Electric Field Enhanced Processing of Advanced Materials II: Complexities and Opportunities

Proceedings

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Effect of the addition of doped-cobalt on the properties of recycled tungsten carbide powder sintered by SPS

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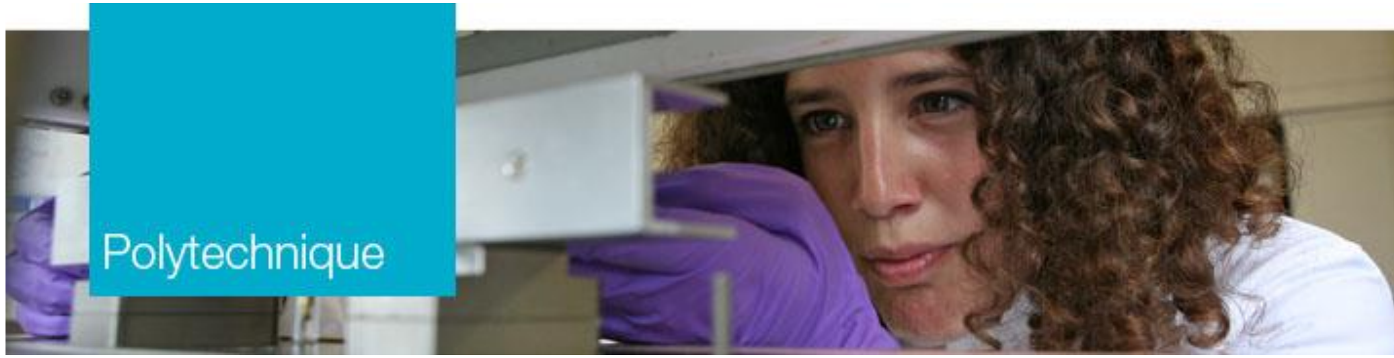

Effect of the addition of doped-cobalt on the properties of recycled tungsten carbide powder sintered by SPS

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POLYTECH MONS

Electric Field Enhanced Processing of Advanced Materials II
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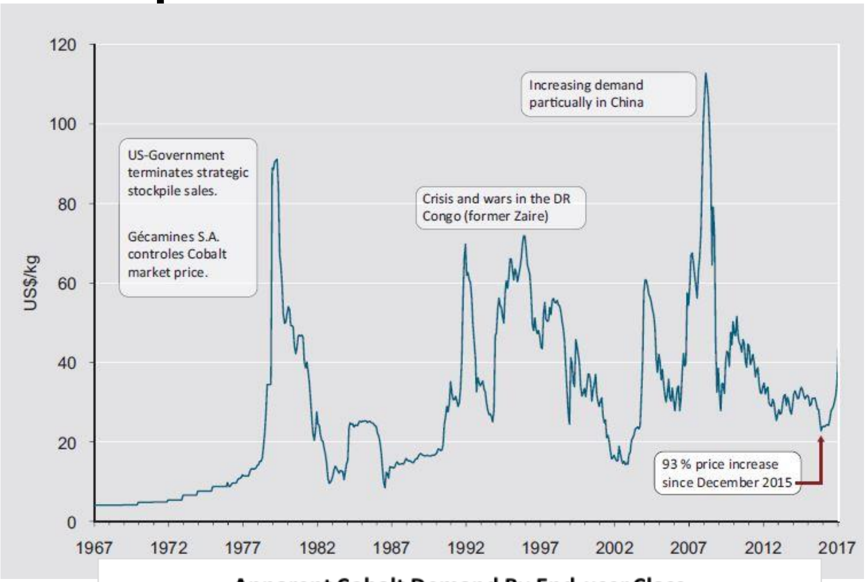
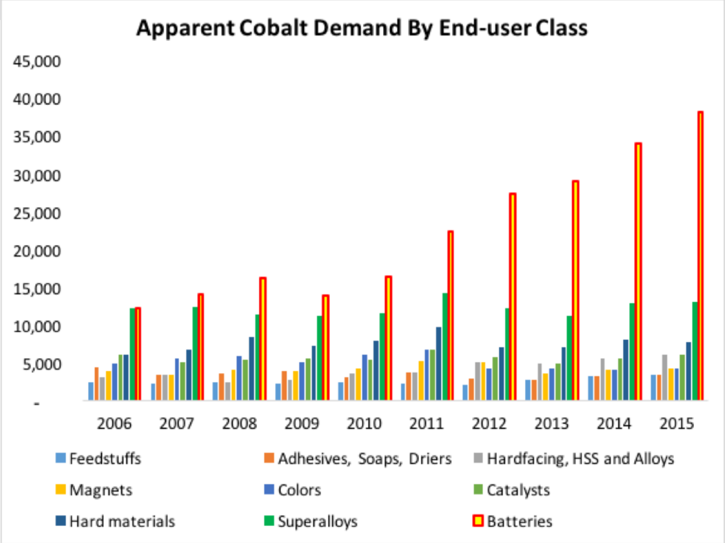
Issues related to WC-Co

1) Large fluctuation of cobalt price!
   - 94% of Co is by-product of Cu and Ni mines.
   - 50% of the world reserves are in RDC and Zambia.



2) W and Co: Critical raw materials since 2011!
   - W: China is the main producer.
   - Co: intensive use in batteries.

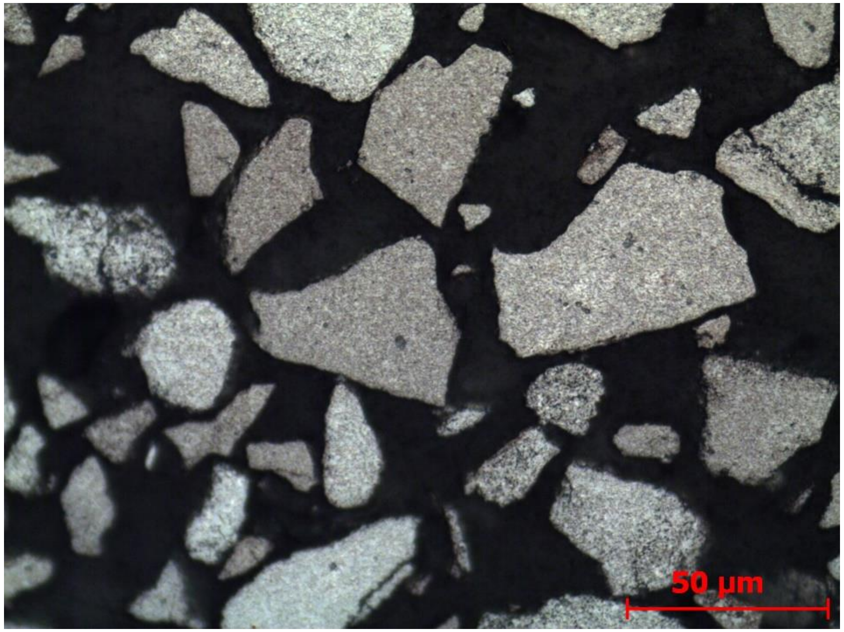


Recycling WC-Co tools is important

Separation of Co and WC is not easy

Alternative: “Coldstream Process”! The tools are crushed and transformed into powder.

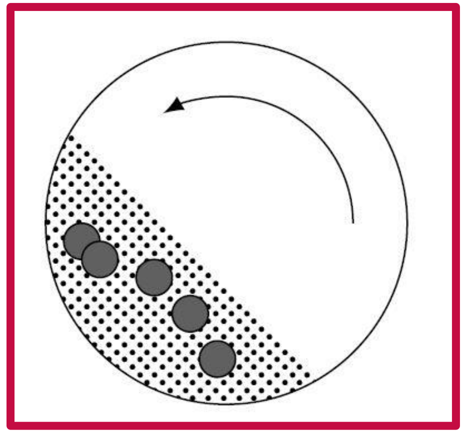
- Company Höganäs Belgium.
- Powder containing WC and Co agglomerates.
- Average size 45 µm.
- Provides good ductility.
- Cheaper than new WC and Co powders



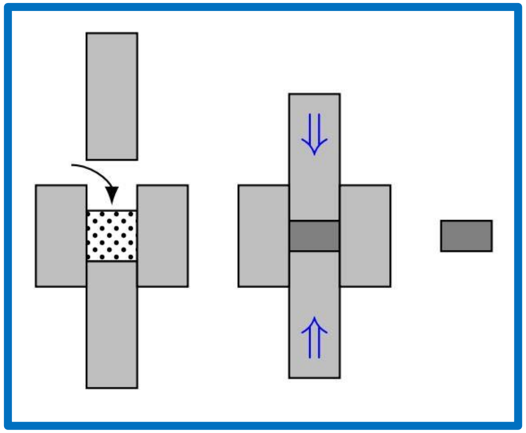
Understanding the recycling of WC-Co requires the knowledge of its process

Mixing of the powders

- WC
- Co
- Additives

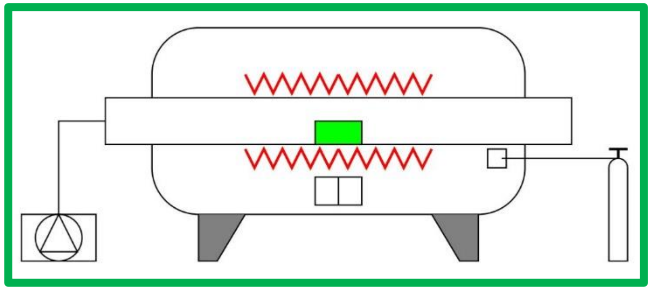


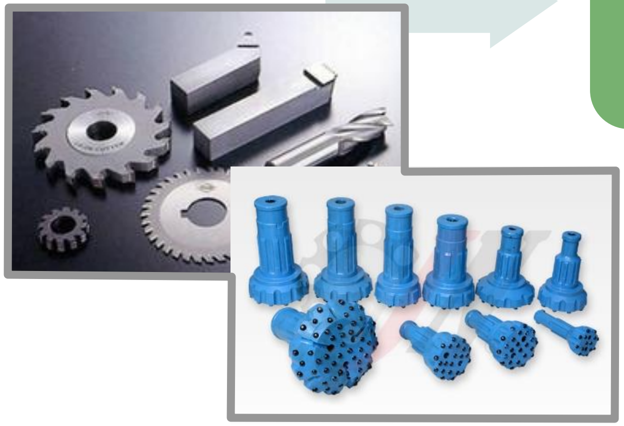
Uniaxial compaction



Liquid Phase Sintering

- Vacuum
- 1350-1550°C
- 30-90 min
- max. 10°C/min





Applications

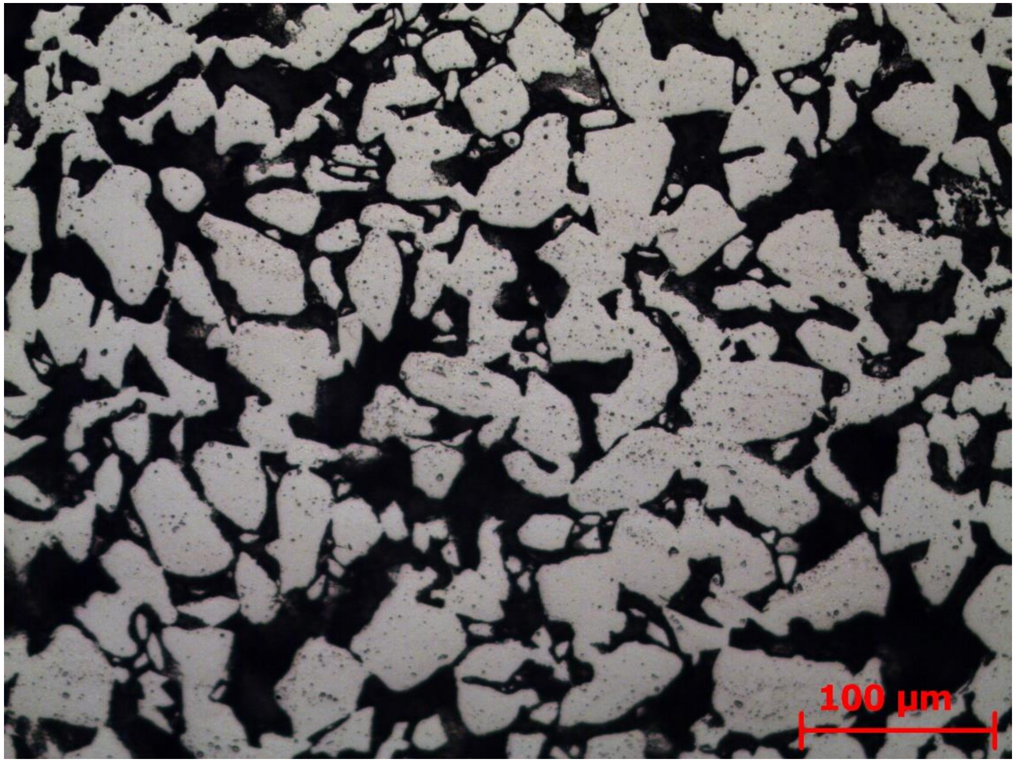
- Cutting tools and inserts
- Mining tools
- Construction tools

Preliminary results on the re-sintering of the recycled powder

Sintering conditions

- 1400°C
- 60 min
- 4°C/min
- Vacuum

Only 65% densification



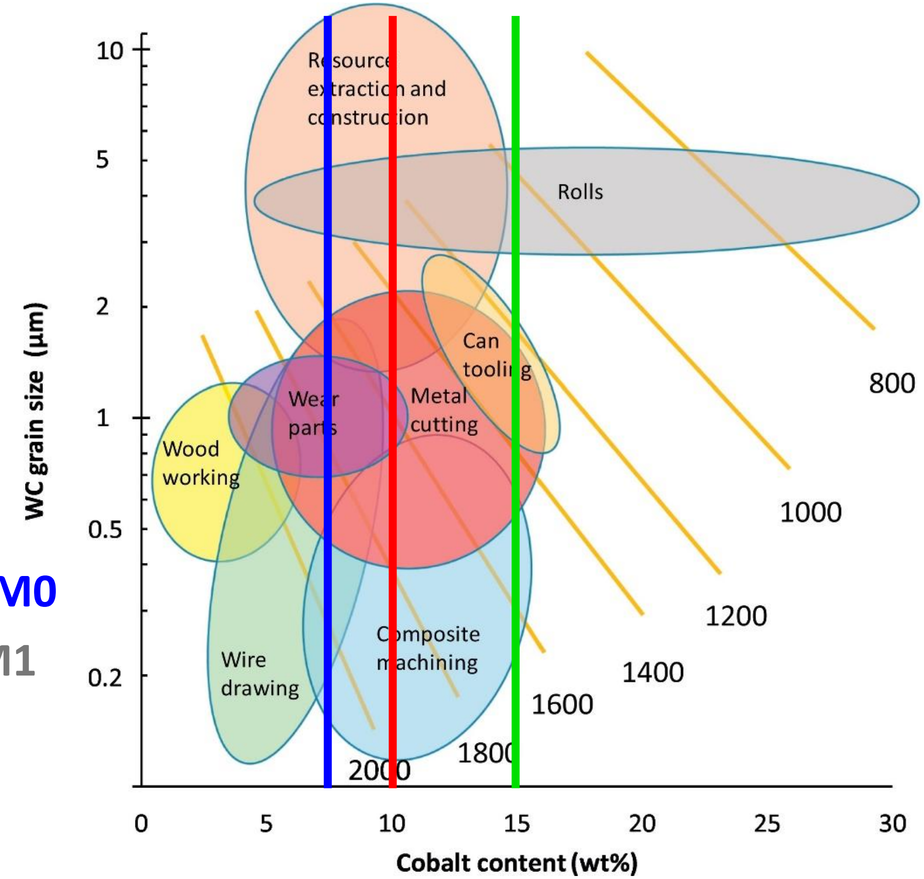
Low sinterability

⇨ must be increased!

How?
- Sintering at higher conditions (T, t)
- Ball milling experiments
- Alternative sintering processes

Strategy

- Ball milling 6h in wet conditions.
- Addition of a small content of doped cobalt.
- 4 Samples:
  - WC-7.5Co (as-received recycled powder) – **M0**
  - WC-7.5Co (ball milled recycled powder) – **M1**
  - WC-10(Co+Cr_3C_2) – **M2**
  - WC-15(Co+Cr_3C_2) – **M3**

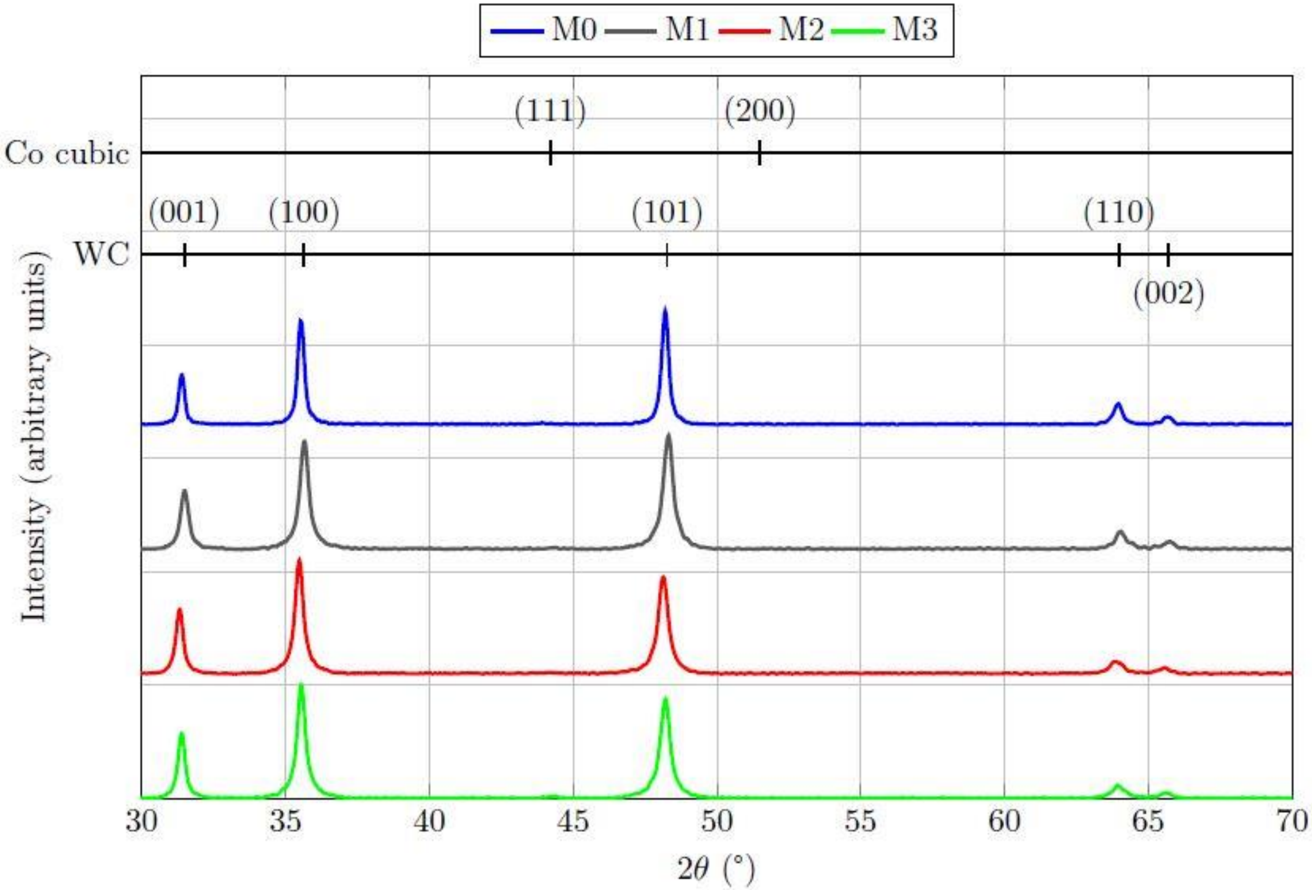


Garcia J. et al., Cemented carbide microstructures: a review, 2019

	SPS (50 MPa)	Vacuum sintering
Temperature	1200°C	1400°C
Time	10 min	60 min
Heating rate	150°C/min	4°C/min

X-rays diffraction on powders

M0: as-received powder (7.5 wt% Co)
M1: milled powder (7.5 wt% Co)
M2: milled powder (10 wt% Co+Cr_3C_2)
M3: milled powder (15 wt% Co+Cr_3C_2)



Crystallites size

49 nm

27 nm

29 nm

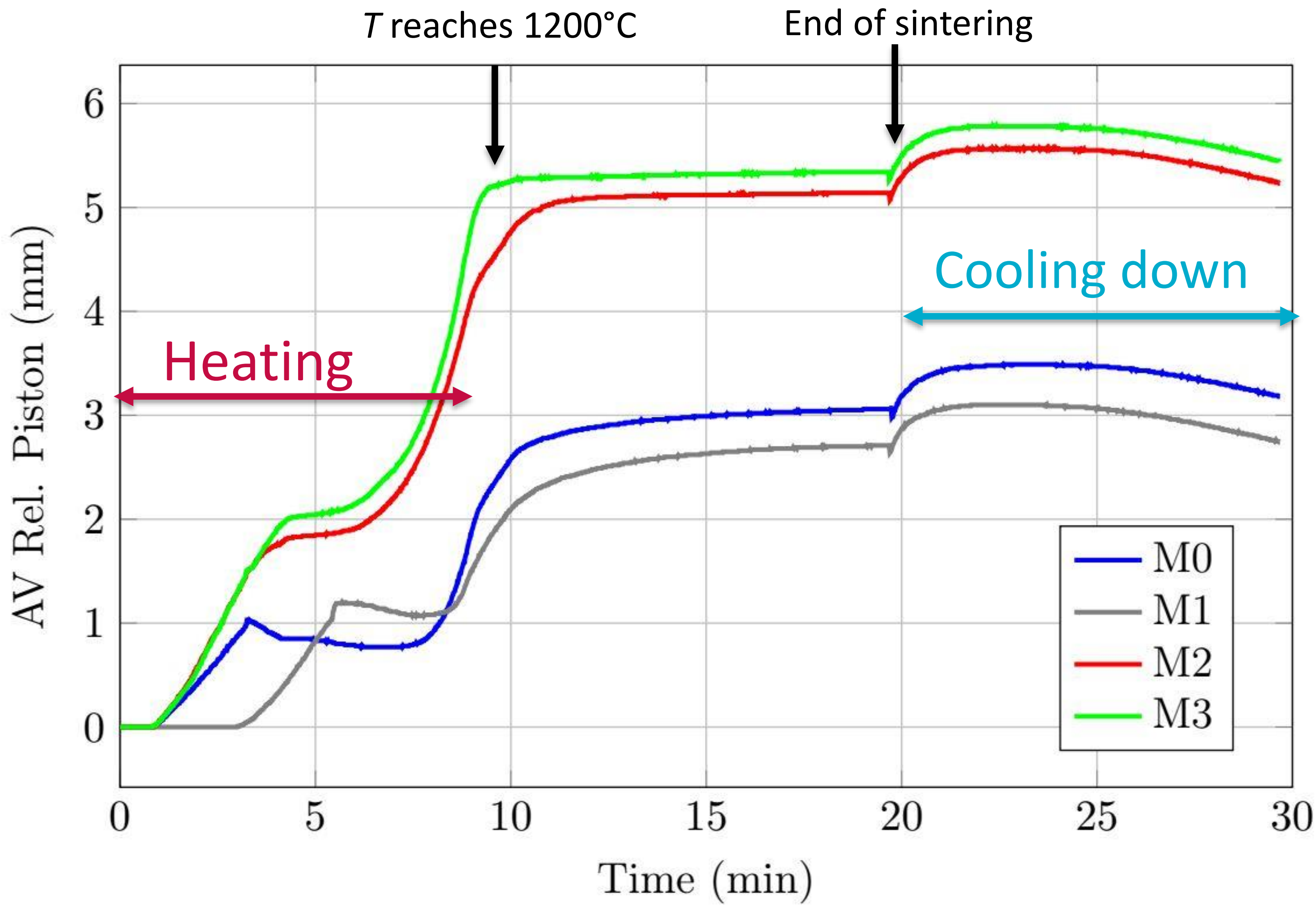
28 nm

Ball milling allows:

- Size reduction of crystallites (ca 60 %)
- Increase of the reactivity of the powder?

SPS densification curves

M0: as-received powder (7.5 wt% Co)
M1: milled powder (7.5 wt% Co)
M2: milled powder (10 wt% $Co+Cr_3C_2$)
M3: milled powder (15 wt% $Co+Cr_3C_2$)



X-rays diffraction on sintered samples

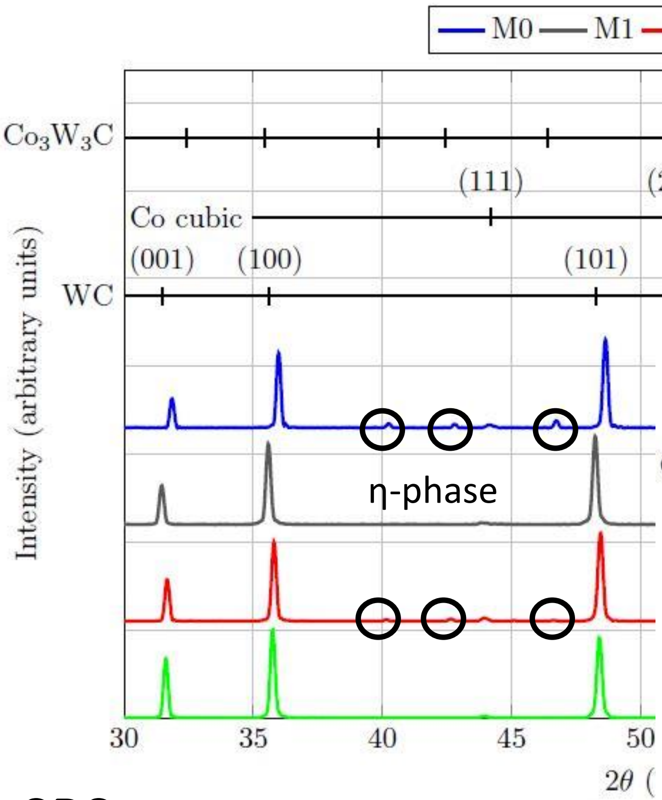
M0: as-received powder (7.5 wt% Co)
M1: milled powder (7.5 wt% Co)
M2: milled powder (10 wt% Co+Cr_3C_2)
M3: milled powder (15 wt% Co+Cr_3C_2)

Vacuum sintering

- Presence of η-phase (brittle carbide)

crystallite growth

- **M0**: 281 nm → 470 %
- **M1**: 147 nm → 444 %
- **M2**: 178 nm → 514 %
- **M3**: 150 nm → 435 %

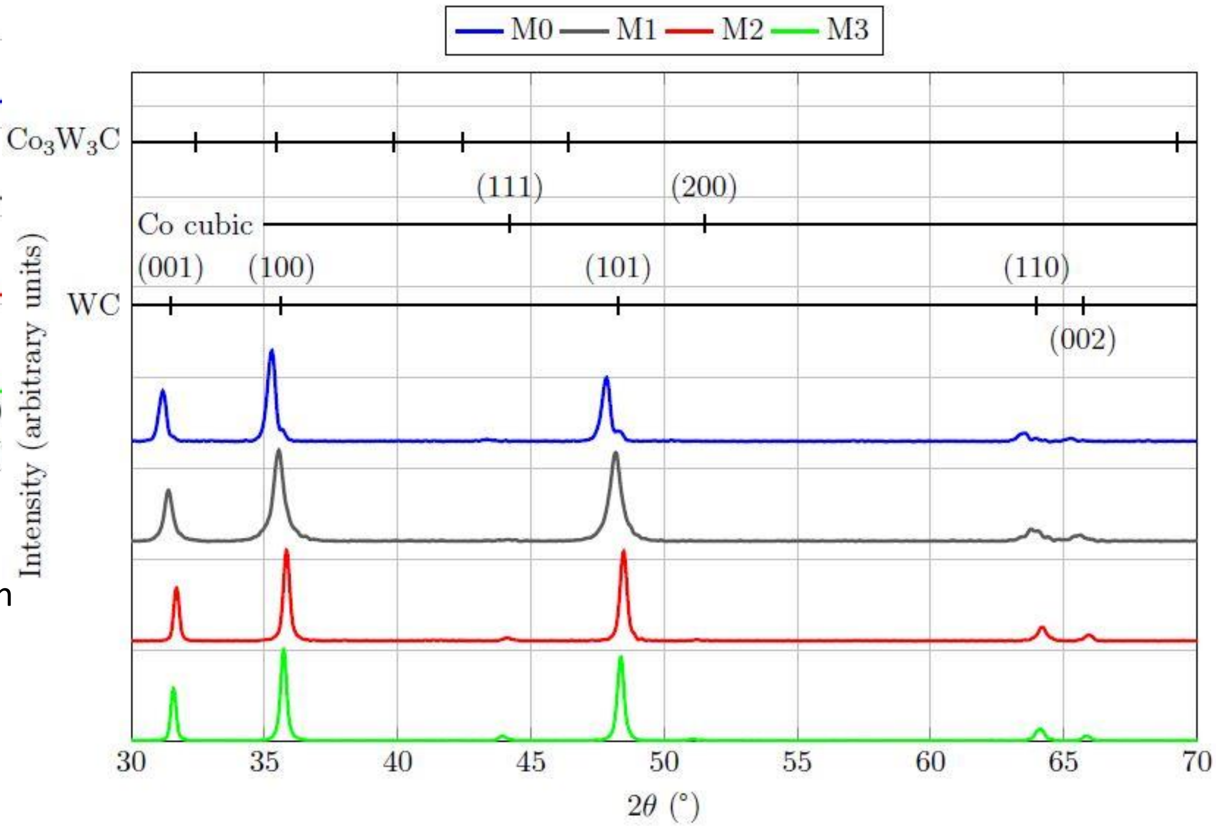


SPS

- No η-phase (brittle mixed carbide)

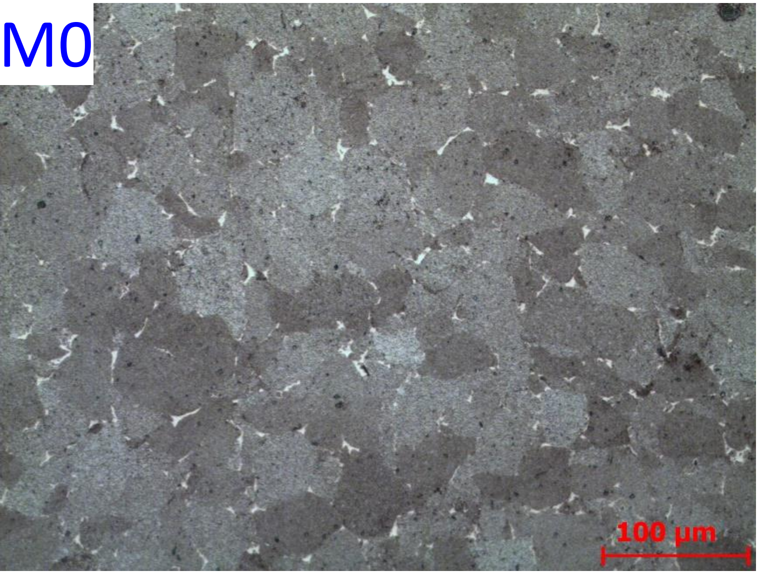
crystallite growth

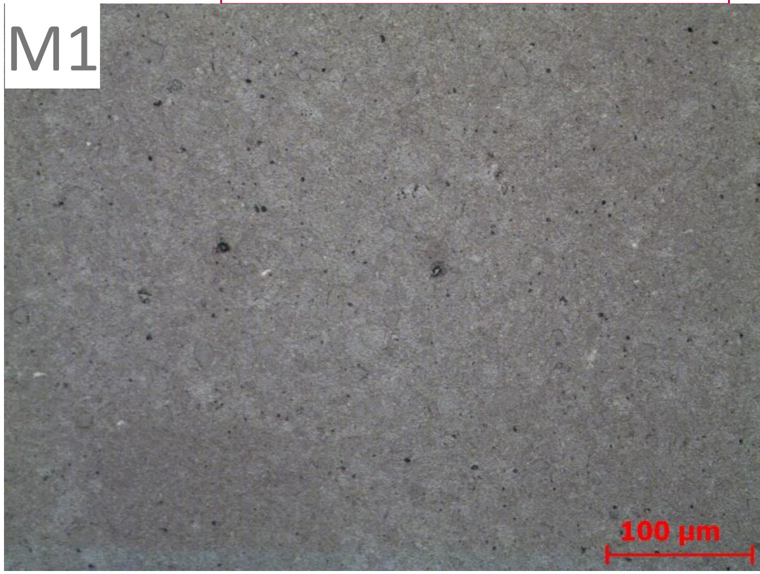
- **M0**: 108 nm → 118 %
- **M2**: 75 nm → 158 %
- **M3**: 82 nm → 197 %



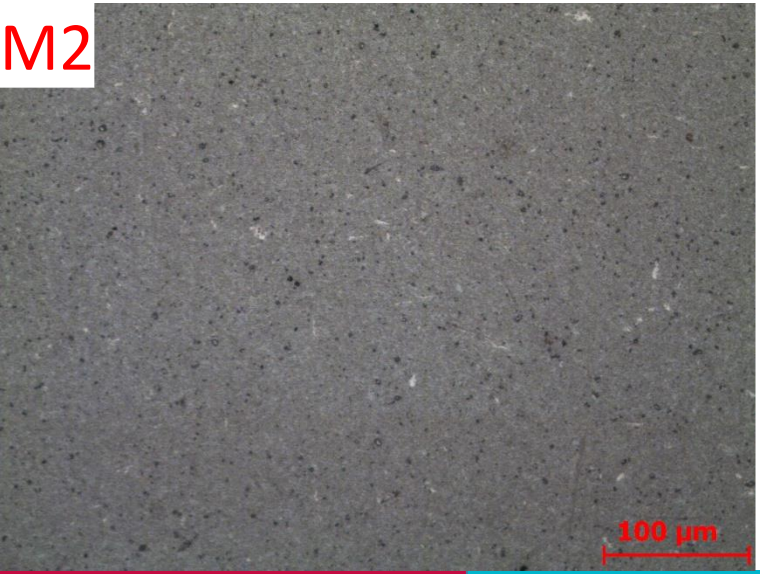
Microstructures

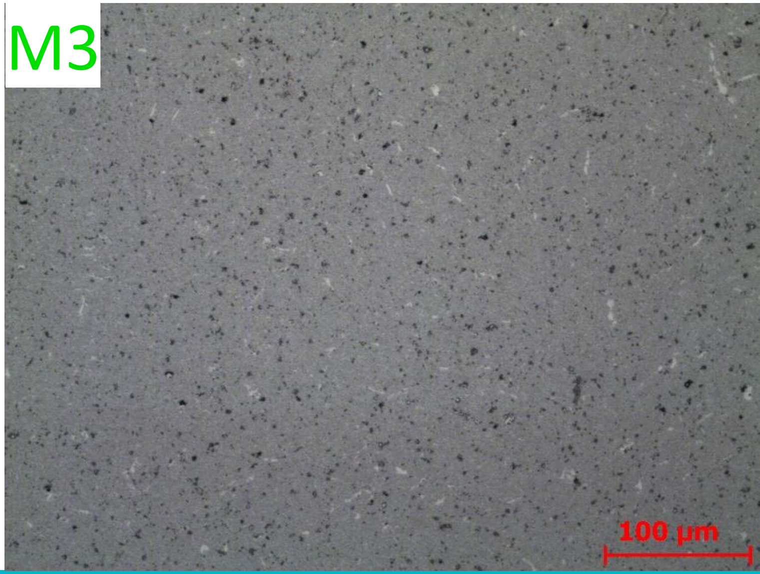
M0: as-received powder (7.5 wt% Co)
M1: milled powder (7.5 wt% Co)
M2: milled powder (10 wt% Co+Cr_3C_2)
M3: milled powder (15 wt% Co+Cr_3C_2)





- Particles are seen only in M0
- Microstructure more homogeneous in M1.

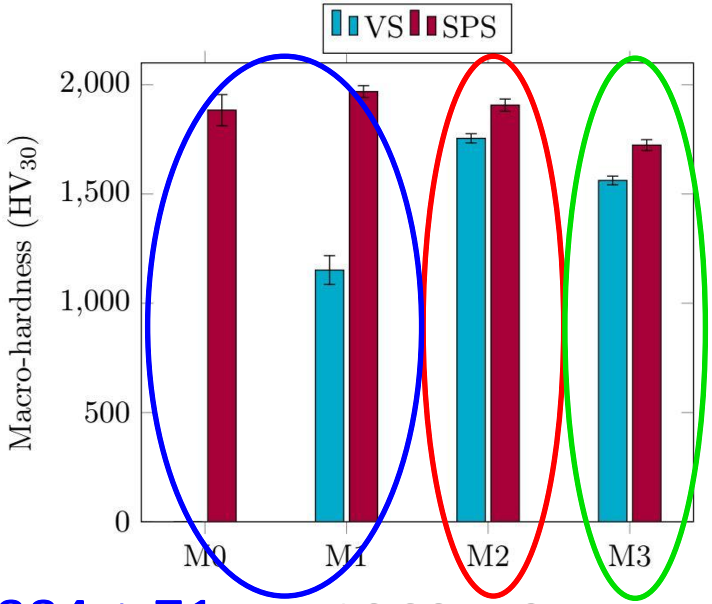




- Presence of micro-porosities in M2 and M3

Hardness

M0: as-received powder (7.5 wt% Co)
M1: milled powder (7.5 wt% Co)
M2: milled powder (10 wt% Co+Cr_3C_2)
M3: milled powder (15 wt% Co+Cr_3C_2)



- Density too low to measure hardness of M0.
- Sintering by SPS:
  - M1: improvement of 71%
  - M2: improvement of 9%
  - M3: improvement of 10%
- Help of the addition of raw cobalt on the sinterability.

1884 ± 71 1969 ± 27

References	Hardness (HV_{30})
Laoui et al. 2011	ca 1700-1800
Zhao et al. 2009	ca 1850-1900
Garbiec et al. 2015	ca 1700-1800
Rumman et al. 2015	ca 1800

1907 ± 28

References	Hardness (HV_{30})
Cha et al. 2003	ca 1600
Zhu et al. 2003	ca 1900
Zhao et al. 2009	ca 1650
Wei et al. 2012	ca 1700

1724 ± 25

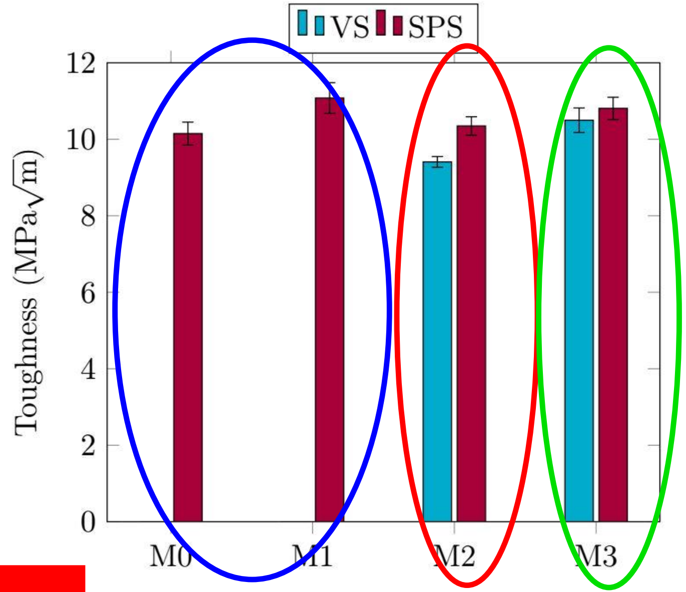
References	Hardness (HV_{30})
Bonache et al. 2011	ca 1800-2000
Laoui et al. 2011	ca 1700
Al-Aqeeli et al. 2015	ca 300 (1200°C) ca 1600 (1300°C)

WC-12Co

Toughness

M0: as-received powder (7.5 wt% Co)
M1: milled powder (7.5 wt% Co)
M2: milled powder (10 wt% Co+Cr_3C_2)
M3: milled powder (15 wt% Co+Cr_3C_2)

- Toughness could not be measured on M0 and M1.
- Sintering by SPS:
  - M2: improvement of 10%
  - M3: improvement of 3%
- M3 contains more Co
  higher toughness



10.15 ± 0.30 11.08 ± 0.40

References	Toughness (MPa $m^{0.5}$)
Zhao et al. 2009	ca 8.5-12.5
Garbiec et al. 2015	ca 11.5-12.5
Rumman et al. 2015	ca 8-10

10.35 ± 0.24

References	Toughness (MPa $m^{0.5}$)
Cha et al. 2003	ca 2
Zhu et al. 2003	ca 11.5
Zhao et al. 2009	ca 12-12.5
Wei et al. 2012	ca 11-13

References	Toughness (MPa $m^{0.5}$)
Bonache et al. 2011	ca 10-10.5
Al-Aqeeli et al. 2015	ca 9 (1200°C) ca 10 (1300°C)

10.81 ± 0.29 WC-12Co

Conclusions…

- 10 wt% cobalt → many applications.
- The use of SPS increases hardness while keeping reasonable toughness.
- The addition of cobalt, coupled with milling, improves the mechanical properties.

… and perspectives

- Add WC to reach 6 wt% Co (comparison literature)
- Optimisation of SPS thermal cycles
  - As-received powder: increase temperature.
  - Milled powders: decrease temperature or shorten times.
- Use other grain growth inhibitors.

Thank you for your attention

Acknowledgments

BCRC member of EMRA

Höganäs