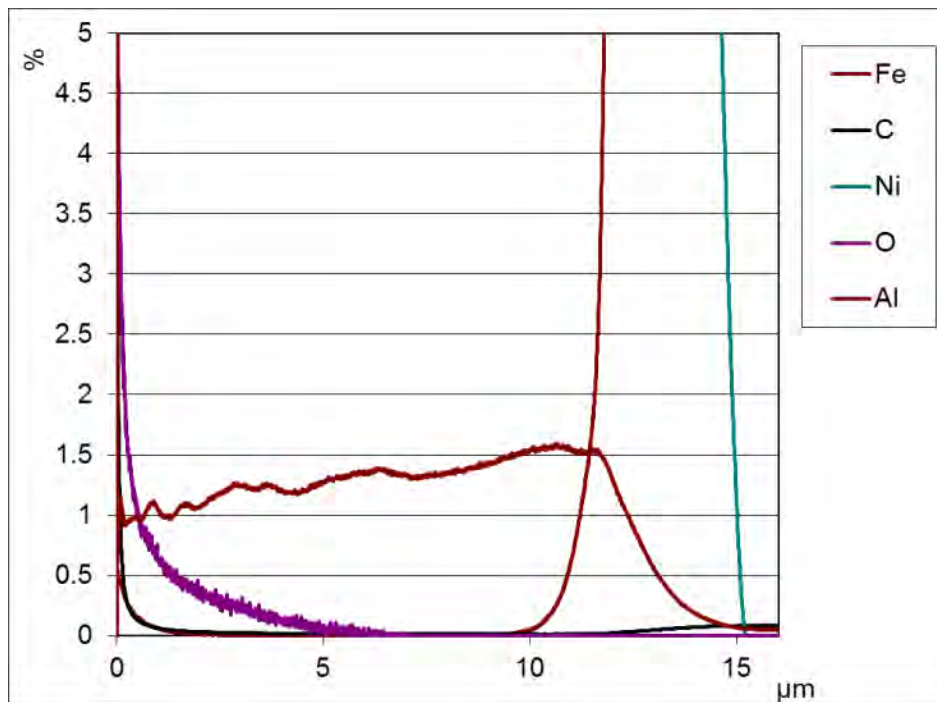
30g/L H<sub>3</sub>BO<sub>4</sub>

**No additives**

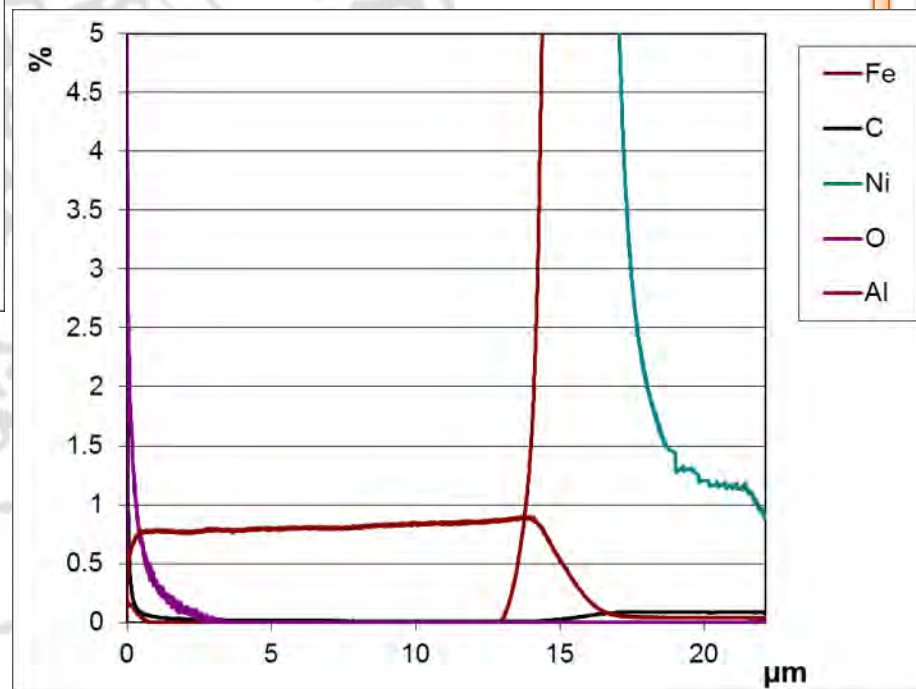
**2A/dm<sup>2</sup>**

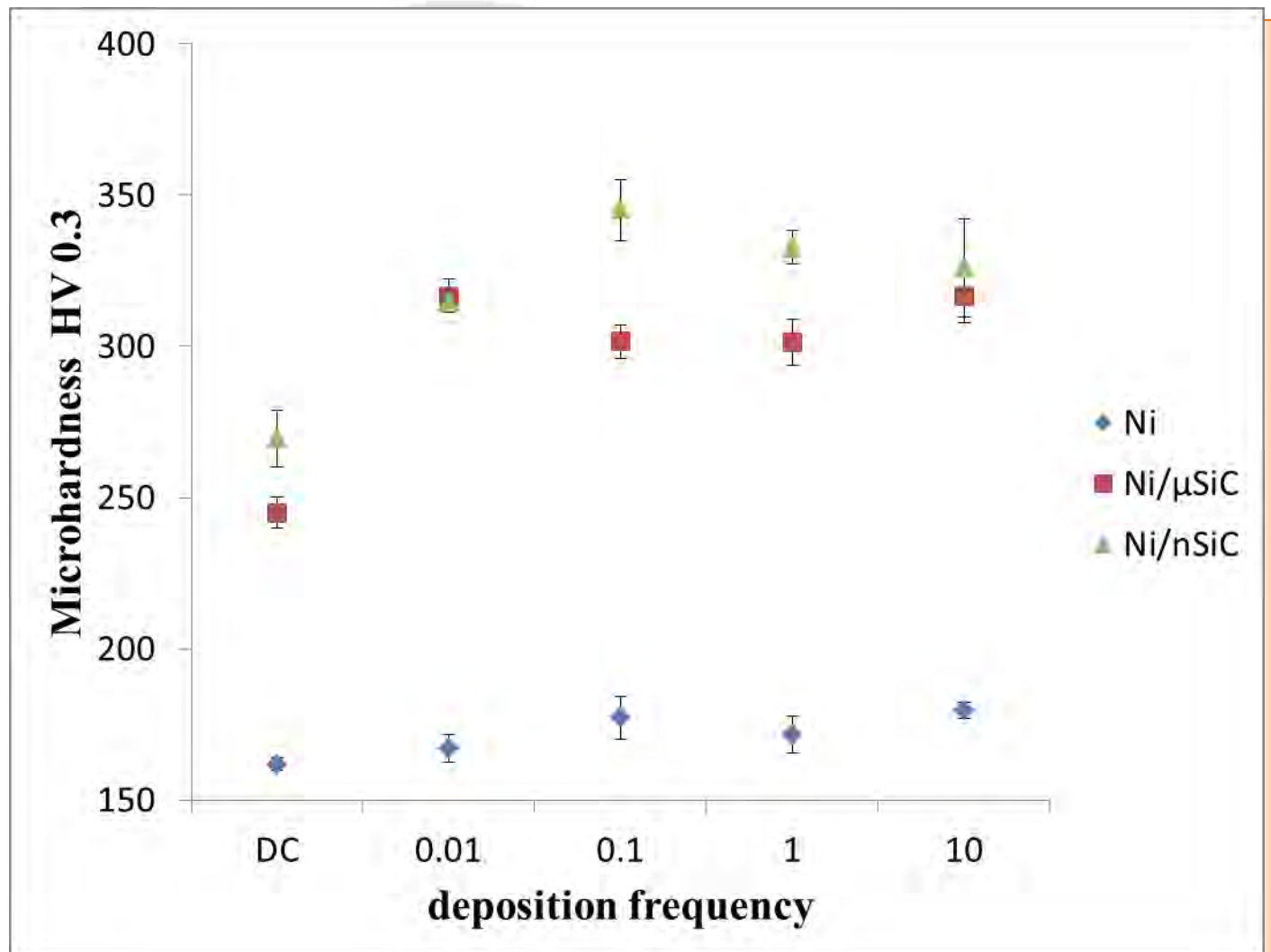
**20g/L of nSiC**

*Ni-nAl<sub>2</sub>O<sub>3</sub>- DC*



*Ni-nAl<sub>2</sub>O<sub>3</sub>- DC - US*

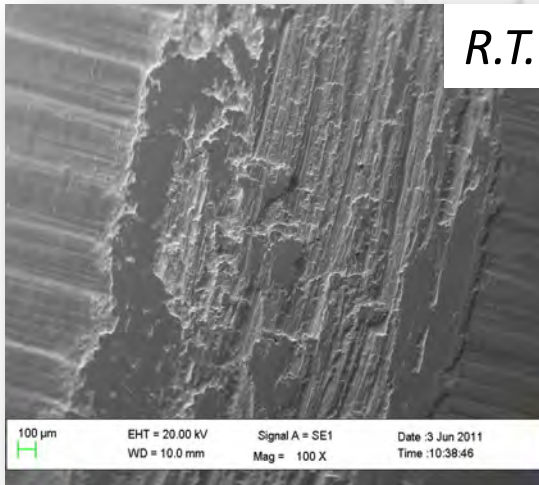
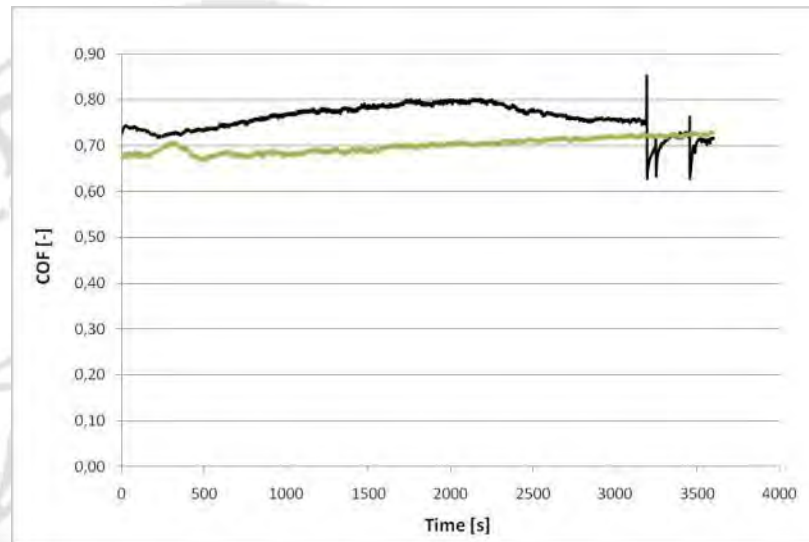


$HV_{0.3}$ 

# Ni/SiC – RESISTENZA AD USURA

## Testing parameters

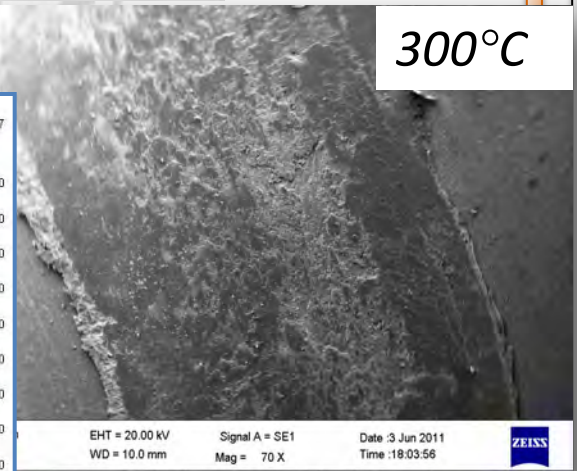
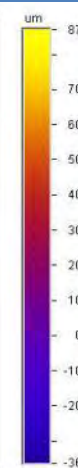
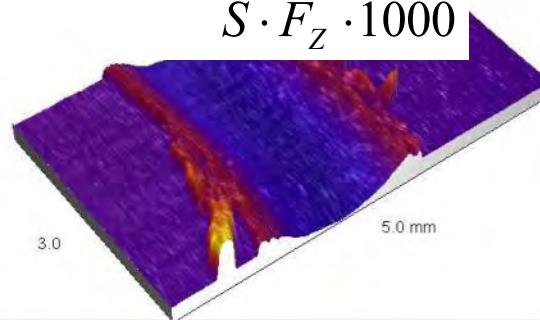
- ✓ Ball on disc configuration
- ✓ Counter: WC/Co
- ✓ Applied load: 70N
- ✓ Test radius: 18mm
- ✓ Sliding speed: 0,45m/s
- ✓ Test duration: 1h
- ✓ Temperature: RT and 300°C



R.T.

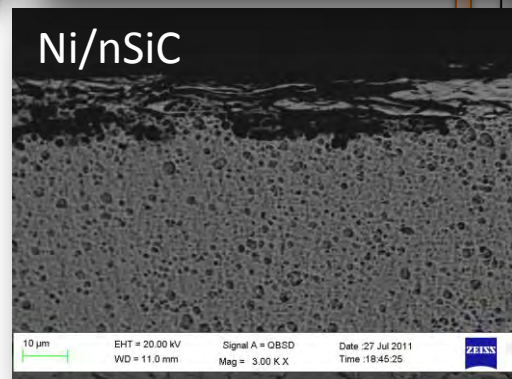
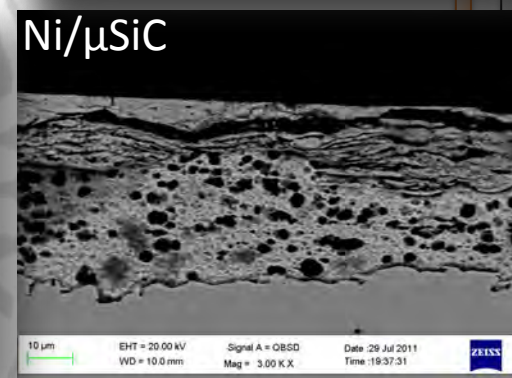
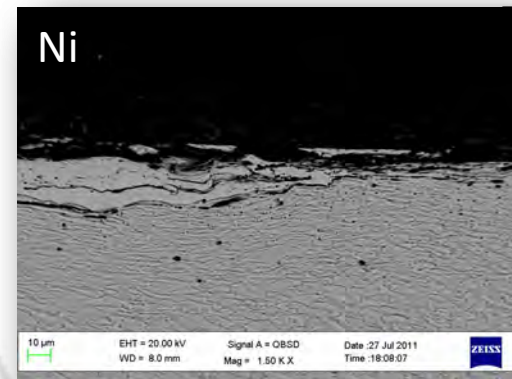
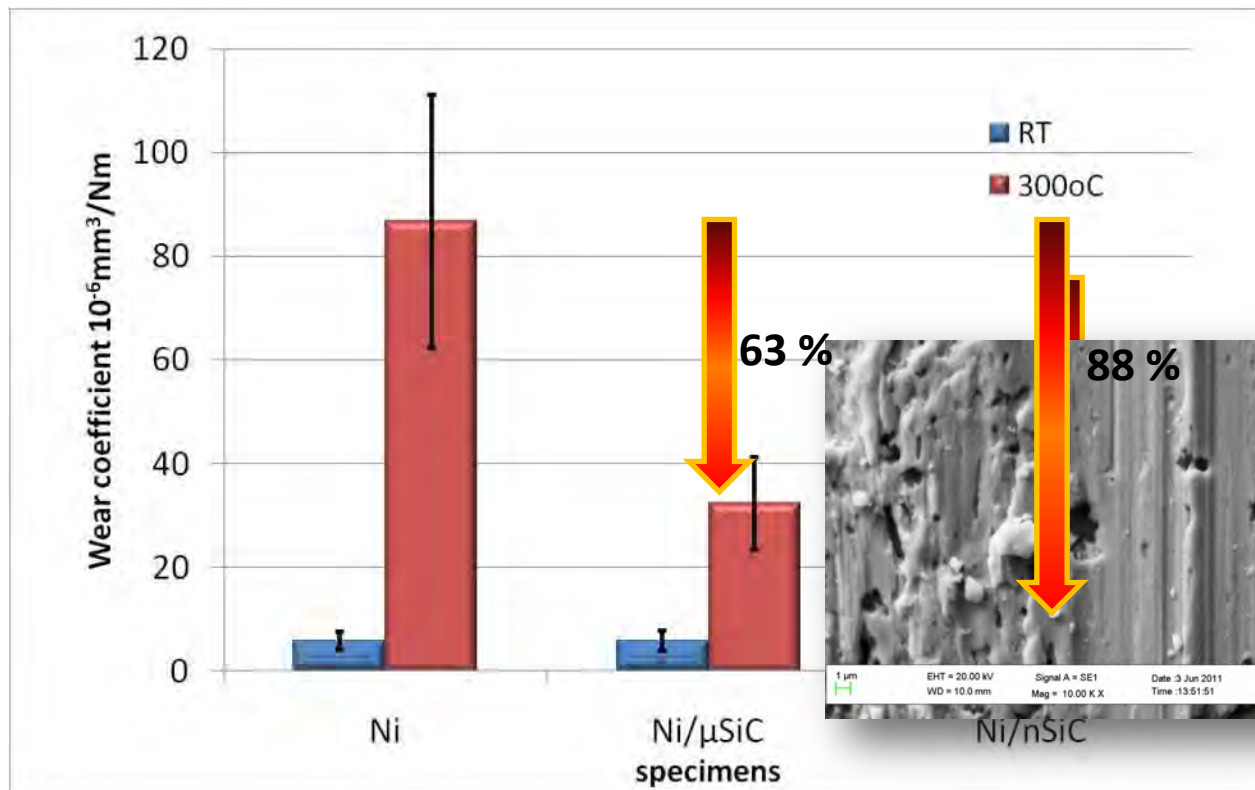
## Wear coefficient

$$K = \frac{V}{S \cdot F_z \cdot 1000}$$



300°C

# Ni/SiC – RESISTENZA AD USURA



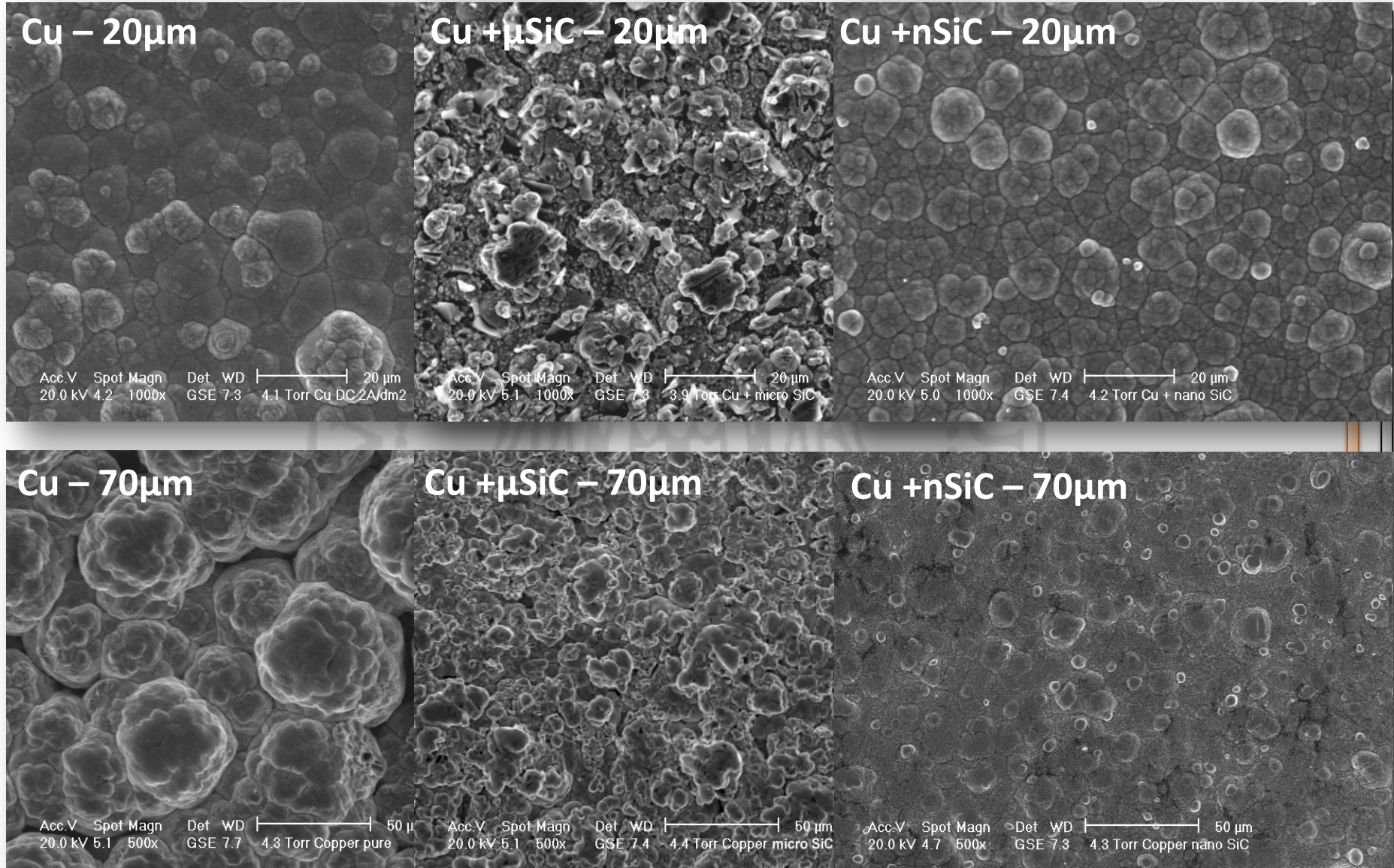
**Plating bath – Nickel sulfamate high speed**

✓  $4 \text{ A}/\text{dm}^2$

✓  $20 \text{ g}/\text{L}$  of either  $\mu\text{SiC}$  or  $n\text{SiC}$

M. Lekka, A. Lanzutti, A. Casagrande, C. de Leitenburg, P.L. Bonora, L. Fedrizzi, Surface & Coatings Technology (2012), doi: 10.1016/j.surfcoat.2012.03.016

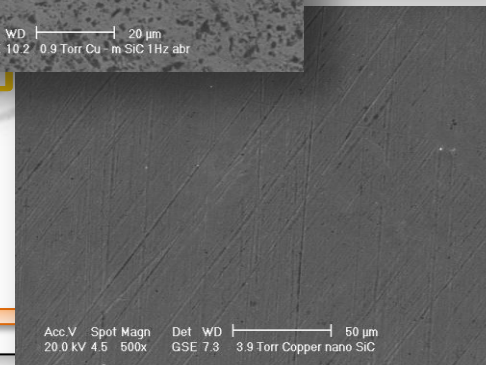
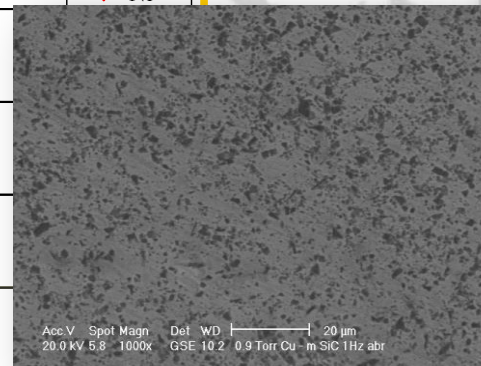
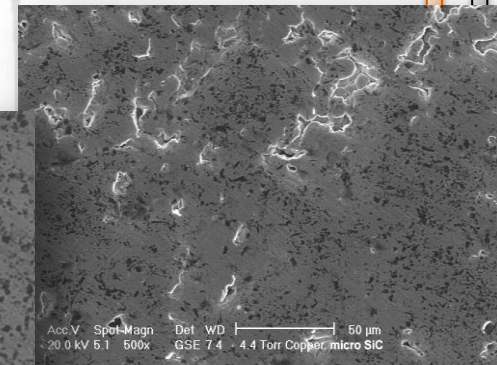
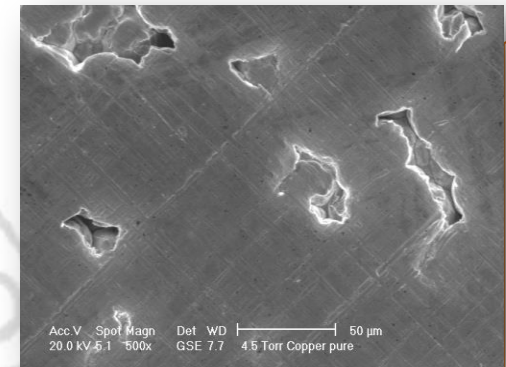
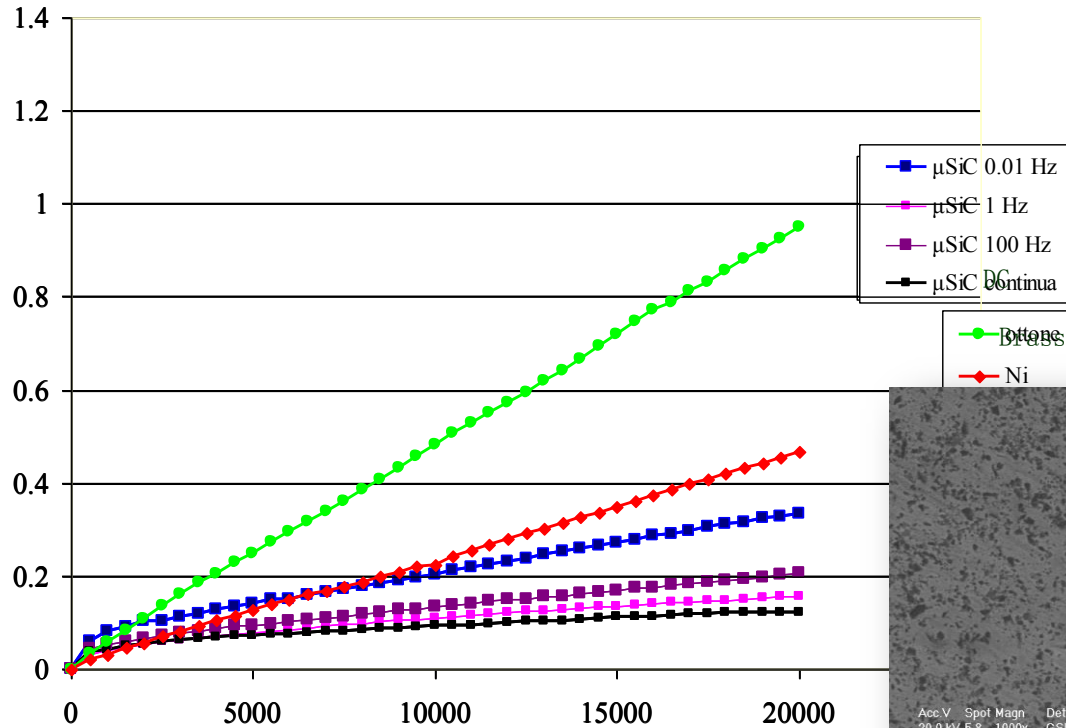
# Cu/SiC - MICROSTRUTTURA



M. Lekka, D. Koumoulis, N. Kouloumbi, P.L. Bonora, *Electrochimica Acta* 54 (2009) 2540-2546

# Cu/SiC – RESISTENZA ALL'ABRASIONE

## Coppio $\mu$ micro SiC

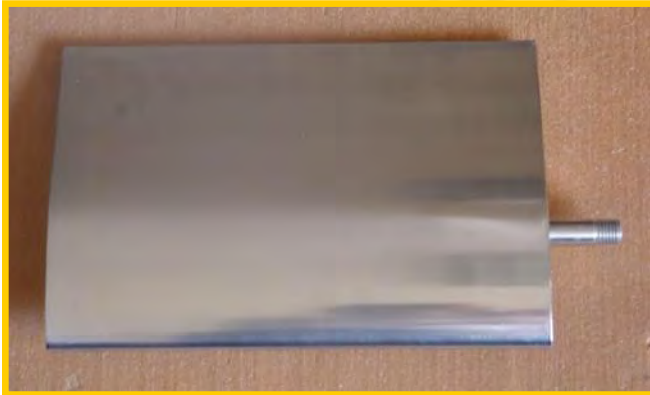


# SCALING UP – INDUSTRIALIZZAZIONE

**Ni + nSiC**



**Propeller models**



**Propeller profiles**



**Train axles**

**Cu +  $\mu$ SiC deposits**



**Pasta extruders**



**Copper moulds –  
Ni/ $\mu$ SiC**

# SCALING UP – INDUSTRIALIZZAZIONE



## Esposizione in nebbia salina

### Nichel



7 d



30 d



45 d

### Nichel + nano SiC



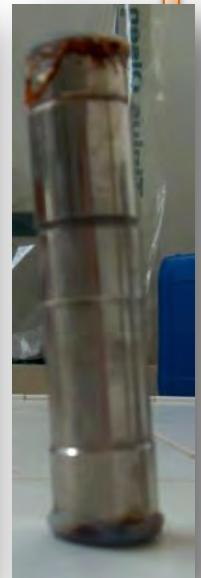
7 d



30 d



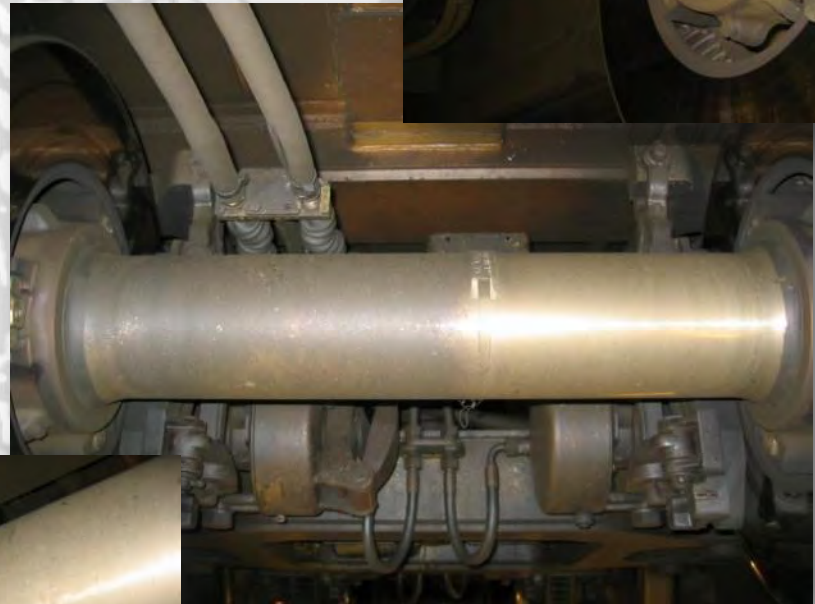
45 d



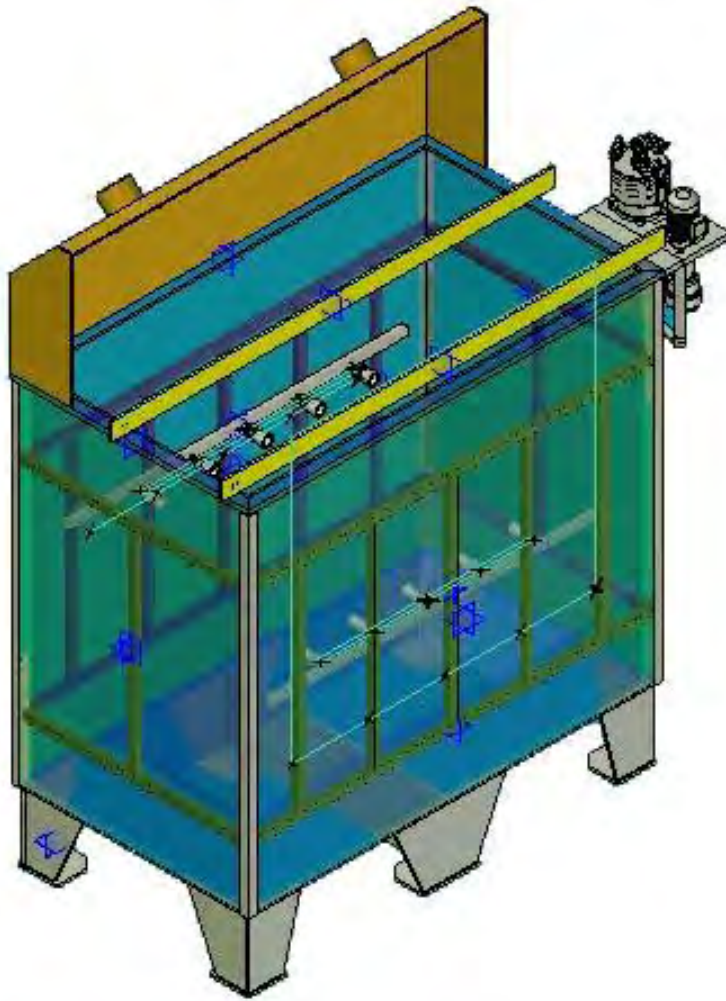
90 d

## Assili ferroviari

Appena montati



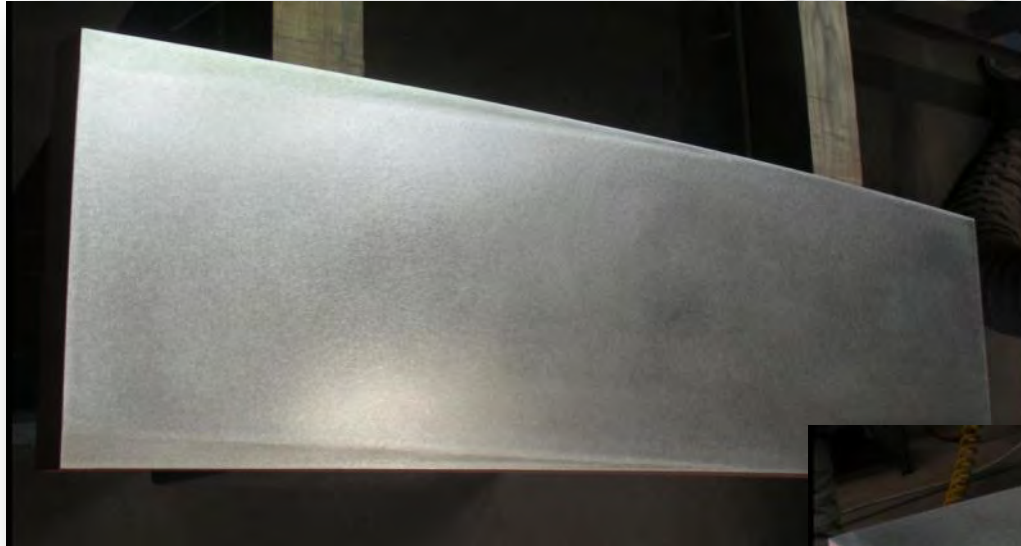
dopo 700.000km



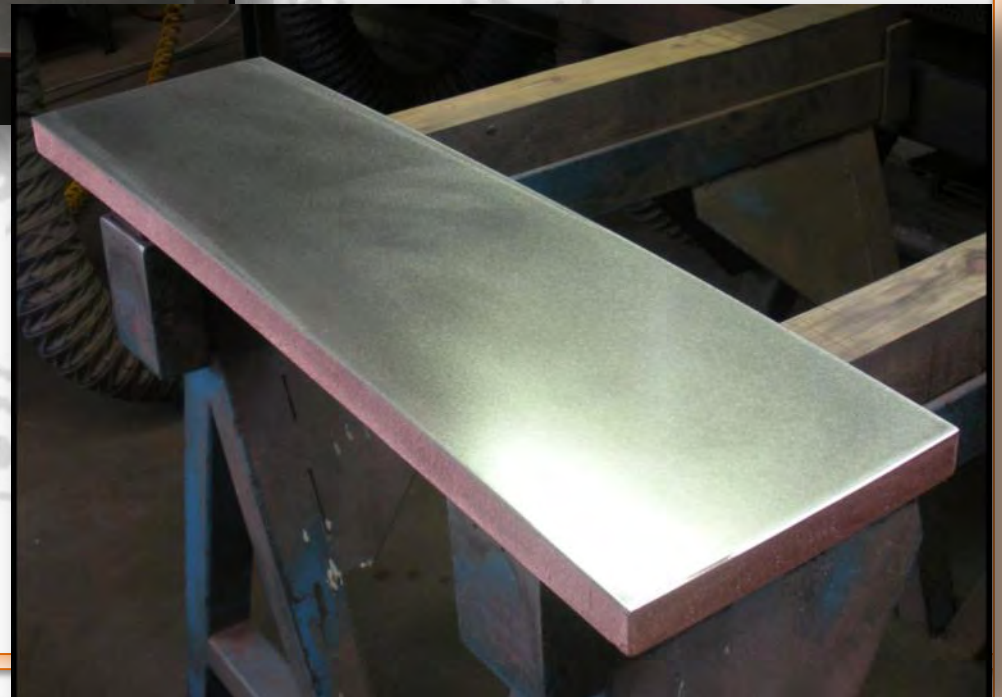
**Pilot plant (1500lt)**

- ➡ **Progettazione dell'impianto: prove iniziali con sfere di vetro colorate e acqua per il corretto posizionamento dei venturi**
- ➡ **riempimento dell'impianto con il bagno galvanico e 20g/l di micro-particelle di SiC – agitazione per 48h prima della deposizione**

# SCALING UP – INDUSTRIALIZZAZIONE



➡ **Prodotto finale**



➡ La codeposizione di nano-particelle in una matrice metallica porta generalmente ad un affinamento della microstruttura e alla formazione di rivestimenti più compatti.

➡ I rivestimenti nano-compositi possono avere una maggiore resistenza ad usura e corrosione.

➡ Le proprietà dei nano-compositi dipendono dalla microstruttura che può essere modificata da:

- composizione del bagno galvanico
- tipo e dimensioni delle particelle
- distribuzione delle particelle
- corrente di deposizione
- agitazione
- uso di tensioattivi
- uso di ultrasuoni

- ➡ **Ogni sistema composto risponde a specifiche esigenze tecnologiche che richiedono specifici parametri di processo per ottimizzare le prestazioni. Ogni sistema esige perciò uno studio particolare.**
- ➡ **La conoscenza di parametri di processo e dei loro aspetti più critici è indispensabile per ottenere con minime modifiche un scaling-up e un'industrializzazione ottimali senza intervenire massivamente sugli impianti esistenti.**



# **Rivestimenti galvanici innovativi per applicazioni anti - usura**

**Dr. M. Lekka**

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