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KOMPOZYTY
COMPOSITES

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MICROSTRUCTURE AND TENSILE PROPERTIES OF COMPOSITES WITH HIGH STRENGTH ALUMINIUM ALLOYS MATRIX REINFORCED WITH SAFFIL™ FIBERS

Metal matrix composites (MMC) were produced by the force infiltration of Saffil™ fiber preforms with high strength AA2024, AA6061 and AA7075. The preforms with ~10 vol.% of fibers were bonded by dipping in liquid glass and heat treated at 800°C/2 hours. Next, the preforms were placed in a mould and the liquid alloy was forced into it. The composites microstructure was investigated using scanning xL30 and transmission Tecnai FEG (200 kV) electron microscopes. The tensile strength was tested with an Instron machine. The microstructure observations confirmed that after heat treatment, the $Na_2SiO_3(H_2O)$ binding phase turns to amorphous silica. The liquid AA2024 reacts with the silica, substituting part of the binder with a fine-crystalline mixture of MgO, Θ–Cu_2Al and silicon crystallites. The AA6061also reacts with the SiO_2 binder, but replaces it with a porous amorphous aluminium oxide. However, the infiltration with AA7075 left the binder mostly intact with discontinuous precipitates of MgO at the silica/matrix interface. The mechanical tests of the AA6061/Saffil™ were inconsistent due to a large scatter of results, but for the other composites they showed that the Saffil™ fibers helped to increase the tensile strength of the castings from 230 to 330 MPa and from 420 to 590 MPa for the AA2024/ Saffil™ and AA7075/ Saffil™ composites (T6 conditions) respectively.

Keywords: MMC, AA2024/ Saffil™, AA6061/ Saffil™, AA7075/ Saffil™, nano-composites

MIKROSTRUKTURA I WYTRZYMAŁOŚĆ KOMPOZYTÓW O OSNOWIE Z WYSOKOWYTRZYMAŁYCH STOPÓW ALUMINIUM WZMACNIANYCH WŁÓKNAMI SAFFIL™

Kompozyty o osnowie metalicznej zostały otrzymane poprzez ciśnieniową infiltrację wysokowytrzymałymi stopami AA2024, AA6061 oraz AA7075 preform zawierających ~10% obj. włókien Saffil™. Preformy zanurzano w roztworze z tzw. ciekłego szkła $Na_2SiO_3(H_2O)$, suszono, a następnie wypalano w 800°C/2 godz. Następnie ceramiczne preformy osadzano we wlewnicy, którą napełniano ciekłym stopem wtłaczanym do niej z wykorzystaniem prasy. Kompozyt badano metodami mikroskopii skaningowej (xL30) oraz transmisyjnej (Tecnai FEG 200kV). Własności wytrzymałościowe mierzono z wykorzystaniem urządzenia Instron. Obserwacje mikrostruktury wykazały, że po obróbce cieplnej ciekłe szkło ulega przemianie do amorficznej krzemionki (SiO_2). Zalanie reformy ciekłym stopem AA2024 powoduje jego reakcję z krzemionką, a w konsekwencji jej zastąpienie drobnokrystaliczną mieszaniną MgO, Θ-Cu_2Al oraz α-Si. Również AA6061 reaguje z krzemionką, ale w rezultacie w jej miejsce tworzy się porowaty i amorficzny Al_2O_3. Jedynie przy infiltracji preform stopem AA7075 większa część fazy krzemionkowej pozostawała w mostkach między włóknami, ale w jej granicy z osnową pojawiały się już warstwy MgO. Pomiary własności mechanicznych dla AA6061/ Saffil™ miały zbyt duży rozrzut, ale w przypadku dwu pozostałych kompozytów stwierdzono, że ich wytrzymałość na rozciąganie rośnie z 230 do 330 MPa oraz z 420 do 590 MPa odpowiednio dla AA2024/ Saffil™ and AA7075/ Saffil™ (po obróbce T6).

Słowa kluczowe: nanokompozyty, AA2024/ Saffil™, AA6061/ Saffil™, AA7075/ Saffil™

INTRODUCTION

Aluminium alloys are already quite widely applied in automotive industry. They serve not only for the production of car bodies and minor fittings but also for more demanding parts like engine blocks or piston heads. Reinforcing high strength aluminium alloys with ceramic particles or fibers may allow the development of even lighter and stiffer materials. It was already proved in the case of AA6061, 2014, 2024, 7075 or AlMgCuAg alloys, where the addition of Al_2O_3 Saffil™ fibers showed up to a 20% increase of UTS and hardness [1-5]. Additionally, all these composites retain their high strength up to a higher temperature range than the alloys serving as their matrix. However, infiltrating a ceramic preform made of such fine fibers without changing their required shape is quite a problem.

The lack of wetting of Al_2O_3 fibers by aluminum was partly overcome by force infiltration and partly by alloying additions, like magnesium, routinely introduced into commercial aluminium alloys. However, switching from the Al–Al_2O_3 system to AlMg–Al_2O_3 may cause a reaction between magnesium and Al_2O_3. It could result in the formation of MgO, detrimental for mechanical properties, or even more brittle $MgAl_2O_4$ [1]. The fixing of a preform with $Na_2SiO_3(H_2O)$ liquid glass only worsens this situation by introducing a large amount of oxygen from the SiO_2 bonding phase, which is easily dissolved in contact with liquid metal.

A few published observations of aluminium alloys like Al4Cu1Mg0.5Ag reinforced with SiO_2 bonded Saffil™ fibers showed that in a multi-component alloy, $MgAl_2O_4$ may indeed form alongside MgO even at very low magnesium additions [3, 6]. Similarly, $MgAl_2O_4$ was found on the surface of Al_2O_3 particles introduced to an AA6262 alloy [7]. Aside from the presence or absence of some types of oxides formed at the Saffil™ fiber/matrix interface, their amount and form may also significantly affect the mechanical properties of these composites. This information could be gained only through more microstructure observations of these materials.

Therefore, the present project was aimed at the microstructure characterization of the composites obtained with AA2024, AA 6061 and AA7075 aluminium alloys reinforced with Saffil™ fibres, frequently used in car industry applications. Special attention was paid to analysis of the phases formed at the fibre surfaces.

EXPERIMENTAL PROCEDURE

The preforms made from Safill™ fibers (10 vol.%) were bonded with liquid glass ($Na_2SiO_3(H_2O)$), dried and fired at 800°C. Next, they were force infiltrated with AA2024, AA6061 or AA7075 alloys (Table 1). The composites obtained with the two former alloys were next solution heat treated and aged to peak hardness, i.e. T6 condition.

TABLE 1. **Chemical compositions (wt.%) of alloys used for infiltrating preforms**

TABELA 1. **Skład chemiczny stopów używanych do infiltracji preform**

Alloys	Mg	Si	Cu	Zn	Mn	Fe	other
AA2024	1.2÷1.8	0.4÷0.6	3.8÷4.9	<0.25	0.3÷0.9	<0.5	<0.1[1)]
AA6061	0.8÷1.2	0.4÷0.8	0.1÷0.4	<0.25	<0.15	<0.7	<0.4[2)]
AA7075	2.1÷2.9	<0.4	1.2÷2.0	5.1÷5.6	<0.3	<0.5	<0.15[3)]

[1)] Cr <0,1, Ti <0,2 [2)] Cr <0,35, Ti <0,15 [3)] Cr<0,3, Zn<0,1, Pb<0,1

The composite microstructure was investigated using scanning eXL30 (relying on a Secondary Electrons (SE) detector) and transmission Tecnai SuperTWIN FEG 200kV electron microscopes with an integrated EDAX microanalysis system. Thin foils were cut using a Quanta 3D focused ion beam equipped with an Omniprobe lift-out attachment.

RESULTS

Dipping Saffil™ fibers into liquid glass, covers them with a thin layer of binder which dries leaving characteristic roughness on their surface (Fig.1a). Subsequent firing at a high temperature simultaneously removes the rest of the water from the bonding phase and smooths the fiber surfaces. Eventually, after the firing process, every strand of Saffil fiber is coated with a thin amorphous layer of silica with some traces of sodium. The bonding phase fixes the fiber connections and stabilizes the preform shape (Fig.1b). The transmission electron microscopy of thin foils cut from such bridges helped to prove that even after heat treatment, the binder preserves its amorphous form.

a)

b)

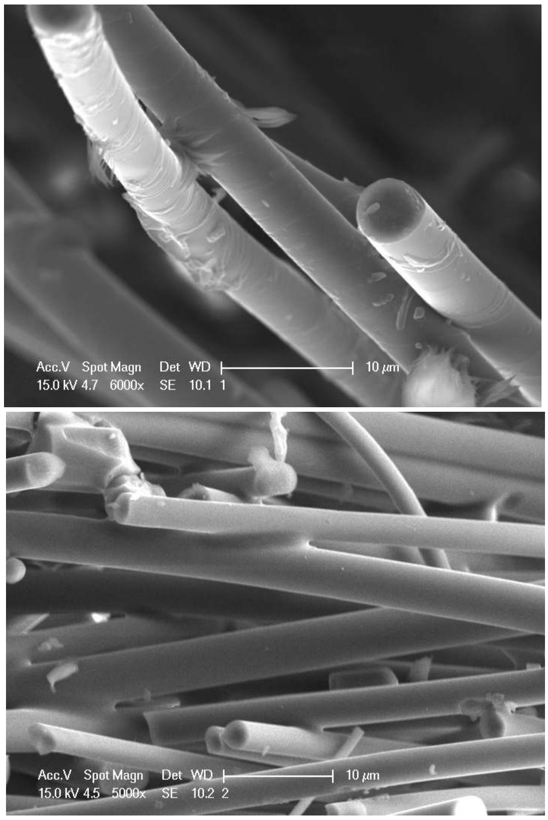

Fig.1. Scanning images (SE) of Saffil™ fibers: a) covered with liquid glass, b) after additional heat treatment strengthening fiber interconnections

Rys. 1. Obrazy mikrostruktur skaningowych włókien Saffil™: a) pokrytych szkłem wodnym, b) poddanych dodatkowemu wyżarzaniu wzmacniającemu ich połączenia

The force infiltration with any of the investigated alloys allowed the filling in of practically all the interfiber areas, preserving their approximately uniform distribution (Fig. 2a). A section obtained with a Focused Ion Beam (FIB), i.e. devoid of standard polishing artifacts like groves or pits, showed that during solidification, the fibers served as preferential nucleation sites for phases of evidently brighter mass contrast, i.e. denser than the matrix (Fig. 2b). Only, in some deep pockets left between adjacent fibers a dark contrast was present, which may correspond to remnants of the $Na_2SiO_3(H_2O)$ bonding phase.

a)

b)

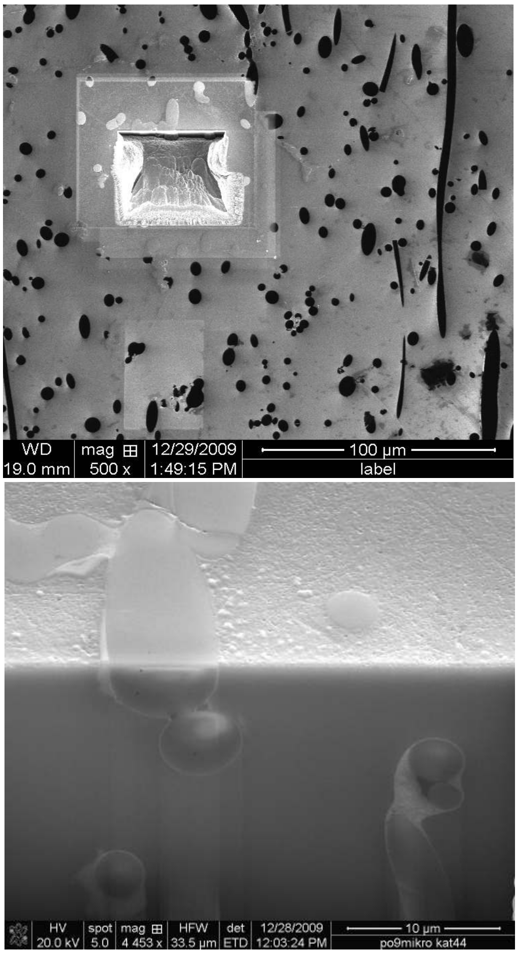

Fig. 2. Scanning images (SE) of: a) polished surface of Saffil™/AA2024 composite and b) its FIB section obtained from place shown in upper left corner

Rys. 2. Obrazy skaningowe (SE): a) polerowanej powierzchni kompozytu Saffil™/AA2024 oraz b) przekroju poprzecznego do powierzchni z miejsca zaznaczonego w lewym górnym rogu wykonanego techniką FIB

The composite microstructure is dominated by sections of nano-crystalline Saffil™ fibers sometimes connected with binder bridges and immersed in a metallic matrix (Fig. 2). The as-cast ones contain some larger precipitates attached to the fibers, as the latter serve as preferred nucleation sites for intermetallic phases during solidification (Fig. 2a). The applied homogenization treatments help to dissolve most of the intermetallic phases leaving the matrix nearly precipitation free (Fig. 2b). The subsequent heat treatment causes the formation of fine Θ phase thin platelets from the supersaturated aluminium on the {100} matrix planes, characteristic for T6 heat treatment (Fig. 3a). These observations also show that at the places where the grain boundary touches the fiber, larger crystals of a/an Θ or Q phase are still present. It indicates that the standard for AA2024 T6 treatment and especially the homogenization temperature is not as effective as in the worked alloy. The precipitates persist as they are much larger than in the worked alloy pieces and their dissolution cannot be completed in time. Simultaneously, the bridges of the amorphous silica bonding phase formed between the fibers in the preform were either substituted in the composites with porous amorphous material (Fig. 3a), a mixture of fine crystalline material (Fig. 3c) or left untouched (Fig. 3b).

a)

b)

c)

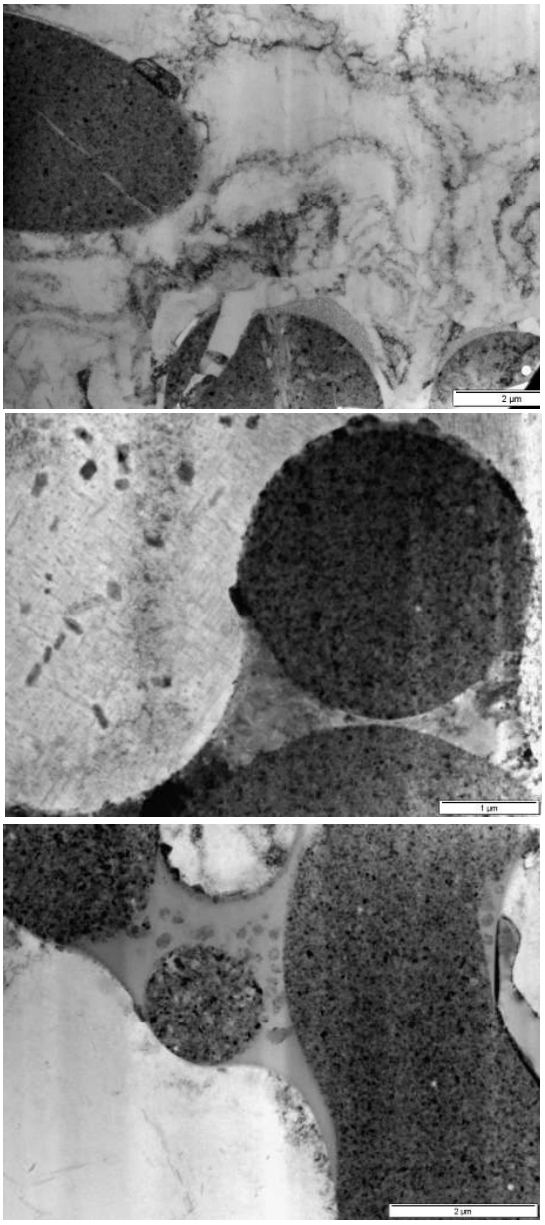

Fig. 3. Transmission images (BF) of Saffil™ fibers: in matrix from a) AA6061, b) AA7075, c) AA2024 alloys

Rys. 3. Obrazy transmisyjne włókien Saffil™, w osnowie ze stopów: a) AA6061, b) AA7075, c) AA2024

The chemical analysis using the EDS system indicated, that the porous material formed in the place of the $Na_2SiO_3(H_2O)$ in the AA6061/Saffil™ fiber composite is indeed an aluminium oxide (Fig. 4a). The swapping during the infiltration of AA6061 with the

AA2024 alloy caused the bridges to be substituted with a mixture of the Θ and practically pure silicon crystallites immersed in remnants of the SiO_2 phase (Fig. 4b).

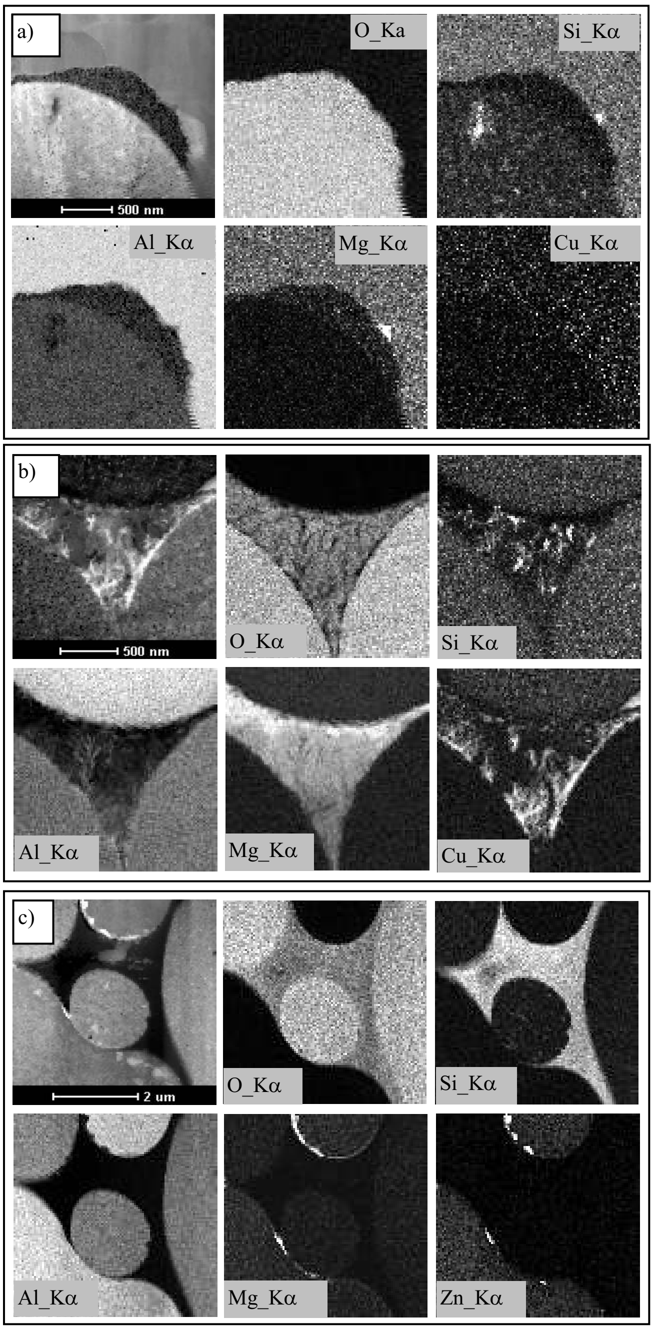

Fig. 4. Scanning-transmission (HAADF) images and maps presenting distribution of O, Al, Si, Cu, Zn and Mg obtained from: a) AA6061/Saffil™, b) AA2024/Saffil™, c) AA7075/Saffil™ composites

Rys. 4. Skaningowo transmisyjne obrazy oraz mapy prezentujące rozkład O, Al, Si, Cu, Zn i Mg uzyskanych z kompozytów: a) AA6061/Saffil™, b) AA2024/Saffil™, c) AA7075/Saffil™

The scanning - transmission image confirms a high density of nano-voids (visible as dark spots) as well as some SiO_2 (added to prevent Al_2O_3 nano-crystallites growth) in the Saffil™ fibers. Outside of these interconnections, i.e. where fibers were covered only with a thin layer of binder, the latter was totally dissolved and substituted with MgO precipitated directly on the fiber surface. The filling in of the preform from Saffil™ fibers with still another alloy, i.e. AA7075, left the glassy SiO_2(NaO) bridges practically untouched (Fig.4c). Zinc or copper-rich or Mg_2Si intermetallic phases indeed form but only at the binder/matrix interface. However, some reaction between SiO_2(NaO) and liquid metal has to take place, as at the Saffil™ fiber surface, the thin layer of binder was substituted with a layer of MgO similar in thickness. The lack of any significant signal from other than silicon and oxygen elements from the central part of the binder areas indicates that the defects in such areas (visible in Fig. 3) are probably voids formed during firing.

The tensile tests performed at ambient temperature using samples of the presently produced composites showed only a moderate strength increase from 230 to 330 MPa and from 420 to 590 MPa for the AA2024 and AA7075 alloys (T6 conditions) respectively, as presented in Figure 5. The above gains roughly correspond to those obtained by Hajjari et al [8] for a direct squeeze cast as compared to gravity casts of the AA2024 alloy, i.e. with no reinforcing phase. However, the composites retain most of their strength up to 200 or even 300°C, which is far outside of any safety operational temperature margin for high strength aluminium alloys.

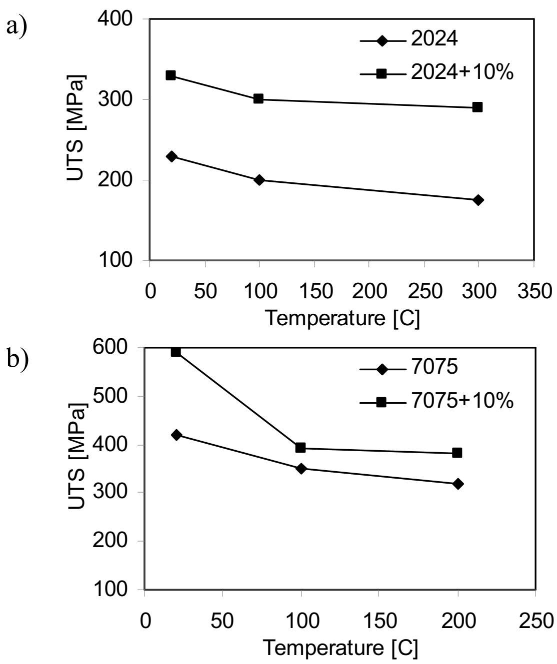

Fig. 5. Ultimate Tensile Strength of alloys and composites with 10 vol. % of fibers with: a) AA2024, b) AA7075 (T6)

Rys. 5. Wytrzymałość (Rm) stopów i kompozytów z 10% włókien Saffil™ z osnową: a) AA2024, b) AA7075 (T6)

DISCUSSION

The reinforcing high strength aluminium alloys of the 2xxx, 6xxx or 7xxx series with even stronger (~2 GPa), long, ceramic fibers like nano-crystalline

Al_2O_3 Saffil™ should help to produce exceptionally strong, stiff and light materials. Equally important is the fact that such composites retain relatively good mechanical properties up to much higher temperatures, i.e. at least 200 MPa at 300°C [2], while standard "duraluminium" loses its properties above 200°C. However, obtaining a roughly uniform distribution of long fibers, guaranteeing these very good properties requires their proper stabilization in the preform, which is a problem in itself. The easiest approach is by wetting the fibers with so called liquid glass, i.e. $Na_2SiO_3(H_2O)$ and next firing them at a high temperature, producing stable silica bridges between the individual fibers. The casting tests showed that such a procedure helps to produce preforms which can withstand force infiltration.

The formation of a strong connection between the matrix and the Saffil™ fibers is another requirement necessary to achieve improvement of MMC mechanical properties. Vaucher and Beffort [1] claim, that proper bonding between Al_2O_3 fibers and the aluminum alloy depends to large extent on the amount of magnesium additions deciding on the type of oxide phases, like MgO or $MgAl_2O_4$. They pointed out also that the presence of a spinel forming from 4<Mg<8 wt.% content is the most detrimental for composite properties. Even though, this amount is higher than usual magnesium additions in commercial alloys, the presence of an oxygen rich silica bonding phase might cause the nucleation of $MgAl_2O_4$, also in the case of such alloys like Al1Mg2Cu0.5Ag [3] or Al12SiCuMgNi [6]. The present experiments with AA6061 alloys containing ~1 wt. % Mg showed only formation of an Al_2O_3 phase in the place of the binder. The AA2024 and AA7075 alloys with a higher magnesium content, i.e. up to 1.8 and 2.9 wt.% respectively do show the presence of MgO at the binder/matrix interface. The differences between literature and the present experiments with AA6061 may be connected with varying casting conditions, like infiltration time and pressure as well as the amount of other alloying additions.

The lack of a $MgAl_2O_4$ spinel at the Saffil™ fiber/matrix interface, generally considered as a necessary condition for obtaining composite strength improvement, is not the only requirement. The porous mixture of an amorphous Al_2O_3 substituting bonding phase in the Saffil™/AA6061 composite definitely stands no chance at keeping the fiber-matrix together. Additionally, occasional larger voids present in this area might serve as crack initiators. The microcrystalline mixture of Θ-Al_2Cu, Si and MgO material found in the Saffil™/AA2024 composite in the places of the bonding phase has close similarity to the one obtained after the infiltration of Saffil™ with Al4Cu1Mg0.5Ag [3]. This composite shows the presence of only a very small amount of the glassy phase located in very deep pockets in-between the Saffil fibers, as in the one showed in the FIB cross section in Figure 2b. The Saffil™/AA7075 composite retained most of the glassy SiO_2 binding phase at the inter-fiber bridges, but at the binder/matrix interface the presence of magnesium oxide is also evident. Even though such a mixed microcrystalline like in Saffil™/AA2024 or amorphous like in the Saffil™/AA7075 microstructure seems of dubious value for load transfer, at least no voids were noted in that area.

The tensile testing at ambient temperature of the samples from the presently produced composites showed only a moderate strength increase from 230 to 330MPa and from 420 to 590 MPa for the AA2024 and AA7075 alloys (T6 conditions) respectively. The above gains roughly correspond to those obtained by Hajjari [8] for a direct squeeze cast as compared to gravity casts of the AA2024 alloy, i.e. with no reinforcing phase. However, the composites retain most of their strength to 200°C and even 300°C, which is far outside of any safety operational temperature margin for high strength aluminium alloys.

SUMMARY

The force infiltration of preforms with 10 vol.% of Saffil™ fibers with AA6061, AA20224 and AA7075 helped to obtain dense, i.e. of negligible macro- or even micro-porosity, MMC composites. The stabilizing of the strands of fiber in the preform with a ($Na_2SiO_3(H_2O)$) liquid glass, improved infiltration but simultaneously introduced a rich source of oxygen for reactions during casting. However, the microstructure observations indicated that infiltration of the Saffil™ preform with the AA6061 alloy with the lowest magnesium addition resulted in partial dissolution of silica and substituting it with a nano-porous amorphous aluminium oxide. Similar experiments with the AA2024 and AA7074 alloys with higher a magnesium content resulted in the formation of magnesium oxide at the remnants of the binder/matrix interfaces.

The reproducible results of mechanical measurements were obtained only for the composites with the AA2024 and AA7074 alloy matrix, while the one with AA6061 gave a large scatter of data probably caused by the presence of nano-porous amorphous alumina formed at the Saffil™ surface. The tensile strength of the produced composites was only at par with squeeze cast alloys, i.e. they reached 330 and 590 MPa for those with the AA2024 and AA7074 matrix, respectively. However, the composites retain most of their properties, i.e. the Saffil™/AA2024 shows ~300 MPa at 200°C and the Saffil™/AA7075 more than 400 MPa ultimate tensile strength at 200°C.

Acknowledgements

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