NANOSTRUCTURAL CHARACTERIZATION OF TERNARY CARBIDES IN CARBON-FIBRE REINFORCED Mg-Al MATRICES AND THEIR INFLUENCE ON THE COMPOSITE PROPERTIES

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SUMMARY: To enhance the interface bonding in C/Mg-Al composites via the formation of aluminium carbides, the interface reactivity has been modified by changing the aluminium content of the matrix and by using carbon fibres with different surface microstructures. The particulars of the fibre/matrix interfaces as well as their influence on the mechanical properties have been explored by investigating the metal matrix composites on different structural levels using in situ three-point bending tests as well as chemical and structural transmission electron microscope analyses. With increasing interface reactivity three characteristic failure mechanisms have been observed (single-fibre fracture, bundle fracture, and brittle fracture), which could be related to different amounts of plate-shaped carbide precipitates of varying size at the fibre/matrix interfaces of the composites. The bundle fracture at a medium reactivity provided the highest bending strength of approximately 929 MPa. Especially, the near-edge fine structures (ELNES) of electron energy-loss spectra have been analyzed to evaluate the bonding characteristics of the elements Mg, Al, and C, revealing that the precipitates at the fibre/matrix interfaces, which govern the composite properties, are not the binary carbides Al$_4$C$_3$ but ternary ones of approximate stoichiometry Al$_2$MgC$_2$.

KEYWORDS: Al$_2$MgC$_2$, Al$_4$C$_3$, carbide formation, interface reactivity, high-resolution transmission electron microscopy, electron energy-loss spectroscopy, three-point bending, microstructure/property relationship.

INTRODUCTION

Metal matrix composites (MMCs) of the system carbon-fibre/magnesium-matrix promise outstanding mechanical properties due to the high strength and the high modulus of carbon fibres and the low density of their components. As neither for a low nor for a high fibre/matrix interface strength the reinforcement will be optimum [1-3], a tailoring of the interface is necessary, including the prevention or reduction of fibre degradation.

The pure system C/Mg is chemically non-reactive, as the two binary carbides MgC$_2$ and Mg$_2$C$_3$ are known to be endothermic compounds, which start to decompose at about 500 or 650 °C, respectively [4-7]. Therefore, their formation during the MMC processing at 700 to 800 °C is very unlikely and, generally, the interface bonding is too weak. Reactive conditions can be
created by alloying the Mg matrix with Al, to initiate the formation of aluminium carbides for enhancing the interface bonding. Moreover, the interface reactivity further depends on the surface reactivity of the fibres, which is related to the fibre type.

**EXPERIMENTAL**

The interface reactivity in the system C/Mg-Al has been varied systematically by changing the aluminium content of the matrix and by using carbon fibres with different surface microstructures. In cooperation with the University of Erlangen [2, 8] three composites have been investigated, with increasing fibre/matrix reactivity: M40J/AM20, T300J/AM20, and T300J/AZ91. The abbreviations M40J and T300J denote carbon fibres of the high-modulus and the high-tensile-strength type, respectively, by Toray, and the acronyms AM20 and AZ91 designate magnesium alloys with 2 or 9 wt.% Al content, respectively.

To explore the particulars of the fibre/matrix interfaces as well as their influence on the mechanical properties, the MMCs have been investigated on different structural levels by means of scanning electron microscope (SEM) in situ three-point bending tests, high-voltage transmission electron microscopy (HVEM), high-resolution transmission electron microscopy (HREM), and scanning transmission electron microscopy (STEM) in combination with energy-dispersive X-ray spectroscopy (EDXS) and electron energy-loss spectroscopy (EELS), especially analyses of the near-edge fine structure (ELNES).

**INTERFACE MICROSTRUCTURE**

According to the degree of interface reactivity, three different interface structures have been observed. The composite M40J/AM20 exhibited no carbides, resulting in a weak interface bonding, which was indicated by a frequent observation of delaminations [1]. At the fibre/matrix interface of the composite T300J/AM20, carbidic precipitates have formed, with a lattice fringe distance of 0.62 nm and dimensions far below 100 nm (cf. Fig. 1).

![HREM micrograph of composite T300J/AM20 reveals precipitates at the fibre/matrix interface, with dimensions of only some ten nanometres and exhibiting a lattice fringe distance of 0.62 nm.]

Fig. 1: HREM micrograph of composite T300J/AM20 reveals precipitates at the fibre/matrix interface, with dimensions of only some ten nanometres and exhibiting a lattice fringe distance of 0.62 nm.
Many of these precipitates have formed in composite T300J/AZ91, some of which reaching more than 1µm into the matrix (cf. Fig. 2). The lateral distribution of the precipitates is clearly visualized by the bright contrasts in Fig. 2b, representing the EDXS elemental map of aluminium.

![Image](image1.png)

Fig. 2: Carbodic platelets at the fibre/matrix interface of a C/Mg-Al composite with 9 wt.% Al in the matrix: (a) bright-field image, (b) elemental distribution of aluminium.

**CARBIDE CHARACTERIZATION**

**Nanochemical analysis**

EDXS and EELS investigations of the precipitates at the fibre/matrix interfaces revealed that they are not the binary aluminium carbide Al₄C₃ but a ternary aluminium-magnesium-carbide of approximate stoichiometry Al₂MgC₂ [9, 10], which often shows planar defects parallel to its (0001) habit plane (cf. Fig. 3).

![Image](image2.png)

Fig. 3: High-resolution micrograph of the intergrowth of a regular ternary carbide (left) with one showing many planar defects parallel to the (0001) habit plane (right).
Detailed knowledge about this new type of carbide is of general interest for the optimization of C/Mg-Al composites as we could show that its formation strongly influences the composite properties [1, 10-12]. Thus, a nanoanalytical study of the nature of the precipitates has been undertaken by analyzing the ELNES in the EEL spectra.

The fine-structures of the ionization edges in the EEL spectra contain information far beyond the composition as the ELNES peculiarities are substantially determined by the bonding states, thus reflecting the bonding partner [13]. The ELNES features of the carbidic precipitate (defect-free part in Fig. 3) are discussed in reference to Fig. 4, where the fine-structures of the Mg-L\textsubscript{23}, Al-L\textsubscript{23}, and C-K ionization edges are compared to those of standard substances.

*Fig. 4: Near-edge fine-structures of a precipitate compared to different standard substances.*

The Mg-L\textsubscript{23} ELNES curves of Fig. 4a show a significant difference in the chemical environment of the magnesium atoms of the precipitate compared to those of metallic (bottom) or oxidic magnesium (top). In addition, the ELNES of the precipitate phase shows a peak structure at about 73 eV (onset), which can be attributed to the L\textsubscript{23} ionization edge of aluminium. In Fig. 4b, this peak structure is compared to that of various Al compounds.
The Al-L\textsubscript{2,3} ELNES (Fig. 4b) of the Al\textsubscript{4}C\textsubscript{3} standard and of the precipitate phase show similar profiles. However, they differ clearly from those of metallic (bottom) and oxidic aluminium (top). In both cases, the onset energy of the Al-L\textsubscript{2,3} ionization edge is at about 73 eV, followed by a small peak at about 77.5 eV after a steep rise in the signal.

At the C-K ionization edge (Fig. 4c), the spectra of the Al\textsubscript{4}C\textsubscript{3} standard and of the precipitate phase show a steep rise in the signal, with its maximum peak at about 291 eV. Only for the precipitate phase, the slope decreases slightly in the left flank of the peak, viz. at about 287 eV. Furthermore, at about 30 eV above the onset energy, another broader peak occurs, which differs by about 3 eV in the energy position of its maximum (at about 305 eV, for Al\textsubscript{4}C\textsubscript{3}, and at about 302 eV, for the precipitate).

These ELNES peculiarities suggest that the precipitate phase is an aluminium-magnesium-carbide, the crystal chemistry of which is closely related to that of the binary carbide Al\textsubscript{4}C\textsubscript{3} because of the strong similarities in the Al-L\textsubscript{2,3} and C-K ELNES (Figs. 4b and c).

Furthermore, the observed lattice fringe distance of 0.62 nm (Fig. 3, left) could be related to the (0002) lattice fringe distance of a polymorph of the ternary carbide Al\textsubscript{2}MgC\textsubscript{2}, which recently was synthesized for the first time and than analyzed by X-ray diffractometry [14].

**Crystallographic structure**

Based on the data of X-ray powder diffractometry [14] and on HREM as well as EELS investigations [9, 10, 12] we propose a crystal structure for this new type of carbide, which in Fig. 5 is presented together with the well-known structure of the binary carbide Al\textsubscript{4}C\textsubscript{3} [15, 16] via a projection of the atomic arrangements in the (1120) plane. In the binary carbide (Fig. 5a) as well as in the ternary carbide (Fig. 5c), the metal atoms form a close-packed arrangement, which is filled with carbon atoms in octahedral or trigonal-bipyramidal interstices.

![Crystal structures](image)

*Fig. 5: Crystal structures represented by cuts along the (1120) plane: (a) Al\textsubscript{4}C\textsubscript{3} [15, 16], (b) building blocks, (c) structure proposal for Al\textsubscript{2}MgC\textsubscript{2}.*

The crystal structures and their relationship are more elucitated by dividing both structures into structural units (Fig. 5b). They are related by the occurrence of a common [Al\textsubscript{2}C] unit (Fig. 5b, middle) and possess similar environments for the aluminium and carbon atoms, respectively, explaining the strong similarities in the ELNES profiles at the Al-L\textsubscript{2,3} and C-K ionization edges.
(Figs. 4b and c). The carbon atoms which are incorporated in the \([\text{Al}_2\text{C}]\) structural unit are octahedrally coordinated by cubic close-packed (c) Al atoms. The carbon atoms in the \([\text{MgC}]\) or \([\text{Al}_2\text{C}_2]\) units are located near the center of trigonal bipyramids, which are made up of the hexagonal close-packed (h) metal atoms. In the ternary carbide \(\text{Al}_2\text{MgC}_2\), with the \([\text{MgC}]\) unit, the Mg atoms form the base triangles of the bipyramids, and the Al atoms form the two tips, one below and one above the Mg layer, respectively.

**Growth mechanisms**

Formed in the C/Mg-Al composites, the ternary carbides have a plate-shaped morphology as they are laterally extended in always perpendicular orientation to their c-axis. As Fig. 6a demonstrates, the interfaces between the side faces of the \(\text{Al}_2\text{MgC}_2\) platelets and the metal matrix show many growth ledges, whereas the interfaces between the (0001) habit planes and the matrix are flat on the atomic scale.

These two distinct interface structures between the carbide platelets and the Mg matrix indicate the action of two different growth mechanisms, which have been observed also for \(\text{Al}_4\text{C}_3\) in Al matrices [17, 18]:

(i) The atomically rough interface moves in a continuous diffusion-controlled growth mode, which is determined by the diffusion rates of the reaction partners.

(ii) In directions normal to the atomically flat interface (i.e., along the c-axis of the carbide), the crystal grows by an interface-controlled ledge mechanism, which requires a multiple two-dimensional nucleation or a spiral growth mechanism.

The observed plate-shaped morphology of the ternary carbides is due to the diffusion-controlled growth process being much faster than the interface-controlled one.

![Fig. 6: High-resolution micrograph of platelets of the ternary carbide in composite T300J/AZ91: (a) carbide/matrix interfaces, (b) carbide/fibre interface.](image)

Besides influencing the interface bonding, the carbides may cause a detrimental embrittlement of the composite, if there are too many large ones. In composite T300J/AZ91, with a strong fibre/matrix reaction, the carbides are grown directly on the fibre surface, as shown in Fig. 6b. Hence, if this composite is loaded in the direction of the fibre axes, the carbide platelets sometimes larger than 1 µm (cf. Fig. 2) may notch the fibre.
With increasing interface reactivity, three characteristic failure mechanisms have been observed: single-fibre fracture, bundle fracture, and brittle fracture (cf. Fig. 7). The bundle fracture at a medium reactivity preserved the highest bending strength of approx. 929 MPa (composite T300J/AM20). The composite with a low interface reactivity (M40J/AM20) showed a bending strength of approx. 544 MPa, which is 1.7 times lower and accompanied with single-fibre fracture. The composite with high interface reactivity (T300J/AZ91), with many large carbidic platelets at its fibre/matrix interface (cf. Fig. 2), showed brittle fracture.

Fig. 7: Load deflection diagrams and SEM images of the fracture surfaces:
(a) composite M40J/AM20 ($\sigma_B \approx 544$ MPa, single-fibre fracture),
(b) composite T300J/AM20 ($\sigma_B \approx 929$ MPa, bundle fracture),
(c) composite T300J/AZ91 ($\sigma_B \approx 158$ MPa, brittle fracture).
CONCLUSIONS

The interface reactions in C/Mg-Al composites lead to the formation of platelets of the ternary carbide Al$_2$MgC$_2$. Thus, the widely held view of the primary role of the binary carbide Al$_4$C$_3$ in the fibre/matrix reactions should be revised.

The interface reactivity can be modified by using carbon fibres with different surface microstructures and by using Mg alloys with different amounts of Al, and it governs the composite properties via controlling the amount and size of the carbidic platelets at the fibre/matrix interface. With increasing interface reactivity, the failure behaviour changes from single-fibre fracture to bundle fracture and to brittle fracture.

An MMC with optimum properties is characterized by the bundle fracture behaviour, which can be achieved by the moderate formation of Al$_2$MgC$_2$ at the fibre/matrix interface via a controlled medium interface reactivity.

ACKNOWLEDGEMENTS

The authors would like to thank Prof. R.F. Singer and Dr. O. Öttinger (University Erlangen-Nürnberg) for providing the MMCs, Dr. M. Füting (Fraunhofer Institute for Mechanics of Materials, branch lab Halle) for the provision of the ESEM-3/bending stage, and their colleague Dr. R. Schneider for his support in recording the EEL spectra.

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