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Microstructural and hardness studies of ZrO_2 reinforced Ni-P nanocomposite coatings for anti-erosion and anti-wear applications

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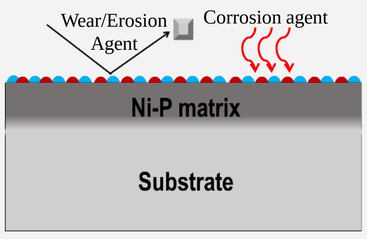
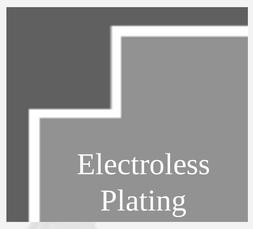
Introduction

Electroless Ni-P coatings are widely employed at industrial scale to protect engineering components from environmental attack and surface degradation thanks to their excellent properties of wear and corrosion resistance, hardness and solderability. Incorporation of ZrO_2 nanoparticles can modify hardness and tribological properties, enhancing performances in terms of reliability and durability of components.



- ✓ High P (HP, 10-13 wt%): amorphous → High Corrosion resistance.
- ✓ Medium P (MP, 6-9 wt%): nanocrystalline → Anti erosion/wear properties.
- ✓ Nano-reinforcement → improves hardness without altering microstructure.



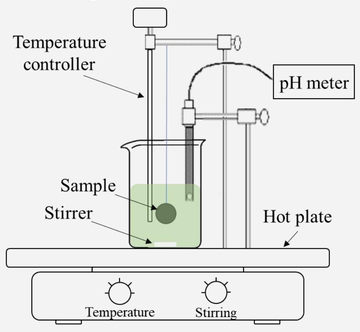
Chemical process, no need of external current:
- ✓ Uniform coating;
- ✓ Non-line-of-sight;
- ✓ *Easy* incorporation of second phase particles.

Effectiveness of nanoparticle reinforcement depends on:
- Quantity of embedded particles
- Dispersion (size of agglomerates) — ⚠ *Difficult to quantify*

Aims:
- ➢ Provide an objective method to quantitatively assess co-deposition features (incorporation and agglomeration) in MP and HP nanocomposites through original image processing and analysis procedure;
- ➢ Relate nanocomposite characteristics to microhardness improvement.

Materials and Methods

Coating Preparation

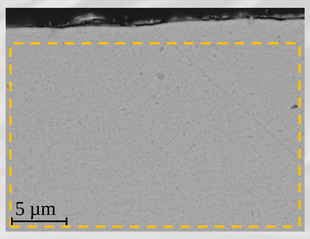


Samples prepared from original lead-free and surfactant-free solution

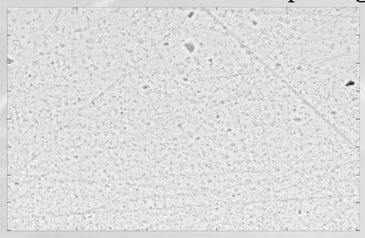
	n-ZrO_2 concentration [g/l]			
	/	4.5	9	13.5
~6 wt% P	MP	MPZ-1	MPZ-2	MPZ-3
~11 wt% P	HP	HPZ-1	HPZ-2	HPZ-2

Image Processing and Analysis

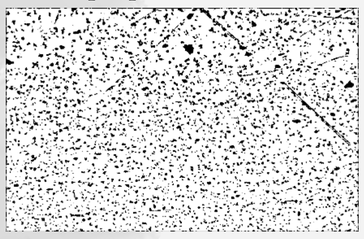
1) ROI selection from original SEM micrograph



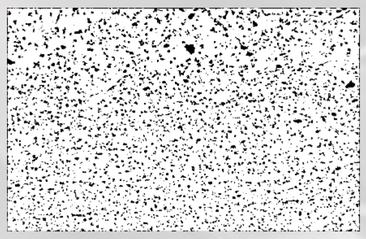
2) Application of a 3x3 Gaussian filter and sharpening



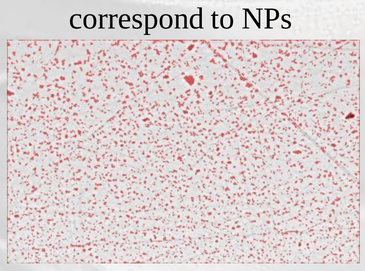
3) Binarizing according to a proper threshold



4) Filter on aspect ratio to remove scratches



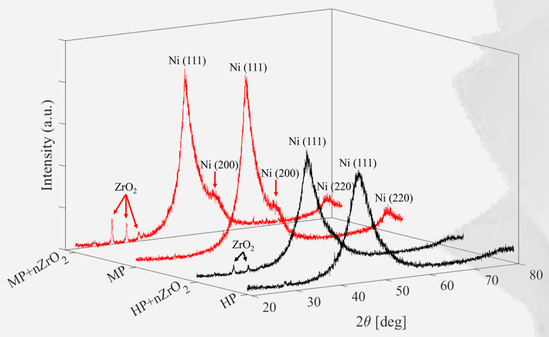
5) Routine output: red spots correspond to NPs



Calculated parameters:
- ➢ **A%:** Area fraction of nanoparticles embedded in the coating;
- ➢ **n_a**: Mean number of particles per agglomerate.

Results and Discussion

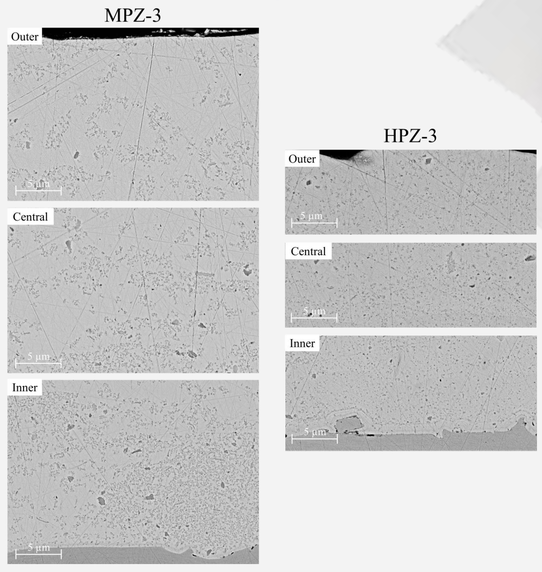
Phase composition

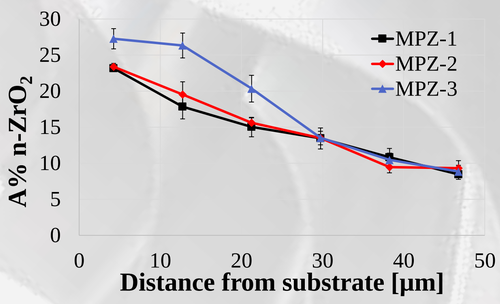


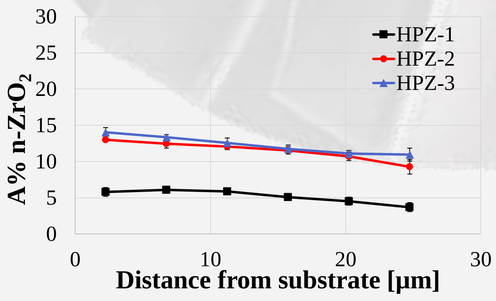
Phosphorus gathers at Ni grain boundaries, limiting grain growth.

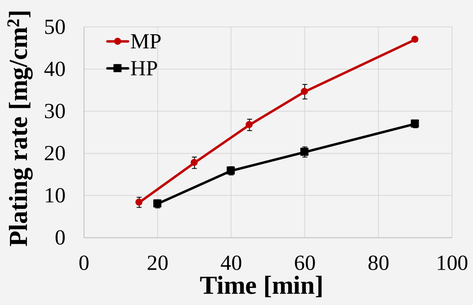
	Grain Size	Microstructure
HP	< 2 nm	Amorphous
HP+nZrO_2	< 2 nm	Amorphous
MP	2.6 nm	Nanocrystalline
MP+nZrO_2	2.9 nm	Nanocrystalline

Cross Section analysis



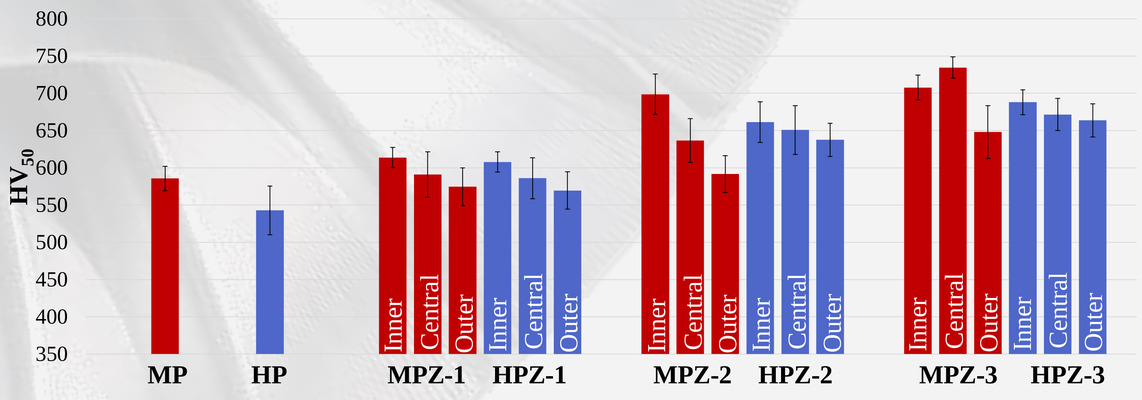


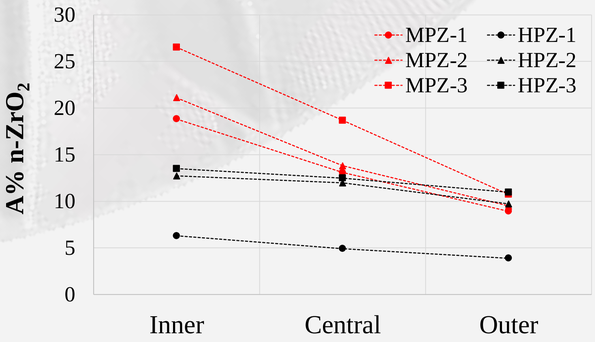


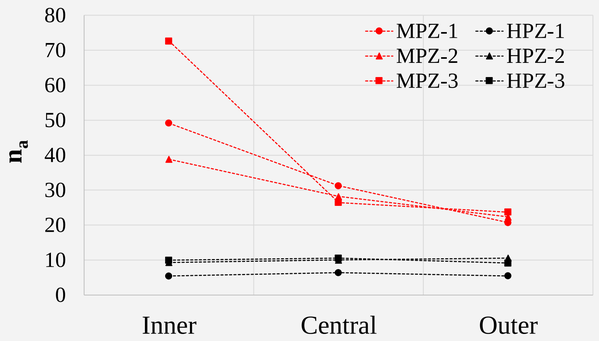


- Faster MP deposition → higher enveloping capability, but incorporation of agglomerated;
- Slower HP deposition → capability of entrapping small clusters only, with lower %A but better dispersion.

Microhardness Studies



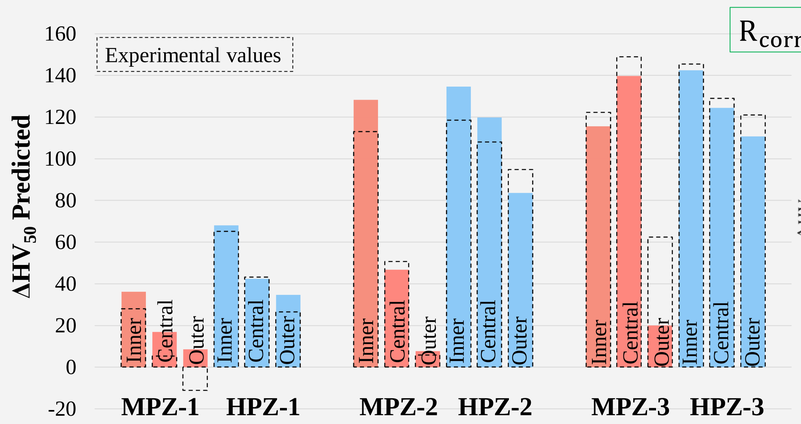


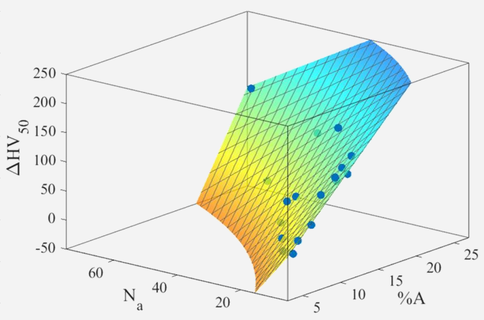


Dispersion hardening effectiveness strongly depends two quantities: (*i*) the volume fraction of nanoparticles embedded in the coating (measured by A%), as it affect the work-hardening behavior of the material, and (*ii*) agglomeration of the reinforcing phase (estimated by n_a), since it is associated to a higher formation of micro voids that ultimately result in poor mechanical behavior.

$$\Delta HV_{50} = f(A\%, n_a) \Rightarrow \Delta HV_{50} = 23.1 + 12.9\,A\% - 7.1\,n_a + 0.61\,A\%\,n_a$$

$R_{corr} = 0.96$





Conclusions

- Particle distribution in MP and HP nanocomposites presented significant differences that could be attributed to the difference in plating rate;
- A mathematical bi-linear relationship demonstrated that the reinforcing capability is first driven by A%, with an important contribution by n_a on its effectiveness;
- HP co-deposition: efficient strengthening, with homogeneous improvement up to 145 HV_{50};
- MP hardening: limited by the excess of agglomeration.