Decomposition of silica binder during infiltration of Saffil fiber preform with Mg and Mg-Li melts

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Abstract

Mg and Mg-Li matrix composites were prepared by the melt infiltration of fibrous preform consisting of Saffil alumina fibers and the silica binder. During this process there has occurred decomposition of silica binder and/or surface silica film by displacement redox reactions and the reaction products were characterized using SEM, TEM, SAED, FTIR and XPS techniques. The only reaction products found in Mg infiltrated Saffil preform were MgO and Mg_2Si. In Mg-Li melt infiltrated Saffil preform there was found besides MgO and Mg_2Si also the non--crystalline phase that appears to be the lithium silicate $xLi_2O \cdot ySiO_2$. Binary lithium silicides and ternary magnesium-lithium silicides were not detected.

K e y w o r d s: Mg-Li composites, Saffil fibers, silica binder, melt infiltration, XPS, FTIR

1. Introduction

Commercial Saffil fibers based on δ-alumina phase are being commonly used as cost effective reinforcement for preparation of light metal matrix composites. These composites are usually fabricated by the melt infiltration technique which involves the filling of fibers assembly with molten metal under action of mechanical forces (e.g., pressurized inert gas) and subsequent metal freezing in interstices. To facilitate the handling with fibers during composite processing, the fibers are arrayed into solid preform using the refractory binder (typically silica). For this purpose, colloidal silica (very fine silica particles in water) is added to the fibers bundle as a binding agent in the amount of $\sim$ 4 wt.% [1, 2]. As a result, colloidal silica creates thin film on individual fibers and sticks them together at the junction points thus creating 3D porous skeleton (preform). On subsequent drying and heating at $\sim 1000\,°C$, the loss of water and the coalescence of silica particles take place resulting in solid silica product with sufficient sticking efficiency [3].

Note that besides the silica binder & film there is present in Saffil fibers also the inner silica (about 4 wt.%) incorporated into alumina structure to stabilize δ-phase against transformation to α-Al_2O_3 during thermal processing of sol-gel fiber precursor [2].

Both the silica binder and the surface silica film react readily with injected light metals (Mg, Al) producing new phases. Although the total volume fraction of new products is quite small, they are located mainly in interfacial fiber/matrix region which plays critical role in mechanical performance and fracture of resultant composites. It is therefore highly relevant to characterize these phases and elucidate their formation chemistry.

When inserting Saffil preform into molten magnesium, silica species decompose rapidly due to displacement redox reactions. Hallstedt et al. [4] concluded that during infiltration of Saffil preform with pure magnesium the silica binder is transformed almost completely to a very fine grained MgO releasing elemental silicon which dissolves in molten matrix and precipitates as Mg_2Si upon cooling. The total reaction scheme is:

$$2Mg + SiO_2 = 2MgO + Si, \qquad (1)$$

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$$2Mg + Si = Mg_2Si. \qquad (2)$$
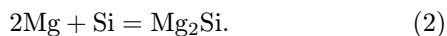
Similarly, Rehman et al. [5] reported that MgO and Mg_2Si are the only products of silica binder decomposition when infiltrating Saffil preform with pure Mg and Mg alloy (AZ91).

Current paper deals with the chemical conversion of silica binder and/or surface silica film during fabrication of Mg and Mg-Li matrix composites by the melt infiltration of Saffil preform. Owing to very high affinity for oxygen, elemental both Mg and Li can decompose the silica species [6]. Nevertheless, till now there are very little data available on the reaction of silica binder with Mg-Li melt. Only Mason et al. [7] had shortly communicated that during infiltration of Saffil with molten Mg-12 wt.% Li alloy a rapid dissolving of silica binder occurred producing Mg_2Si. On the other hand, MgO and Mg_2Si were the only reaction products detected by XRD in Mg-Li matrix composites prepared by insertion of SiO_2 powder into molten Mg-Li alloys [8].

The aim of present study is to characterize the products of redox decomposition of silica binder & film during contact of Saffil preform with Mg and Mg-Li melts. There have been used as the analytical techniques transmission electron microscopy (TEM) coupled with selective area electron diffraction (SAED), Fourier transform infrared spectroscopy (FTIR) and X-ray photoelectron spectroscopy (XPS). Hence, besides traditional diffraction method (SAED) there has also been applied the ex-situ approach (FTIR, XPS) for analyzing of fibers chemically isolated from Mg and MgLi matrices to detect non--crystalline and/or glassy phases.

2. Experiment

2.1. Composite preparation and fibers isolation

Commercial Saffil preform (Saffil Ltd, UK) containing $\sim$ 10 vol.% discontinuous Saffil fibers and $\sim$ 4 wt.% silica binder & film was infiltrated with pure Mg and MgLi alloys with different Li contents (4, 8 and 12 wt.%) to prepare related metal matrix composites. Individual Saffil fibers are typically 3–5 μm in diameter and about 300 μm in length [9]. They consist of nanocrystalline δ-Al_2O_3 phase ($\sim$ 96 wt.%) and a small amount of dissolved inner silica ($\sim$ 4 wt.%) [2]. Melt infiltration was carried out in labor autoclave by the gas pressure technique (argon, 6 MPa) at 690 °C for 120 s. To be ex-situ investigated by XPS and FTIR, the fibers were isolated by dissolving of Mg and MgLi matrices in 10 % bromine – methylacetate solution at the room temperature followed with filtration, decantation and drying at $\sim$ 50 °C under vacuum.

2.2. TEM and SAED analysis

The structure of Mg- and MgLi-matrix composites were studied in as-prepared state using TEM and SAED techniques (JEOL, JEM-100C) to identify the reaction products of silica conversion. The samples for TEM were prepared by standard ion-thinning technique (Balzers).

2.3. FTIR analysis

FTIR analysis of as-received and isolated Saffils was conducted under vacuum using Bruker JFS 66v set (DTGS MIR detector, KBr beam splitter, Globar source). Standard KBr pellet sampling technique was applied in which the fibers were mixed with KBr powder (1 : 300 ratio) and pressed into KBr disc. FTIR spectra (128 scans, resolution 4 cm^{-1}) were acquired within 900–1400 cm^{-1}.

2.4. XPS analysis

Isolated fibers (500 mg) were mechanically pressed into indium foil (4N purity) and analyzed in XPS SYSTEM PHI-5600 spectrometer on the area of 800 $\times$ 800 μm^2. The XPS spectra were excited by Al Kα radiation (350 W) with analyzer pass energy of 29 eV. The positions of spectra recorded were corrected to C(1s) peak.

3. Results

3.1. SEM and TEM investigation

Figures 1a–c show surface morphologies of as--received Saffil fibers as well as those affected with Mg and Mg-Li melts. While as-received Saffil is continuously covered with fairly smooth silica film (Fig. 1a), Mg and Mg-Li affected Saffils exhibit rugged surfaces with the population of submicron particles that are attributable to the conversion of silica species. Accordingly, Mg affected Saffil is uniformly covered with very fine crystallites with an approximate size of 50–70 nm (Fig. 1b) while on the surface of Mg-Li affected Saffil there are visible detached large particles (200–300 nm) besides numerous small crystallites (Fig. 1c).

To characterize these products, interfacial region in Mg and Mg-Li composites was investigated using TEM and SAED. Figure 2a shows TEM micrograph of matrix area between two neighboring fibers in Mg composite displaying small well-faceted crystallites that have been identified as MgO and Mg_2Si and, in some cases, also as coupled MgO/Mg_2Si products (Figs. 2b,c). Ring SAED patterns indicate that MgO is present as a polycrystalline phase while Mg_2Si particulates appear mostly in the single-crystalline form.
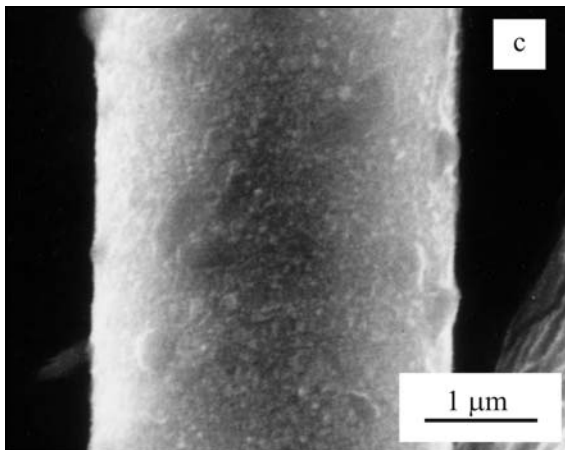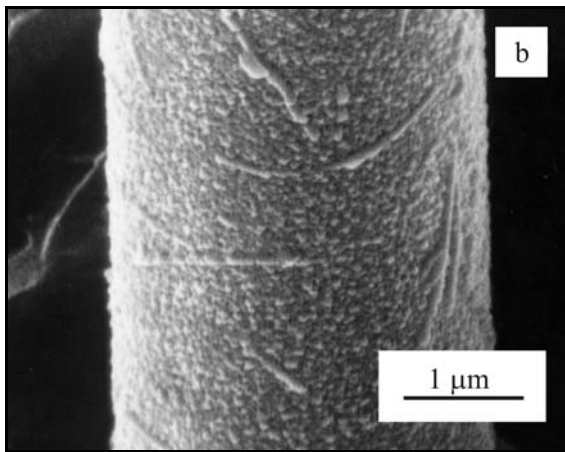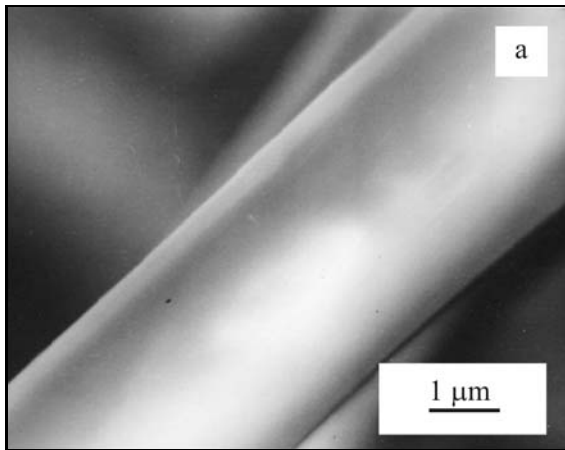
Fig. 1. SEM micrographs showing the surface morphologies of as-received Saffil (a), Saffil isolated from pure Mg (b) and Saffil isolated from Mg-8 wt.% Li alloy (c).

These submicron particles occur typically in narrow matrix areas between close lying fibers where initial silica binder was preferentially localized. In case the fibers are well spaced apart, the particles reside usually directly on fiber surfaces.
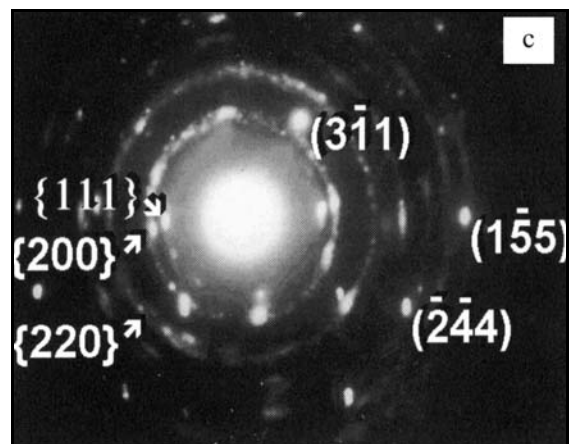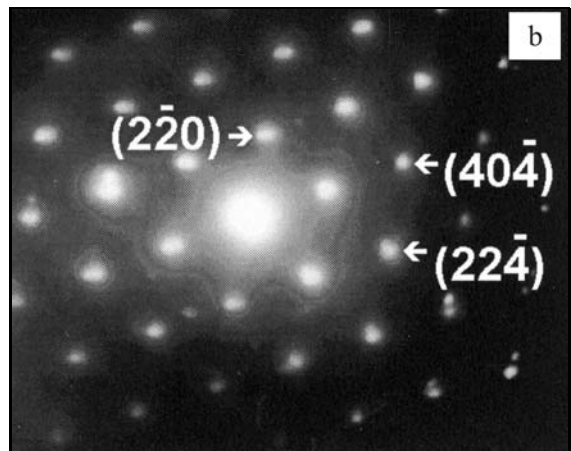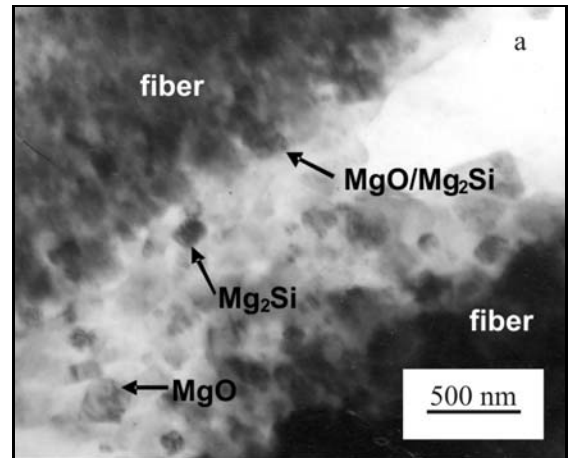
The only reaction products detected by SAED in

Fig. 2. Bright-field TEM image of the matrix region between two close-lying Saffil fibers in pure Mg matrix composite showing submicron crystallites of MgO, Mg_2Si and MgO/Mg_2Si (a), together with SAED patterns of [111] zone of Mg_2Si crystals (b), and [011] zone of Mg_2Si superimposed on ring patterns of MgO in coupled MgO/Mg_2Si particles (c).

matrix area of Mg-Li composites were MgO and Mg_2Si and very seldom also Li_2O. Equilibrium phase diagram Mg-Li-Si implies that in the magnesium-rich

corner, which is relevant to our study, besides Mg_2Si also Li_2MgSi and Li_xMg_2Si ($x \leq 0.91$) should precipitate [10]. However, neither lithium silicides nor ternary magnesium-lithium silicides were positively identified herein by SAED. Note that Li_xMg_2Si denotes interstitial solid solution of Li in binary Mg_2Si phase so that it is hardly discernible from Mg_2Si due to great similarity of their SAED patterns. Some of particles have been almost unidentifiable due to very poor SAED patterns indicating their glassy nature.

3.2. FTIR and XPS study

Because of limited capability of SAED to identify non-crystalline and/or glassy species, isolated Saffil fibers have been ex-situ analyzed by FTIR and XPS to gain complementary chemical information. Generally, crucial problem of ex-situ approaches is selection of appropriate solvent to minimize possible chemical attack of reaction products studied. Bromine--methylacetate solvent used in current study can partly dissolve both Mg- and Li-silicides so that FTIR and XPS results obtained are merely of qualitative significance.

As-received Saffil fibers and those isolated from Mg- and Mg-8 wt.% Li matrices were FTIR analyzed focusing on Si-O bond stretching region around $1000–1100\,cm^{-1}$ wherein the as-received Saffil preform with silica binder is expected to exhibit absorption band at about $1080\,cm^{-1}$ belonging to SiO_2 [11]. As already mentioned, besides the "outer" silica binder & film there occurs in Saffil fibers also crystallographically incorporated "inner" silica preserving δ-alumina phase on fibers processing. Obviously, the transmission FTIR spectrum of as-received Saffil preform comprises contributions of both outer and inner silica species.

Figure 3 compares FTIR spectra recorded from various Saffils: (a) as-received Saffil with silica binder, (b) as-received Saffil without silica binder, (c) Mg melt affected Saffil, and (d) Mg-8 wt.% Li melt affected Saffil. Spectrum (a) shows striking absorption band with the maximum at $1085\,cm^{-1}$ while spectra (b) and (c) display almost unrecognizable Si-O absorptions. Spectrum (b) demonstrates that contribution of inner silica is almost negligible although its amount is roughly the same as that of outer silica which reflects different structure of these silica species. While the silica binder is constituted solely of silica domains consisting of aggregated SiO_4 tetrahedra, inner silica can be modeled in terms of isolated SiO_4 tetrahedra randomly distributed within AlO_4 and AlO_6 groups of δ-alumina phase [12]. Amount of inner silica (~ 4 wt.%) corresponds to molar composition of $\sim SiO_2 \cdot 15Al_2O_3$ which indicates very dilute solution of SiO_4 groups in δ-alumina structure. As a result, striking Si-O absorption around $1080\,cm^{-1}$ is produced by silica binder (line a) while
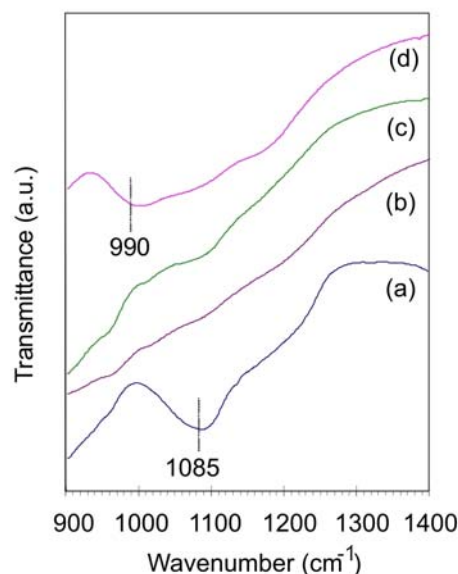

Fig. 3. FTIR spectra of different Saffils in the region of Si-O stretching vibrations: (a) as-received Saffil with silica binder, (b) as-received Saffil without silica binder, (c) Saffil isolated from pure Mg, (d) Saffil isolated from Mg-8 wt.% Li alloy.

the extremely poor ones belong to inner silica (line b). Very weak IR pattern at $1085\,cm^{-1}$ in spectrum (c) indicates almost total decomposition of silica binder due to Mg attack. Nevertheless, the traces of residual SiO_2 are still recognizable. On the other hand, the spectrum of Mg8Li affected Saffil (line d) exhibits broad and relatively strong Si-O absorption band centered at about $990\,cm^{-1}$ which is markedly less intensive than that of as-received Saffil (line a). Its shape and position corresponds to some Li_2O-rich silicate specified tentatively as orthosilicate Li_4SiO_4 [13, 14]. The latter consists of isolated SiO_4 tetrahedra connected with LiO_n polyhedra ($n = 4, 5, 6$) [15]. Broadening of absorption band (line d) may be due to the vibrational interference of SiO_4 units with LiO_n groups. As compared to spectrum of as-received Saffil (line a), maximum of Si-O absorbance (line d) is shifted to lower wavenumbers by $\sim 90\,cm^{-1}$ thus giving an evidence for the formation of silicate type compound [16]. Moreover, broad IR absorption spanned between $950–1070\,cm^{-1}$ appears to overlap also the SiO_2 related absorption at $1085\,cm^{-1}$ thus indicating incomplete decay of silica binder.

XPS analysis has been used to identify silicon species on the surface of Saffils isolated from MgLi matrices with different Li content. Figure 4 shows detailed XPS records of fibers isolated from Mg-4 wt.% Li (line a), Mg-8 wt.% Li (line b) and Mg-12 wt.% Li (line c) in the binding energy (BE) region of 95–110 eV comprising two Si(2p) photoelectron peaks at 98.5 eV and 102.5 eV. Both these Si(2p) patterns are nearly
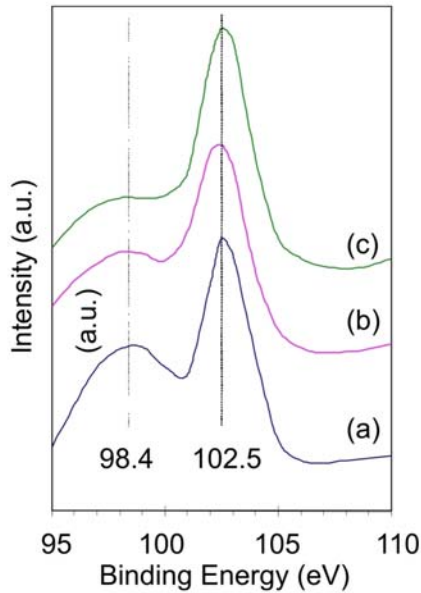
Fig. 4. XPS records of Saffils isolated from Mg-4 wt.% Li (a), Mg-8 wt.% Li (b) and Mg-12 wt.% Li (c) alloys in the region of Si(2p) photoelectrons indicating the presence of Mg$_2$Si and Li-silicate by 98.4 eV and 102.5 eV binding energy positions.

symmetric without any overlapping features thus indicating the presence of single silicon-related species. The first peak is positioned close to Si(2p) core level of Mg$_2$Si reported in the literature (98.3 eV) [17]. BE value of 102.5 eV of the second peak is quite well fitted with Si(2p) of lithium disilicate [18]. Neither elemental Si (99.5 eV) [19] nor SiO$_2$ (103.5 eV) [20] have been found. These results indicate that magnesium silicide Mg$_2$Si and some Li-Si-O phase are the only Si(2p) silicon species detected on the surface of MgLi affected fibers. XPS patterns in Fig. 4 suggest that Mg$_2$Si formation tends to be suppressed with increase in Li content in MgLi matrix alloy.

4. Discussion

Despite certain inferiority of ex-situ investigations resulting from possible attack of reaction products with bromine-methylacetate solvent, FTIR and XPS results can be usefully combined with SAED analysis to gain more complete picture on conversion of silica binder in Mg and Mg-Li melts affected Saffil. In both cases MgO and Mg$_2$Si were the major reaction products. In addition, in Mg-Li affected Saffil also the lithium silicates were found. Note that FTIR and XPS results cannot be fully compatible with each other because FTIR is a bulky analytical method while XPS is restricted only to surfaces.

SAED analysis has shown that pure magnesium

transforms the silica binder towards MgO and Mg$_2$Si which corresponds to earlier observation of Hallstedt et al. [4]. Accordingly, silicon released by the displacement reaction (1) is dissolved in molten Mg and enters the reaction (2) producing Mg$_2$Si. Morphological features of Mg$_2$Si and MgO crystallites suggest that they have been formed by the primary crystallization from the melt, typically via heterogeneous nucleation on the surface of Saffil fibers. Nevertheless, Mg$_2$Si crystals can also precipitate on primarily formed MgO phase as demonstrated by the occurrence of MgO/Mg$_2$Si couples. However, the amount of elemental Si released by the silica binder in current Mg matrix composite (10 vol.% Saffil) seems to be too low for formation of primary Mg$_2$Si crystals directly from the melt because it is well below the eutectic concentration (1.3 mol.% Si) reported for binary Mg-Si system [4]. Hence, infiltration time was too short for achieving uniform concentration of dissolved Si within entire Mg matrix so that primary Mg$_2$Si might locally crystallize only in silicon-rich regions followed with secondary Mg$_2$Si precipitation from supersaturated solid solution on the cooling.

On the other hand, FTIR analysis of MgLi affected Saffil indicates the presence of some silicate-type compound that however could not be precisely identified. Its formation can be outlined by common shrinking core model [20]. Accordingly, lithia produced by displacement reaction

$$4Li + SiO_2 = 2Li_2O + Si \qquad (3)$$
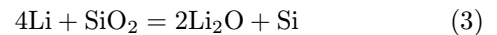
creates the reacted shell on the core of unreacted silica thus forming the reaction couple Li$_2$O/SiO$_2$ in which the solid state reaction:

$$xLi_2O + ySiO_2 = Li_{2x}Si_yO_{x+2y} \qquad (4)$$
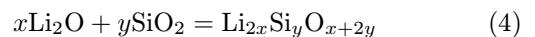
can proceed. This result corresponds to observations of Maschhoff et al. [21] establishing that lithium silicate can be formed by reaction between SiO$_2$ and elemental Li. It is nevertheless quite surprising that relatively mild reaction conditions (690 °C/120 s) in present experiments are sufficient to accomplish this solid state reaction. Reaction (4) may proceed by counter migration of Li$^+$ and Si^{4+} ions in the framework of O^{2-} ions array, as usual in formation of mixed oxides [22]. Accordingly, extremely fast kinetics of reaction (4) seems to be linked with very fast diffusion of Li$^+$ ions. Similar silicate forming reaction in pure Mg affected Saffil preform, despite thermodynamically favorable, has not been observed, probably due to slower mobility of Mg^{2+}. As known, monovalent cations in oxidic ceramics migrate much faster than polyvalent ones [22]. FTIR spectrum (Fig. 3, line d) suggests that besides silicate products there is still present some amount of residual silica. Silicate phases

$x\mathrm{Li_2O} \cdot y\mathrm{SiO_2}$ have not been detected by SAED so they appear to be of glassy nature. Elemental Si released by reaction (3) is thought to be dissolved in MgLi matrix and precipitate as $\mathrm{Mg_2Si}$.

$\mathrm{Mg_2Si}$ was the only silicide identified in MgLi affected Saffil while any of possible lithium silicides reported in literature ($\mathrm{Li_{22}Si_5}$, $\mathrm{Li_{13}Si_4}$, $\mathrm{Li_7Si_3}$, $\mathrm{Li_{12}Si_7}$) have not been found. These silicides appear in Li-rich corner of Mg-Li-Si ternary diagram which, however, lies too far from current Mg-Li compositions so that precipitation of above mentioned binary lithium silicides is hardly expectable. On the other hand, the precipitations of $\mathrm{Mg_2Si}$ as well as $\mathrm{Li_2MgSi}$ and $\mathrm{Li_xMg_2Si}$ seem to be possible [10]. However, negligible crystallographic differences between $\mathrm{Mg_2Si}$ and $\mathrm{Li_xMg_2Si}$ (Li-doped $\mathrm{Mg_2Si}$ in fact) makes the latter silicide hardly identifiable by SAED method. Proposed model of Li insertion into host $\mathrm{Mg_2Si}$ is interstitial solid solution in which $\mathrm{Li^+}$ ions occupy vacant octahedral positions [23]. That is why the formation of $\mathrm{Li_xMg_2Si}$ phase in MgLi affected Saffil cannot be excluded.

5. Conclusions

SEM and TEM observations as well as SAED, FTIR and XPS analysis were used to characterize reaction products of the silica binder decomposition during infiltration of Saffil fibers preform with Mg and Mg-Li melts. Dominant reaction products in both cases are MgO and $\mathrm{Mg_2Si}$ formed by displacement redox reaction. In Mg-Li melt infiltrated Saffil preform there was found besides MgO and $\mathrm{Mg_2Si}$ also the non-crystalline phase that appears to be lithium silicate $x\mathrm{Li_2O} \cdot y\mathrm{SiO_2}$. Precise characterization of these silicate products needs, however, further study. Binary lithium silicides and/or ternary magnesium-lithium silicides were not identified.

Acknowledgement

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