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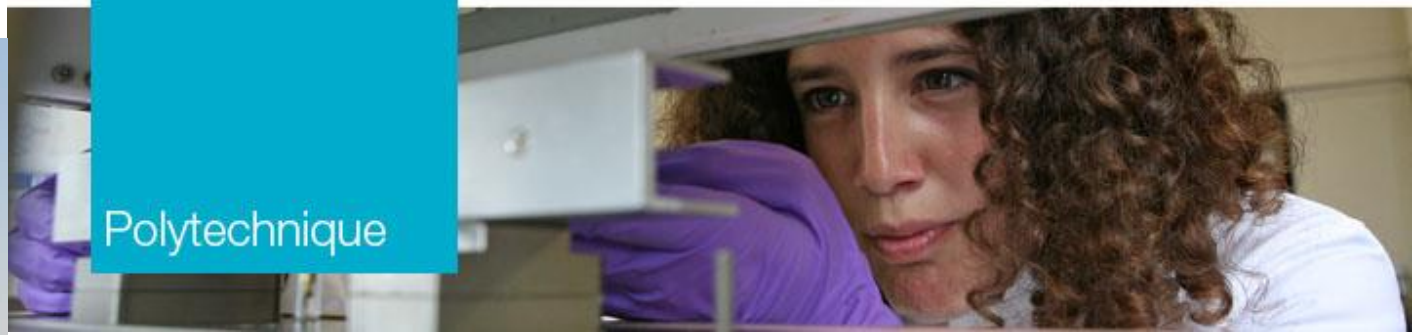

Impact of WC-Co powder preparation on the SPS sintering behavior

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- Context about « mechanical alloying »
- Powder preparation
- Analysis of sintered products

Conclusions and perspectives

Study motivation

Data from literature about WC-Co composite powder preparation:
Mixing parameters extremely variable

Mixing time

- Extremely variable: between 30 minutes and 48 hours

Milling installations

- Low-energy mixers :
  - Turbula
- High-energy mills
  - Different balls size
  - Balls made of different materials
  - From 150 to 700 rpm mixing speed

Milling environment

- Different environments:
  - Dry
  - Paraffin
  - Various alcohols
- Liquid milling medium in various proportions

Context of the study

Co
Produced in laboratory

Cr_3C_2
WC
WO_3
Purchased Inframat

Planetary ball milling

Doped binder preparation **1: Co + Cr_3C_2**

Préparation WC
2a: Mechanical milling
WC brut

2b: Mechanical alloying
$2WO_3 + 5C \rightarrow 2WC + 3CO_2$

Mixing 1+2=3

Sintering

Planetary ball mill
Pulverisette 7 Premium line

Purpose of work

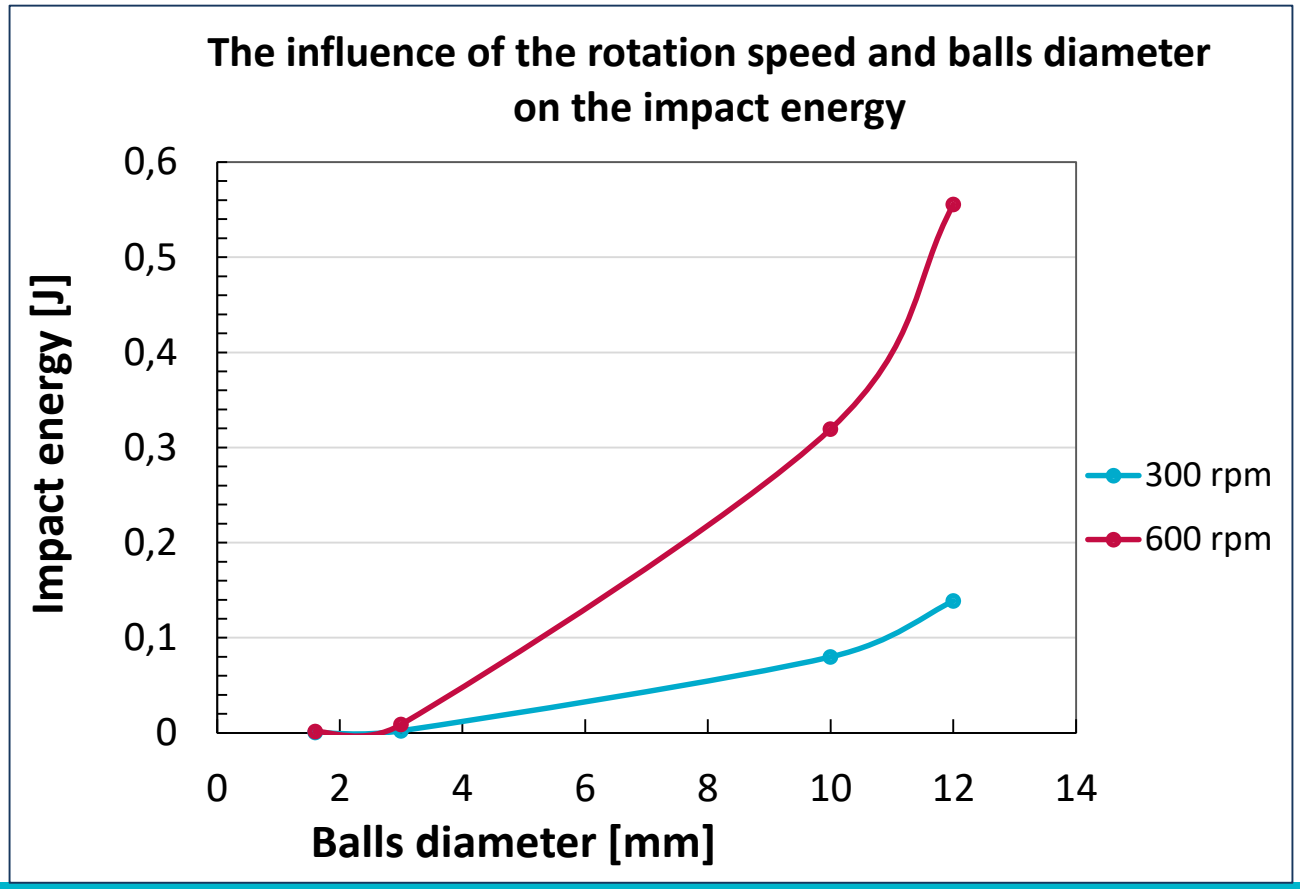
Use of the mechanical alloying method to obtain a nanostructured tungsten carbide - cobalt powder using a simple and easy to use technology at no prohibitive cost, directly by an end-user.

Application of modeling for Pulverisette 7 Premium Line planetary ball mill

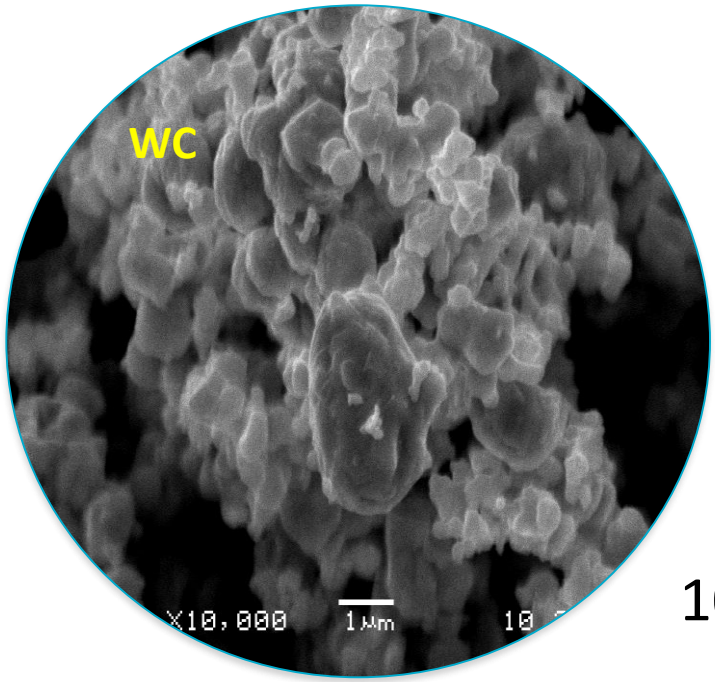
Bowl diameter	dm [mm]	46.25
Balls diameter	db [mm]	10 ; 12
Number of balls	nB [-]	15 ; 25
Weight of sample	W [g]	20
Speed of revolution	Nr [rpm]	300 ; 600
Balls density	ρ [g/cm^3]	14.89

The impact energy of a ball can be calculated with the formula :

$$E_i = \frac{1}{2} m v_r^2$$



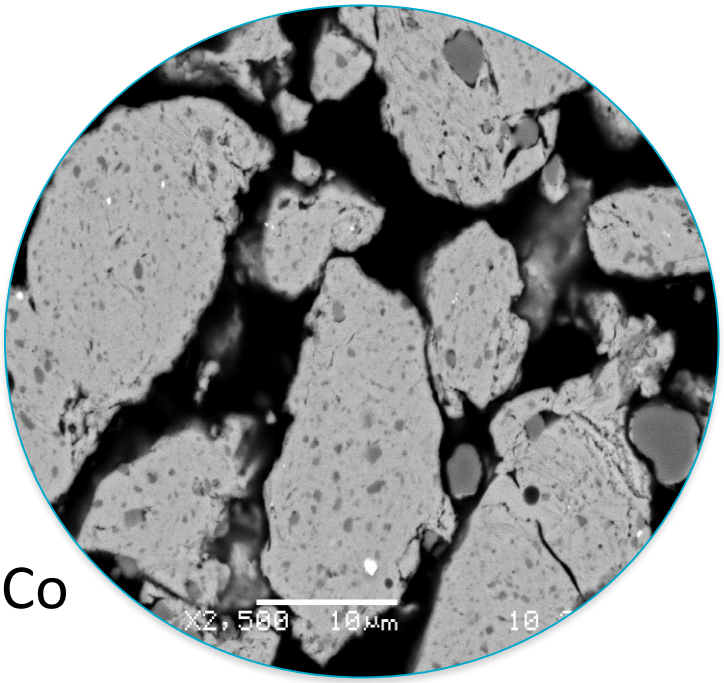
Powder preparation



90 wt.% WC

+

10 wt.% doped Co



Tungsten carbide powder with a particle size of about 1 µm (grain size : 378 nm).

Cobalt powder mixed with 10 wt.% chromium carbide (Cr_3C_2) and milled for 10 h.

Milling time: 10 hours

Balls /powder ratio: 4:1

Jar 1: 200 g of 10 mm balls

Jar 2: 200 g of 12 mm balls

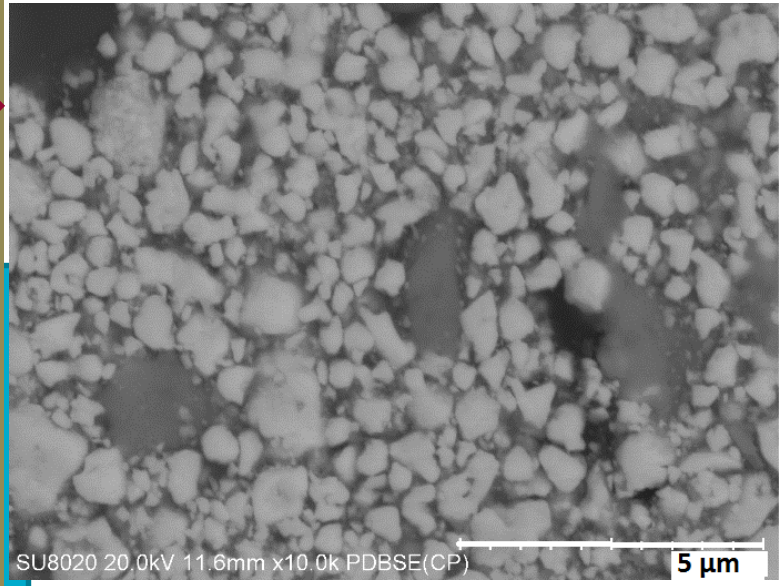
10 ml of ethanol added as anti-caking agent

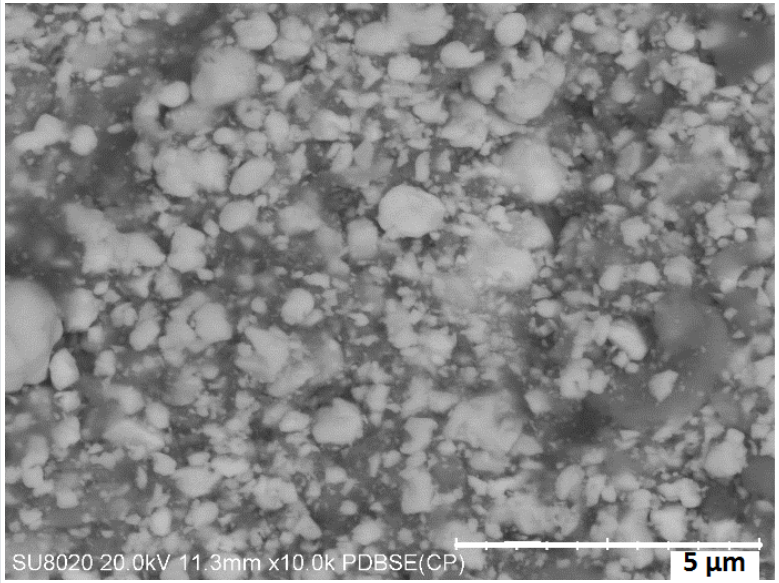
Analysis of powders

Φ 10 mm balls

Φ 12 mm balls

300 rpm

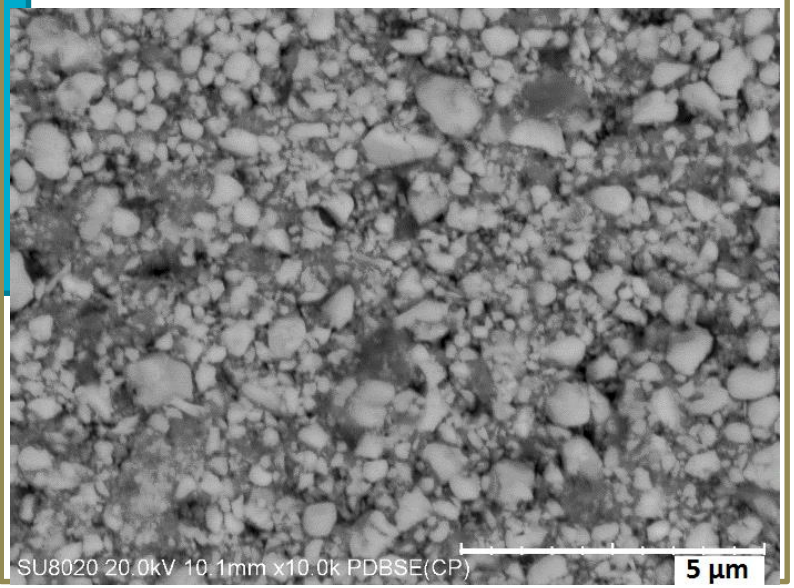


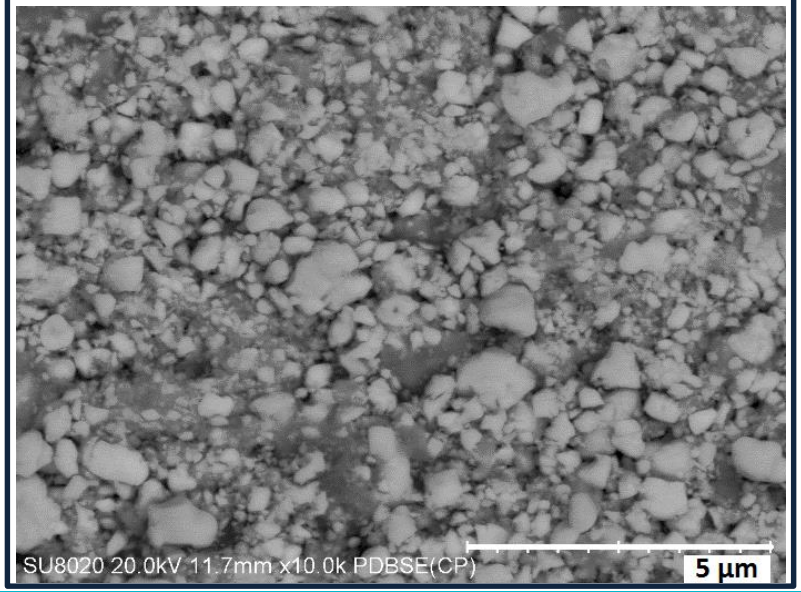


At 300 rpm, there is a size effect of the balls diameter: the larger balls provide better homogenization

The powders milled at 600 rpm are more homogeneous.

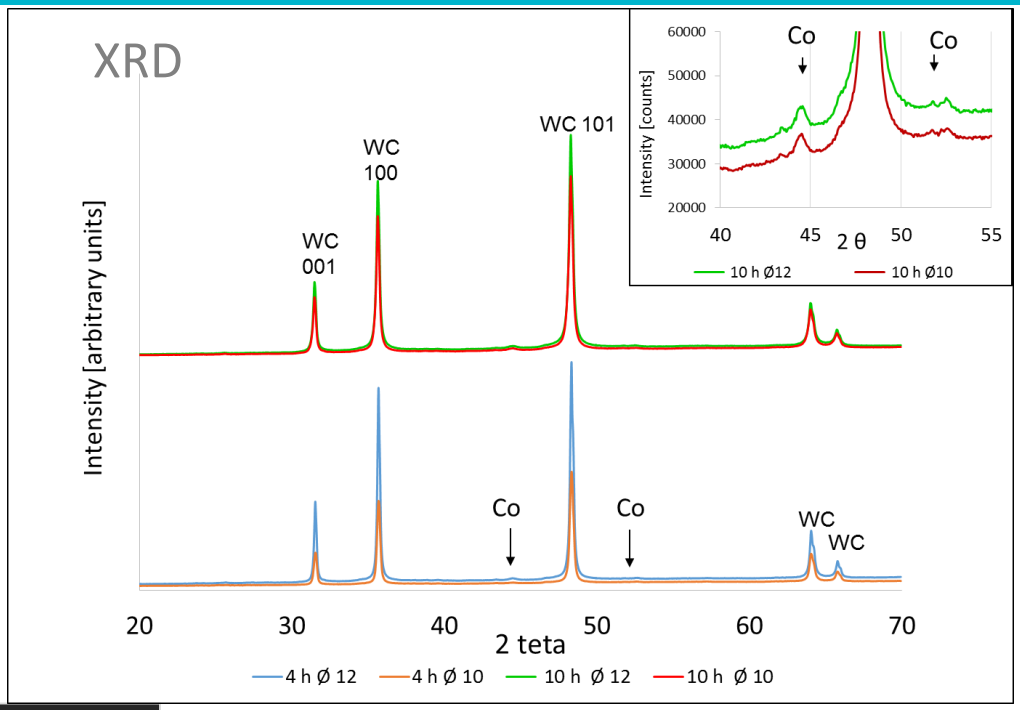
600 rpm

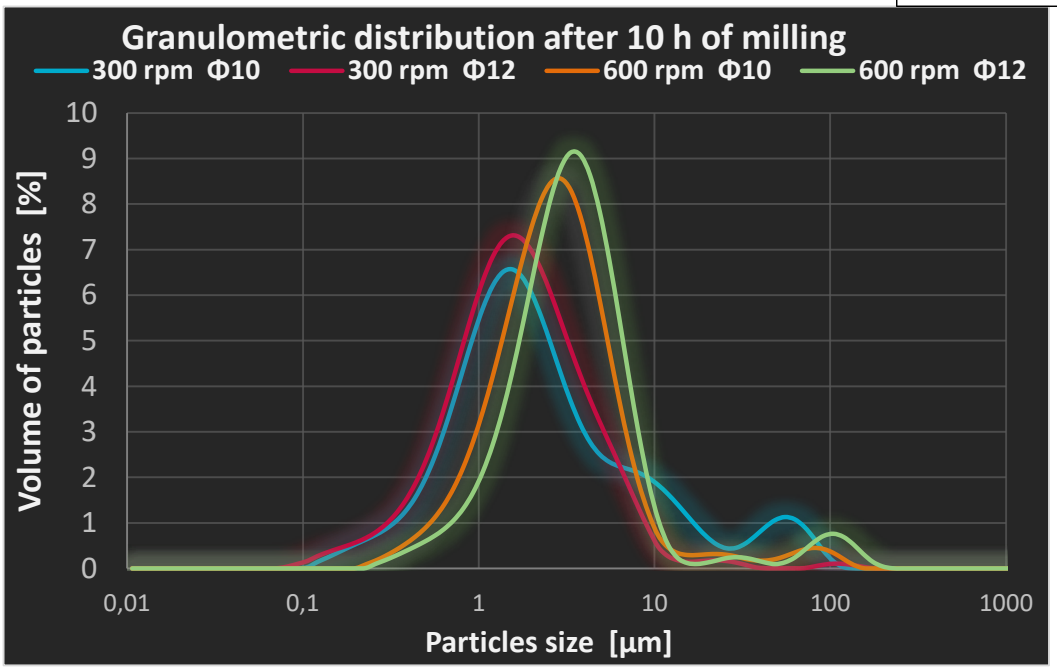


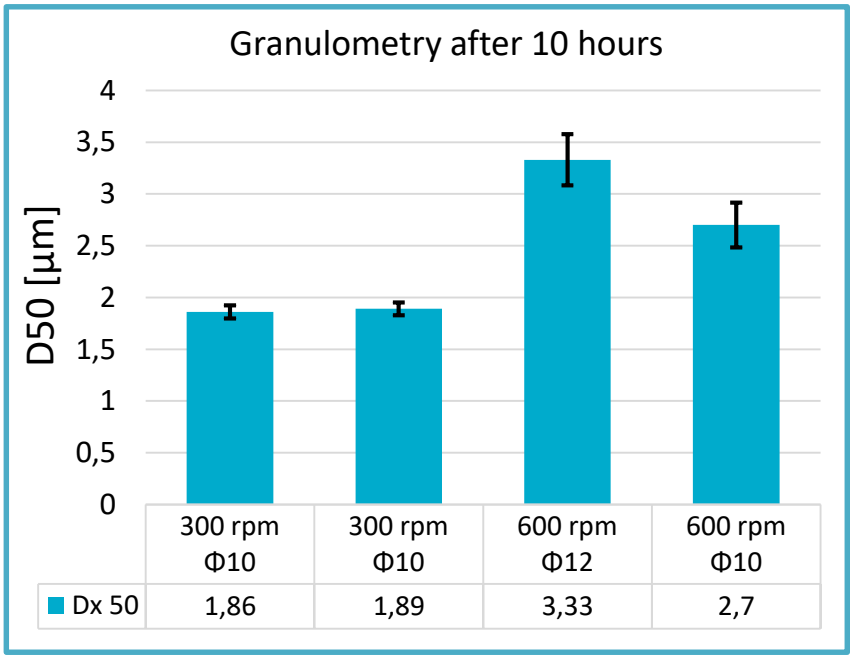


Analysis of powders

Crystallites size after 10 hours of milling				
	300 rpm, Ø10	300 rpm, Ø 12	600 rpm, Ø 10	600 rpm, Ø 12
Grains size [nm]	**303**	**280**	**181**	**177**







Preparation of sintered samples

SPS HPD10 machine from FCT System GmbH, Germany.

SPS sintering

Heating rate: 50°C/min

Sintering temperature: 1150°C

Holding time: 15 min

Atmosphere: vacuum

Sample weight: ±20 g

Sample diameter: 20 mm

Pressure: 50 MPa

Analysis of sintered samples

SEM and EDX analysis

Hitachi SU8020

Vickers micro and macro-hardness measurements

Mitutoyo, EMCO

X-rays diffraction

Siemens D5000, cobalt cathode

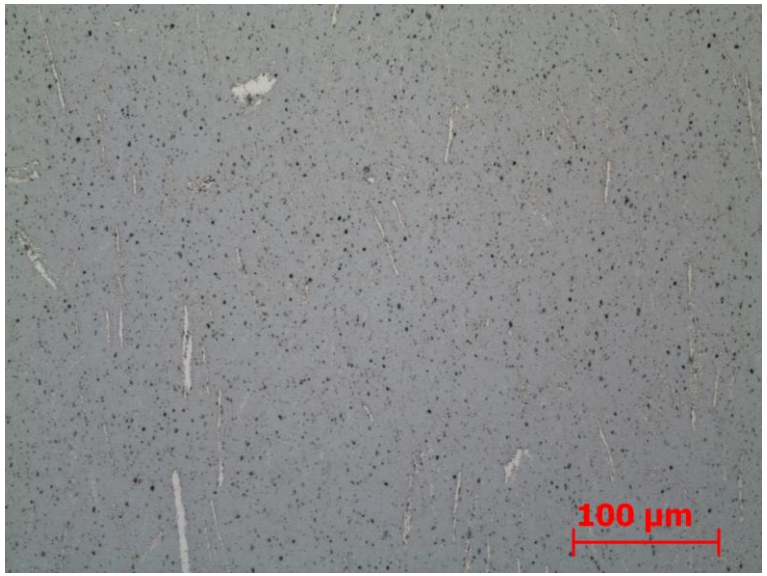
Analysis of sintered products – optical microscopy

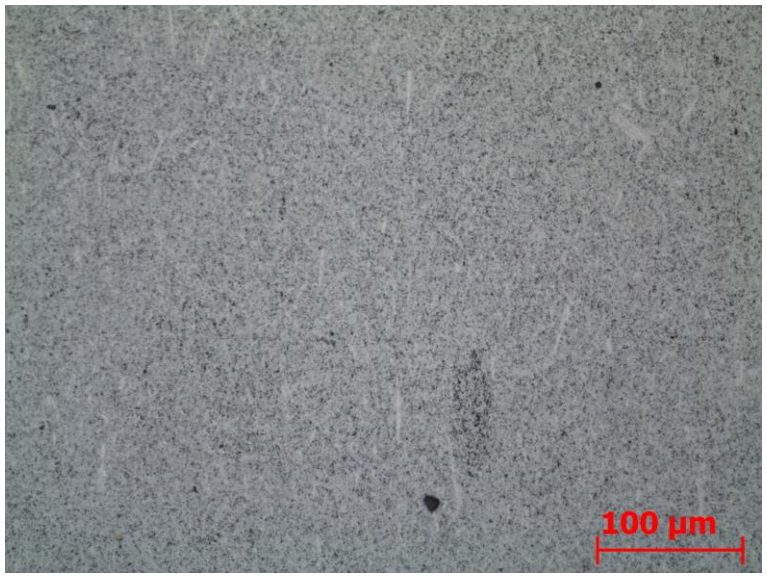
300 rpm

The samples milled at 300 rpm present a less homogeneous microstructure unlike those milled at 600 rpm whatever the balls diameter.

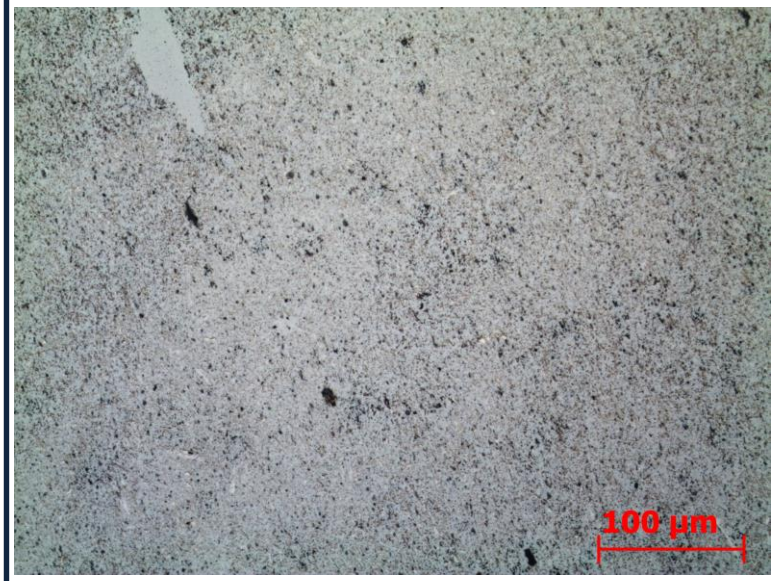
600 rpm

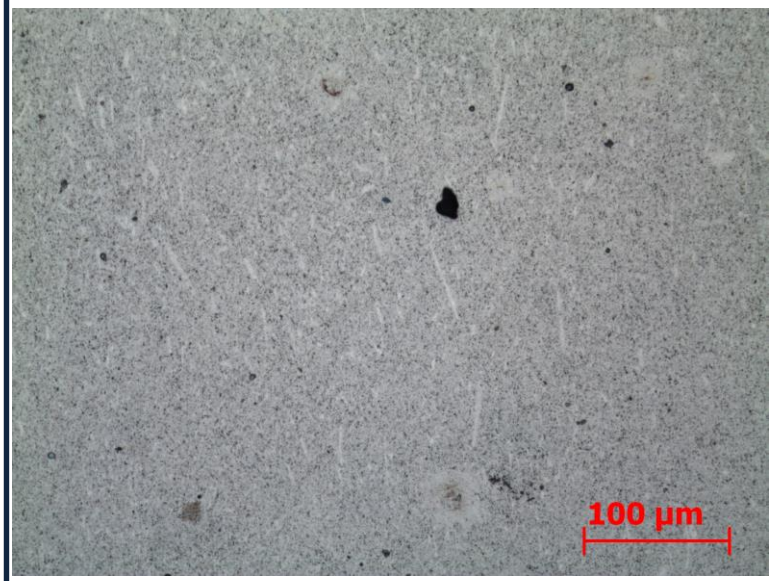
Ø 10 mm balls





Ø 12 mm balls



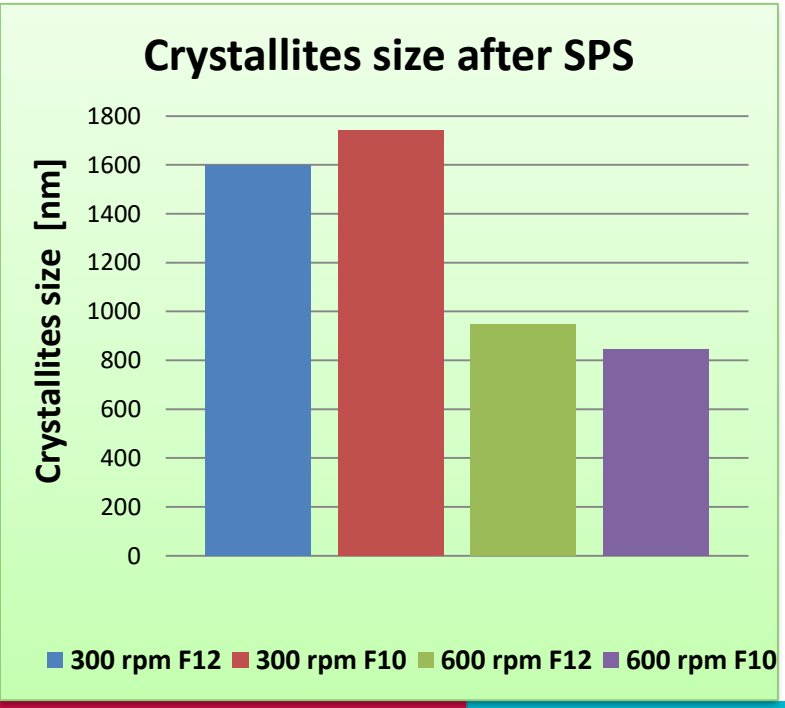


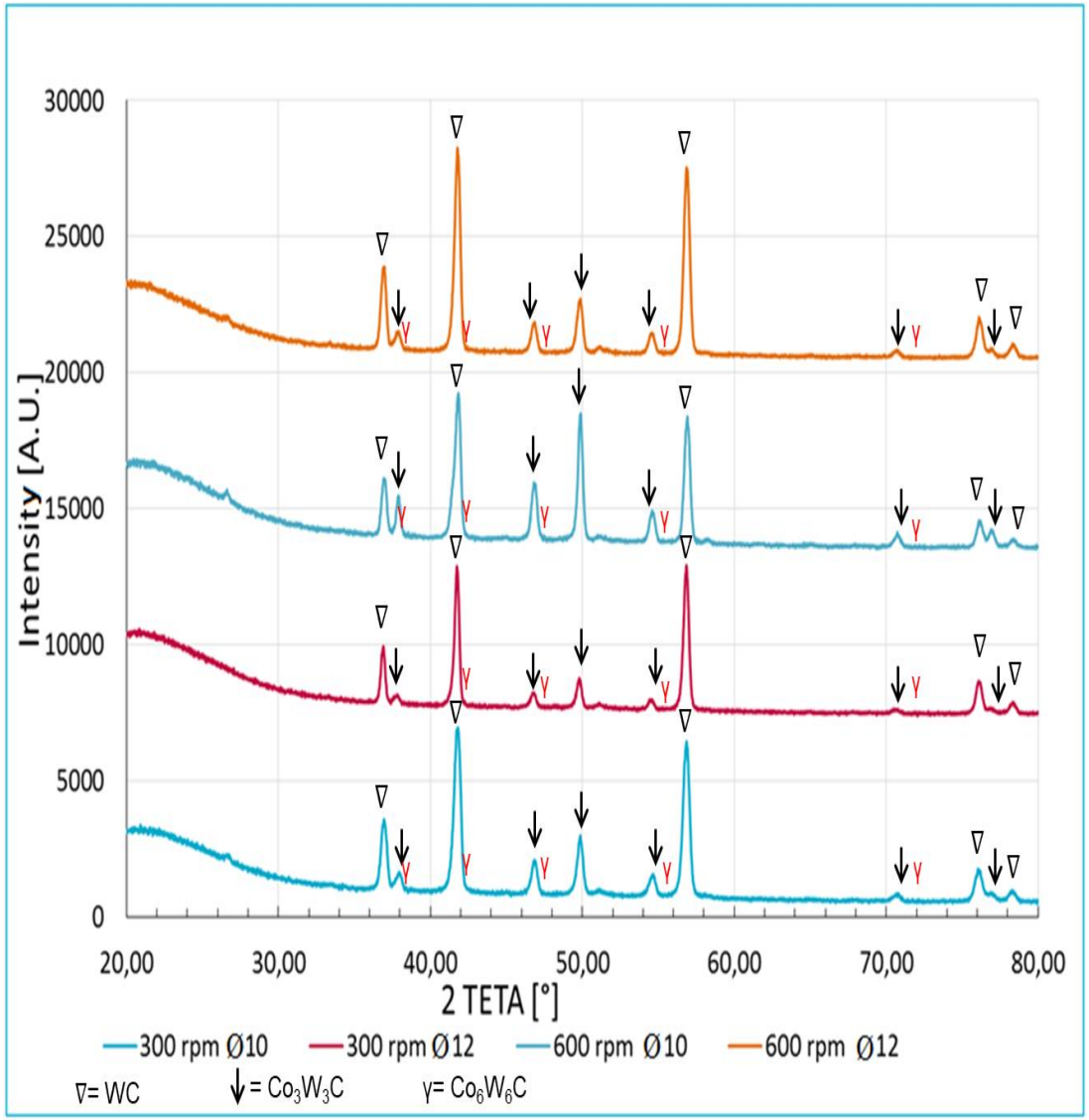
Analysis of classic sintered products : crystallites size

Evolution of the WC crystallites size

Grains size [nm]	Samples			
	300 rpm		600 rpm	
	Ø 12	Ø 10	Ø 12	Ø 10
Initial grains size	280	303	177	181
After sintering	1598	1742	948	846
Grains growth after sintering[%]	570	570	530	470

The size of crystallites appears to be influenced rather by the milling speed than by the size of the balls.





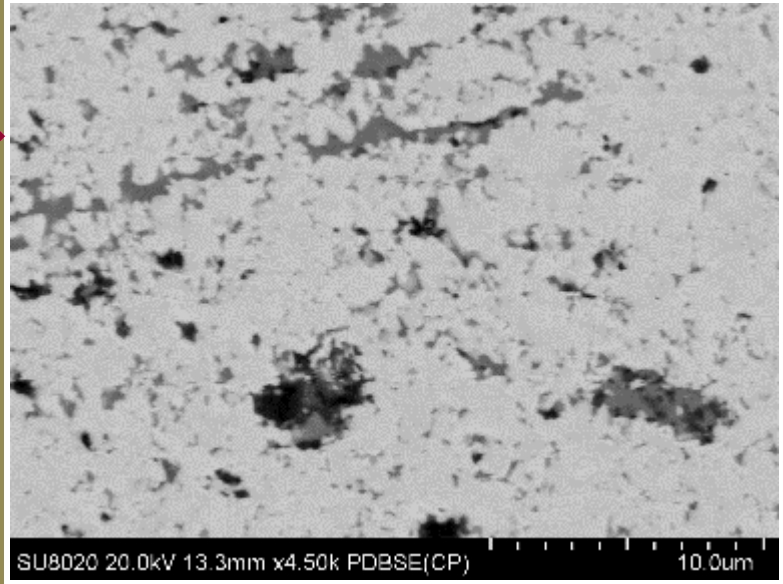
Analysis of SPS sintered samples - SEM

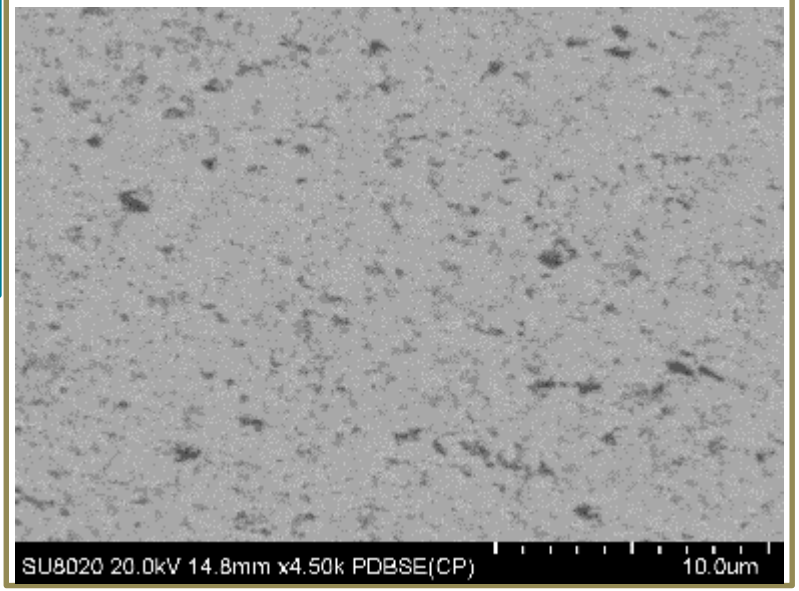
300 rpm

Samples milled at 300 rpm are less homogenous than those milled at 600 rpm whatever the balls size.

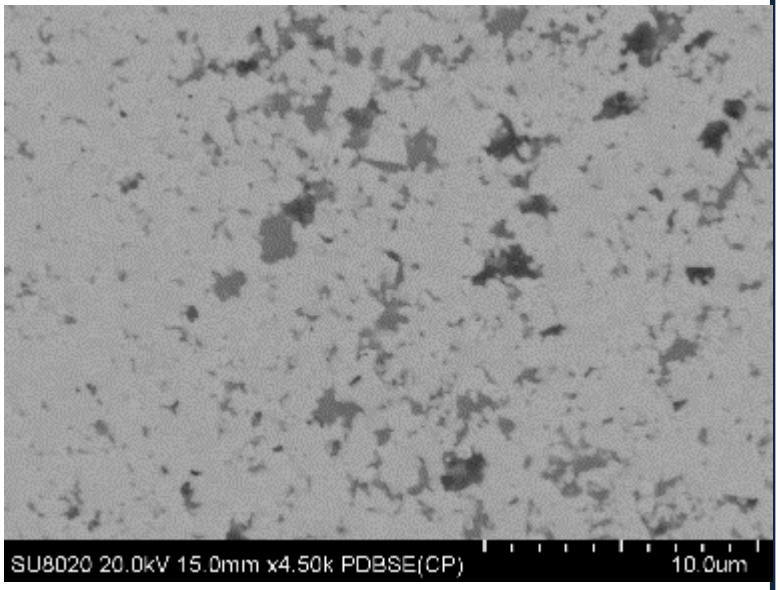
600 rpm

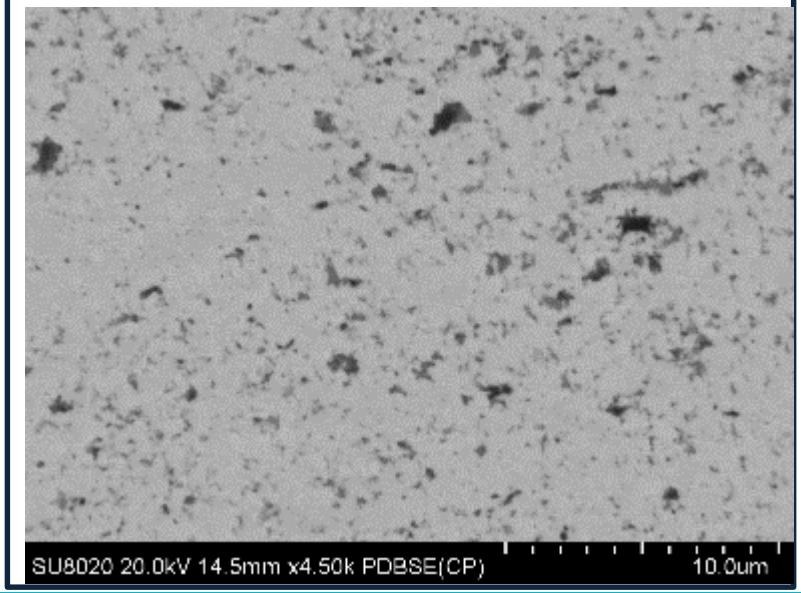
Balls Φ 10 mm



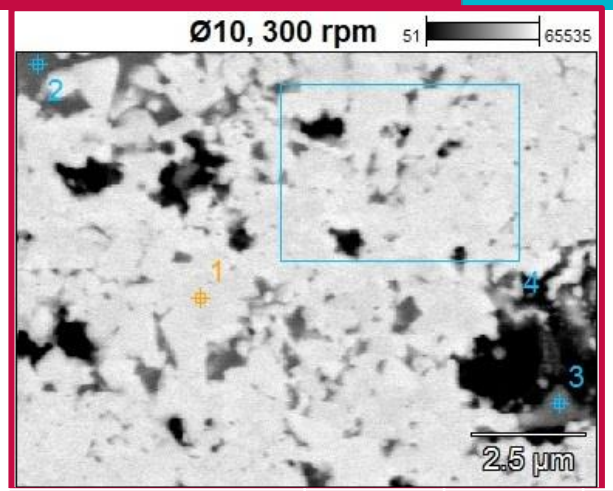


Balls Φ 12 mm

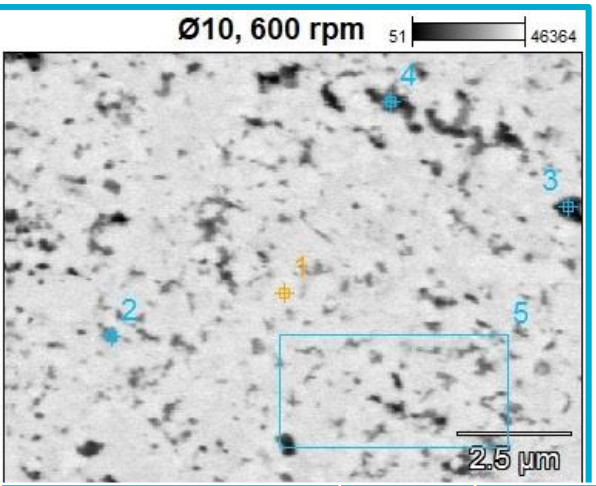




Analysis of sintered products - EDX

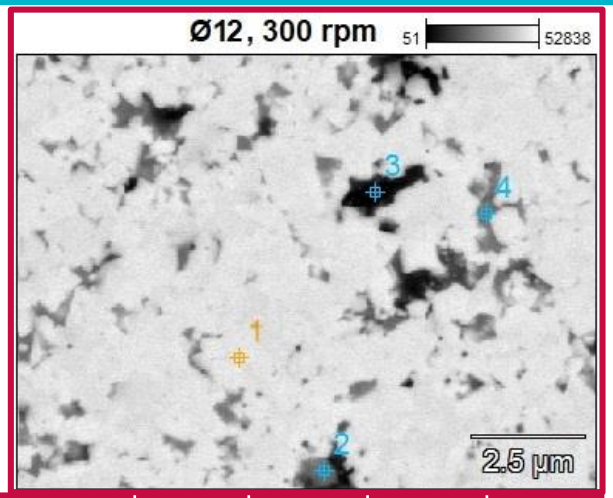


Weight %	Cr	Co	W
Ø10, 300 rpm_pt1		4.3	95.7
Ø10, 300 rpm_pt2	0.2	55.2	44.5
Ø10, 300 rpm_pt3	14.5	56.0	29.5
Ø10, 300 rpm_pt4	1.4	6.5	92.1

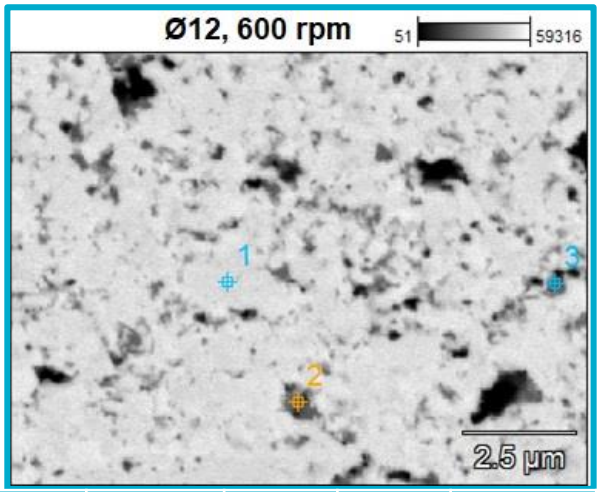


Weight %	Cr	Co	W
Ø10, 600 rpm_pt1		6.0	94.0
Ø10, 600 rpm_pt2	0.4	15.9	83.7
Ø10, 600 rpm_pt3	8.3	10.6	81.0
Ø10, 600 rpm_pt4	4.2	12.2	83.6
Ø10, 600 rpm_pt5	1.0	9.5	89.4

Phases:
WC –white
Co_3W_3C – gray
Co_6W_6C – black

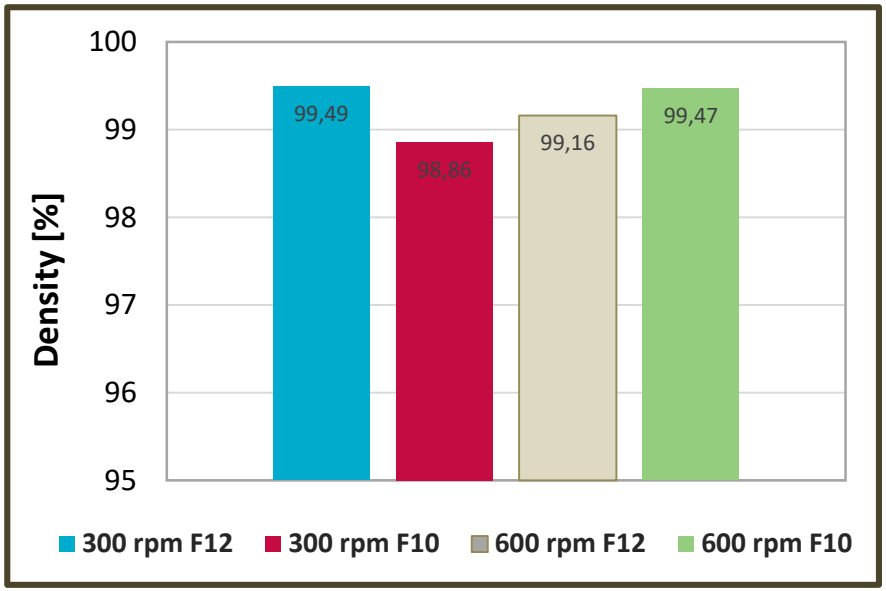


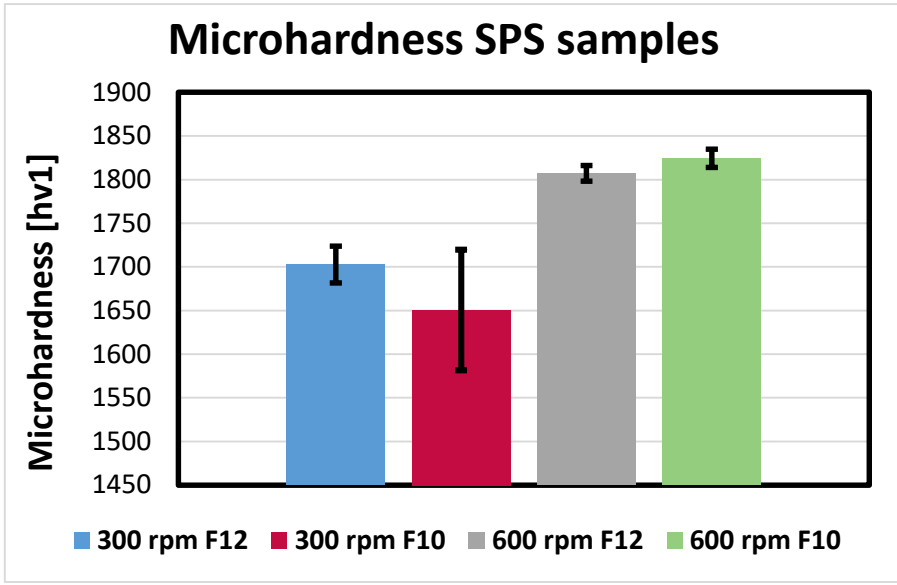
Weight %	Cr	Mn	Co	W
Ø12, 600 rpm_pt1			3.0	97.0
Ø12, 600 rpm_pt2	10.0	0.2	19.8	70.0
Ø12, 600 rpm_pt3	15.8		5.4	78.8
Ø12, 600 rpm_pt4	0.5		24.3	75.2

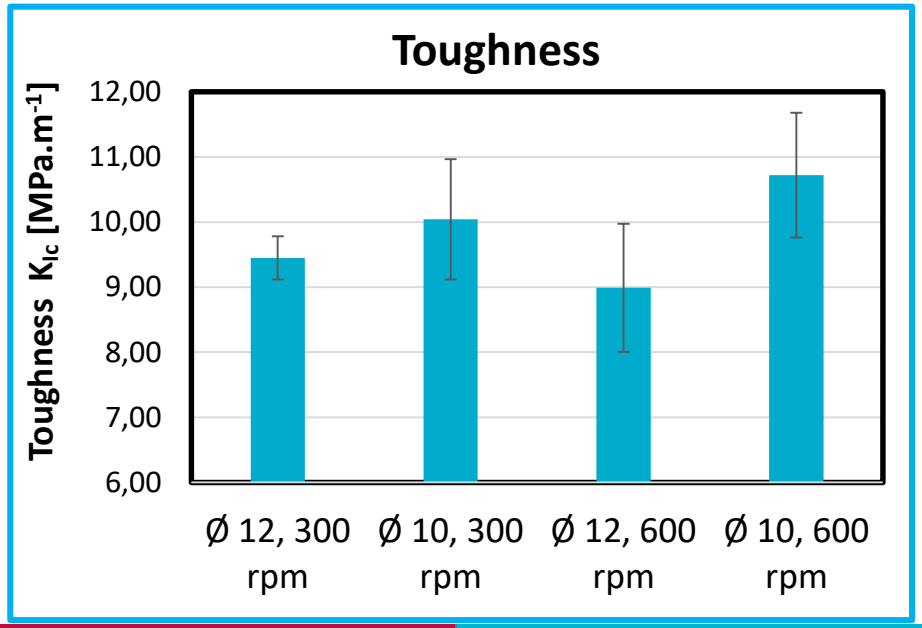


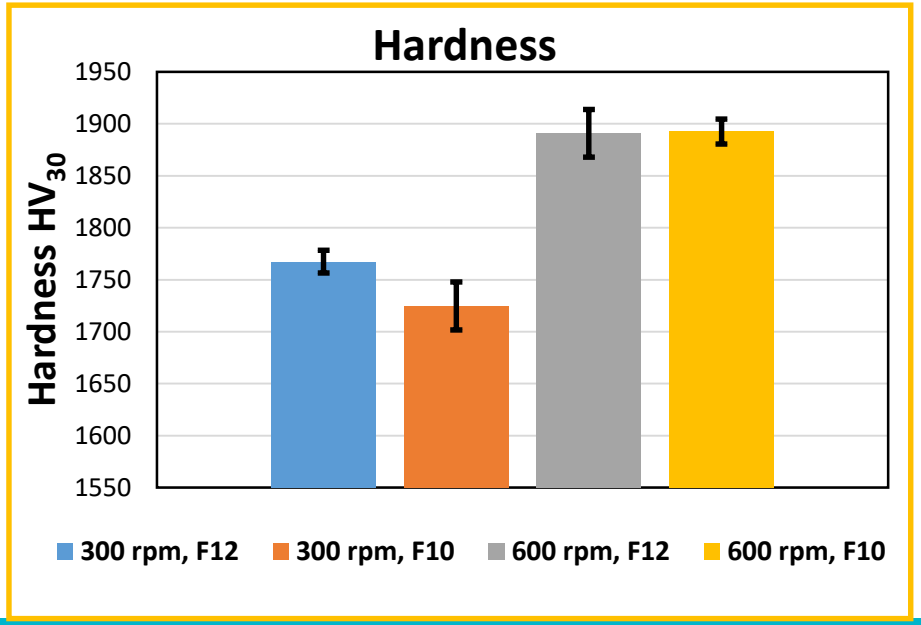
Weight %	Cr	Mn	Co	W
Ø12, 600 rpm_pt1			5.0	95.0
Ø12, 600 rpm_pt2	3.4	0.2	16.2	80.3
Ø12, 600 rpm_pt3	1.1		18.1	80.8

Analysis of SPS sintered samples



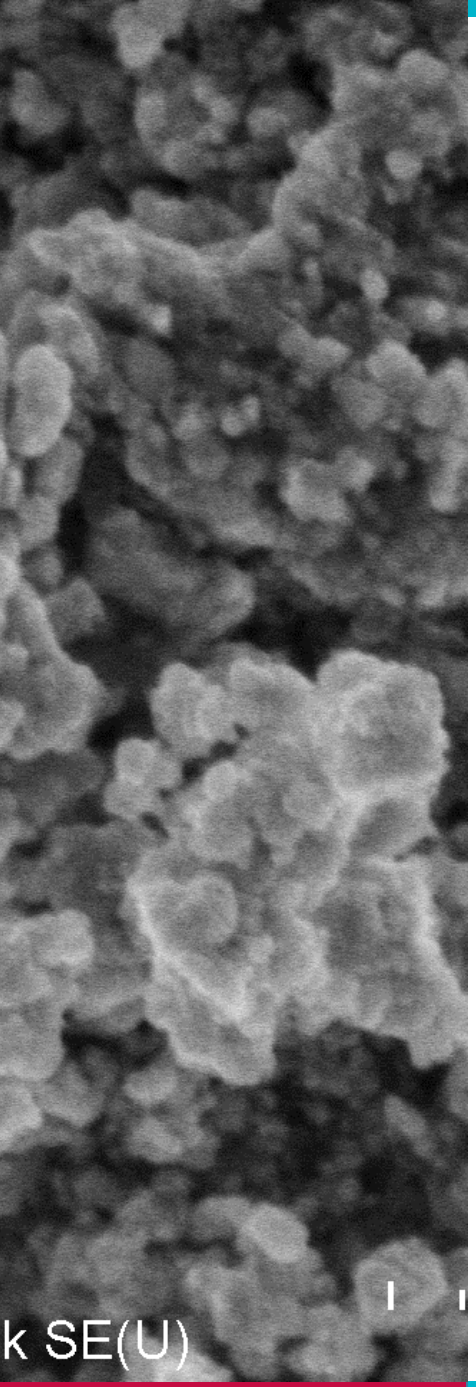






Conclusions

- The hardness of the samples is influenced by the speed and size of the grinding balls.
- The homogeneity is greatly improved with the increase of grinding speed.
- At low speed homogenizing, the balls size is important: the balls with 12 mm in diameter provide better homogenization than those of 10 mm.
- A control of the carbon balance is important to avoid the appearance of the η phase.
- With the SPS sintering, the size of the crystallites decreases with the increase of the grinding speed.



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Thank you for your attention!
Questions?