XRD and EDS Investigations of Metal Matrix Composites and Syntactic Foams

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ABSTRACT

Metal matrix composites (MMCs) of different composition were produced and investigated by X-ray diffraction (XRD) and energy dispersive spectrometry (EDS) analysis. Firstly unidirectionally reinforced MMCs were produced using two type carbon fibre reinforcement and commercial purity aluminium matrix. In MMCs the interface layer has significant effect on the mechanical properties of the composites therefore need to be correctly explored. The investigations showed chemical composition changes in the composites, especially at the interface layers. In the case of carbon fibre reinforced composites Al_4C_3 phase was formed. The amount of Al_4C_3 depended on the temperature and the time at temperature of the composite during production and on the quality of carbon fibres. As the second investigated MMC, SiC fibre reinforced aluminium matrix composite wires were produced by continuous pressure infiltration. In SiC reinforced MMC wires the effect of interface diffusion was observed. After long term thermal ageing at 300°C alumina was formed and Si and Ti of SiC fibres moved into the matrix. Finally, metal matrix syntactic foams were manufactured which are particle-reinforced composites, but also known as porous materials (foams), because they contain high amount of hollow ceramic microspheres. Four type hollow spheres from different suppliers with different chemical composition and mean diameters were used. In syntactic foams an exchange reaction took place between the aluminium alloy matrix and the Si content of ceramic inclusions. The reaction resulted in significant alumina formation.

KEYWORDS

X-ray diffraction analysis, energy dispersive spectrometry analysis, metal matrix composite, syntactic foam, interface layer, aluminium-carbide

INTRODUCTION

Nowadays MMCs are widely used in many fields. They can be found in every engineering application, where increased mechanical properties and low density are required. Their unique properties make them competitive in transportation industry

(train and other vehicles), in aeronautics, astronautics. Many structural elements in modern devices exchanged for MMCs during years of development [1]. MMCs' main advantages are their very good specific properties and thermal stability. Their modulus to weight and strength to weight ratio are outstanding. The constituents of the composites and the interface layer between the reinforcement and matrix material determine these properties. In the case of MMCs lightweight metal alloys (usually aluminium) are used as matrix material, which can ensure the low self-weight of the composite. MMCs can be either particle- or fibre-reinforced. Particles can be easily embedded in metals by mixing into liquid metal or using infiltration technique. However when the loading is direction specified, fibre reinforcement, aligned in the main loading direction is better choice than particles, or randomly aligned short fibres. Fibre-reinforced composites usually have steel, alumina, SiC or carbon fibre reinforcement. MMC blocks can be made by pressure infiltration technique [2]. The main parameter in this case is the infiltration pressure, which can be approximated by numeric calculations and influenced by wetting [3, 4]. MMCs with fibre reinforcement can also be produced by a continuous infiltration technique [5]. In this case temperature and wetting are extremely important and have great influence on the required infiltration pressure. Composite wires have exciting mechanical properties [6, 7] and are investigated according to various applications [8]. In composite materials the interface layer has special role on the mechanical properties. This layer is responsible for load transfer from matrix to reinforcement. If the interface has week zones, the load transfer cannot be accomplished. Therefore the investigation of interface is an important task in characterization of the composites [9].

Particle-reinforced MMCs have a special class, called metal matrix syntactic foams; they can be classified as closed-cell foams also. The first publications on this material were presented in the late sixties. In the case of syntactic foams porosity is originated from hollow ceramic spheres, which are composed of various oxides (mainly SiO_2, Al_2O_3, K_2O, Fe_2O_3 and MgO). Syntactic foam blocks can be also made by pressure infiltration [10, 11, 12]. The required pressure can be estimated by numerical methods and depends on the wetting similarly as in the case of fibre-reinforced MMCs [13]. The main advantages of these materials are low density, high specific compression strength and thermal stability. The compression strength can be estimated by mathematical method [14]. Syntactic foams loaded in compression show a plateau region and absorb high mechanical energy [15, 16]. Therefore they are used as energy absorbers, sound absorbers or as material of hulls in naval applications and aeronautics. In the case of metallic syntactic foams the matrix materials are usually aluminium alloys because of their low density. Between the hollow ceramic spheres and matrix an interface layer can be formed. It has – again – a very important role on mechanical properties, because this layer ensures the load transfer between the microspheres and matrix material. Load partitioning was investigated by neutron and synchrotron X-ray diffraction analysis in previous study. By calculating an effective stress from the measured lattice strains, the degree of load partitioning between phases was determined [17].

As one can see the interface layers formed during production have at least the same importance in MMCs as the constituents themselves. Therefore the investigation of interface layer should be one of the most important tasks in characterization of the MMCs. From the results of XRD and EDS investigations on MMCs and their constituents one can deduce conclusions about the interface layers and therefore

about the properties of composite itself. The aims of this paper are to develop different methods for the investigations of interface layers and to characterize the interfaces of the produced MMCs.

EXPERIMENTAL

Investigated materials

Unidirectionally reinforced MMCs were produced in different manner. As first examined material, MMC blocks were produced by pressure infiltration. These MMC blocks contained 60 vol% carbon fibres in AlSi12Mg matrix. Dimensions of the blocks were 25×75×170 mm. The infiltration pressure was 8.5 MPa (85 bar) and the infiltrating temperature was 600 °C. The difference between the produced blocks was the difference between the applied carbon fibres. Two types of fibres were used: Thornel P25 4K and Zoltek 12K. The mean diameters of the fibres were 13 μm and 7 μm respectively. According to X-ray diffraction analysis, the “xSize” parameter (which has connection with the grain size) of carbon fibres was 3.2 and 2.5 in the case of Thornel and Zoltek fibres respectively (T and Z in the followings).

The second examined material was a reinforced MMC wire, which was also produced by continuous pressure infiltration method. This MMC wire contained 60 vol% Nicalon type polymer-melt spun SiC fibre. Bleay et al. examined Nicalon-type SiC fibres; electron probe microanalysis showed that the fibres consist of 54.9 wt% Si, 32.1 wt% C and 11.6 wt% O. Fine structure analysis of the X-ray emission bands showed that these elements were combined as 46 vol% silicon carbide, 34 vol% silicon oxycarbide and 20 vol% free carbon, with the oxycarbide in the outermost regions of the fibre being significantly richer in oxygen. The silicon carbide was composed of microcrystallites several micrometres in diameter and the remaining material formed an amorphous network of material surrounding the microcrystallites [18]. The matrix was commercial purity Al (cp-Al, Al99.5) and the fibres had 16 μm mean diameter. The composite wire’s diameter was 1.6 mm and it had high strength and Young’s modulus [6, 7]. The infiltration pressure and temperature was 2 MPa (20 bar) and 710°C respectively. After production, long term ageing (262 h, 720 h and 1155 h) were done at 300 °C in atmospheric environment.

Finally, as the third examined material, metal matrix syntactic foams were produced by pressure infiltration. Matrix materials were cp-Al or AlSi12, nearly eutectic aluminium alloy. Four type of hollow ceramic microspheres were used, SSI, SLG, SL150 and SL300 respectively. In summary eight types of syntactic foams blocks were manufactured. Dimensions of the blocks were 36×55×170 mm. The microsphere content was maintained at 60 vol%. The hollow ceramic spheres were supplied by Sphere Services Inc. (SSI) and Envirospheres Pty. Ltd. (SLG, SL150 and SL300). Table 1 shows the constituent phases and mean diameters of the hollow spheres. The infiltration pressure was 0.5 MPa (5 bar), the infiltration temperature was 600 °C and 710 °C in the case of AlSi12 and cp-Al matrix respectively. The specimens were investigated in as manufactured state and they were named after their constituents. For example the name AlSi-SSI means the specimen has AlSi12 aluminium alloy matrix and approx. 60 vol% SSI type hollow microspheres.

Table 1. Morphological properties and phase constitution of the applied hollow ceramic spheres

Sphere type	Diameter	Al_2O_3	SiO_2	Mullite	Quartz	Other
[-]	[μm]			[phase%]		
SSI	10-350	25-30	55-60	6	2	bal.
SLG	20-300					
SL150	20-150	30-35	45-50	19	1	bal.
SL300	150-300					

Specimen preparation, XRD- and EDS analyses

X-ray diffraction and energy dispersive spectrometry analyses were applied in order to get information about the interface between the reinforcement and matrix material. All XRD analyses were done on powdered specimens at the Chemical Research Centre of the Hungarian Academy of Sciences using a Phillips X-Pert type diffractometer. A small, but representative part of the composites were dry powdered in alumina mortar. The EDS investigations were done by using a Phillips XL-30 type scanning electron microscope with EDAX Genesis analyser. These measurements needed careful preparation. Carbon fibre-reinforced MMC blocks showed high stiffness, but they were brittle. Due to the brittleness newly generated and cleaned fracture surfaces could be investigated by EDS analysis. The centre and the edge of the filaments, and the interfilamental matrix were analysed by spot measurements at 5 kV excitation voltage. The same preparation was done in the case of SiC reinforced cp-Al wires, but the specimens were cooled in liquid nitrogen in order to minimize the plastic deformation of matrix during fracture. Spot measurements were done on one single fibre and on the separated interface layer. In the case of syntactic foams EDS line analysis was done on polished samples. The length of the lines was approx. 17 μm measured at 30 points. The lines started from the matrix materials and crossed the wall of the hollow sphere.

RESULTS AND DISCUSSION

Carbon fibre reinforced MMCs

XRD measurements revealed that in MMCs with carbon fibre reinforcement Al_4C_3 phase was formed during production of the composites according to the following endothermic reaction (ΔG= -168 kJmol^{-1}).

$$4Al_{(liq)} + 3C_{(sol)} \rightarrow Al_4C_{3(sol)}$$

Al_4C_3 is a brittle acicular phase growing perpendicular from the surface of carbon fibres. This can have beneficial effect on the compressive strength, because Al_4C_3 crystals can constrain the lateral deformation and therefore the compressive strength will be higher. In the Al-diamond systems Al_4C_3 formation has distinguished planes, which are {100} planes of the diamond, while the aluminium-carbide precipitation is suppressed on the {111} planes [19, 20]. The measurements showed that in Z-type

carbon fibre reinforced composite (having lower “xSize” parameter) 18 times higher quantity of Al_4C_3 was formed, see Fig. 1 and 2.

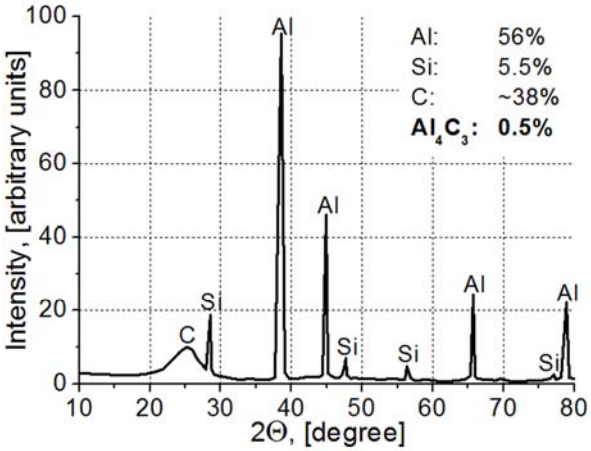

Figure 1. Diffractogram of AlSi12Mg+60 vol% Thornel type carbon fibre reinforced composite

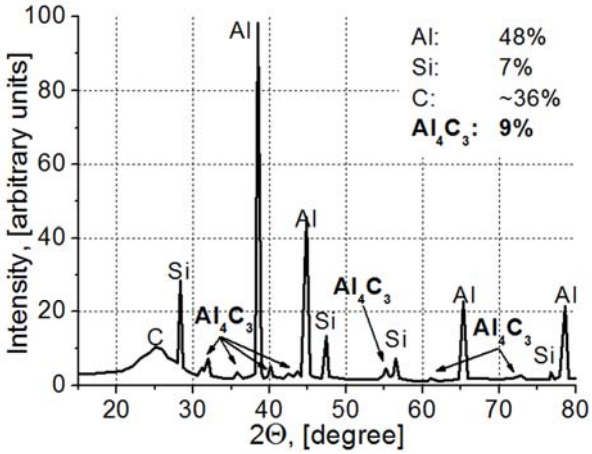

Figure 2. Diffractogram of AlSi12Mg+60 vol% Zoltek type carbon fibre reinforced composite

Lower “xSize” parameter means lower grain size and higher probability of occurrence of distinguished planes on the fibre surface (similar as in Al-diamond systems). The more ideally oriented planes are available the more Al_4C_3 will form. This was ensured by EDS investigations. The results of these measurements are shown in Fig. 3 and Table 2.

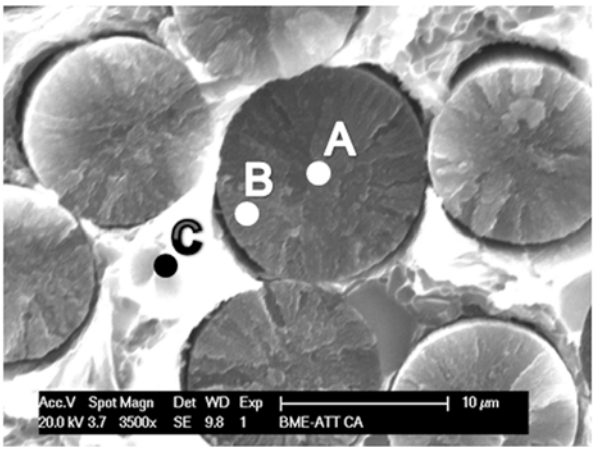

Figure 3. Fractograph and arrangement of measured spots on carbon fibre reinforced materials

Table 2. Chemical composition in analysed points of carbon fibre reinforced composites

Spot		C	Al	Si	O
[-]		[weight%]			
T	A	93.5	1.94	0.34	4.22
	B	88.1	7.81	0.54	3.17
	C	28.4	66.7	4.92	0
Z	A	87.4	9.21	0.85	2.59
	B	81.1	16.6	0.91	1.36
	C	15.1	80.1	4.79	0

EDS measurements showed decreasing carbon content from the centre of the fibre to the matrix. At the edge of the fibres carbon content decreased by 5-6% showing carbon diffusion to the matrix. This strengthens the possibility of Al_4C_3 formation at the interface layer.

SiC fibre reinforced MMC wires

Al_4C_3 formation is also possible in Al-SiC systems during pressure infiltration, therefore in composite wires as well, according to the following equation.

$$4Al_{(liq)} + 3SiC_{(sol)} \rightarrow Al_4C_{3(sol)} + 3Si_{(sol)}$$

Despite of the reaction above, XRD analyses did not show any Al_4C_3 formation, but revealed gamma-Al_2O_3 and mullite ($3Al_2O_3 \cdot 2SiO_2$) development in the crystalline part of the thermally aged composite wires. The results summarized in Table 3.

Table 3. Constituents of the crystalline phases of the thermally aged composite wires

Specimen [-]		Al [phase%]	SiO_2 [phase%]	γAl_2O_3 [phase%]	Mullite [phase%]
300 °C	262 h	95	1	0	0
	720 h	95	0.5	0	2
	1155 h	65	2	30	3

After 1155 hours at 300 °C the amount of gamma-Al_2O_3 strongly increased in the composites. High alumina development implies oxygen diffusion from the outer, oxygen rich region of the fibres to the interface layers as silicon oxycarbide was reduced by Al. Besides this, getting of oxygen into the interface layer is also possible. Some alumina and silica combined to mullite at the interface layer. There was no crystalline SiC observed, so the heat treatment did not change the amorphous part of SiC reinforcement. This process was confirmed by EDS analysis (see Fig. 4 and 5). The results of EDS measurements are listed in Table 4.

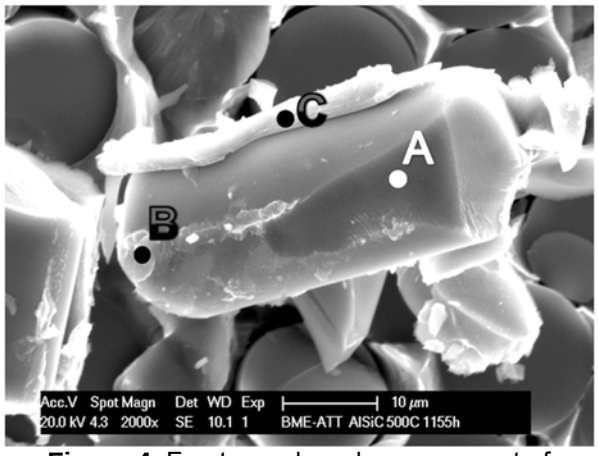

Figure 4. Fractograph and arrangement of measured spots on SiC reinforced MMC wires

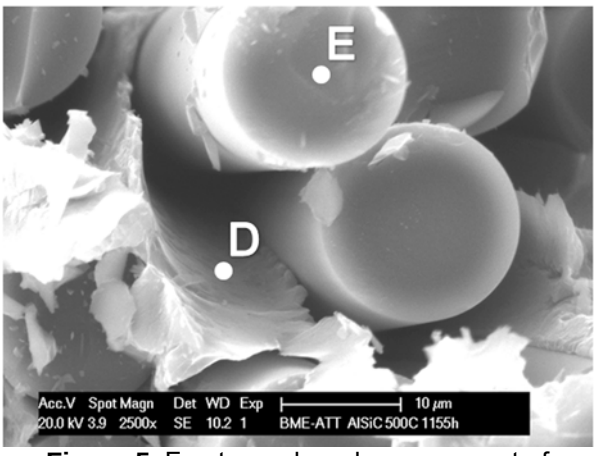

Figure 5. Fractograph and arrangement of measured spots on the cross section of SiC reinforced MMC wires

Table 4. Results of EDS measurements of heat treated SiC reinforced metal matrix composite wires

Spot [-]	Al [wt%]	Si [wt%]	C [wt%]	O [wt%]	Ti [wt%]
A	2.5	75.3	5	14	3.2
B	10.9	75.9	5	4	4.2
C	86.1	8.1	3	2	0.8
D	53.2	39.2	3	2	2.6
E	2.3	75.4	6	13	3.3

These results showed that after 1155 h heat treatment at 300 °C the middle of the fibre (spot A and E) almost did not change and contains lot of Si. The same result can be observed in spot B, but a very thin layer of Al remained on the fibre's surface, so more Al can be noticed. In spot C a thin layer of matrix was analysed which contains mainly Al. The inner surface of the separated interface layer (spot D) is rich in Si, which proves the diffusion process mentioned above. Another diffusion process

was also observed: Ti content of fibres was relatively high in the centre and on the edge of the fibres and also in the inner surface of the separated interface layer. This indicates that during heat treatment titanium moved out from the surface of fibres and diffused to the matrix.

Metal matrix syntactic foams

In the case of metal matrix syntactic foams XRD analyses revealed an exchange reaction, which processed between hollow ceramic spheres and matrix material during the composite production. The results of XRD analyses are given in Table 5 and 6.

Table 5. Results of XRD measurements of cp-Al matrix syntactic foams

Specimen	Al	Si	Mullite	γ-Al_2O_3	α-Al_2O_3	Amorphous glass
[-]				[phase%]		
Al-SSI	65	8	5	15	3	0
Al-SLG	60	6	12	12	4	0
Al-SL150	65	8	10	10	3	0
Al-SL300	75	0	10	0	0	10

Table 6. Results of XRD measurements of AlSi12 matrix syntactic foams

Specimen	Al	Si	Mullite	Quartz	Amorphous glass
[-]				[phase%]	
AlSi-SSI	80	10	2	1	5
AlSi-SLG	72	7	12	0	8
AlSi-SL150	72	7	12	0	8
AlSi-SL300	72	7	12	0.5	8

Due to the exchange reaction SiO_2 was reduced by the Al according to the following equation (ΔG= -310 kJmol^{-1}).

$$4Al_{(liq)} + 3SiO_{2(sol)} \rightarrow 2Al_2O_{3(sol)} + 3Si_{(sol)}$$

This reaction strongly depends on the infiltration temperature and the exposure time. In the case of cp-Al matrix, Al_2O_3 was formed during the exchange reaction while the amorphous glass and mullite phase content was decreased significantly. Al_2O_3 was developed mainly as gamma-Al_2O_3, and less Al_2O_3 developed as alpha-Al_2O_3 due to rapid cooling and diffusion process. The driving force of diffusion was the Si-concentration difference between microballoon walls and matrix material. As one can see in Table 5 Al-SL300 type composite was an exception. In that case the mullite content decreased, but no Al_2O_3 and Si were formed, and some amorphous glass remained. This can be explained by the smaller relative surface of the SL300 type microspheres and somewhat lower infiltration temperature (690 C). In the case of AlSi12 matrix the mullite and Si content were decreased too but in smaller degree, and there was no Al_2O_3 formation. This fact implies that the exchange reaction mentioned above was suppressed or blocked by something.

The only thing what changed was the matrix material's Si content. The driving force of the exchange reaction was the silicon concentration difference between the hollow sphere walls and matrix material. This difference was decreased when using AlSi12

matrix, which contains considerable amount of silicon. Due to this, the driving force decreased and the rate of the exchange reaction decreased also. Line EDS measurements were done on the polished specimens. The line-scan profiles showed the alternating of chemical elements along the line. This is a very good chance to examine the interface layer and the changes in the microsphere wall and in the matrix. Examples for cp-Al and AlSi matrices are shown in Fig. 6 and 7 respectively.

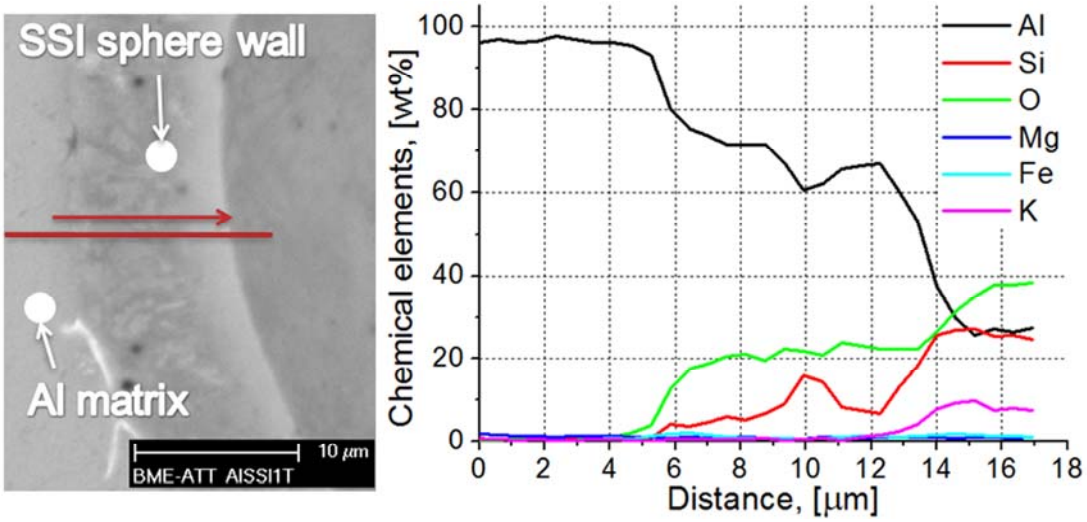

Figure 6. BSE image and EDS line-scan profiles of Al-SSI syntactic foams

In Fig. 6 the wall of a SSI type hollow sphere can be observed in high magnification back-scattered electron (BSE) image. It can be noticed that the outer edge of the wall is not very well defined. This means the surface is disordered. As mentioned above the exchange reaction produces Al_2O_3, what is advantageous, but not at a price of disordering the microballoon's wall. The Si and Al content were decreased and increased respectively in the direction of radius pointing outward from the centre as expected due to diffusion process. In Fig. 6 a lighter grey zone in the BSE image can be observed at the inner side of the microsphere. This zone had different chemical composition and was rich in Si, O and K. In the case of AlSi12 matrix the Al and Si content can be observed at the beginning of the diagram (Fig. 7).

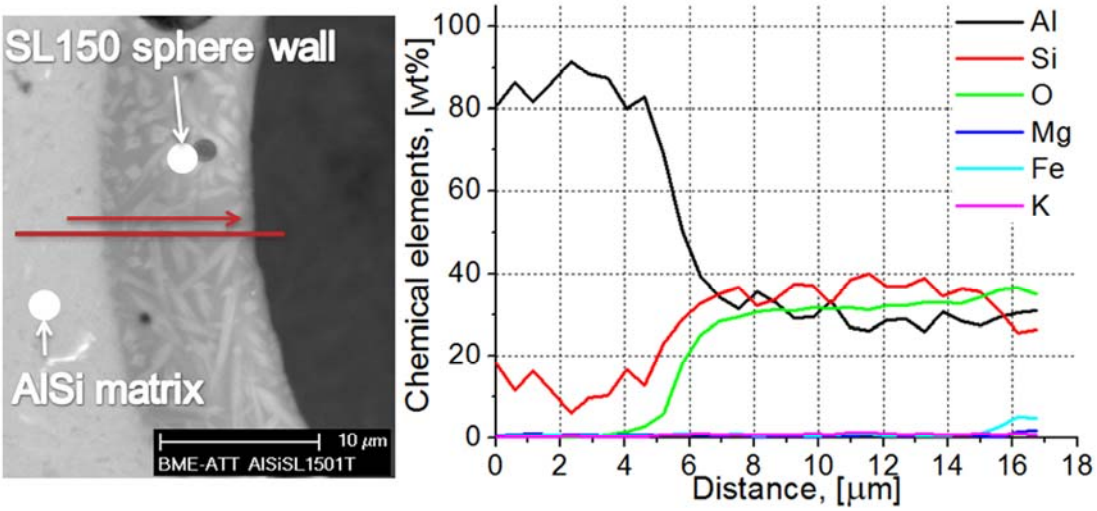

Figure 7. BSE image and EDS line-scan profiles of AlSi-SL150 syntactic foams

The outer surface was unharmed as the exchange reaction was suppressed. In the concentration-sensitive BSE image lighter needle-like phases can be observed in the wall of SL150 spheres. According to this a well defined Al and Si alternation occurred in the line EDS analysis diagram. In the lighter areas Si and Al content decreased and increased respectively while the oxygen content remained constant. This implies that lighter phases in the sphere wall are Al_2O_3 rich particles embedded in SiO_2 rich matrix. Again a very narrow Fe, Mg and K rich inner band exists at the inner side of the microballoon wall.

CONCLUSIONS

From the results of XRD and EDS measurements described above the following statements can be concluded.

- In carbon fibre reinforced MMCs Al_4C_3 was formed. The Al_4C_3 content depends on the crystallinity of carbon fibres and mainly on the manufacturing temperature and exposure time.
- In SiC reinforced MMC wires Al_4C_3 was not observed, but after long term ageing at 300 °C Al_2O_3 was formed that originated from the solid state aluminium induced decomposition of the silicon oxycarbide. A diffusion process of Si and Ti was observed and resulted in the Si and Ti rich interface layer. The SiC of the fibres remained amorphous and its amount was not changed at the applied ageing temperature.
- In cp-Al matrix syntactic foams intensive Al_2O_3 development was occurred due to an exchange reaction except in the case of SL300 reinforcement. The driving force of the diffusion ruled reaction was the Si concentration difference between reinforcement (microballoon) and matrix. The microballoon-matrix interface was damaged and not very well defined. The reaction between microballoon and matrix degraded the microballoons' wall. At the inner surface of microballoons a Si, O and K rich band was observed.
- In AlSi matrix syntactic foams the exchange reaction was suppressed by the considerable amount of Si content in the matrix. When aluminium contains about 12 wt% silicon, the silica containing hollow spheres remained stable.

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