INFLUENCE OF REACTIVE ALLOYING ELEMENTS ON THE MECHANICAL PROPERTIES OF CARBON/MAGNESIUM COMPOSITES

Sarala Djanarthany[1], Marie-Hélène Vidal-Sétif[2], Roger Valle[2], Jean-Louis Raviart[3], Maurice Rabinovitch[2]

[1]*Université de Marne-la-Vallée, IFI, 2 rue de la Butte Verte, 93166 Noisy-le-grand, France*
[2]*ONERA/DMSC,* [3]*ONERA/DMMP, BP72, 92322 Châtillon Cedex, France*

SUMMARY : Magnesium matrices containing carbon reactive elements are tested to improve the fibre/matrix bonding in C/Mg composites. Unidirectional composites reinforced with K139 fibres are fabricated by liquid infiltration of RZ5 and WE43 magnesium alloys under moderate pressure (25 MPa). As-cast and heat-treated composites are tensile tested in longitudinal and transverse directions. The interface microstructure is revealed through scanning and transmission electron microscope observations: a good wetting is observed between fibre and matrix. In both as-cast composites, second phases, Zn rich or rare earth rich, resulting from solidification are strongly concentrated at some fibre/matrix interfaces. These phases are not reaction products. However in both composites, Zr has reacted and a continuous layer of ZrC is observed at some interfaces but not in the whole composite. The presence of these numerous phases lying along the fibre/matrix interface, although being partly dissolved during the heat treatment, degrades the composite mechanical properties. Process improvements are suggested.

INTRODUCTION

Carbon-magnesium composites reinforced with high modulus K139 fibres exhibit interesting properties such as specific stiffness, high thermal conductivity and low coefficient of thermal expansion, particularly useful for space applications such as supports of satellite antennae which require high dimensional stability. Moreover, these composites can be processed through casting routes, allowing the fabrication of net shape components at a relatively low-cost. The major problem with these materials is the weak fibre-matrix bonding that results from a lack of chemical reaction between magnesium and carbon. Although, in this case, cracks that appear in the weakest fibres can be easily deflected along the interface, thus cancelling the stress concentration effect on the adjacent fibres, the load transfer from matrix to fibre fragments is not much efficient and the mechanical strength of the composite is not optimum. It results that unidirectional C/Mg composites (50% volume fraction) can exhibit a longitudinal ultimate tensile strength as high as 1400 MPa but poor transverse characteristics (ultimate tensile strength between 5 to 30 MPa) [1].

The first approach used to improve the interfacial bonding, was to investigate the influence of different fibre coatings on the fibre-matrix interface properties and transverse tensile properties of the composites [2]. Due to the necessity of using a CVD reactor and to the difficulty of coating continuously and uniformly fibre bundles, the number of available coatings was very limited [3-5]. Consequently, only few coatings such as SiC, TiC or B_4C have been tested and have not demonstrated an effective increase in the interfacial bonding. The present investigation aims at attempting to improve the interfacial bonding by using matrices containing reactive alloying elements in order to promote a chemical reaction with the carbon fibres. Moreover, the tailoring of process parameters such as infiltration

temperature and contact time between fibres and liquid metal would permit to control the chemical reaction and thus the interfacial bonding.
In this paper, two magnesium based matrices containing rare-earth alloying elements have been considered. Both matrices contain at least one element reactive with carbon : zirconium for RZ5 and zirconium and rare earth elements (RE) for WE43. This investigation is focused on the microstructural study of the two composites RZ5/K139 and WE43/K139 in order to correlate the tensile behaviour of these systems to the presence of interfacial compounds formed either from a chemical reaction between the carbon fibre and the alloying elements or during the alloy solidification or heat treatment.

MATERIALS AND EXPERIMENTAL METHODS

Composite constituents

The composition (wt %) of the two industrial alloys RZ5 and WE43 (Magnesium Elektron, UK) is given in Table 1. RZ5 and WE43 alloys are respectively T5 and T6 heat-treated .

RZ5	Zn	Zr	Ce	La	Other rare earth elements
composition	4.2	0.73	0.78	0.32	0.7

WE43	Y	Nd	Gd	Dy	Er	Yb	Ce	Sm	Zr
composition	3.8	2.2	0.16	0.25	0.12	0.07	0.05	0.05	0.49

Table 1 : Composition of the RZ5 and WE43 alloys.

The K139 Pitch based fibre (Mitsubishi, Japan) has been selected for its high modulus (760 GPa) and strength (3700 MPa). These fibres (1000 filaments bundles) are 5-7 μm in diameter and 2.15 in density.

Composite processing

Metal matrix composite plates (130x70x1 mm in size) with unidirectional reinforcement have been fabricated at ONERA by liquid infiltration of carbon fibre preforms under moderate pressure (25 MPa). The main characteristic of this original process described in [1, 6] is that it is isothermal in nature (the mould, the fibre preform and the liquid metal are all at the same temperature). The pressure-temperature-time cycle is adequately chosen and is computer monitored. It allows to optimise the fabrication cycle and improve its reproducibility. Two processing conditions have been used : a "soft" one ($T_{infiltration}$ = 645°C, $t_{contact}$ = 20 to 30 min) and a "hard" one ($T_{infiltration}$ = 670°C, $t_{contact}$ = 70 min) in order to enhance a potential chemical reaction .
A T5 heat treatment is performed on the RZ5/K139 composite (2 hours at 330°C followed by 16 hours ageing at 200°C). As regards the WE43/K139 composite, the following T6 heat treatment is performed : solution treatment of 8 hours at 525°C followed by water quenching and 16 hours ageing at 250°C.

Composite tensile tests

Longitudinal and transverse strengths have been determined from tensile tests performed on 80x8x1 mm specimens. The tests were conducted on a Roell-Korthaus testing machine (50 kN static load capacity). Fibre volume fractions were determined by matrix dissolution.

Microstructural observations

The preparation of samples for metallography was conducted using methods such as mechanical cutting, grinding and polishing. Due to magnesium reactivity with water, alcohol based coolant has been used during the mechanical preparation. Transparent specimens for transmission electron microscopy (TEM) studies have been prepared by mechanical polishing and ion milling on both sides at an angle of 12° and an energy of 6 kV using a liquid nitrogen cold stage. To prevent any contamination, specimens are stored in a desiccator under vacuum. The thin foils are examined in the CM20 Philips transmission electron microscope and analyses were performed using energy dispersive X-ray spectroscopy (EDS system from Tracor).

PROPERTIES AND CHARACTERISTICS OF RZ5, WE43 ALLOYS AND K139 FIBRES

Magnesium is rarely used for engineering applications in its unalloyed form and a variety of elements are added to improve its properties. Mg-Zr alloys are not strong enough for commercial applications and the addition of other alloying elements is necessary. Among the commercial alloys developed from Mg-Zr alloys, the magnesium-rare earth-zinc-zirconium alloys of RZ5 type and magnesium-yttrium-rare earth-zirconium alloys such as WE43 are well-known for their high corrosion resistance. Moreover, with such alloys, it is possible to obtain a wide range of mechanical properties by combining alloy compositions and heat treatments [7, 8].
Zirconium is added to refine the grain size and to increase the strength levels owing to the interference hardening mechanism [9]. The presence of rare earth elements improves the corrosion resistance as well as the behaviour in moulding and casting. However, both zinc and rare earth additions have to be limited as they weaken the alloy by forming brittle precipitates at the grain boundaries [7]. The association of both Y and Nd in the WE43 alloy allows to obtain the optimum mechanical properties and an appropriate toughness [10].
RZ5 and WE43 alloys are generally heat-treated in order to optimise their mechanical properties (table 2).

Alloy	0.2 % proof stress (MPa)	Tensile strength (MPa)	Elongation (%)	Characteristics
RZ5	175	180	2	Sand castings, good room temperature strength, improved castability
WE43	187	263	4	High corrosion resistance, Max strength at ambient temperature, Short term high strength to 300 °C

Table 2 : Tensile properties of the WE43 and RZ5 alloys [7-10].

In Mg-RE systems, precipitation processes are frequently complex and are not completely understood [7]. As regards the RZ5 alloy, an independent formation of Mg-Zn precipitates can occur although part of the zinc is associated with RE elements. The RZ5 alloy thus behaves both as a Mg-RE(Ce) alloy and a Mg-Zn alloy. In Mg-RE(Ce) type alloys, hardening is associated with the ageing sequence $Mg_{SSSS} \Rightarrow \beta'' \Rightarrow \beta' \Rightarrow \beta$, the equilibrium precipitate β being described as $Mg_{12}Ce$ or $Mg_{27}Ce_2$. Here, the role of zirconium is limited to grain refinement. As regards the WE43 alloy, hardening is associated with the ageing sequence

$Mg_{SSSS} \Rightarrow \beta''(DO_{19}) \Rightarrow \beta'(bco) \Rightarrow \beta(fcc)$ described in the literature concerning Mg-Y-lanthanides [11, 12].

Concerning the K139 fibres, the subbuilding units of these carbon fibres are graphite crystals which are more or less preferentially arranged about the longitudinal axis of the fibre : (0001) basal planes of the graphite crystallites parallel to the fibre axis. The bonding between the basal planes is of the weak Van der Waals type. This anisotropy of structure leads to the anisotropy of the mechanical properties in particular the Young's modulus. In the graphite single crystal, the Young's modulus in the basal plane is 1000 GPa whereas in the normal direction it is about 30 GPa [13]. In the case of the K139 fibre, it leads to a longitudinal modulus of 773 GPa and to a much lower transverse modulus. High modulus Pitch fibres are less reactive than high resistance PAN fibres [14, 15]. Carbon atoms inside the fibre subbuildings are weakly reactive since they are sp^2 hybrided and bound through strong covalent bonds to three neighbour carbon atoms. However, the atoms on the edge of the subbuilding units or near a stacking fault in the hexagonal lattice have only two nearest neighbours and present a free valence. They thus constitute reactive sites [16, 17], which are less numerous in the less distorted structure of the Pitch fibre. Due to its microstructure, the K139 fibre is thus inherently weak in the transverse direction and difficult to wet by liquid metals [18].

RESULTS

Matrix microstructure

The RZ5 alloy microstructure, as revealed through optical microscope observations and SEM analysis, is formed of equiaxed grains about 50-100 μm in size, the centre of each grain being zirconium rich. Two types of phases are observed in TEM : one is Zn rich and moreover contains Ce and La and the other is probably $Mg_{102.8}Zn_{39.60}$ with some cerium included. As regards the Mg_7Zn_3 phase identified by Lavernia [19] in the Mg-5.6Zn-0.3Zr (weight %), it is not observed in the RZ5 alloy.
Optical microscope observations and SEM analysis performed on the WE43 alloy indicate that the microstructure is also formed of equiaxed grains about 40-100 μm in size (Fig.1), with locally a coarse Nd rich intergranular precipitation and some Y-(Nd) rich cubic shaped particles about 1-3 μm in size. Outside the coarse intergranular precipitate area, grain boundaries appear as thin ribbons.

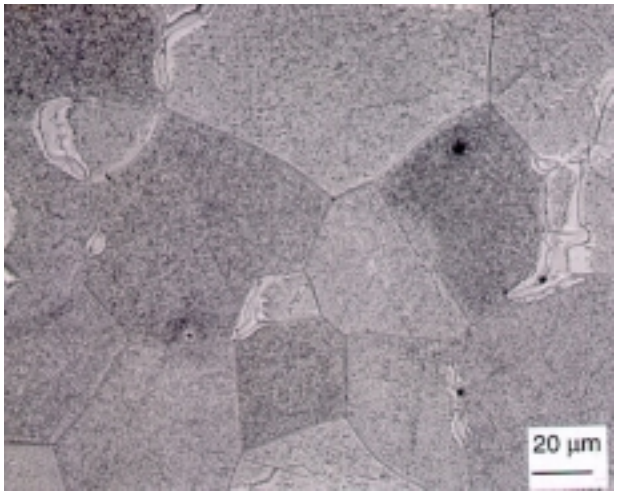


Fig.1 : WE43 T6 heat-treated isolated matrix, optical micrograph.

The TEM observations reveal the presence of the following precipitates :

- a dense precipitation of platelets within the magnesium matrix (Fig. 2a). On the matrix $[2\bar{1}\bar{1}0]$ zone axis diffraction pattern, extra spots on the <1100> row are observed corresponding to the base-centred orthorhombic β' phase of lattice parameters a = 6.4 Å, b = 22.5 Å and c = 5.2 Å, the [200] zone axis of which coincides with the matrix $[2\bar{1}\bar{1}0]$ zone axis (Fig. 2b). The precipitation of this phase, favoured by annealing at 250°C, is that observed in Mg-Y-lanthanides alloys [11, 12];
- a dense precipitation at grain boundaries identified by diffraction as the face-centred cubic β phase of lattice parameter 22.5 Å;
- coarse elongated precipitates (5-7 μm in length and 2-3 μm in width) already observed at grain boundaries and triple points at the optical microscope scale, rich in the rare earth elements Mg-Nd-Y-La or Y-Nd-Mg (Fig. 2c).
In both alloys, the presence of MgO is revealed in the diffraction patterns.

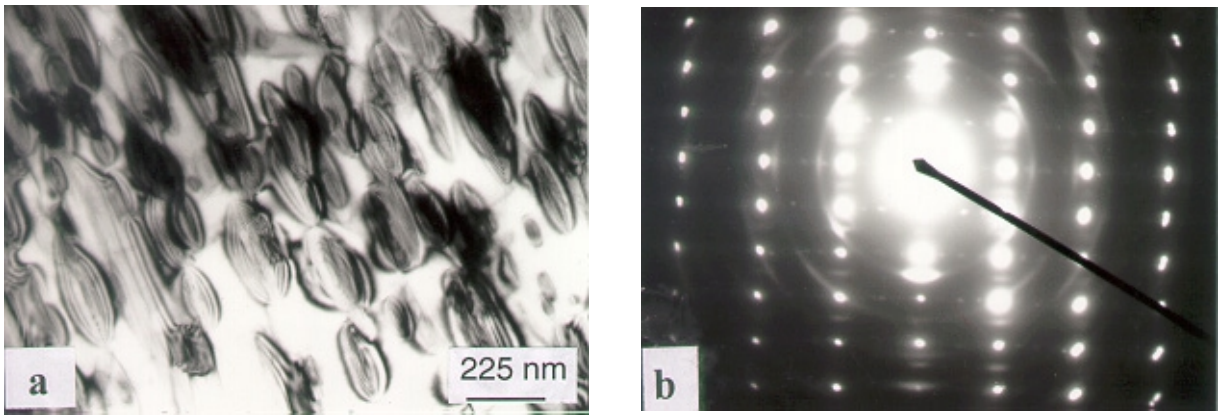


Fig. 2 : (a) Bright field TEM micrograph showing β' platelets (b) $[2\bar{1}\bar{1}0]$ zone axis diffraction pattern of the magnesium based matrix revealing the presence of extra spots on the [1100] row.

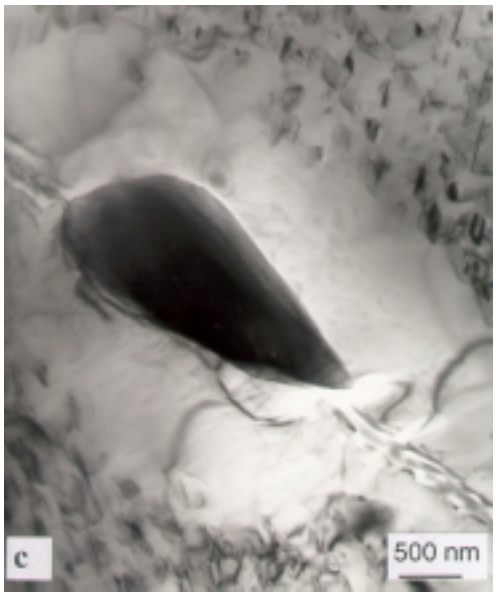


Fig. 2c : Rare earth rich phases observed at the grain boundary.

Tensile tests results and microstructure of the composites

RZ5/K139 composite

The mechanical properties of the composites fabricated in the "soft" and "hard" conditions are reported in table 3.

Processing conditions	Longitudinal Mean Rupture Strength (MPa)	Transverse Mean Rupture Strength (MPa)
Soft conditions	900	30
Soft + heat treatment	1350	8
Hard conditions	1037	14
Hard + heat treatment		15

Table 3 : Tensile properties of the RZ5/K139 composites.

SEM studies performed on the as-cast composite reveal the microstructure of the fibre/matrix interfaces : numerous Zn rich and rare earth rich phases are observed (Fig. 3).

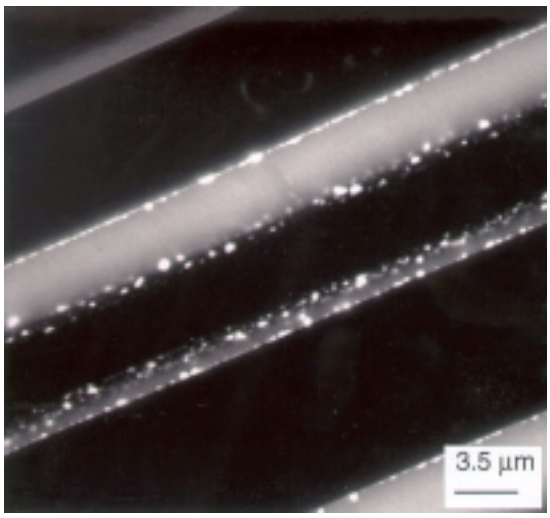


Fig. 3 : Interface microstructure in the RZ5/K139 as-cast composite ("soft" conditions).

Moreover, locally, on the edge of the composite plates, the fibres are coated with a continuous zirconium rich layer. TEM observations confirm and clarify the SEM observations: at the fibre/matrix interface, cubic shaped phases rich in zinc and rare earth elements such as Mg-Zn-(Ce-La), Mg-Zn-(Ce) and Ce-La-Zn are observed (Fig. 4a). A magnesium oxide layer is also sometimes detected. In the matrix, a fine inhomogeneous Zn rich precipitation is observed. Finally, a continuous layer of zirconium carbide is identified at some interfaces (Fig. 4b-c).

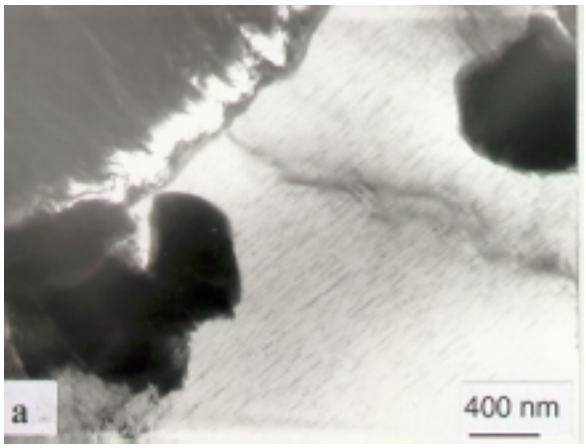


Fig. 4a : Rare earth rich phases at the RZ5/K 139 interface (TEM bright field micrograph).

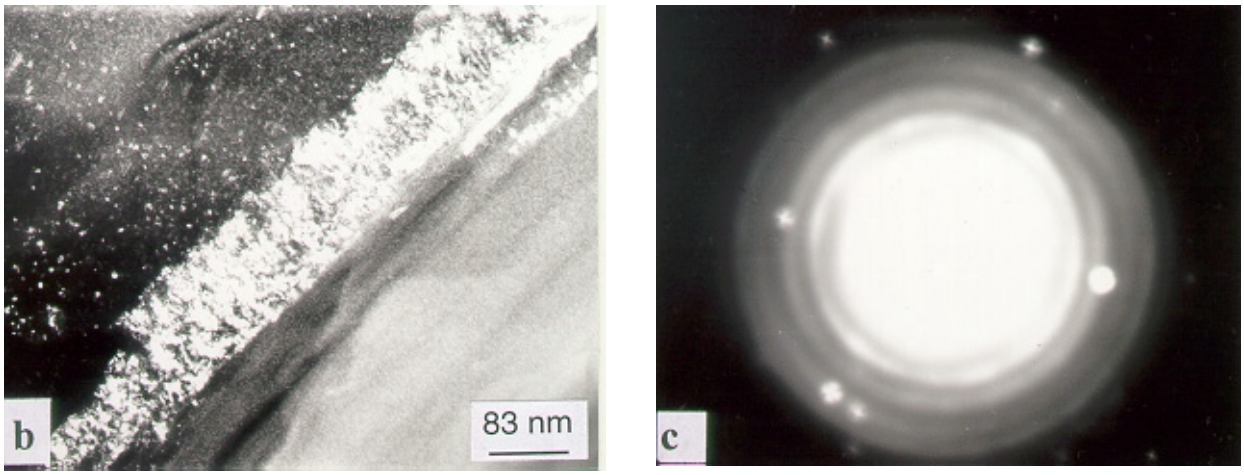


Fig. 4: (b) ZrC interfacial layer at the RZ5/K139 interface (dark field micrograph) (c) corresponding diffraction pattern.

WE43/K139

The mechanical properties of the composites are reported in table 4.

Processing conditions	Longitudinal Mean Rupture Strength (MPa)	Transverse Mean Rupture Strength (MPa)
Soft conditions	821	22
Soft + heat treatment	1124	
Hard conditions	639	15
Hard + heat treatment		8

Table 4 : Tensile properties of the WE43/K139 composites.

SEM observations performed on as-cast composites show a good wetting between fibre and matrix and numerous rare-earth rich phases at the fibre /matrix interface (Fig. 5). As in the RZ5/K139 composite, a continuous Zr rich layer is locally observed on the fibres.

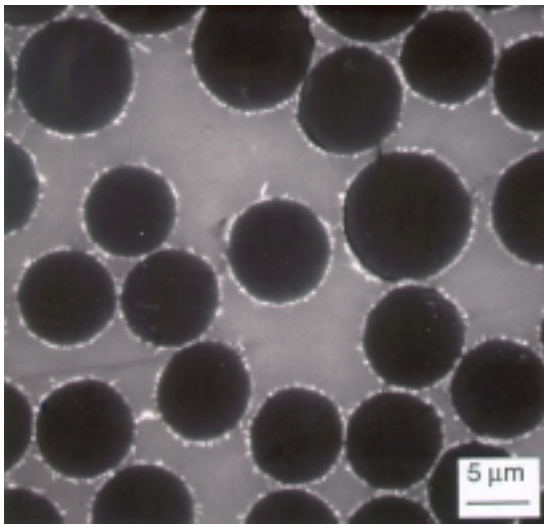
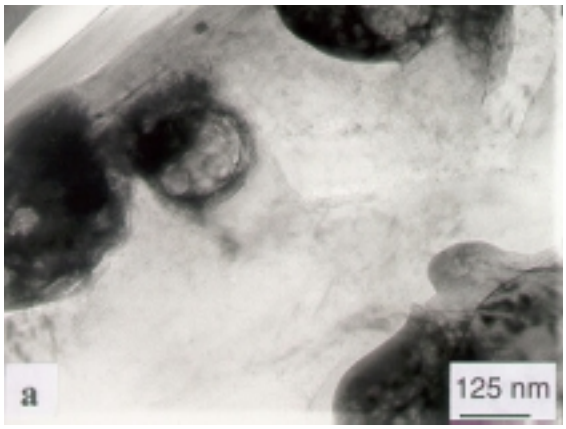


Fig. 5 : Interface microstructure in the WE43/K139 as-cast composite ("soft" conditions).

TEM observations of composite transverse sections reveal different types of round, cubic and rectangular shaped phases at the fibre-matrix interfaces :

- around some fibres, a continuous 0.45 µm thick layer, constituted of small crystalline MgO grains;
- round shaped aggregates of yttrium oxide particles Y_2O_3 (Fig. 6a-b);
- rectangular and cubic shaped phases containing rare earth elements Mg-Y-(Nd-La) and Y-Nd-(Mg-La) (Fig. 6c);
- the zirconium carbide layer is not observed, but this layer being only locally present in the composite plate, it could be absent in the observable areas of the thin foils.



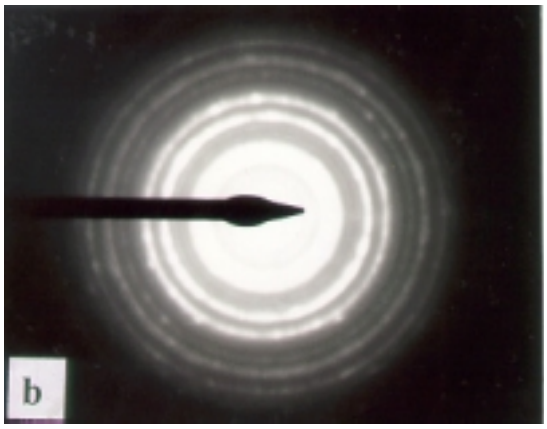


Fig.6 : (a) Y_2O_3 aggregates at the WE43/K139 interface (TEM bright field micrograph) (b) corresponding diffraction pattern.

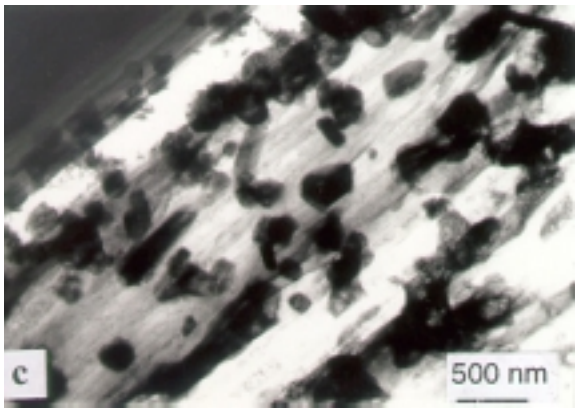


Fig 6c : Concentration of rare earth rich phases between two closely spaced fibres.

DISCUSSION AND CONCLUSIONS

WE43/K139 composite

The continuous MgO layer and the Y_2O_3 phases observed at the fibre/matrix interface certainly result from the reaction of magnesium and yttrium with oxygen trapped in the matrix or, most probably, with oxygen present in the casting equipment during processing. Indeed, though a primary vacuum is maintained in this equipment before metal infiltration, oxygen is still present. This oxide formation will be difficult to avoid even if the vacuum quality is improved since magnesium and yttrium have a high affinity towards oxygen.
In the "soft" processing conditions, the longitudinal as-cast composite tensile strength is poor and increases after heat treatment. When "hard" processing conditions are used, degradation of both longitudinal and transverse properties occurs. In the isolated WE43 matrix, the rare earth rich phases are responsible for the alloy hardening. During composite heat treatment, these phases are dissolved and further precipitate as β' or β phases. This suggests that these numerous phases lying along the fibres in the as-cast composite are responsible for the rather low mechanical properties of this composite. Reducing the amount of rare-earth elements in the matrix could possibly limit the number and size of these phases at the fibre/matrix interface and thus limit the composite degradation.

RZ5/K139 composite

In the "soft" processing conditions, the longitudinal as-cast composite tensile strength is also poor though higher than that of the WE43/K139 composite. It increases after heat treatment but the transverse properties are markedly degraded. In this alloy, the Zn rich phases are known to be responsible for hardening. In the present case, due to the rather low heat treatment temperature (330°C), rare earth rich phases are not affected by the heat treatment which only modifies the size and microstructure of the Zn rich phases. This suggests that these Zn rich phases, most probably brittle and located near the fibre/matrix interface in the as-cast composite, are responsible for the rather bad mechanical longitudinal properties of the as-cast composite. The ZrC layer identified at some F/M interfaces results from the reaction between Zr present in the RZ5 matrix and the carbon fibre. The formation of such a ZrC_x layer at the fibre/matrix interface has already been observed in C/Mg composites (matrix containing 0.15 to 0.2 at % Zr) : it is formed by chemical reaction between the carbon fibre and the liquid Mg-Zr alloy and its growth is explained according to a solid state diffusion mechanism [20]. In the present case, the ZrC layer is only locally observed in the composite i. e. present on some fibre interfaces, it is consequently difficult to evaluate its effect on the mechanical behaviour of the composite. Increasing the Zr content in the matrix and/or performing a homogenisation heat treatment of the composite could be a possibility to favour the homogeneous formation of the ZrC layer throughout the composite.

REFERENCES

1. Rabinovitch M., Daux J.-C., Raviart J.-L., Vidal-Sétif M. H., Mévrel R., Abiven H. and Peltier J.-F., in Proceedings of the. International Symposium on Advanced Materials for Lightweight Structures, ESTEC, Noordwijk, The Netherlands (1992) p. 135.

2. Allio N., ”Contribution à l’étude du comportement mécanique en sens travers de composites à matrice magnésium renforcée par fibres longues de carbone”, Thesis, Université Paris-Sud, June, (1993).

3. Vidal-Sétif M. H., Gérard J. L. in Proceedings of the 8th European Conference on Chemical Vapour Deposition, Glasgow, Scotland (edited by M. L. Hitchman and N. J. Archer), Les Editions de Physique, Les Ulis, France, J. Phys.II 1 (1991) C2-681.

4. Bertrand P., Vidal-Sétif M.H., Mevrel R., Surface and Coatings Technology 96 (1997) pp 283-292.

5. Vincent H., Bonnetot B., Bouix J., Mourichoux H. and Vincent C. in Proceedings of the 7th European Conference on Chemical Vapour Deposition, Perpignan, France (edited by M. Ducarroir, C. Bernard and L. Vandenbulcke), Les Editions de Physique, Les Ulis, France, J. Phys. supplément au n° 5 (1989) C5-249.

6. Rabinovitch M., Daux J.-C., Raviart J.-L. and Mévrel R., in Proc. 4th Eur. Conf. Comp. Mater., Stuttgart, Germany (edited by J. Füller, G. Grüninger, K. Schulte, A.R. Bunsell and A. Massiah), Elsevier Applied Science, London and New York (1990) pp 405-410.

7. Polmear I. J., Magnesium Alloys, "Light Alloys : Metallurgy of the Light Metals", ed. Edward Arnold, Londres (1987) pp 127-161.

8. King J. F., Unsworth W., "Development of Magnesium-Yttrium containing alloys", Technical Status Report, MR 10/807, MEL, Feb. 1988.

9. Forester G. S., Met. Eng. Q., 12 (1) (1972) pp 22-27.

10. Notice MEL, n°467, Elektron WE43 (1989).

11. Lorimer G. W., "Magnesium Technology", The Institute of Metals, Londres (1987) pp 47-53.

12. Sanchez C., Private communication.

13. Joucquet G., Bull. Inf. Scient. Techn., CEA, 192 (1974) p. 25.

14. Yoon H. S. and Okura A., SAMPE J. 26 (1990) p. 19.

15. Suzuki M. T, Comp. Sci. Technol. 56 (1996) p. 147.

16. Ehrburger P.,. Lahaye J., High Temp. High Press. 22 (1990) p. 309.

17. Sanchez M., "Traitements de surface de fibres de carbone ; effets sur l'adhésion carbone-époxyde", Thèse de Doctorat de l'Université Paris 6, May, (1986).

18. Guigon M., Oberlin A., Desarmot G., Fibre Science and Technology, 20 (1984) pp 177-198.

19. Lavernia E. J., Gomez E., Grant N. J., "The Structure and Properties of Mg-Al-Zr and Mg-Zn-Zr Alloys Produced by Liquid Dynamic Compaction", Materials Science and Engineering, 95 (1987) pp 225-236.

20. Bouix J., Berthet M. P., Bosselet F., Favre R., Peronnet M., Viala J. C., Vincent H., "Interface Tailoring in Carbon Fibres Reinforced Metal Matrix Composites", J. Phys. IV, C6 (1997) pp 191-205.