TiN interlayers in carbon fibre reinforced magnesium were investigated using high-resolution electron microscopy (HREM), scanning transmission electron microscopy (STEM) and electron energy loss spectroscopy (EELS), including analyses of near-edge fine structures (ELNES) and corresponding quantumchemical calculations. The nanocrystalline TiN fibre coatings of thicknesses between 10 and 30 nm were chemically vapour deposited from a TiCl$_4$-N$_2$-H$_2$ atmosphere. Detailed ELNES measurements across the fibre/matrix interregion with a point-to-point distance of 1.3 nm in combination with quantumchemical calculations reveal in the fibre-near interlayer region interactions of the Ti-3d electrons with both the N-2p and the C-2p electrons resulting in mixed p-d-$\pi$ and p-d-$\sigma$ bondings. This hints to the formation of a TiC/TiN mixture of varying composition or of a titanium carbonitride (TiC$_x$N$_y$) with a high carbon content at the fibre/coating interface during the first steps of the coating by interaction of the carbon atoms of the fibre surface with the reactor gas. In this way the excellent adhesion of the TiN layers on the fibres can be understood which makes them appropriate for the important application in Mg matrices, where the layers have to serve as a suitable coupling medium between fibre and matrix.

Keywords: bonding, TiN

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1. Introduction

In previous work (FELDHOFF et al. 1997, 1999, ÖTTINGER et al. 1995) on the possibilities of interface tailoring in the initially non-reactive system C-fibre/Mg-matrix we demonstrated that appropriate interface properties can be achieved by adjusting the interfacial bonding with small amounts of Al and carbon fibres of the high-tensile-strength type via the moderate formation of the ternary carbide Al$_2$MgC$_2$ in the fibre/matrix interlayer.

Another possibility to generate an appropriate interlayer is the direct fibre coating prior to the composite processing where the coating serves as a suitable coupling medium between fibre reinforcement and metal matrix providing an adequate adhesion effect. As it is necessary to achieve appropriate films on each filament in the multifilamentous carbon-fibre-yarn, chemical vapour deposition (CVD) is an adequate coating technique. A further requirement determining the kind of the coating is a good wetting of the metal on the coating which also correlates with the tendency to form bonds with the constituents of the coating (NAIDICH 1981, DELANNAY et al. 1987). Generally, the wettability of metal-like compounds by metals is better than that of covalent ones as a high percentage of delocalized electrons in the solid phase favours the electron exchange, which is necessary for the formation of chemical bonds with the liquid-phase metal. The electronic structure of TiN indicates metal-like properties because of its small band gap, resulting from weak bonding molecular orbitals...
immediately below the Fermi level $E_F$ (originating from N-2p atomic orbitals) and unoccupied Ti-3d-levels immediately above $E_F$. Moreover, TiN is of the rock-salt structure, which is the simplest structure of interstitial compounds. Thus, an isotropic growth during CVD could be expected, which would lead to a homogeneous covering of the fibres, even for thin films of some ten nanometers in thickness.

In the present paper, we focus on the bonding specifics within the coating at its interface with the fibre surface. Very recently it was shown (Feldhoff et. al. 2000a, 2000b) that a proper TiN coating simultaneously can act as a coupling medium and as an efficient diffusion barrier. A corresponding successful interlayer tailoring would enable an important potential application of the resulting light-weighted C/Mg composites with a strength of 1 to 2 GPa, namely the partial reinforcement of highly loaded parts in mechanical hybrid components:

In those parts of the components where the loads are lower, the strength of Mg alloys with 5 to 9 wt.% Al (approx. 250 MPa at room temperature) suffices, but, according to our above mentioned observations, Mg-Al alloys with such large amounts of Al cause an extensive formation of the ternary carbide $\text{Al}_x\text{MgC}_y$ in contact with carbon fibres, leading to a drastic embrittlement of the composite. Coating the fibre surface to slow down the deleterious mass transfer across the interface is a promising way to suppress carbide formation as well as fibre degradations and to provide a mechanical protection of the fibres.

2. Experimental

The composite material was prepared at the University of Erlangen (Wurm et al. 1997, Wurm 1998) using the carbon-fibre-yarn Tenax 5331 HTA (Toho/Akzo) of the high-tensile-strength type (6000 single filaments, tensile strength $\sigma_f = 3.95$ GPa, Young’s modulus $M_f = 238$ MPa) which was thermally desized and passed through a CVD counter-current reactor using a mixture of TiCl$_4$, N$_2$, and H$_2$ as the precursor gas. The parameters of the CVD process were chosen to yield an invariance in the fibre properties, compared to the as-received state, and a complete and uniform covering of all the filaments in the yarn with TiN. Unidirectionally wound carbon-fibre preforms were infiltrated with matrices of commercial purity magnesium (cp-Mg) via a gas-pressure melt-infiltration process (Öttinger and Singer 1993, Öttinger 1996) at 720 °C and 10 MPa employing a 5-minute fibre/melt contact to obtain metal matrix composites with a fibre content of approx. 58 vol.%. Cross-sections of the fibre/matrix interface area were prepared by cutting thin (500 µm) slices of 3 mm in diameter, planar grinding and double-mould dimpling to a thickness of about 20 µm. To prevent galvanic attack on the Mg, a water-free lubricant was used. Final thinning was performed by ion milling (Ar$^+$, 5 kV) down to electron transparency. For the HREM, STEM, and EELS investigations, a combined (scanning) transmission electron microscope of the type Philips CM 20 FEG operating at 200 kV was used, which was equipped with a post-column electron energy-filter (Gatan Imaging Filter GIF 200, model 667) as well as with a digital scanning module (Gatan Digiscan). To minimize contamination effects, a liquid-N$_2$ cooling specimen holder (Gatan model 668) was used during the STEM procedures. For image processing and EEL spectrum treatment the Gatan Digital Micrograph and EL/P software, run on a Power Macintosh 7200/75, were employed. The thermally assisted field emission gun enables an energy resolution of the EEL spectra of 0.7 to 1 eV, which were acquired at dispersions of 0.1 and 0.5 eV per channel.

For good lateral resolution in the STEM-EELS procedures, only sample regions of the composites which have been suitable for HREM have been analyzed. Additionally, to minimize multiple scattering effects on core-loss spectra in EELS, here, the sample thickness has been counter-checked by the peak intensity ratios of the zero-loss to volume plasmons in
corresponding low-loss spectra. Using dispersions of 0.1 and 0.5 eV per channel, the exposure time per spectrum was 4.0 s and 0.8 s, respectively.

As standard substances, powders of TiC (Aldrich, purity 98%, -325 mesh) and TiN (Aldrich, purity 99%, < 10 micron) were dispersed onto supporting grids. EEL spectra of the standards were acquired at a spectral dispersion of 0.1 eV per channel with 4 s exposure, respectively. For noise reduction, spectra taken on 10 different points on a crystallite were added, yielding an effective exposure time of 40 s. As in the spectra taken on the composite material, no deconvolution treatment was applicable, for reasons of comparability, none were applied to the spectra of the standards. The only additional spectra treatments were background subtraction using a polynomial fit and scaling to allow a better comparison of ELNES features.

3. Quantumchemical calculations

Measuring the ELNES of the relevant core-shell ionization edges allows, to a certain degree, a mapping of the partial local density of states (PLDOS) above the Fermi level which contains subtle information on the respective bonding specifics and the coordination of the next neighbour atoms (e.g. WILLIAMS and CARTER 1996). The ELNES features are caused by excitations of core-shell electrons into unoccupied states above the Fermi level (BRYDSON et al. 1991, REZ 1992) and can be interpreted by comparison with standard spectra or by partial local densities of states, derived by quantumchemical calculations (e.g. LICHTENBERGER et al. 1995, SCHNEIDER et al. 1996 a,b). For our calculations simple clusters, simulating the crystal structures of TiC, TiN, and a hypothetical titanium carbonitride have been used, considering the correct octahedral coordination of the central titanium atom. At first a quantumchemical calculation using the semiempirical PM3(tm)-method (parameterized method 3 for transition metals, cf. STEWART 1990) including d-electrons, with geometry optimization has been performed, in order to obtain cluster geometries with minimized formation enthalpy. These preoptimized clusters have been submitted to a calculation using the density functional theory (DFT) with the non-local self-consistent Becke-Perdew model (BP) (BECKE 1988, PERDEW 1986) including a double numerical basis set (DN*), i.e. one function for core-electrons (as, e.g., 1s), two functions for valence electrons (as, e.g., 2s, 2p for C and N; 4s, 3d for Ti) and one set of polarisation functions (for example five 3d-functions for N and C). Calculations of such kind result in an energy level diagram of molecular orbitals (MOs) This MO scheme is used for the interpretation of the measured ELNES curves.

One way of understanding correlation effects in molecules and solids is the so-called back-bonding, that is the back transfer of charge from the electronegative bonding partner (as nitrogen) to the electropositive partner (as titanium), especially into its electron levels which are unoccupied in the ground state (HEHRE 1995). This is one reason that large underlying basis sets are necessary for correlated models, as, e.g., DFT, including functions with a larger quantum number than occupied in the ground-state system, in order to achieve reasonable results (HEHRE and LOU 1997). The differences of the energy eigenvalues of the core electrons and of the unoccupied electron levels of the clusters have been chosen for the interpretation of the number of peaks in the observed ELNES, their onsets and energy positions.

4. Results and discussion

Fig. 1 shows in lattice plane resolution the turbostratic carbon of the fibre (left) and the (1010) lattice fringes of the Mg matrix (right) ending at the coating (middle part). The
polycrystalline nature of the coating with grain sizes in the range of the film thickness is clearly revealed.

Fig. 1: HREM image of the composite material showing the (10\,10) lattice fringes of the Mg matrix ending on the coating (left: fibre, right: matrix).

Fig. 2: Composite T5331HTA / TiN / cp-Mg: (a) Three-dimensional plot of EEL spectra taken at 30 equidistant points (1.3 nm) across the fibre/matrix interregion, arranged from fibre (back) to matrix (front), (b) STEM bright-field image showing the analysis distance as a white line.
A three-dimensional plot of EEL spectra is given in Fig. 2a, which were recorded across the fibre/matrix interregion at 30 equidistant points along the white marker in the STEM bright-field image (Fig. 2b), with the point-to-point distance amounting to about 1.3 nm and at a dispersion of 0.5 eV per channel. In the energy interval between 250 and 750 eV, there appear the C-K, N-K, Ti-L\(_{2,3}\), and O-K ionization edges and their associated fine-structures. In the region of the fibre (spectra in the background, Fig. 2a), only the C-K ionization edge at 284 eV arises from the exponentially decreasing background. At the fibre/coating interface, a Ti-L\(_{2,3}\) ionization edge appears and the C-K ELNES changes. Within a gradient of approximately 5 nm, an N-K ionization edge arises and the C-K edge disappears. The Ti-L\(_{2,3}\) ELNES is very clear above the background due to the presence of sharp white lines, which occur at the L\(_{2,3}\) ionization edges of the transition metals and at the M\(_{4,5}\) ionization edges of the rare-earth elements, because the Fermi energy is located in the narrow 3d resp. 4f valence band (REZ 1992).

Changes in the C-K, N-K and Ti-L\(_{2,3}\) fine-structures across the coating in the composite material were observed in more detail at a dispersion of 0.1 eV per channel and are compared with those of TiC and TiN standards in Figs. 3 to 5.

The C-K ELNES of TiC (lowest spectrum of Fig. 3) has its onset at about 280 eV and shows three main peaks: Two narrow peaks at about 4.5 eV and 14 eV above the onset energy (the first one is split by 2.1 eV), and a third broader peak at about 34 eV above the onset energy. The spectra from the composite material were taken across the fibre/coating interface with a point-to-point distance of about 2 nm. Two examples of these spectra are presented in Fig. 3: The topmost spectrum shows the signal from the fibre, and the spectrum in the middle that from the coating. Going from the fibre to the coating, a shift in the edge-onset of about 2 eV to lower energies is observed. Simultaneously, the second peak in the fine-structure becomes narrower, and the first one becomes broader. The splitting of the first peak (as observed in case of the TiC standard) is not resolved in the spectrum from the coating because there is more noise in the latter by the effective exposure time being a factor of ten smaller. The characteristic features of the C-K ELNES of TiC can be interpreted using the MO scheme derived by the DFT-calculations, represented in Fig. 6 (right): The interaction of carbon 2p electrons with titanium 3d electrons leads to two unoccupied molecular orbitals with t\(_{2g}\) and e\(_{g}\) symmetry, 2.3 eV and 4.5 eV above the Fermi-level, respectively. The denotations t\(_{2g}\) and e\(_{g}\) arise from the group theory based symmetry fitting of linear combinations of atomic orbitals (AOs) (SHRIVER et al. 1990): t\(_{2g}\) and e\(_{g}\) represent MOs of octahedrally coordinated central atoms as Ti with d-like AOs, forming bonds which are \(\pi\)-like in case of t\(_{2g}\) and \(\sigma\)-like in case of e\(_{g}\). The t\(_{2g}\)-MOs are threefold degenerated orbitals consisting of d\(_{xy}\), d\(_{yz}\), and d\(_{zx}\) AOs of the central atom and p AOs of the bonding partners. The e\(_{g}\)-MOs are twofold degenerated orbitals with contributions of d\(_{x^2-y^2}\) and d\(_{z^2}\) AOs of the central atom and p AOs of the bonding partners. As both types of MOs contain contributions of p-like AOs (angular quantum number \(l = 1\)), an excitation of an 1s electron (\(l = 0\)) into these MOs will give rise to an observable peak in the ELNES of a K edge: The excitation of a carbon 1s electron in these two unoccupied MO’s leads to the observed splitting of the first peak in the C-K ELNES. The next main peak results from the excitation of a C 1s electron in empty states with 2p-, 3p- and 3d-like symmetry, localized at the carbon atom.

In Fig. 4, the spectrum at top was taken from the middle region of the coating and corresponds well with those of the TiN standard (bottom). The N-K ELNES of TiN has its onset at about 396 eV and shows essentially the same features as that of TiC which was also reported by other authors (CRAVEN 1995, CRAVEN and GARVIE 1995, HOSOI et al. 1986, PFLÜGER et al. 1982). The split of the first peak by about 1.8 eV is slightly smaller than that in TiC. The interpretation of the N-K edge of TiN using the MO scheme obtained by the
DFT calculations is similar to that of the C-K edge of TiC (Fig. 6, left): The split of the first peak is due to the excitation of an N 1s electron in unoccupied energetically contiguous $t_{2g}$ and $e_g$ MOs, formed by the interaction of N 2p and Ti 3d electrons.

Fig. 3: C-K ELNES features taken across the fibre/coating interface in the composite material and those of TiC standard (background subtracted and scaled spectra).

Fig. 4: N-K ELNES features taken across the coating in the composite material and those of TiN standard (background subtracted and scaled spectra).

In Fig. 5, the Ti-L$_{2,3}$ ELNES of TiN and TiC are shown as the lowest and the topmost spectra, respectively. Due to the spin-orbit coupling a split of the Ti-L edge in two distinct peaks (L$_3$ and L$_2$) is observed. In case of TiC, an additional split of the L$_3$ peak by 1.8 eV is indicated which can be interpreted as a crystal field splitting. In principle, this splitting should also be observed in other titanium compounds, as, e. g., TiN. However, in this case, the transition metal - non metal hybridisation is assumed to be weaker (FINK et al. 1990) and therefore the splitting is not found.

Spectra from the composite material were taken across the coating from the fibre to the matrix at a point-to-point distance of about 2.5 nm. Two examples of a fibre-near and a
middle position are given in Fig. 5. Essentially, the Ti-L\textsubscript{23} features from the coating correspond all to that of TiN. In addition, in the fibre-near spectra, a broadening of the L\textsubscript{3} peak is indicated, which possibly hints to carbidic bonding.

![Fig. 5: Ti-L\textsubscript{23} ELNES features taken across the coating in the composite material and those of TiC and TiN standards (background subtracted and scaled spectra).](image)

Fig. 6: Calculated energies of core and unoccupied levels for TiN (left), TiC (right) and a hypothetical TiC\textsubscript{x}N\textsubscript{y} (middle) of octahedrally coordinated titanium. DFT-BP-DN*-calculation.

![Fig. 6: Calculated energies of core and unoccupied levels for TiN (left), TiC (right) and a hypothetical TiC\textsubscript{x}N\textsubscript{y} (middle) of octahedrally coordinated titanium. DFT-BP-DN*-calculation.](image)
Altogether, the ELNES features shown in Figs. 2 to 5 reveal that the coating consists of a TiC/TiN mixture of varying composition or of a titanium carbonitride (TiC_xN_y) with a high carbon content at the fibre/coating interface and gradually becoming richer in nitrogen on going towards the middle of the film. As demonstrated by the calculated energy levels (cf. Fig. 6), a distinction between a mixture of TiN and TiC, and a real TiC_xN_y (titanium bonded simultaneously to carbon and nitrogen) will not be possible by an ELNES analysis: The expected differences between these bonding states result in energy shifts of the measured ionisation edges smaller than 0.1 eV, which are not detectable with the usual EEL spectrometers.

5. Conclusions

The measured and calculated bonding-specific and compositional changes within the coating hint to a reaction of the reactor gas mixture (TiCl_4, N_2, and H_2) with carbon from the fibre during the initial state of the CVD process, i.e. the Ti-3d electrons interact with both, the N-2p and the C-2p electrons, forming a mixture of (i) p-d-π bonds resulting in the t_2g-MOs and (ii) p-d-σ bonds resulting in e_g-MOs. Thus, the term "reactive chemical vapour deposition", which was proposed by Vincent et al. (1992), seems to be suitable here, and the chemical processes during the deposition are much more complex as it may be assumed by simply considering the gas phase reaction TiCl_4 + 1/2 N_2 + H_2 → TiN + 4 HCl.

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