Microstructural characterization of Ti-Al-C MAX phases obtained by SPS

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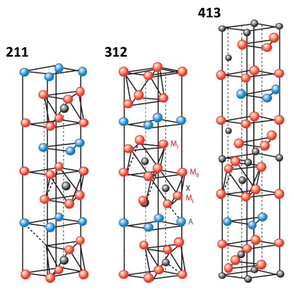
This work is a part of FEDER IMAWA-CeraMAX project that aims at developing by Spark Plasma Sintering (SPS) technology, optimized Ti-Al-C and Ti-Al-N MAX phases for various applications .

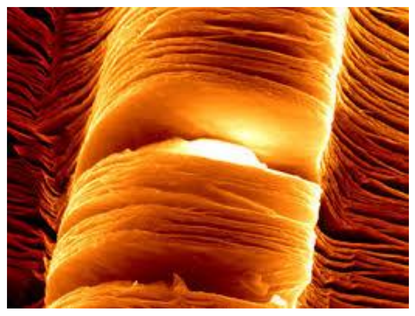
⇨ **Problem**: layered crystal structure of MAX phases gives rise to preferred orientation phenomena of lamellar crystallites which can affect characterization of these materials and then, the optimization synthesis process.

⇨ **Objective of this work**: to provide, by Rietveld method applied to XRD patterns, a complete and reliable microstructural characterization of Ti_2AlC/Ti_3AlC_2 MAX phases obtained according to various SPS conditions.

MAX phases

M : Early metal transition
A : groupe A (IIIA et VIA)
X : C ou N





M_2AX = 211
M_3AX_2 = 312
M_4AX_3 = 413

MAX phases are ternary carbides and nitrides with general formula $M_{n+1}AX_n$ (n=1, 2, 3). They are a new class of layered materials with hexagonal crystal structure. MAX phases present exceptional and unusual combination of metallic and ceramic properties due to their layered structure and their alternating strong covalent M-X and relatively weak metallic M-A bonds [1].

Rietveld refinement principle

Rietveld analysis applied to XRD patterns is widely use for structure refinement, microstructural and quantitative analysis. The principle is to minimize by a least square method, the residual function R between an experimental XRD pattern (I_i) and a calculated profile (I_i^{calc}):

$$R = \sum w_i (I_i - I_i^{calc})^2) \quad \text{with } w_i = 1/I_i \quad \text{and} \quad I_i^{calc} = S_F \sum_{j=1}^{Nphases} S_j \sum_{k=1}^{Npeaks} |F_{k,j}|^2 G_J(2\theta_i - 2\theta_{k,j})\, P_{k,j} A_{j,i} L_i + bkg_i$$

$S_J = f_j V_j$ = phase scale factor
f_j= phase volume fraction
V_j= phase cell volume

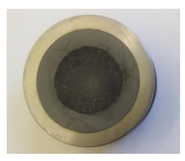
$G_j(2\theta_i - 2\theta_{k,j})$ = profile shape function
Instrument, micro-strains, crystallites size

P_k= preferred orientation function
- March-Dollase (MD)
- Standard functions (SF)

⇨ Experimental Procedure

XRD analysis

- Sample preparation:



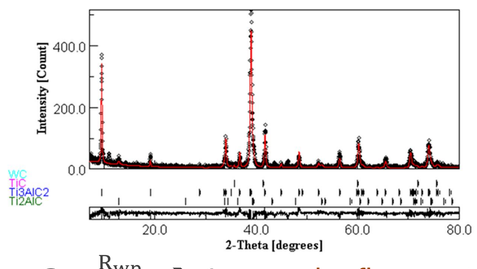
Free sintered powders pressed in the holder

- XRD acquisition (Diffractometer)
- Phases identification (EVA)

Rietveld refinement (MAUD software)

Experimental parameters
→ Structural parameters
→ Microstructural parameters
Crystallites size: Scherrer formula
→ Texture parameters
MD/SF models (P_{00l} factor in mrd unity)

Quality of refinement



$S = \frac{R_{wp}}{R_{exp}}$ ➔ 1 = good refinement

R_{wp}: weighted profile and R_{exp}: expected R-factor

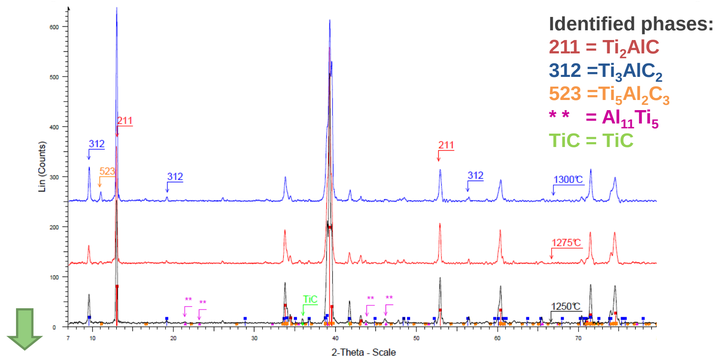
Compositions and sintering conditions tested in SPS

TiC : Al : Ti	1 :1.1 :1	1 :1.5 :1
Sintering temperature (°C)	1250, 1275 1300	1250, 1275 1300
Rate (°C/min)	150	150
Holding time (min)	15	15
Pressure (kN)	10	10

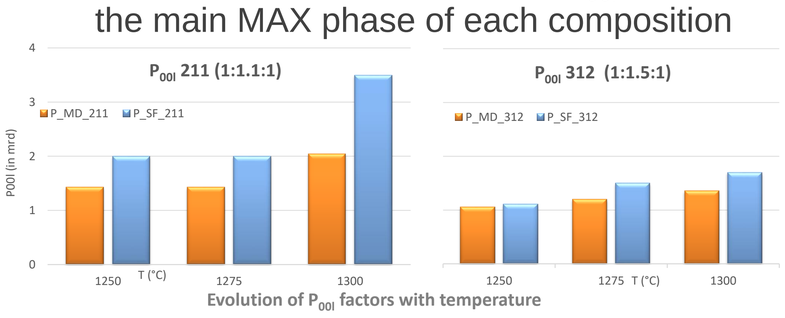
The excess Al aiming at compensating possible mass loss of this low melting element (T= 660°C) during sintering at high temperature.

Results

XRD patterns obtained for TiC:Al:Ti = 1:1.1:1 samples

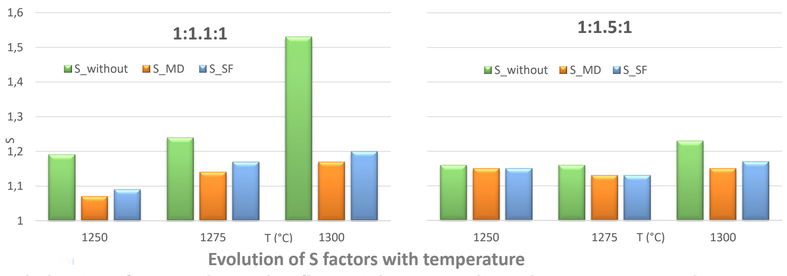


- **Texture analysis:** Evaluation of P_{00l} factor for the main MAX phase of each composition



∞ Relatively weak (00l) P.O of crystallites
∞ Slightly higher orientation for 1:1.1:1 than for 1:1.5:1 samples
∞ SF overestimate the P_{00l} parameter with respect to MD model

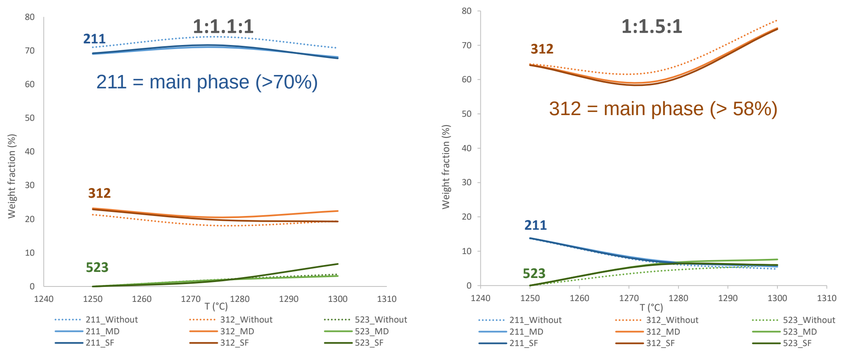
- **Quality refinement:** Evaluation of S factor



∞ High S values when (00l) P.O is not taken into account for 1:1:1
∞ Global good refinement when S is taken into account (S<1.2)
∞ MD gives slightly better refinement than SF

- **Quantitative analysis:** Weight fractions

Main phases: 211, 312 and 523 MAX phases

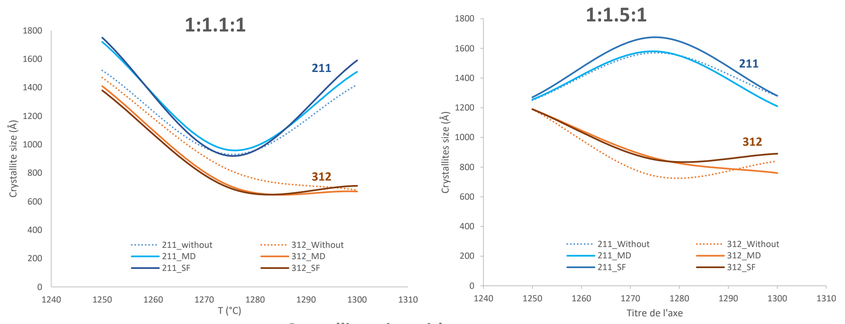


Weight fractions with temperature

Secondary phases: TiC ($0.7 \leq \%TiC \leq 1.4$) and $Al_{11}Ti_5$ ($5 \leq \%Al_{11}Ti_5 \leq 27$) are the main impurities

∞ SF and MD give practically the same results
∞ Slight gap (≤ 4%) when (00l) P.O is not considered

- **Microstructure analysis:** Crystallites size for the 211 and 312 MAX phases

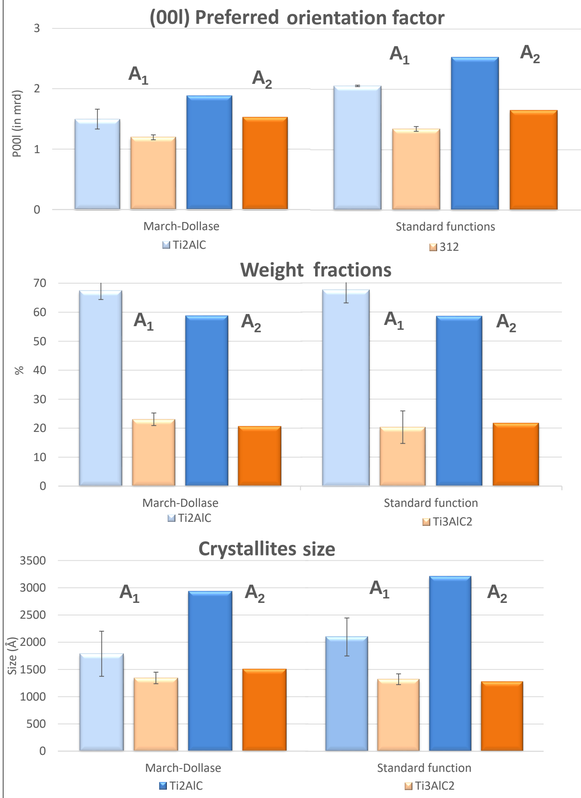


Crystallites size with temperature

∞ Crystallites size: $120 \leq 211 \leq 180$ (nm) and $70 \leq 312 \leq 140$ (nm)
∞ Gaps between SF and MD results higher than those obtained for the weight fractions
∞ More significant gaps when (00l) P.O is not taken into account for the 312 phase

Repeatability (standard deviation evaluation) and Reproducibility (comparison between A_1 and A_2):

case of 1:1.1:1 composition/1250°C



∞ Good Repeatability
∞ Weak reproducibility
∞ ± Good Repeatability
∞ ± Good reproducibility
∞ ± Good Repeatability
∞ Weak reproducibility

A_1: series of 3 calculations using the same XRD experimental pattern (means values of parameters are reported)

A_2: just 1 calculation applied to a different XRD experimental pattern

Conclusion

- ✓ Do not take into account (00l) P.O phenomena reduces the quality of refinement
- ✓ (00l) P.O phenomena affect more crystallites size calculations than weight fractions
- ✓ MD and SF models give slight different results
- ✓ Calculations of crystallites size are weakly reproducible

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[1]: W. Barsoum *et al.*:Annu. Rev. Mater. Res. 2011. 41:195–227