Interface reactions and fracture behaviour of fibre-reinforced Mg/Al alloys

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Summary

In the composite system carbon fibre/magnesium alloy the interface reactivity was varied over a wide range by adding different amounts of the alloying element aluminium (alloys: AM20, AZ91) and by using carbon fibres of different surface properties (fibres: M40J, T300J). The structure and composition of interlayers in these composites down to the atomic scale as well as their effect on the mechanical properties were studied systematically by the combination of high-voltage electron microscopy, high-resolution electron microscopy, energy-dispersive X-ray spectroscopy and electron energy-loss spectroscopy with scanning electron microscope in situ bending tests. As resulting microstructure and nanochemistry correlate with the micromechanical fracture behaviour of the metal matrix composites, the interface reactivity can be used as a parameter governing the composite properties.

In addition to precipitates of aluminium carbide, strongly influencing the fracture behaviour, there are also graphitic carbon ribbons and layers of nanocrystalline magnesium oxide at the fibre/matrix interface.

Increasing the reactivity of the composite system, three characteristic modes of fracture behaviour are observed: single fibre pullout, bundle fracture (the optimum composite) and brittle failure.

1. Introduction

A metal matrix composite (MMC) enables the high strength and high Young's modulus of ceramic or carbon fibres to be exploited in a compact and relatively tough material by embedding the fibres in the metal. The effectiveness of reinforcement is mainly influenced by the properties of the transition regions between the components, especially those based on the interface bonding. Depending on the characteristics of the individual constituents of the interlayer regions, the origin of the bonding may be chemical or physical (including frictional), or a combination of both. Interfacial reactions strongly influence the interface bonding, e.g. by precipitation at the interface, but they also influence the properties of the metal matrix and the fibre (e.g. by degradation).

In contrast to ceramic matrix composites (CMCs) or fibre-reinforced glasses, where the initial process of composite failure is a multiple matrix cracking (Grathwohl et al., 1994), in MMCs the strain to fracture of the fibres is smaller than that of the matrix. The primary microprocesses of failure are therefore ruptures of single fibres according to the Weibull statistics of their strength, whereas the metal matrix deforms elastically and plastically up to fracture. The aim of the present paper is to show how the failure mechanisms at higher strains (secondary microprocesses) are affected by interfacial reactions that influence the effective fibre strength and the interface bonding, and which may cause an embrittlement of the matrix.

Depending on the strength of the fibre/matrix interface, in general, there are two extreme modes of fracture in MMCs (Shorshorov et al., 1983). For a very low interface strength the rupture of several fibres is followed by an extensive pullout of the fibres without a sufficient load transfer. For a very high interface strength, a fibre crack continues to propagate into the matrix, and the composite fails without any pullout of the fibres from the matrix, similar to brittle fracture behaviour. Thus these two fracture modes cannot provide the expected benefit of full fibre strength in a compact material. Preserving the fibre characteristics up to high strains requires an appropriate load transfer from matrix to fibre. Thus, the interface strength has to assume an optimized median value between these two modes, which should be provided by an appropriate adjustment of fibre/matrix reactions. The carbon/magnesium system, as an example of a special fibre/matrix combination of low weight and therefore
promising excellent specific properties, is treated to be more or less chemically inert because the two magnesium carbides MgC₂ and Mg₂C₃ are supposed to be endothermic compounds, which start to decompose at 450 and 700°C, respectively (Irmann, 1948). A promising way to enhance wettability and attain suitable fibre/matrix bonding in C/Mg composites seems to be the alloying of the magnesium matrix with carbide-forming elements, e.g. aluminium, which is known to form the stable carbide Al₄C₃.

Results of microstructural and microchemical investigations of different carbon-fibre-reinforced Mg/Al alloys, produced by a gas pressure infiltration process, are presented in this paper. The investigations were carried out by high-voltage electron microscopy (HVEM), high-resolution electron microscopy (HREM), energy-dispersive X-ray spectroscopy (EDXS) and electron energy-loss spectroscopy (EELS). Moreover, information on the chemical bond state of the elements present was gained by

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**Fig. 1.** HREM image of cross-sections of two PAN-base carbon fibres embedded in an epoxy resin: (a) high-tensile-strength carbon fibre T300J; (b) high-modulus carbon fibre M40J.

**Fig. 2.** Load deflection diagram of an in situ bending test on an M40J/AM20 composite. The SEM image (inset) shows extensive single fibre pullout.

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analysing energy-loss near-edge structures (ELNES), which can be attributed to transitions of core-shell electrons into unoccupied states above the Fermi level (Brydson et al., 1991; Rez, 1992). As characteristic ELNES details the edge onset as well as the shape, the energy position and the intensity of individual fine-structure features are used. In addition, results of micromechanical scanning electron microscope (SEM) in situ bending tests are presented.

2. Experimental

Unidirectionally carbon-fibre-reinforced magnesium/aluminium alloys (explicitly in order of increasing reactivity: M40J/AM20, T300J/AM20, T300J/AZ91) were produced via a gas pressure melt infiltration process with $\approx 63$ vol% fibre content (Öttinger & Singer, 1993; Öttinger et al., 1995).

Here M40J and T300J are designations of commercially available sized PAN-base carbon fibres (Toray) that differ mainly in their order of graphitization. The HREM images of as-received carbon fibres in Fig. 1 correspond well to the structure models of high-tensile-strength and high-modulus carbon fibres proposed by Oberlin (1989): M40J as the graphitized high-modulus carbon fibre possesses a relatively smooth surface with the graphitic basal planes orientated parallel to the fibre surface. However, the surface of the less graphitized high-tensile-strength fibre T300J is rougher, with basal planes ending free on it. Owing to the higher chemical reactivity of the free-ending graphite layers in comparison with the graphitic basal planes, the T300J fibre is more reactive than the M40J fibre.

The designations AM20 and AZ91 denote magnesium alloys with different amounts of the alloying element aluminium and adopt a description method used by the American Society for Testing and Materials, where AM20 contains 2 wt% Al and 0.4 wt% Mn and AZ91 contains 9 wt% Al and 0.7 wt% Zn (Polmear, 1981).

For the transmission electron microscope investigations, specimens were prepared by cutting thin (500-μm) slices 3 mm in diameter using a water-free lubricant, planar grinding and double mould dimpling to a thickness of about 20 μm, followed by ion milling (Ar, 5 kV) down to electron transparency.

The HVEM investigations were carried out using a JEOL 1000-06 microscope operating at 1 MV. For the HREM, EDXS and EELS procedures a combined transmission/scanning transmission electron microscope (TEM/STEM) of type Philips CM 20 FEG running at 200 kV and equipped with a light-element X-ray detector (Tracor Voyager II) and a parallel recording energy-loss spectrometer (Gatan PEELS).
model 666) was used. According to the characteristics of the thermally assisted field-emission gun the energy resolution (half-width of the zero-loss peak) is about 0.8–1 eV. Usually EEL spectra were acquired at 0.5 eV per channel and subsequently deconvoluted with the zero-loss peak to increase the resolution. To minimize contamination effects, which are generally strong for small electron probes of some nanometres, a cooling specimen holder (Gatan model 668) was used for the analytical procedures.

In situ bending tests (Feldhoff et al., 1995) were carried out using a special micro bending table (Raith, Dortmund), which was incorporated in the environmental scanning electron microscope (ESEM-3, Electro Scan, Wilmington). Load deflection diagrams on metal matrix composites cut into $23 \times 5 \times 1.5$ mm$^3$ rectangular specimens were recorded at a cross-head speed of $1 \mu m s^{-1}$ and at a span length of 17 mm. In the middle the samples were notched to 100 $\mu m$ using a 50-$\mu m$ tungsten wire saw for two reasons: first, to localize stress intensities, thus enabling the direct observation of failure mechanisms; and second, to minimize shear stresses that could be expected from the low span length over specimen thickness ratio of 11 (Ottinger et al., 1994). The broken samples were subjected to fractographic examination in an SEM (JEOL, JSM-6300F).

3. Results and discussion

3.1. Composite M40J/AM20

The combination of the low reactive magnesium alloy AM20 with a high-modulus carbon fibre M40J results in an M40J/AM20 composite of middle strength in the in situ bending test (marked by $F_{max} = 240$ N in Fig. 2). The composite behaves more like a loose bundle of fibres than like a compact material, as can be seen from the fracture surface (insert in Fig. 2) which is characterized by an extensive single fibre pullout. The fibre/matrix interface of this composite of low fibre/matrix reactivity is completely free of precipitates and most fibres are debonded from the matrix, as can be seen in Fig. 3. Although the debonding may be influenced by the preparation procedure, it clearly demonstrates the weak interface bonding.

The EDXS intensity maps of C-K$_\alpha$, O-K$_\alpha$ and Mg-K$_\alpha$ X-rays shown in Fig. 4 reveal an enrichment of oxygen at the fibre/matrix interface (Fig. 4c). Note that a segregation of aluminium to the interface could not be observed. Furthermore, in EDXS point analyses in the matrix and at the fibre/matrix interface only a small amount of aluminium of less than 0.5 wt% was observed, which should be compared with a nominal aluminium content of 2 wt% in the AM20
alloy. This anomaly is assumed to be caused by absorption of the Al-$K_\alpha$ X-rays (1.487 keV) by magnesium with Mg-$K_\alpha$ absorption edge at 1.305 keV, slightly below the Al-$K_\alpha$ emission energy. Nevertheless, the investigations clearly show that no dissolution of the matrix alloy took place.

The HREM image in Fig. 5 reveals the oxygen in the fibre/matrix region to be present as MgO crystallites. The polycrystalline nature of the MgO interlayer could also be shown by dark-field imaging under tilted illumination using the 200 and 220 Debye–Scherrer rings of MgO.

3.2. Composite T300J/am20

By increasing the reactivity of the fibre/matrix system by changing the carbon fibre to the high-tensile-strength T300J, the resulting T300J/AM20 composite possesses a higher strength obviously related to a bundle fracture behaviour typical for this combination (inset in Fig. 6). After reaching a maximum at $F_{\text{max}} = 410$ N, the load decreases by characteristic steps (Fig. 6), which are correlated with the successive failure of fibre bundles.

Fig. 5. HREM image of an M40J/AM20 composite reveals an interlayer of polycrystalline MgO (some crystallites are indicated by circles) at the fibre/matrix interface (fibre below).

Fig. 6. In an in situ bending test on a T300J/AM20 composite a high strength is achieved. The SEM image (inset) shows bundle fracture.
The T300J/AM20 composite of medium reactivity shows some precipitates at the fibre/matrix interface (Fig. 7; for details concerning the nature of the precipitates see Section 3.3). In addition, a graphitic interlayer ≈20 nm thick on the fibre surface is revealed by the high-resolution image in Fig. 8. This layer may act as a mechanical fuse, and furthermore it may prevent the fibres being exposed to notching by the precipitates.

3.3. Composite T300J/AZ91

The addition of 9 wt% aluminium to the magnesium matrix (AZ91) in combination with the highly reactive T300J fibre results in a change of fracture behaviour to brittle failure, as the SEM image of the fracture surface in Fig. 9 shows. The AZ91/T300J composite fails during the in situ bending test at a low load (marked by $F_{\text{max}} = 70$ N in the load deflection diagram) and is reminiscent of the fracture behaviour of a brittle ceramic.

The heavy formation of precipitates of different morphology extending from the fibre/matrix interface into the matrix, as shown in Fig. 10, is considered to cause not only a strong interface bonding but also an embrittlement of the matrix. The precipitates grew directly from the fibre surface without any interlayer of magnesium oxide or graphite, as can be seen in Fig. 11. The EDXS intensity maps of C-K$_\alpha$, Mg-K$_\alpha$, and Al-K$_\alpha$ X-rays at the fibre/matrix interface in Fig. 12 show an enrichment of aluminium and slightly of carbon inside the precipitates, so it was assumed that they probably consist of Al$_4$C$_3$. However, there was always a contribution of Mg-K$_\alpha$ X-ray intensity detectable. In EDXS point analyses taken on the precipitates the intensity of the magnesium signal was comparable with that of the aluminium signal. It is assumed that most of the Mg-K$_\alpha$ X-rays arise from the matrix magnesium, in a manner analogous to the EDXS investigations of Hall (1987) on aluminium-rich precipitates in T300/Mg–1% Al. Additionally, absorption effects of Al-K$_\alpha$ and C-K$_\alpha$ X-rays by the matrix magnesium, which are especially strong for the C-K$_\alpha$ X-rays, comparable with that reported by Carpenter & Lo, (1992) for C-K$_\alpha$ X-rays from Al$_4$C$_3$ precipitates in an aluminium matrix, exclude the possibility of quantitative EDXS analysis.

Therefore, a phase analysis by characterizing ELNES details was chosen to elucidate the chemical nature of the precipitates. The EEL spectra (nanoprobe mode with about 2 nm probe diameter) taken from the precipitates show the
Al-L_{2,3} and the C-K edges as dominant features with an Mg-L_{2,3} edge of low intensity. A phase identification was achieved by a detailed analysis of both the Al-L_{2,3} and the Al-K ELNES, in which the respective edges were compared with those of an Al_{4}C_{3} standard material in a fingerprint manner. The results are shown in Fig. 13 where near-edge structure details of aluminium and Al_{2}O_{3} are also given. The features taken from the precipitate are in fairly good agreement with those of Al_{4}C_{3}, particularly for the Al-K ELNES. Slight differences in the curve shapes of the Al-L_{2,3} ELNES of the phase of interest and of the Al_{4}C_{3} powder standard can be explained by a partial oxidation of the latter, as indicated by a small O-K edge. Furthermore, the Al-L_{2,3} ELNES of the precipitate shows good conformity with the EEL spectrum reported by Carpenter & Lo (1992) for Al_{4}C_{3} in an aluminium matrix.

Fig. 8. HREM image of the fibre/matrix interface in a T300J/AM20 composite shows the formation of a graphitic interlayer ~20 nm thick (left: fibre).

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Fig. 9. A T300J/AZ91 composite fails at a low load of $F_{\text{max}} = 70$ N and the SEM image of the fracture surface (inset) points to brittle failure.
Fig. 10. HVEM bright-field image of a T300J/AZ91 composite shows heavy formation of Al₄C₃ precipitates at the fibre/matrix interface (middle: matrix).

Fig. 11. HREM image of the fibre/matrix interface in a T300J/AZ91 composite reveals an Al₄C₃ precipitate extending from the fibre surface into the matrix.
4. Conclusions

The electron microscopical and micromechanical investigations clearly reveal that the mechanical properties of unidirectionally carbon-fibre-reinforced magnesium alloys can be varied over a wide range by changing the fibre/matrix reactivity of the composite system by the use of carbon fibres of different surface structures and of magnesium alloys with different contents of aluminium. The micromechanical behaviour was found to be highly correlated with the resulting precipitation of Al₄C₃ in the fibre/matrix region.

An MMC of optimum properties is obviously characterized by a bundle fracture, which can be governed by medium interface reactions.

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References


