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Interfacial phenomena in carbon fibre reinforced magnesium alloys processed by squeeze casting and thixomolding

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Topics

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   II. Casting techniques
   III. Wetting low energy surfaces
2. **Experimentation – Results – Discussion**
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   II. Sol/Gel & $Al(H_2PO_4)_3$ coating on C fibres
   III. Mechanical properties
3. **Conclusion**
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Introduction to Mg/C MMC

I. General expected properties (law of mixture)

UD case : 50/50 HR/AZ91D vs 50/50 HR/Epoxy

T300 Fibres: UTS: 3500 MPa; E: 230/15 GPa; δ: 1.8
AZ91D Mg alloy: UTS: 140 MPa; YS: 90 MPa; ε_r: 5% E: 45 GPa: δ: 1.75
Epoxy resin: UTS: 40 MPa; E: 2.5 GPa; δ: 1.5

Orientation	Ultimate Strength (MPa)		Young's Modulus (GPa)	
	MMC	PMC	MMC	PMC
0°	1806	1752	137	116
45°	-	-	**84***	**15***
90°**	34	34	**23**	**4**

*Approximated values
** 90° assumes full F/M adhesion

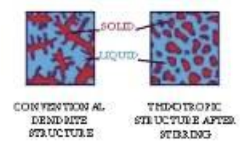
	MMC	PMC
Anisotropy index (E_0/E_{90})	**6**	**29**
Specific E 0/90°	77/**13**	70/**2.5**

Introduction to Mg/C MMC

II. Casting techniques

a. Thixomolding

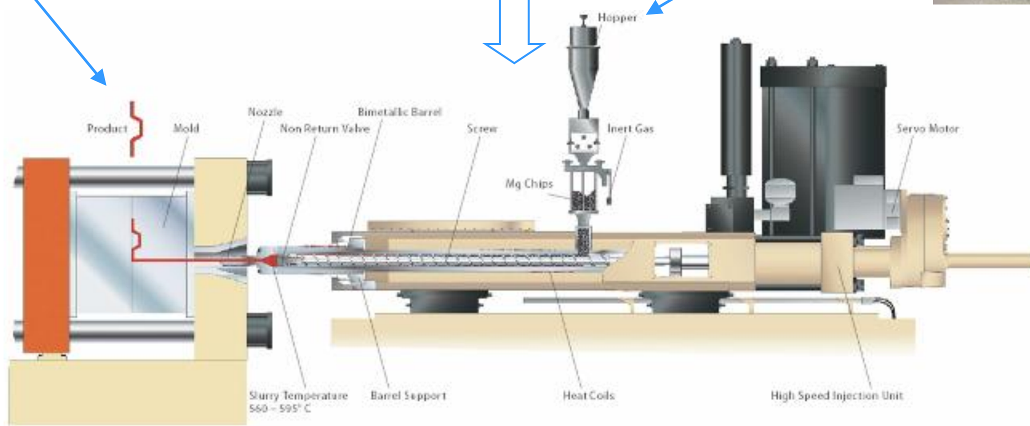
2 Mg partial melting



1 Mg feeding

3 Injection

4 ejection



5 cooling

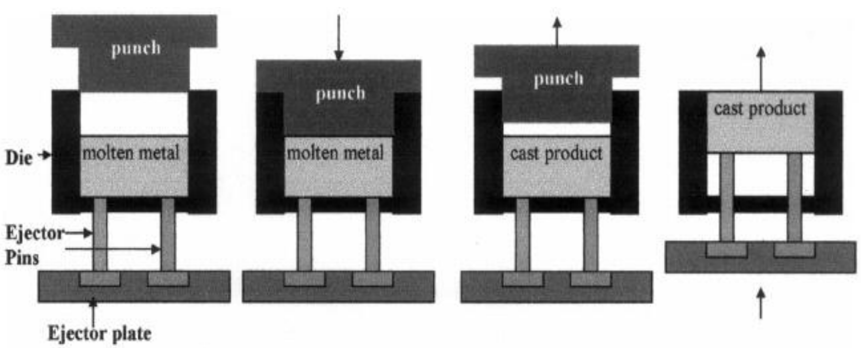
6 Part finition

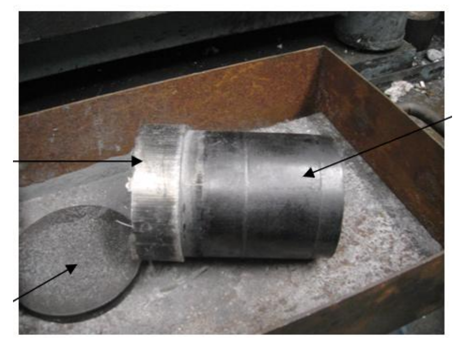
Courtesy Sirris

Introduction to Mg/C MMC

II. Casting techniques

b. Squeeze Casting





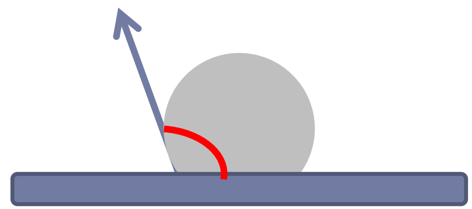
Courtesy UCL

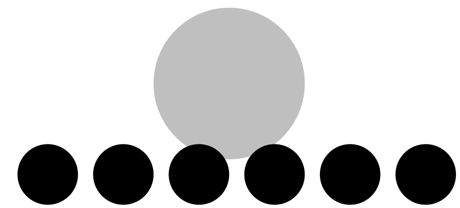
Introduction to Mg/C MMC

III. Wetting low energy surfaces

$$\gamma_{SV} = \gamma_{SL} + \gamma_{LV}\, cos\theta$$

< >> θ > 90°





$$\gamma_{SV} = \gamma_{SL} + \gamma_{LV}\, cos\theta$$

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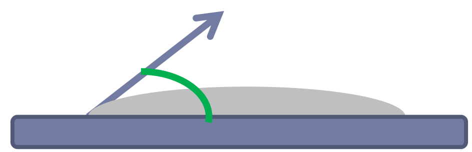
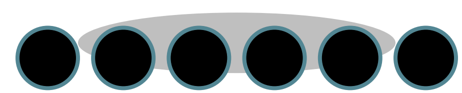




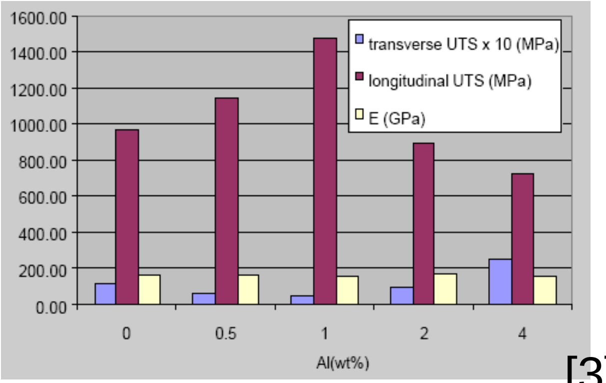
T (°C)	γ_{LV}[1] (Nm^{-1})
650	0.570
700	0.542
750	0.526

[1]For molten Mg, values are lowered with +Ca, Li, Sr, Sb, Pb, Ba & Bi
Source: International Magnesium Association

$$\gamma_{LV,Mg} \cong 0.721 - 0.149\ 10^{-3} T(K) [Nm^{-1}]$$

Introduction to Mg/C MMC

III. Wetting low energy surfaces



[3]

$$Mg + 2\,\underline{Al} + 2\,C \rightarrow Al_2MgC_2$$

$$\cos\theta = \cos\theta_0 + \frac{\gamma_{SL} - \gamma_{SL,0} - \Delta G}{\gamma_{LV}}$$ [10]

$$Mg\,(l) + SiO_2 \rightarrow MgO + \underline{Si}$$ [5]

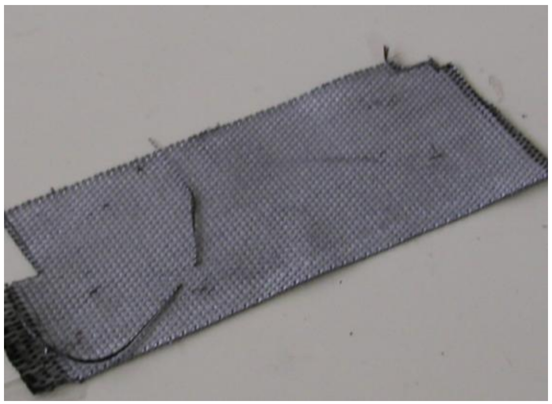
e.g. : Sol/Gel Silica Coating on C fibres

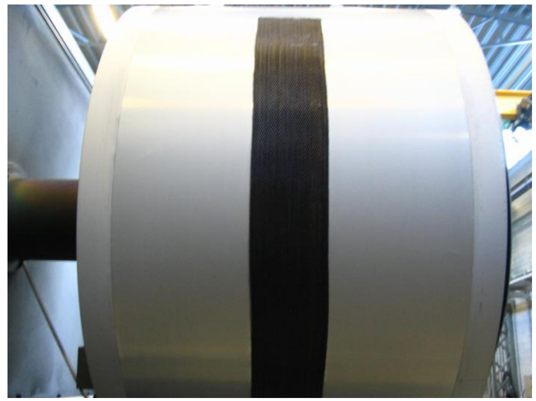
[2]Addition of reactive elements in the alloy:
Al, Zr, Ti

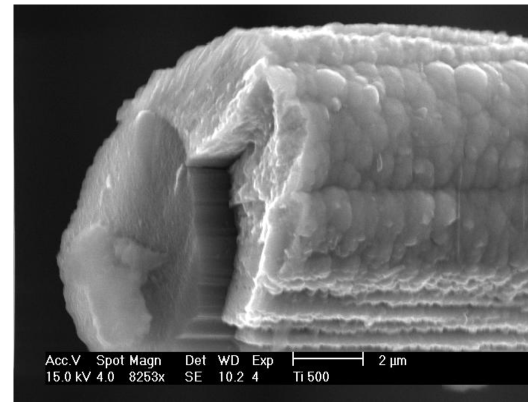
Capillarity effect and adhesion energy are related to contact angles
→ Coat the fibres with reactive oxides/metals
→ Overheat the liquid alloy
→ Add some alloying elements[1,2]

Experimentation – Results - Discussion

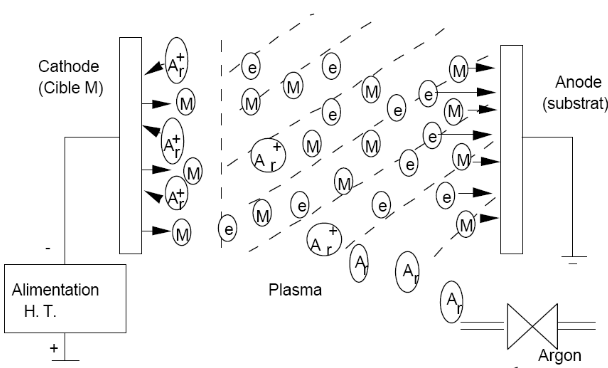
I. Ti/Zr/Mg sputtering coating on C fibres







Ti



Zr

T300 unsized carbon fibres

Flow of Ar+ ions erodes a metallic target

No metal ions

Thin (5-10 µm) surface coating

Experimentation – Results - Discussion

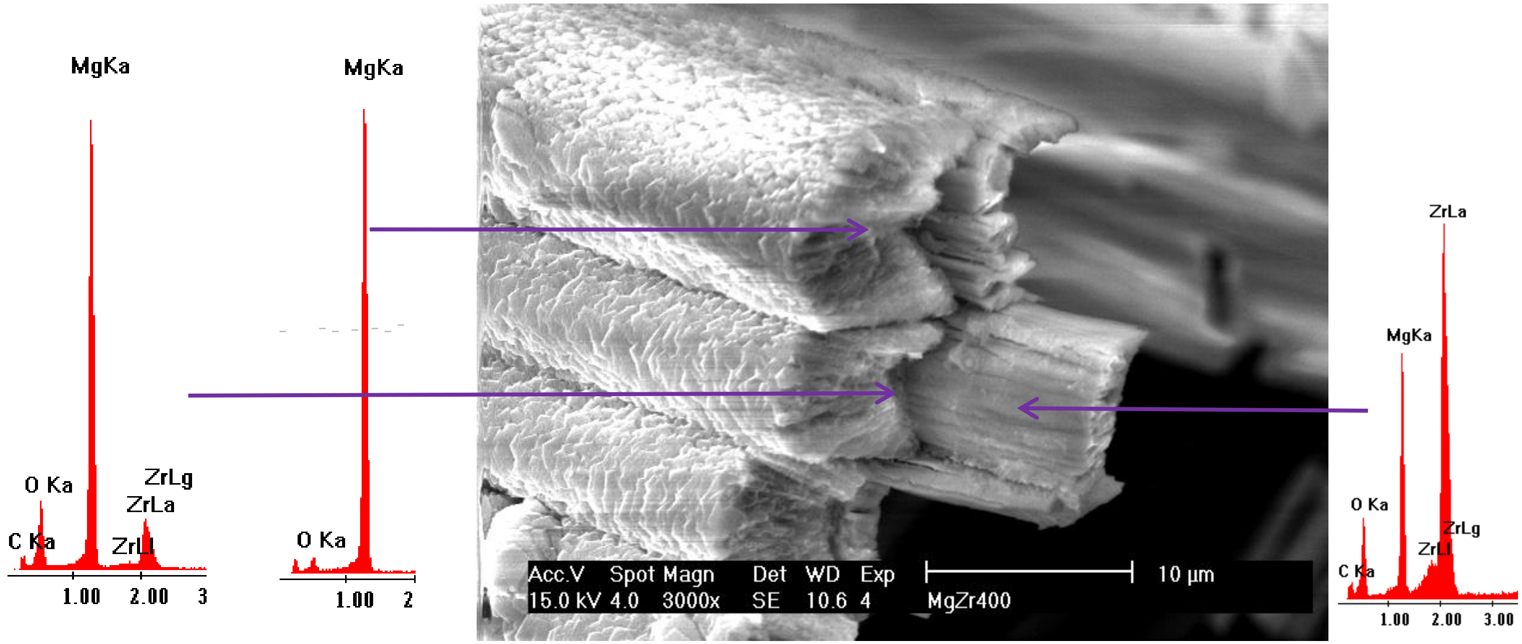
I. **Ti/Zr/Mg sputtering coating on C fibres**

- Experimental
- Coating:
  - Zr (5 µm) + Mg (10 µm)
  - Ti (5 µm) + Mg (10 µm)
  - Ti (5 µm)
  - Zr (5 µm)
- Heat Treatment (3h, Ar) :
  - From 250 °C up to 500 °C
    - $Ti + x\,C \rightarrow TiC_x$
    - 1) $Zr \rightarrow ZrC$; 2) $(1-x)\,Zr + x\,Mg + C \rightarrow Zr_{(1-x)}Mg_xC$ [12]

Experimentation – Results - Discussion

I. **Ti/Zr/Mg sputtering coating on C fibres**

- <u>Results</u>
- Interaction bw. Zr (5 µm) and Mg (10 µm) + 400 °C HT



Experimentation – Results - Discussion

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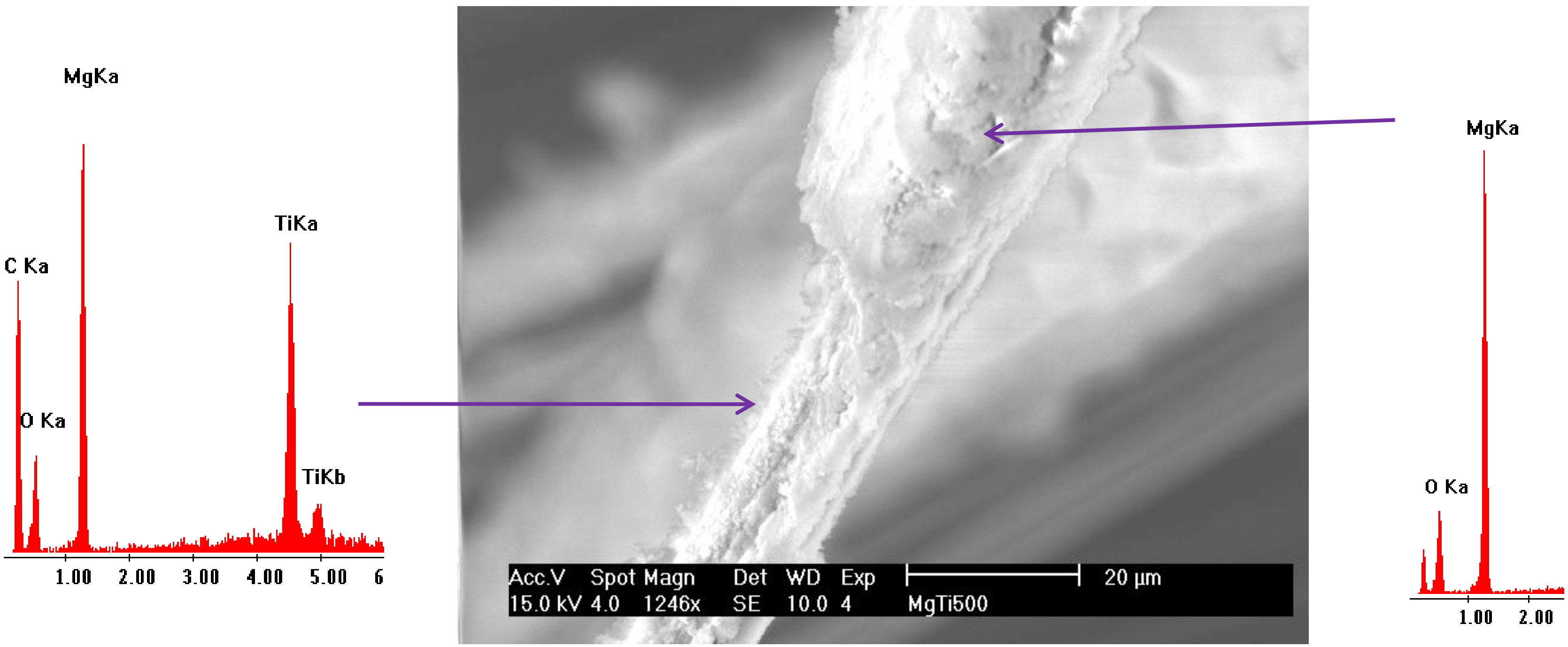
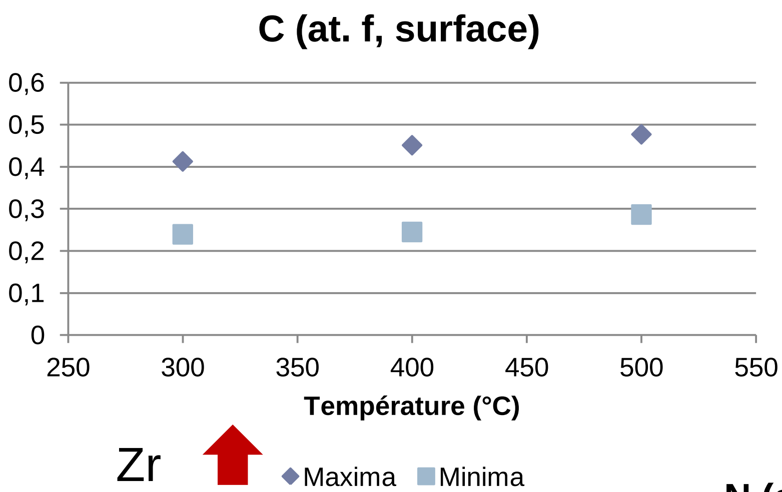
- Interaction bw. Ti (5 µm) and Mg (10 µm) + 400 °C HT



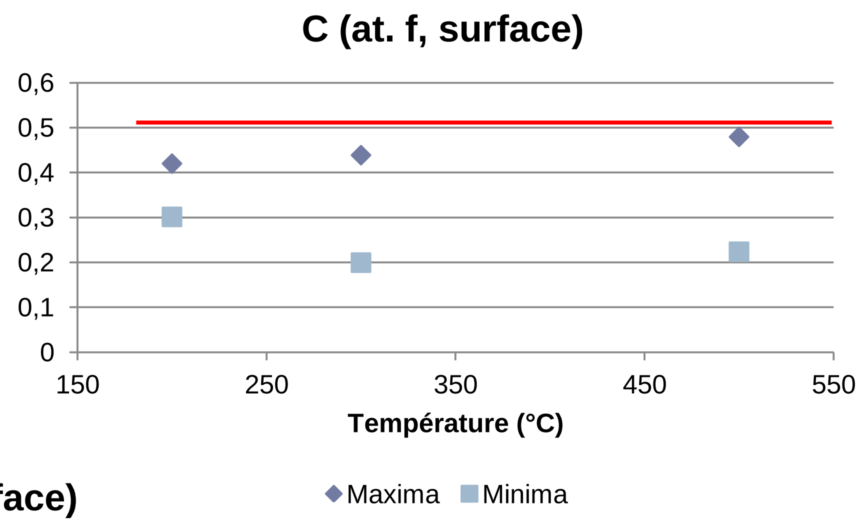
Experimentation – Results - Discussion

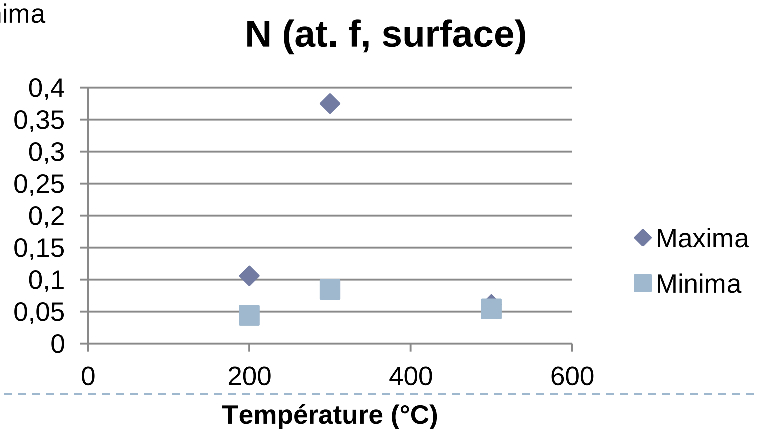
I. Ti/Zr/Mg sputtering coating on C fibres

- <u>Results: </u>Diffusion of C through Zr and Ti layers



Zr





Ti / TiCx

Experimentation – Results - Discussion

II. **Sol/Gel & $Al(H_2PO_4)_3$ coating on C fibres**

- Silver oxide modified silica sol/gel [5]

  TEOS (+ AgNO3)

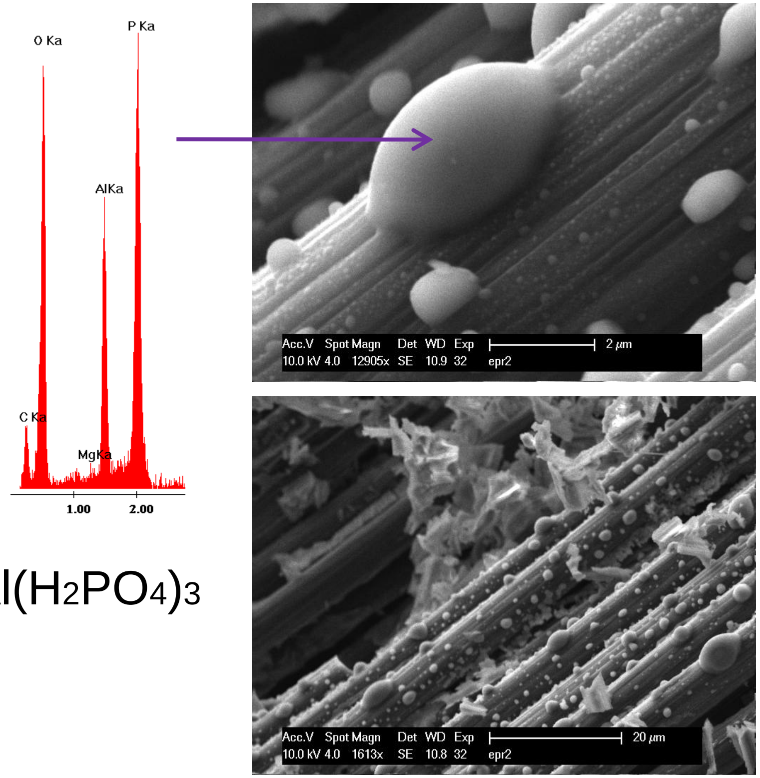
  - $Si(C_2H_5OH)_4 + H_2O \rightarrow Si(OH)_4 + ROH$
  - $Si(OH)_4 \rightarrow SiO_2 + H_2O$ (80 °C)

- Aluminium dihydrogenophosphate
  - Coating (H_2O, H_3PO_4, $Al(H_2PO_4)_3$)
  - 2 heating steps :
    - 100 °C (demoisturization)
    - 1200 °C ($AlPO_4$)

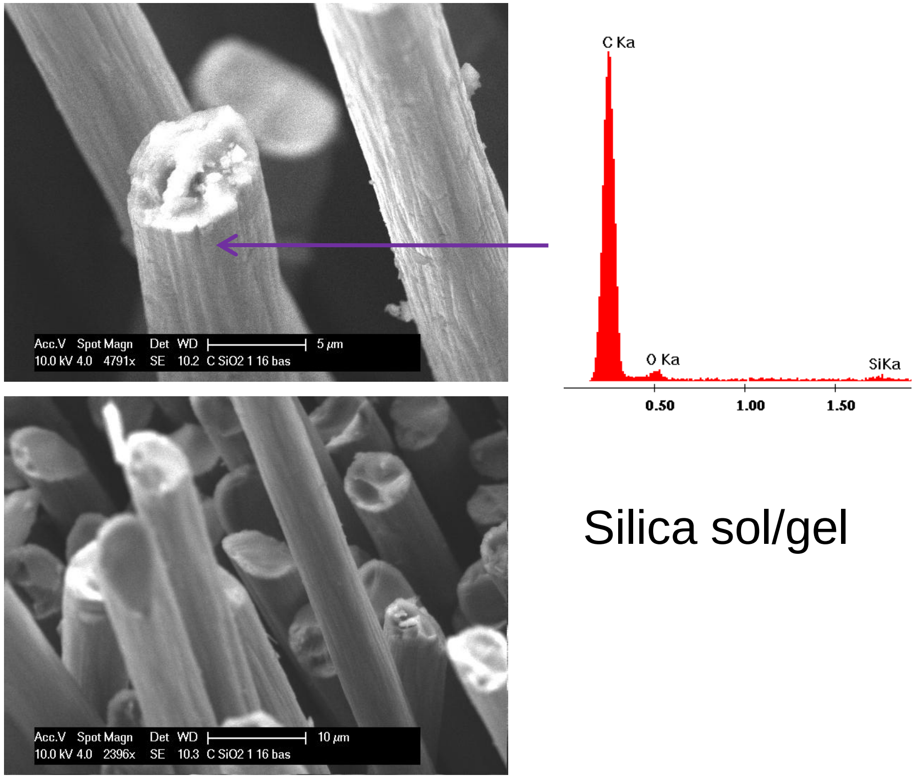
Experimentation – Results - Discussion

II. Sol/Gel & $AlPO_4$ coating on C fibres

- <u>Results</u>
- Caracterisation



$Al(H_2PO_4)_3$

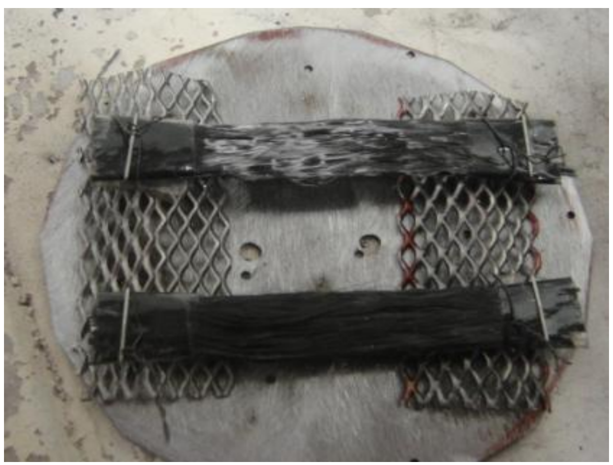


Silica sol/gel

Experimentation – Results - Discussion

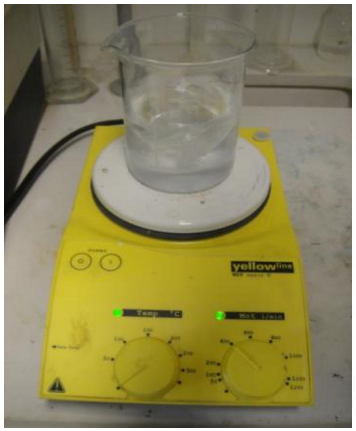
III. Mechanical properties

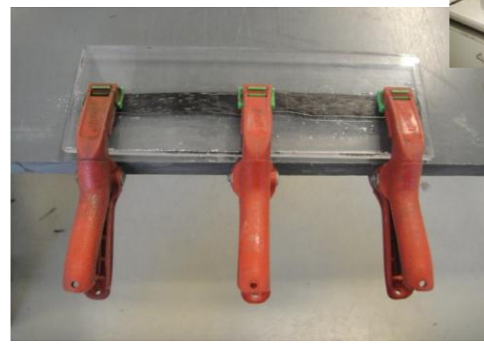
- Preparation of UD preforms with silica sol/gel or $Al(H_2PO_4)_3$ coating
- Squeeze casting (AZ91, 20 MPa, 750 °C, 200 °C preform preheat)
- Sample machining
- Tensile test (ISO527) for the measure of UTS and ~E



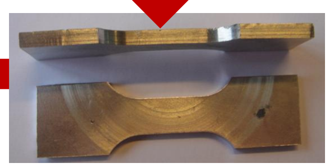
Experimentation – Results - Discussion

III. Mechanical properties








Experimentation – Results - Discussion

III. **Mechanical properties***

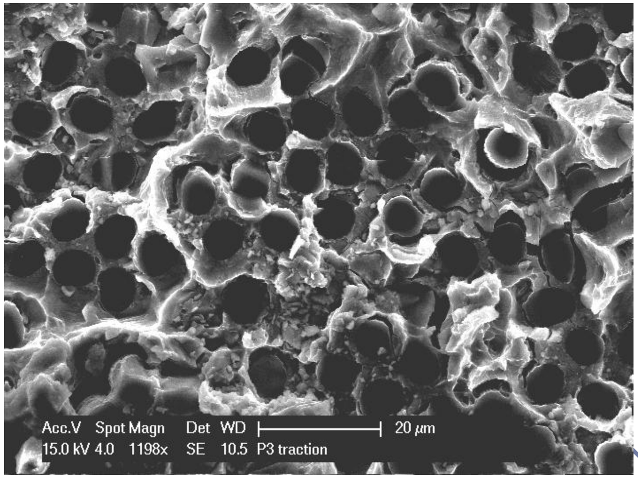
- Min. 5 samples/treatment (unless ( ))

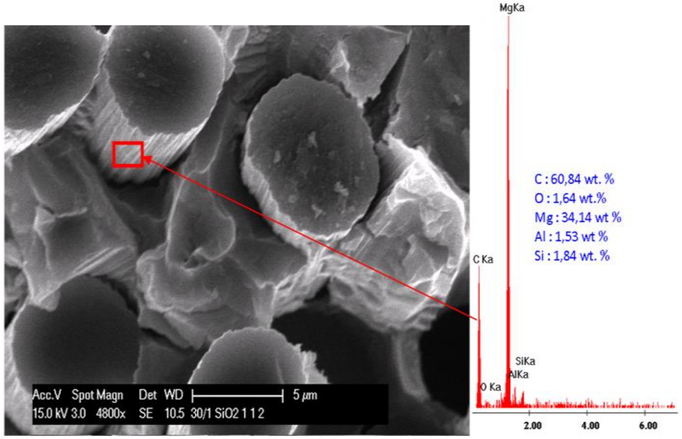
Treatment	E (GPa)	UTS (MPa)	Vol. % fibres
-	21	140	0 %
9 Al/P BD	14	70	3.5 %
9 Al/P UD	27	135	3.5 %
30 SiO_2 1:1:2 UD	65	150	11 %
80 SiO_2 1:1:2 UD	(16)**	112	30 %
80 SiO_2/Ag_2O 1:1:2:0.3 UD	(96)***	(70)***	30 %

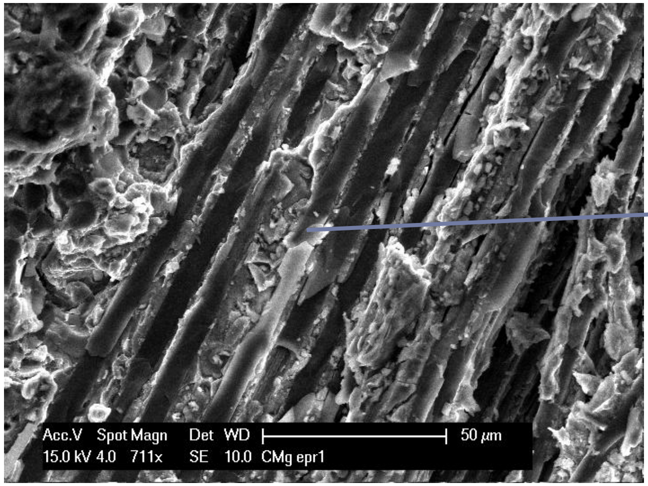
* With respect to ISO527 standard
** Low impregnation
*** Samples were not broken

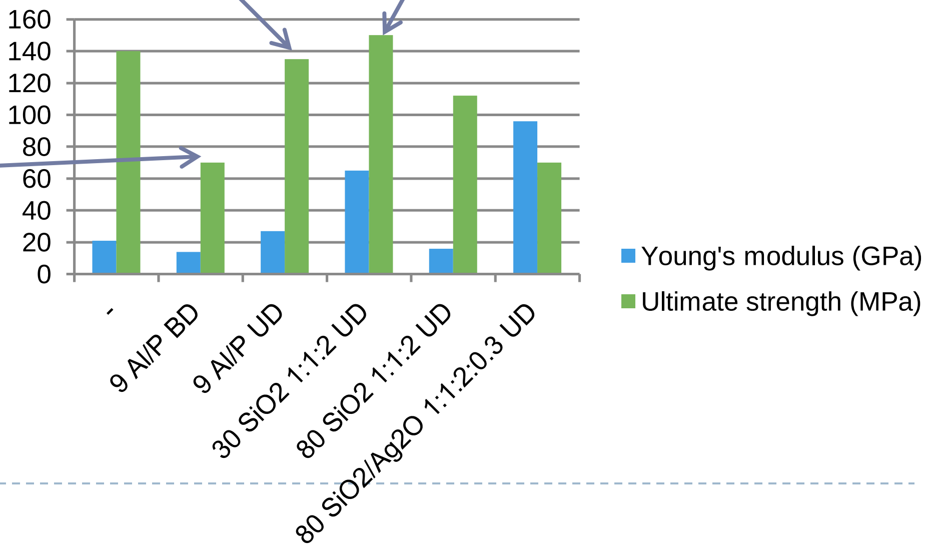
Underestimation of E (ε=0.05-0.25)
E rises with V_f
Ag_2O is helpful for good infiltration

Experimentation – Results - Discussion

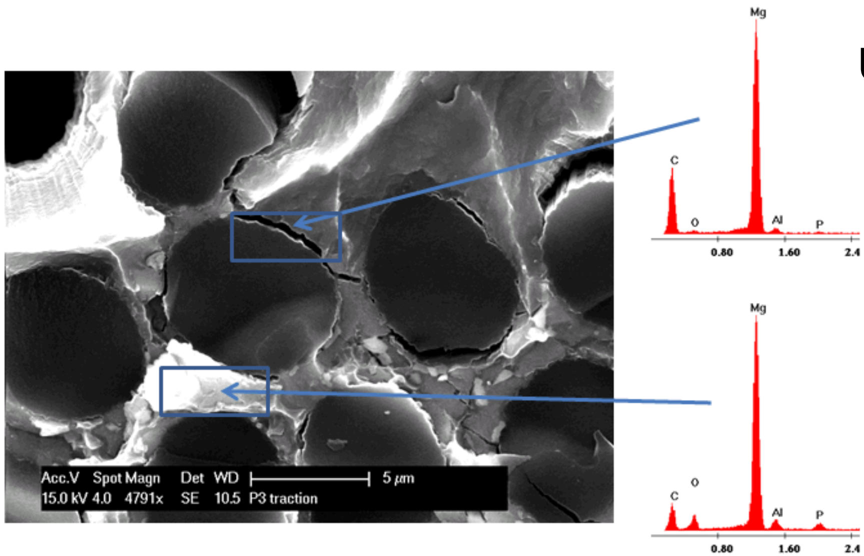








Experimentation – Results - Discussion



Uncoated

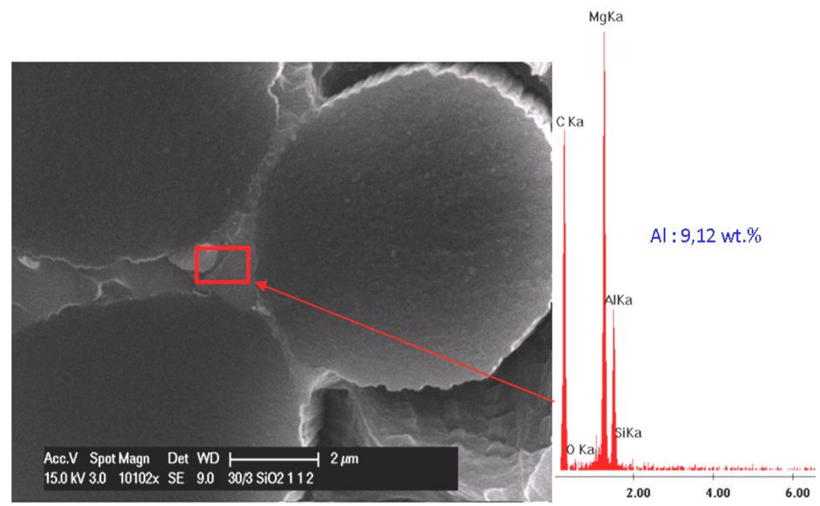
0.15 wt%P

Coated

1.35 wt%P

AlP treatment increases cohesion
Uncoated areas are critical

Partial reaction (too low infiltration T)
Decohesion of fibres



Conclusion

- **We plan to manufacture C/Mg MMC with <u>high specific mechanical properties</u>. Our work is not finished.**

- **Litterature and experiments say <u>wettability</u>, fibre-matrix <u>adhesion</u> and <u>reactivity</u> are linked. When the fibres are really passivated high reactivity does not damage the fibres but promotes enhanced infiltration and mechanical properties.**

Conclusion

- **As the affinity of molten magnesium for carbon is quite low we tried to coat the carbon fibres with some species to improve fibre/matrix adhesion in the MMC.**

- **Metal coating (Ti or Zr): We have shown carbon can diffuse through the coatings to form more compliant species such as TiC_x (x<1) or $Zr_{1-x}Mg_xC$. However the presence of nitrogen and oxygen could strongly limits the reactivity of the coating for short contact times with Mg.**

Conclusion

- **Phosphate coating: as it is not uniform alloying elements such as Al can react (and damage the fibres) or no reaction could occur. In both cases the <u>mechanically weak area</u> is the <u>uncoated zone</u>.**
- **Silica Sol/gel coating: the carbon fibres are <u>totally passivated</u> and the <u>best fibre/matrix adhesion</u> is related to fibre/coating <u>reaction areas</u>. AZ91 seems to be compliant with this treatment. <u>Addition of Ag</u> in sol/gel could help for infiltration especially when <u>V_f is high</u>.**

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