

Tribochemical study of $\text{Ni}_{62}\text{Nb}_{33}\text{Zr}_5$ metallic glass depending on the Cr content of steel counterparts

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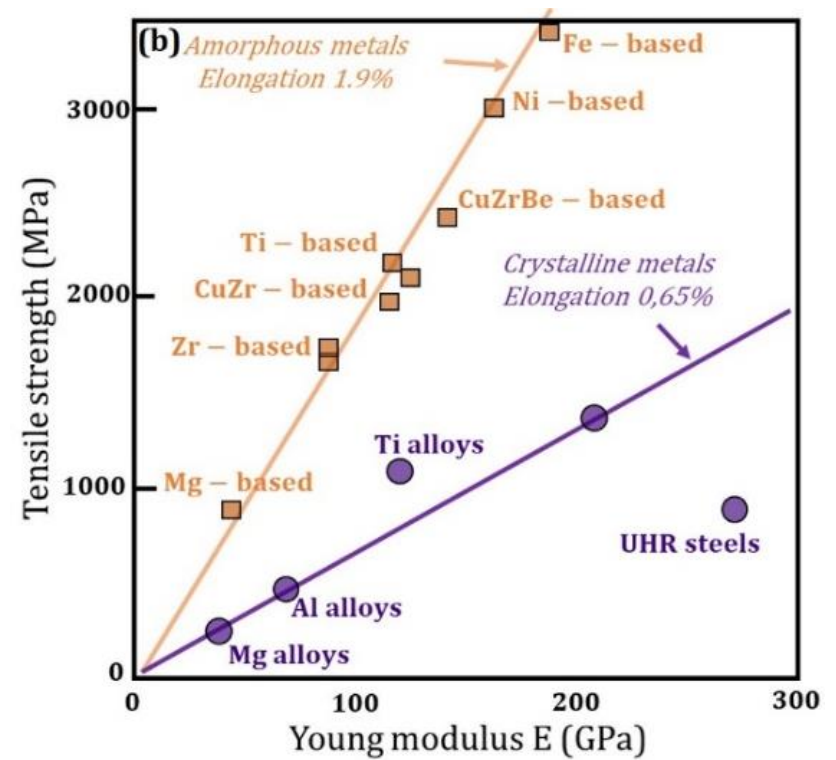
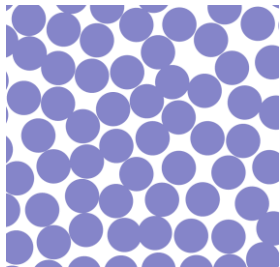
CONTEXT



Amorphous Metallic Alloy → *Bulk Metallic Glass*

Direct solidification
well-defined pure metals
mixture
through extremely fast cooling

amorphous



CONTEXT



Amorphous Metallic Alloy → *Bulk Metallic Glass*

- Erratic tribological behaviours ...

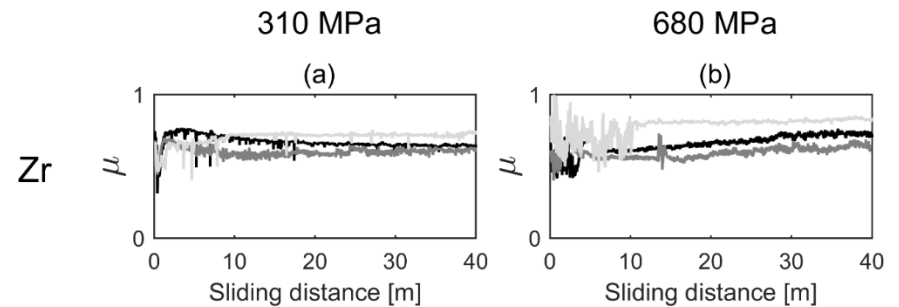
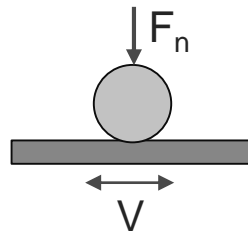
Usually relatively high friction (0.3 to 0.7)

*High and low wear independently of the friction coefficient and hardness ...
even for a single composition*

Particular crack propagation impeding and accentuating wear

... Really ? ... No ! As long as contact conditions are well controlled

Pure sliding, 100Cr6 steel ball against BMG Plate



Cornuault et al, 2019, Trib. Int.

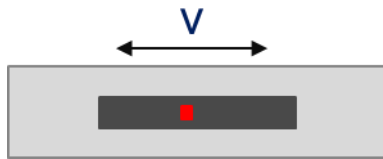
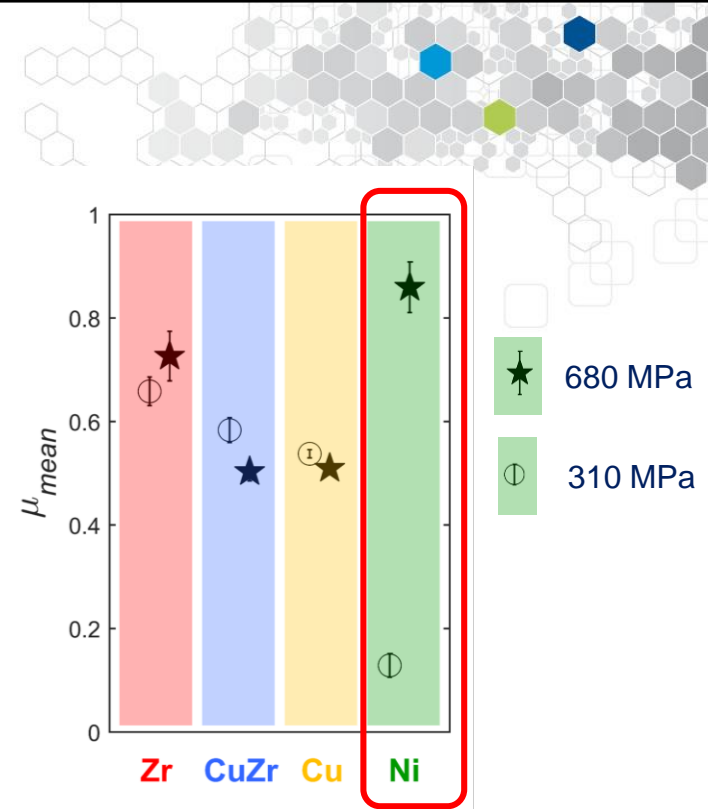
Zr52.5Ti5Cu17.9Ni14.6Al10

CONTEXT – Our previous study

$Zr_{52.5}Ti_5Cu_{17.9}Ni_{14.6}Al_{10}$ – *mechanically driven wear*

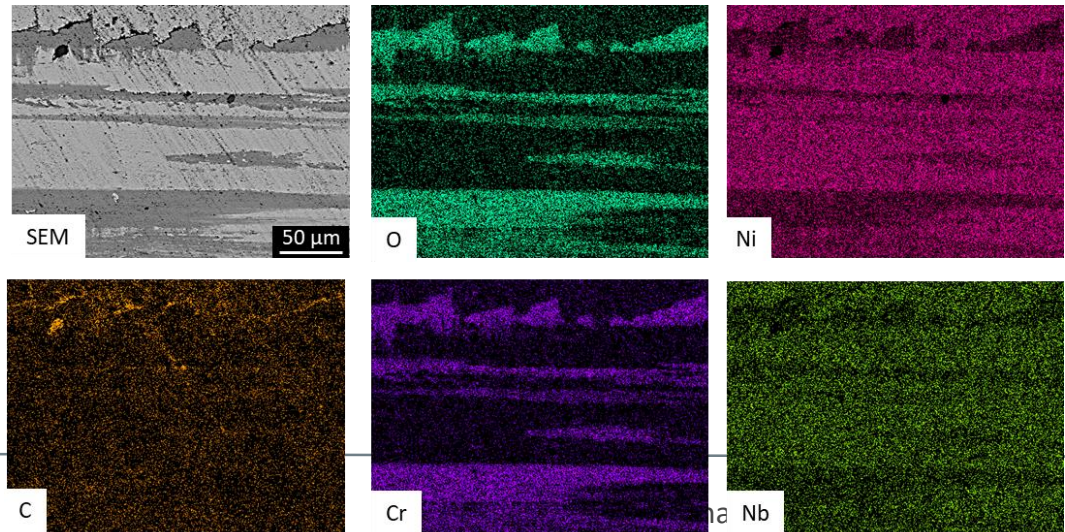
$Cu_{60}Zr_{33}Ti_7$ & $Cu_{47}Zr_{46}Al_7$ – *mechanically and/or chemically driven μ and wear (C, Zr migration, change in accommodation)*

$Ni_{62}Nb_{33}Zr_5$ – *mainly chemically driven μ and wear (Cr migration, C detected, Nb migration like Zr)*

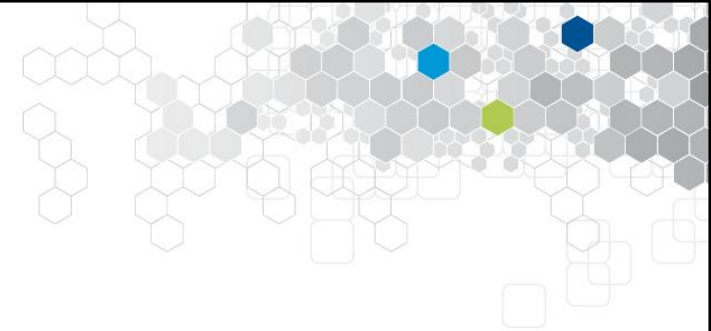


At high loads lots of Cr in the friction track

The steel slider had 1.5% Cr...



OBJECTIVES



Study the effect of Cr content in the steel slider on the tribological behaviours of the $Ni_{62}Nb_{33}Zr_5$ BMG in pure sliding conditions

Why? to further explore the possibility to control friction of the BMG by finely tuning the composition of the counterparts



3 Steel compositions (Ball)

Steel	Fe	C	Cr	Mo	Mn	Si	Ni	Cu
X105CrMo17	Balance	0.95-1.20	16.00-18.00	0.75 max	1.00 max	1.00 max	-	-
100Cr6	Balance	0.95-1.05	1.40-1.65	-	0.25-0.45	0.15-0.35	0.30 max	0.20 max
C90	Balance	0.9	-	0.6	1	0.6	-	-

1 Amorphous Alloys (Plate)

Sample denomination	Composition [at%]	Young's modulus [GPa]	Yield strength [MPa]	Hardness [HV]
Ni	Ni ₆₂ Nb ₃₃ Zr ₅	135	2750	798

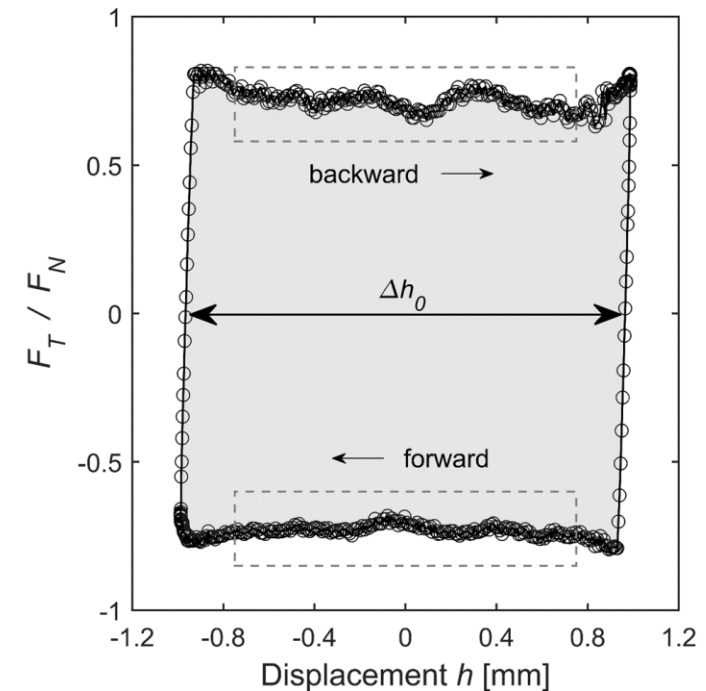
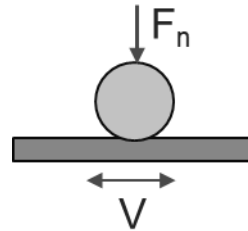
Mechanical properties

Steel	E (GPa)	Y (MPa)	H (HV)
X105CrMo17	210	~1850	750
100Cr6	210	~1700	800
C90	210	~	800

METHODS

Reciprocating linear ball-on-plate friction tests

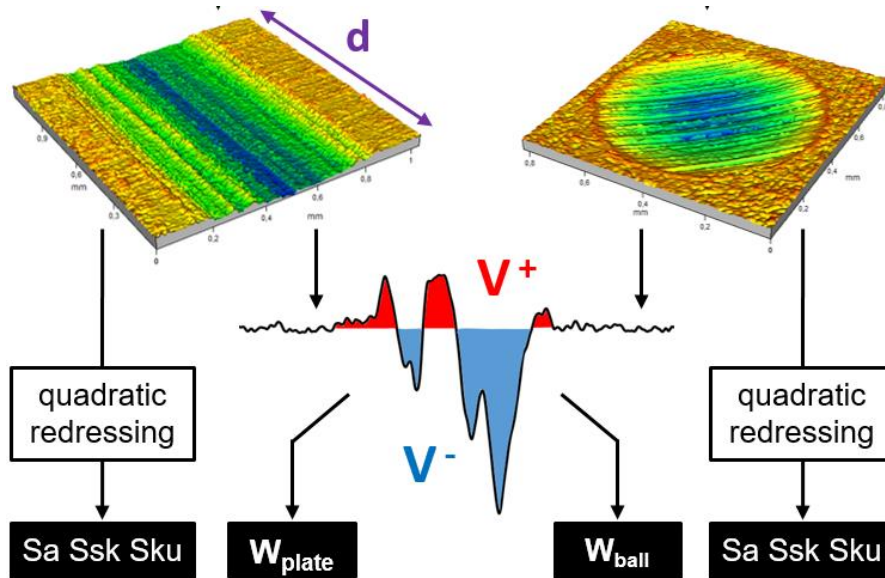
- **Plate:** $\text{Ni}_{62}\text{Nb}_{33}\text{Zr}_5$
- **Ball:** 3 Steels - \varnothing 6 mm
- Contact pressure **P = 680 MPa**
- Displacement stroke **$\Delta h = \pm 1$ mm**
- Motion frequency **f = 1 Hz**
- Sliding speed **V = 4 mm/s**
- Sliding distance **Sd = 40 m** (10,000 cycles)
- Friction coefficient calculated as :



$$\mu = \frac{1}{2 \Delta h_0} \int \left| \frac{F_T}{F_N} \right| dh$$

METHODS

« Wear » and roughness analysis using variable focus microscope



$$W_{plate} = \frac{V_p^- - V_p^+}{2 d N_{cycles}}$$

$$W_{ball} = \frac{V_b^- - V_b^+}{4 N_{cycles}}$$

$$W_{tot} = W_{plate} + W_{ball}$$

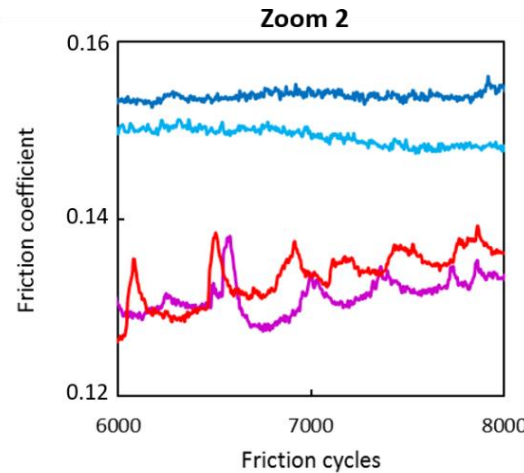
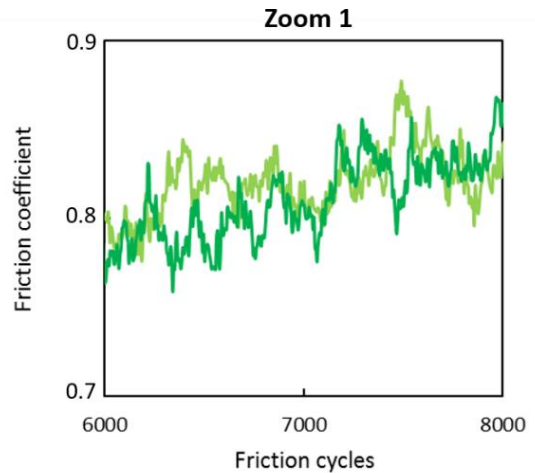
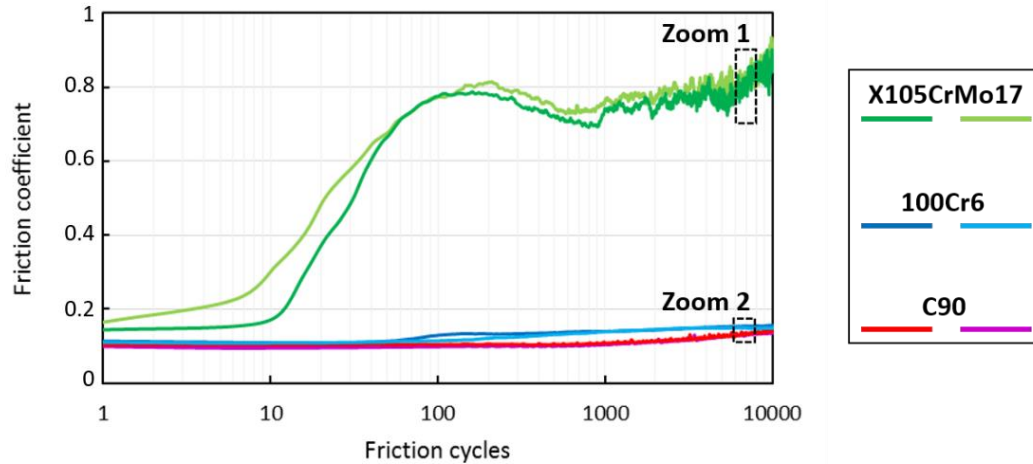
Morphologies and compositions of the tracks analyzed with

SEM/EDX, Raman spectroscopy, XPS, and NanoSIMS



Results

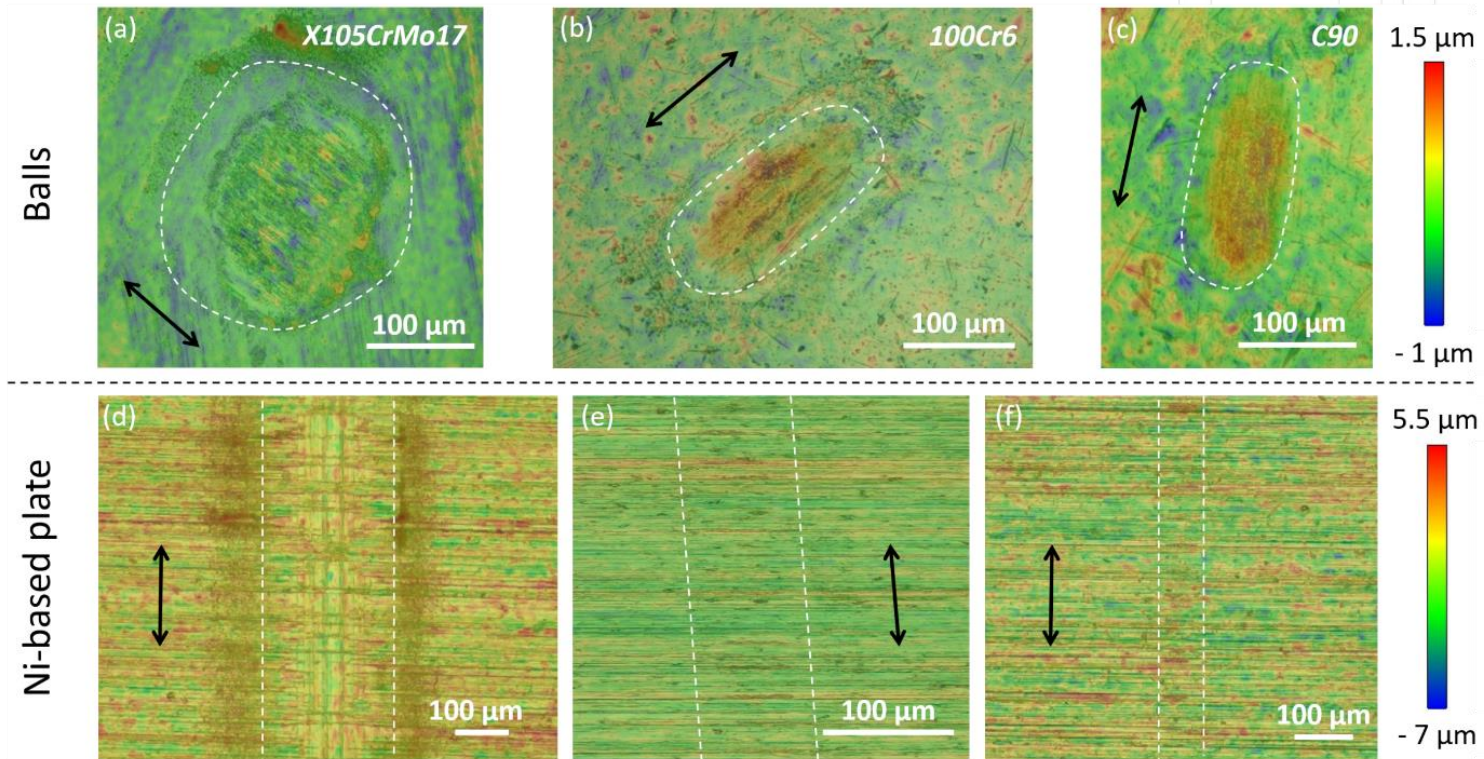
RESULTS – Friction coefficient



Increased Friction in line with increased Cr content ?

=> Confirmation of the effect of Cr content on Ni based BMG tribological behaviour ?

RESULTS – Wear

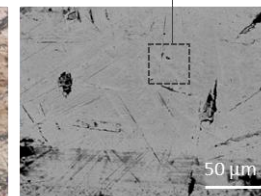
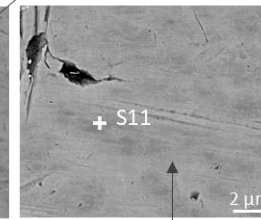
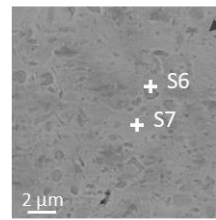
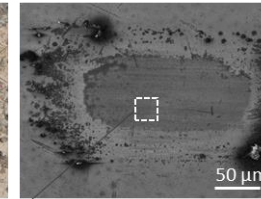
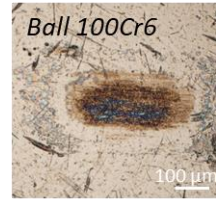
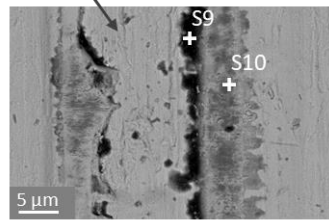
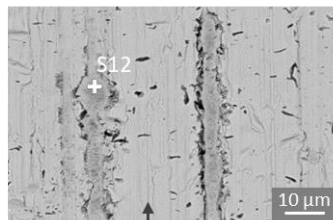
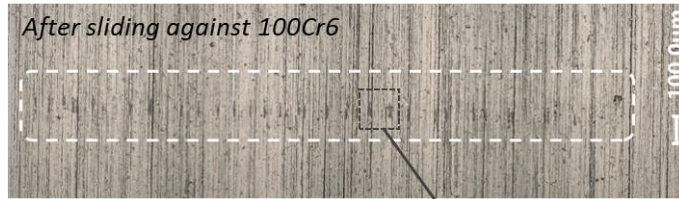
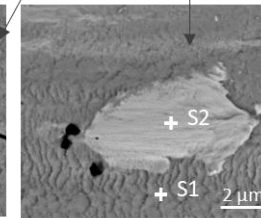
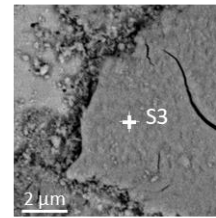
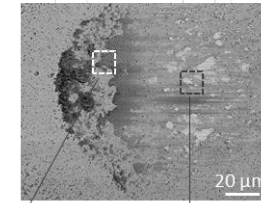
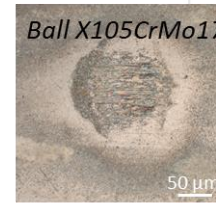
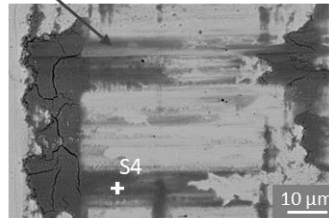
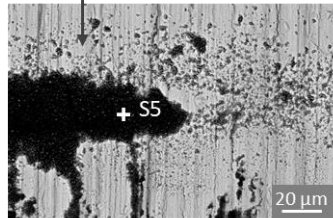
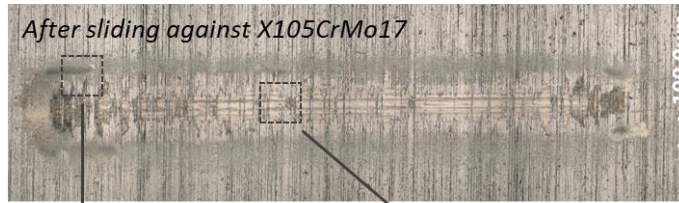


Extremely low wear, impossible to evaluate wear volumes

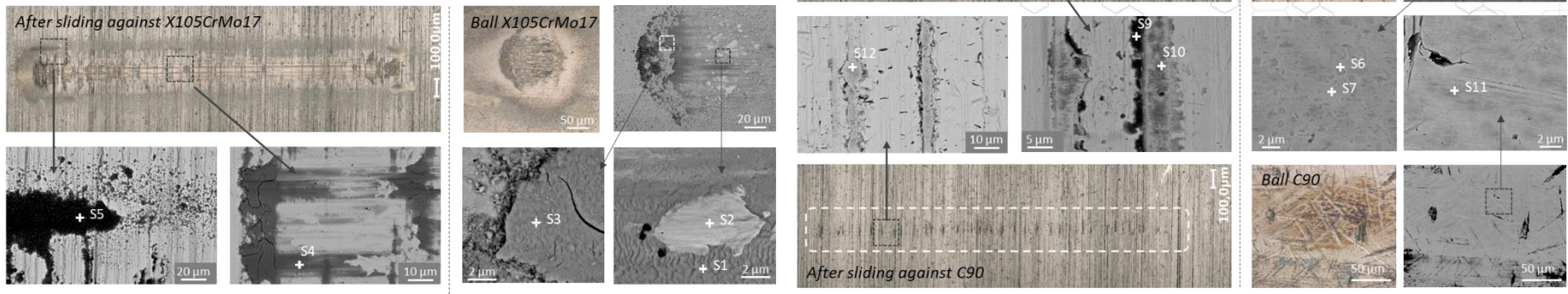
Even for test with X105CrMo17

=> But visible patches of material inside tracks (all) and on the edges (X105CrMo17)

RESULTS – SEM



RESULTS – SEM + EDS



Counterpart	Sample	Spectrum	Elemental composition (atomic %)						
			Ni	Nb	Zr	Fe	Cr	O	C
X105CrMo17	Ball	S1	16.9	5.7	1.0	15.1	3.4	48.0	10.0
		S2	69.4	1.5	0	6.5	1.4	6.8	14.5
		S3	13.0	12.6	2.1	3.0	0.7	63.0	6.7
	Plate	S4	18.2	12.6	2.2	4.8	1.0	54.4	6.9
		S5	12.2	17.7	3.1	4.3	1.1	51.6	10.0
100Cr6	Ball	S6	4.4	0.8	0.1	62.0	4.5	8.0	19.8
		S7	3.3	0.7	0.1	76.8	0.8	5.12	12.3
		S8	0.3	0	0	56.6	0.7	0.9	41.0
	Plate	S9	6.1	3.7	0.1	2.3	0.1	16.4	70.5
		S10	11.4	11.0	2.0	11.5	0.5	58.2	4.3
C90	Ball	S11	6.6	1.3	0.2	63.8	0.2	16.3	11.0
	Plate	S12	24.3	20.9	3.7	3.6	0	39.1	8.4

Ratio of at% significantly changed

Ni transfers a lot on X105CrMo17

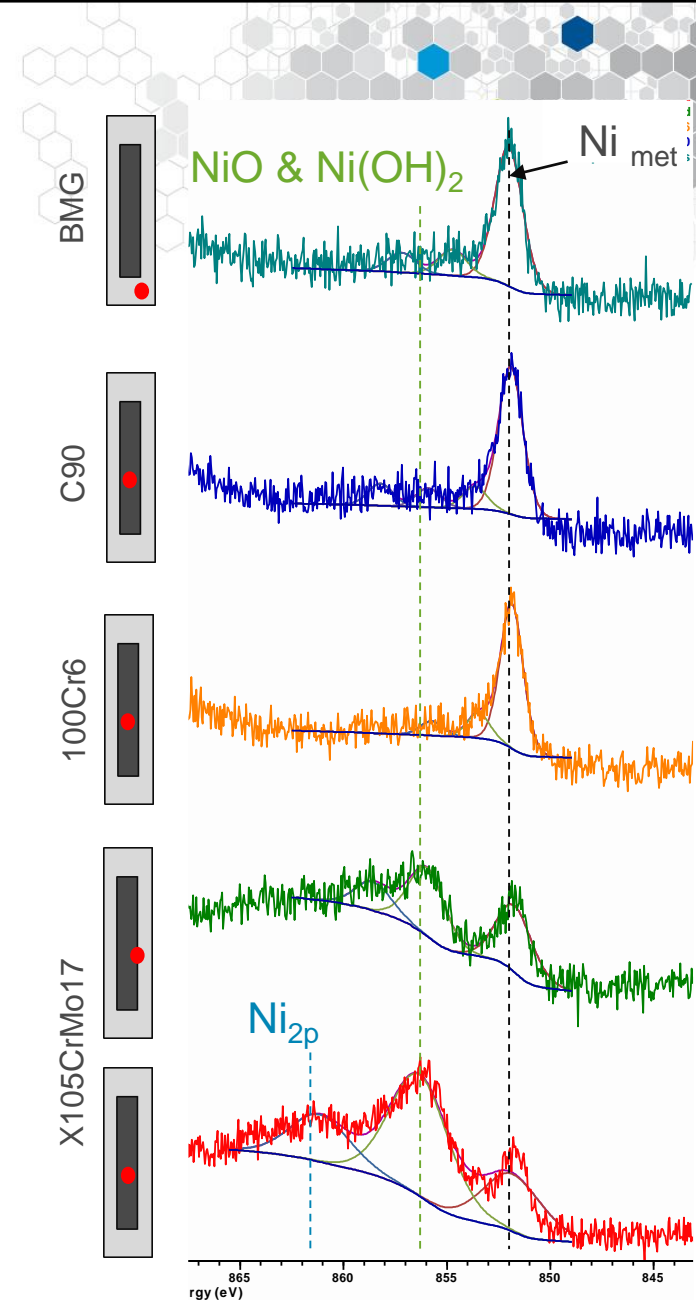
O highly detected

Cr detected ?

RESULTS – XPS

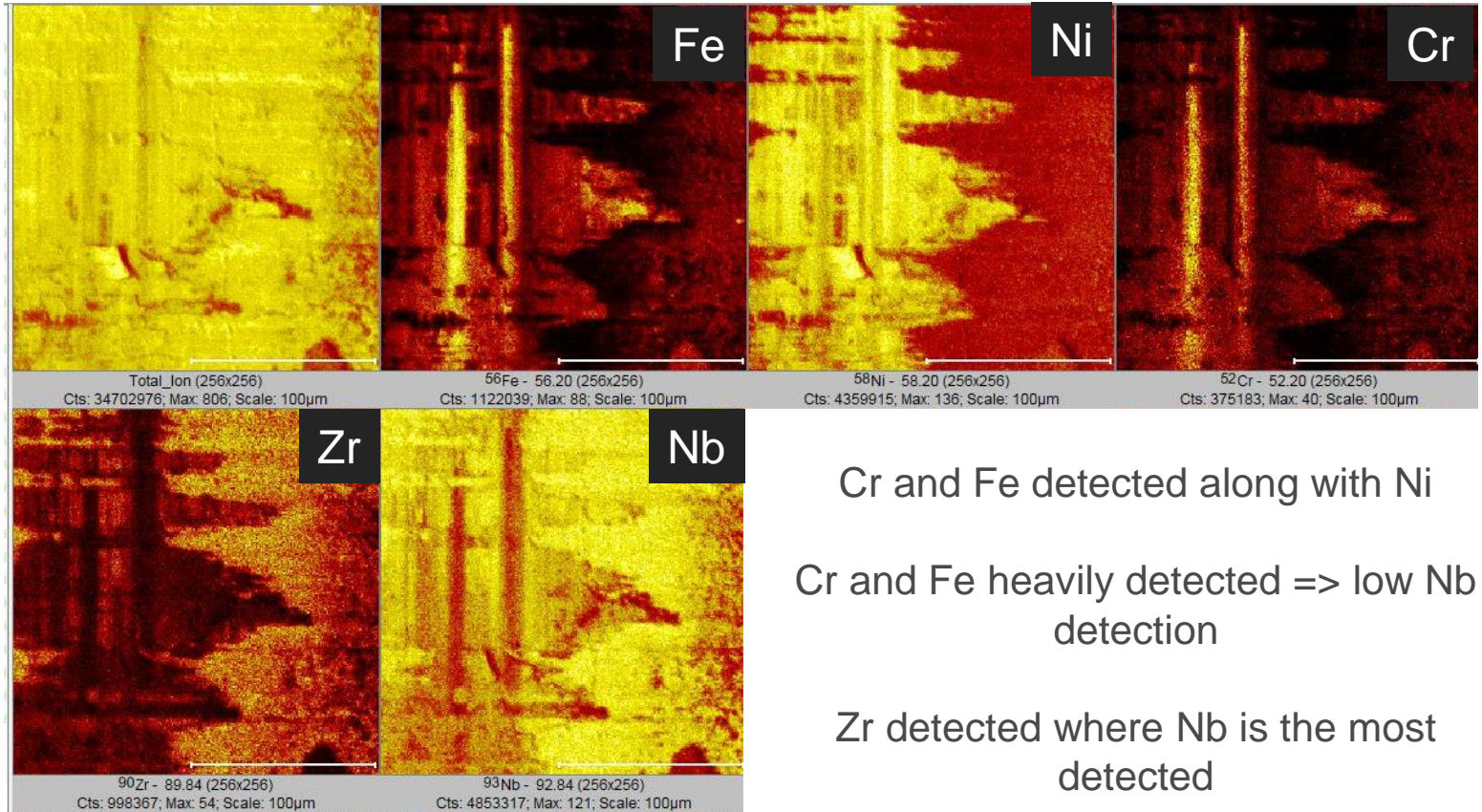
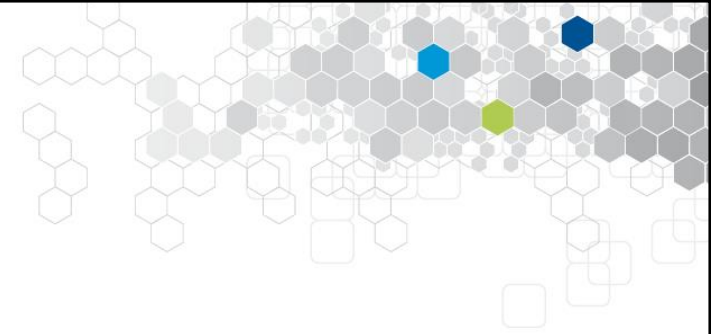
Top Surface analysis (5 nm in depth), averaging over $\varnothing 200\mu\text{m}$ spot

- ⇒ X105CrMo17 :
 - ⇒ oxide et hydroxyde of Ni more detected than Ni metal inside the track and on the edge of it
- ⇒ C90 et 100Cr6 :
 - ⇒ Ni met >> oxide and hydroxyde Ni
 - ⇒ Detection similar to the outside
- ⇒ O and C heavily detected => contaminations + oxides ?
- ⇒ Cr not detected => hidden by C contaminations ?
 - ⇒ *Agree with EDS except Cr was slightly detected*
- ⇒ Native oxide of BMG : Nb_2O_5 & ZrO_2 => OK
- ⇒ Nb_2O_5 and ZrO_2 detected inside friction tracks as well
 - ⇒ *Large spot size and very low wear*



RESULTS – NanoSIMS

Analysis over 2 to 5 nm in depth, \varnothing few μm



Cr and Fe detected along with Ni

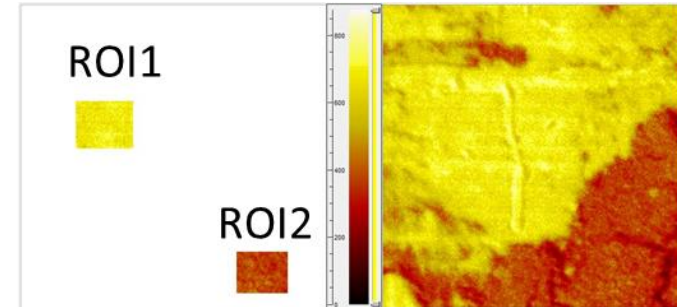
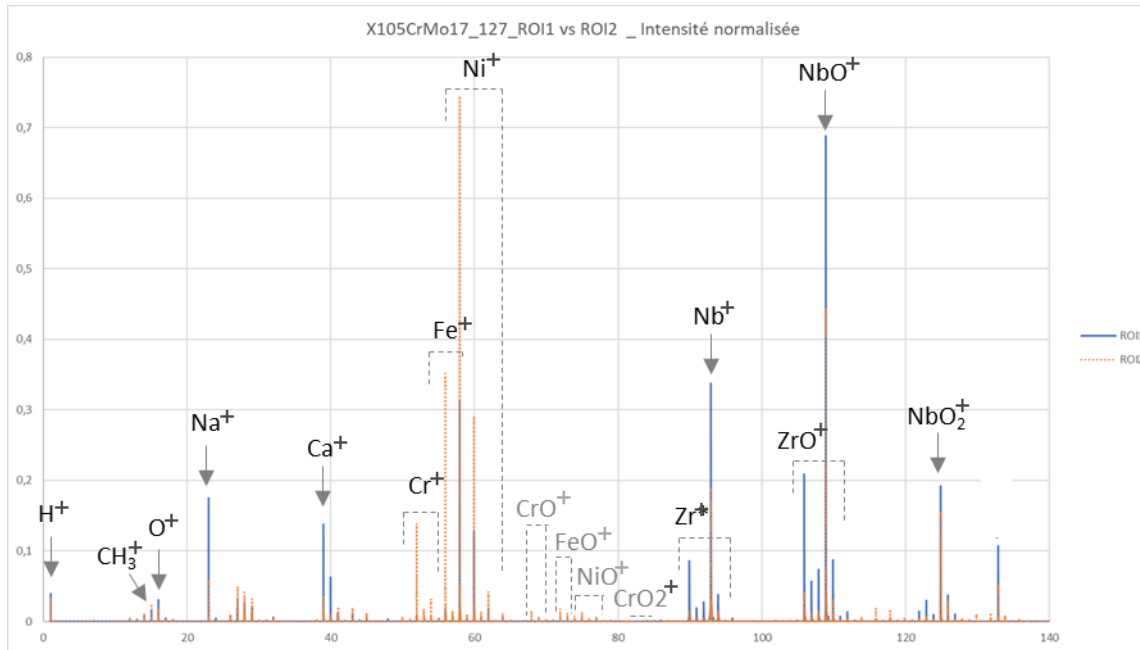
Cr and Fe heavily detected => low Nb detection

Zr detected where Nb is the most detected

RESULTS – NanoSIMS

Definition of region of interest and in depth analysis of spectra

In both positive and negative analysis modes to get access to all fragments



ROI 1 : almost pristine BMG

ROI 2 : patch of worn/transferred material

- ⇒ Clear evidence of reverse detection of Ni vs ZrO_2 and Nb_2O_5 between pristine and transferred material
- ⇒ Ni detected along with Fe and Cr.
- ⇒ + Detection of hydrocarbon contaminant.

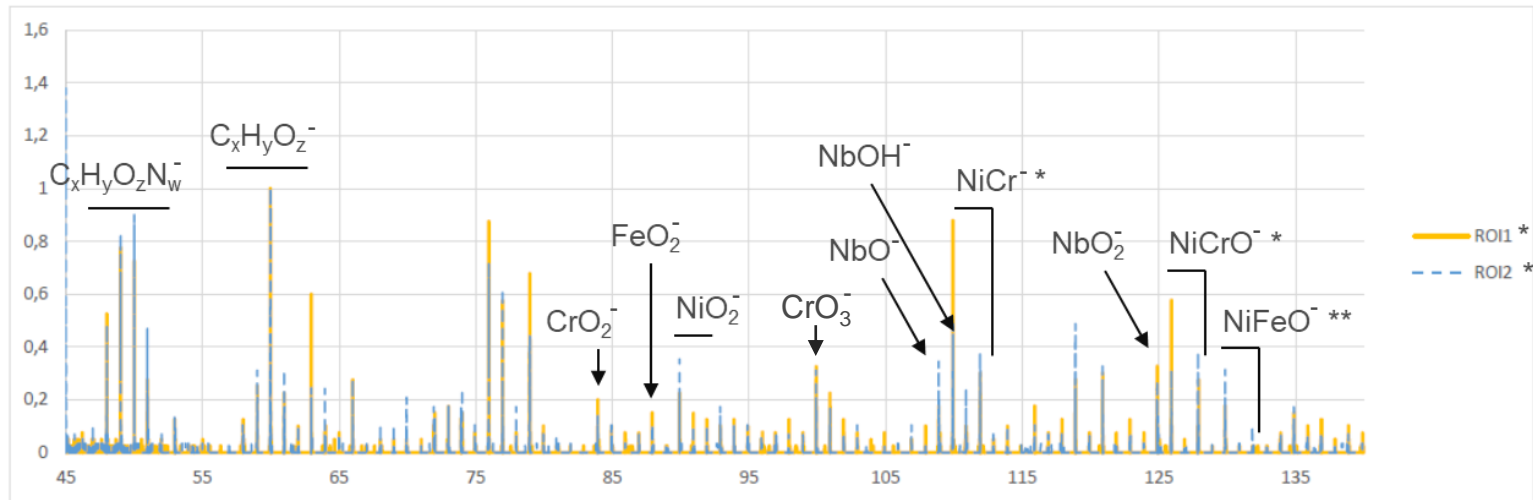
Agree well with EDS and XPS

RESULTS – NanoSIMS

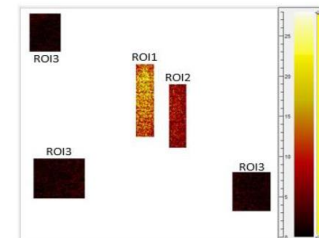
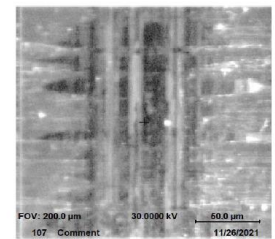


⇒ X105CrMo17

- ⇒ Clear evidence of reverse detection of Ni vs ZrO_2 and Nb_2O_5 between pristine and transferred material
- ⇒ Ni detected along with Fe and Cr. *Agree well with EDS and XPS*
- ⇒ + Detection of hydrocarbones contaminant.
- ⇒ Detection of NiO, NiCrO, and NiFeO compounds, some Cr oxide.



X105CrMo17 ROI1 vs ROI2 & ROI3 _ Pos



⇒ C90 and 100Cr6

- ⇒ No reverse detection: differences inside/outside tracks on Fe and Fe oxide
- ⇒ Nb_2O_5 is mostly detected in C90 friction tracks, followed by 100Cr6, then X105CrMo17
- ⇒ 100Cr6: very low detection of Cr oxide and NiCrO compound

RESULTS – Raman (532nm , power < 1 mW)

⇒ No peaks for C90 and 100Cr6 tests

⇒ X105CrMo17

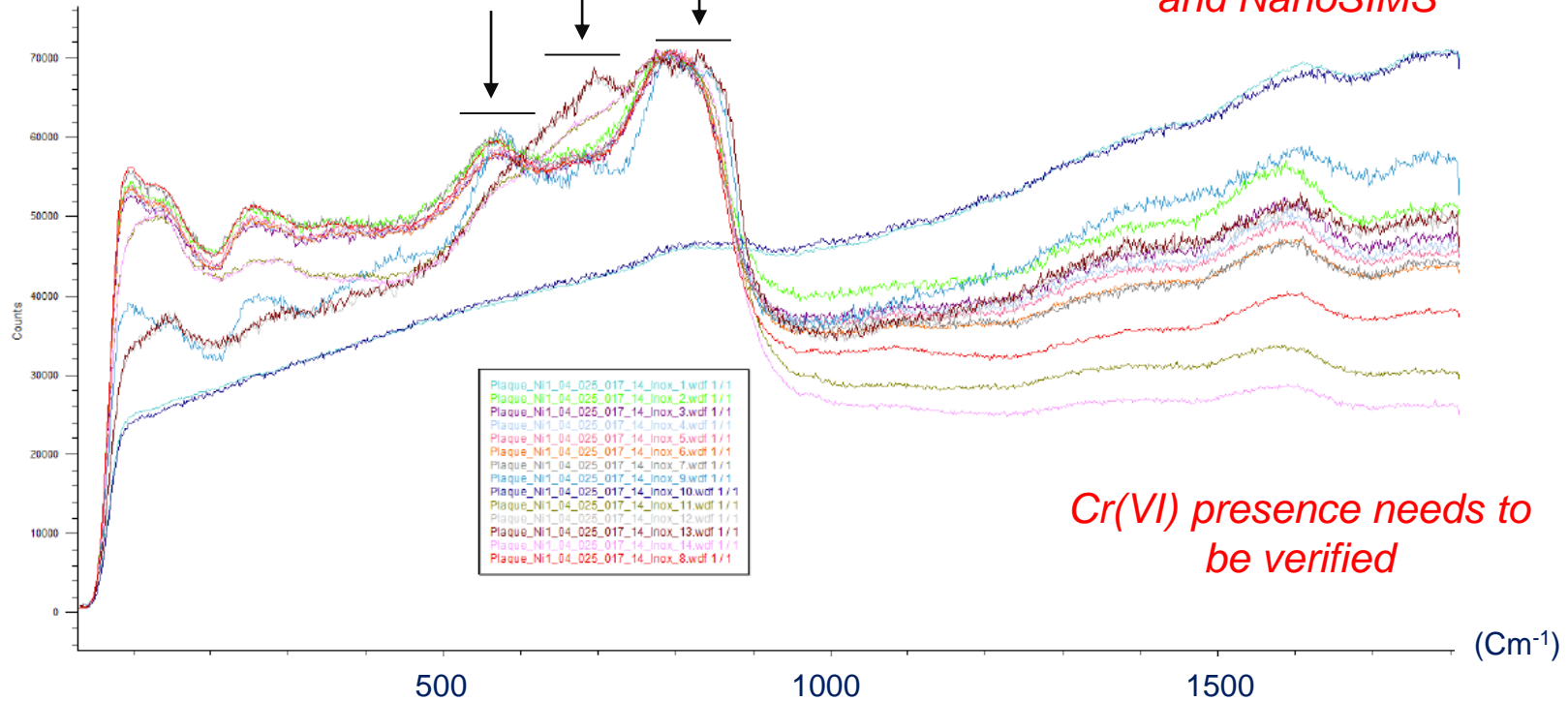
NiFeCrO with residual stress ?

NiCrO

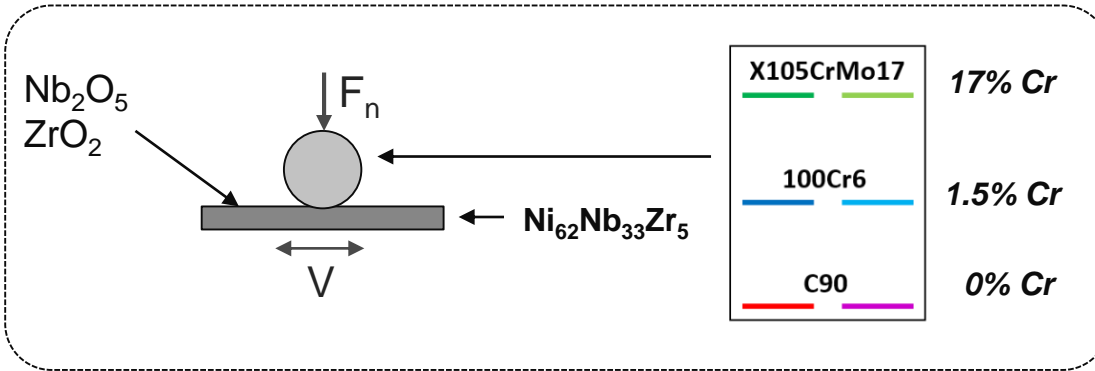
Cr(VI) oxide ?

NiO, CrOOH

*Agree well with EDS, XPS,
and NanoSIMS*

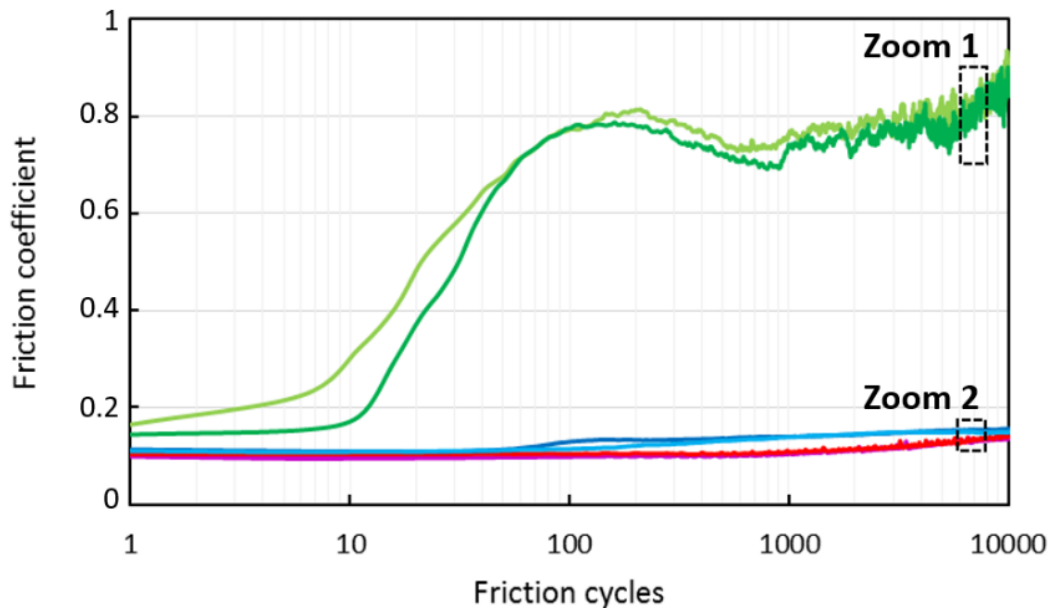


CONCLUSION



Optical profilometry = no wear

SEM/EDS
 XPS
 Raman
 NanoSIMS



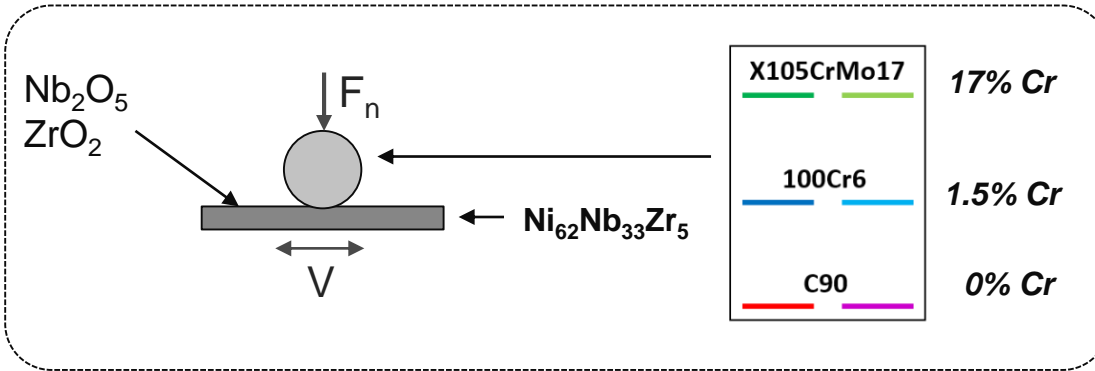
CoF

- Ni ↑ ↑ ↑, $Nb_2O_5 + ZrO_2$ ↓ ↓ ↓,
- Fe, Cr, NiO(H), NiCrO, NiFeO
- traces of Fe oxide, and Cr oxide

- Ni ↑ and Fe, $Nb_2O_5 + ZrO_2$ ↓,
- traces of Cr, Fe oxide, Cr oxide, NiCrO

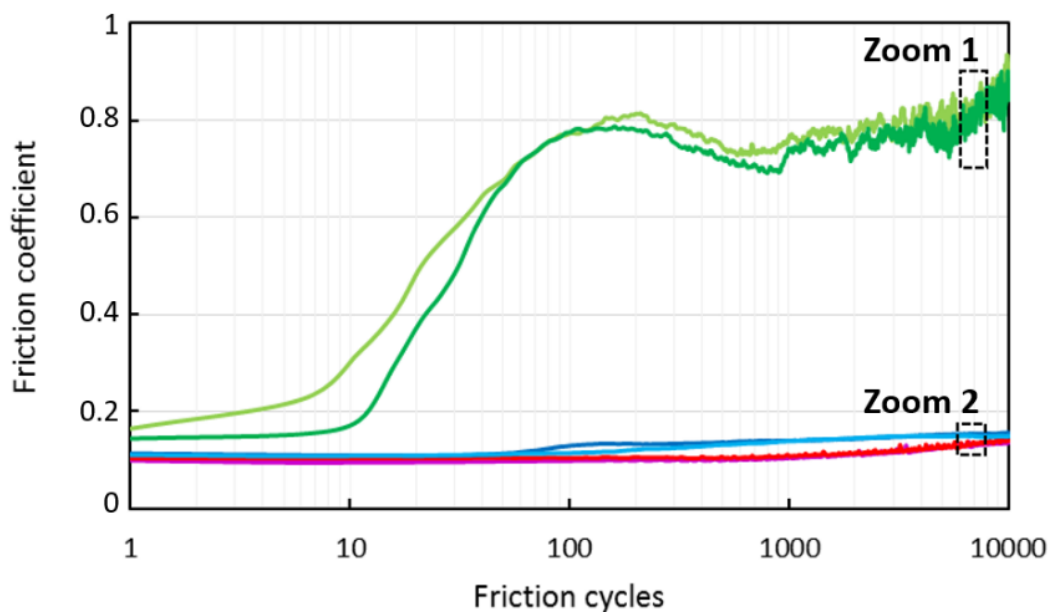
- Ni ↑ and Fe, $Nb_2O_5 + ZrO_2$ ↓,
- traces of Fe oxide

CONCLUSION



Optical profilometry = no wear

SEM/EDS
 XPS
 Raman
 NanoSIMS



CoF



Increased Cr content

Favors Ni selection inside the contact

Loss of Nb_2O_5 which is ductile (potentially good lubricant)

Creation of NiCrO, NiFeO, NiO(H), Cr oxide (obviously less lubricious)

Remains... why Cr(VI)?



Thanks for your attention