A study of the composition and microstructure of aluminum matrix composites reinforced with alumina fibers

D Zolotova¹, V Serpova², M Prokofiev¹, L Rabinskiy¹ and A Shavnev²
¹ Moscow Aviation Institute, 4, Volokolamskoe shosse, Moscow, 125993, Russia
² All-Russian Scientific Research Institute of Aviation Materials, 17, Radio st., Moscow, 105005, Russia
E-mail: f9_dec@mai.ru

Abstract. This article presents the results of a study of the microstructure and the composition of aluminum-based metal matrix composites (MMC) reinforced with continuous alumina fibers. An Al-Mg-Cu alloy similar to that of AA 2024 was used. X-ray diffraction and X-ray fluorescence analyses were used for investigation of a probable volume fraction of a spinel phase in MMC. Scanning electron microscopy and an X-ray microanalysis were used to study a change of the elemental composition of the composites microstructure on the polished cross sections. The constant mass fractions of magnesium (0.65 wt. %) and copper (1.25 wt. %) were found in the interphase area within radius of 1 µm around fibers.

1. Introduction
Enhancement of metallic materials strength nowadays is a topical issue of materials science due to a sharp rise of requirements in the leading-edge aerospace engineering. One of the effective ways of solution of this problem is design of composite materials based on a metallic matrix and, in particular, MMC based on an aluminum matrix reinforced with continuous Al₂O₃ fibers.

The main method of production of Al/Al₂O₃ fiber composites is vacuum impregnation. The main problem of this method is to ensure a reliable contact between fibers and the matrix [1]. The interface properties, first of all adhesion between fibers and the matrix, determine the level of macroscopic properties of composites and preserve it throughout the lifecycle. Local stresses in a composite reach maximum values exactly near or immediately at an interface where material destruction usually starts. Therefore, to reach high mechanic performance, it is necessary to provide effective load transfer from the matrix to the reinforcing agent in the composite material. An adhesive bond at the interface should not be destroyed under the impact of external loading and in case of thermal and shrinkage stress arising due to the difference of matrix and fibers coefficients of thermal expansions. High strength of MMC is achieved in case the reinforcing component is properly moistened with the matrix alloy. However, as a rule, the interphase interaction causes the formation of intermetallic compounds that account for brittle fracture of MMC [1].

In case of production of Al-Al₂O₃ system of MMC, interphase layers consisting of MgAl₂O₄ and/or CuAl₂O₄ (depending on the matrix composition), spinel phases may be formed around fibers in the matrix [2-7]. There is an assumption that if magnesium is added to an aluminum alloy, it is segregated at the inter-phase border thus improving moistening and adhesion in Al/Al₂O₃ MMC [7-9].
The MgAl\(_2\)O\(_4\) spinel may be formed by two identical reactions: in case of interaction of magnesium with aluminum and magnesium with Al\(_2\)O\(_3\) fibers or \(\alpha\)-Al\(_2\)O\(_3\) polycrystals are formed in case of aluminum oxidation [2]:

\[
\begin{align*}
\text{Mg + 2Al + 2O}_2 & \rightarrow \text{MgAl}_2\text{O}_4 \\
3\text{Mg + 4Al}_2\text{O}_3 & \rightarrow 3\text{MgAl}_2\text{O}_4 + 2\text{Al}.
\end{align*}
\]

The purpose of this work is to study the detailed elemental composition and thickness of the interfacial zone in the structure of MMC aluminum based composites armed with alumina fibers.

2. Experimental procedure

Experimental MMC samples were manufactured using a liquid-phase vacuum impregnation technology. Reinforcement was performed using unidirectional continuous Al\(_2\)O\(_3\) fibers. Russian D16 Al-Mg-Cu system aluminum, which is an analog of 2024 aluminum alloys, was used as a matrix. The volumetric content of fibers in MMC was 55 \% wt.

The process operations used to produce MMC samples were: fibrous workpiece formation of the continuous Al\(_2\)O\(_3\) fiber using the winding method, vacuum-compressor impregnation of a fibrous workpiece with a melt of a matrix alloy, machining.

The X-ray analysis was performed using the ALR X’TRA (TermoFisher) device of Cu-K\(_\alpha\) radiation with the \(\theta\)-\(\theta\) scanning method using the PDF -2 data base and the Crystallographica Search-Match Version 3.1.0.0 software. The analysis was performed with the samples of longitudinal and transversal arrangement of fibers towards the radiation source. The quantitative X-ray phase analysis was performed using the Siroquant v.3 program. Aluminum oxide fibers have been also studied separately. This test was performed for estimation of sensitivity and precision of the performed X-ray phase analysis of a composite material.

The chemical X-ray fluorescent analysis was performed using ARL-Optim-X (TermoFisher) along with the UQuant program. At the same time, substances with a content of aluminum less than 0.2 \% were not taken into consideration. The analysis was performed with allowance for backward scattering. The equipment used does not enable revealing a volume fraction of light elements, hydrogen and fluorine. In this case, the volumetric content of oxygen is not explicitly taken into consideration. The analyzing program only enables estimation of the volumetric content of elements or oxides thereof.

The composite microstructure was studied by the example of the cross-sections of samples using the EVO 40 Karl-Zeiss microscope. The X-ray microanalysis of the composition was performed using electronic scanning microscope Versa 3D LoVac DualBeam.

3. Results

For unidirectional samples oriented longitudinally and transversely to the radiation source X-ray diagrams were obtained (Figure 1a, b). Data given in table 1 has been acquired as a result of the analysis of X-ray diagrams. The results of intensity measurements for two types of samples are slightly different. It was established that a sample is mostly two-phase and consists of (-Al\(_2\)O\(_3\) and a solid solution of copper in Al.

The results of the chemical X-ray fluorescent analysis are given in Table 2. It contains the weight fractions of components that are a part of the material in terms of the metallic phase and in terms of oxides. The analysis has revealed that a fraction of copper and magnesium (or oxides thereof) in a metal composite is approximately half as high as compared with the original fraction in the matrix alloy.
Figure 1. X-ray analysis results in case of longitudinal orientation of fibers (a), transversal orientation of fibers (b). In the upper part of the figures (blue lines) – X-ray diagrams obtained from experiments; given below – from the data base (green and black lines).

Table 1. Results of the X-ray analysis of composites.

|                        | Aluminum Oxide | Aluminum |
|------------------------|----------------|----------|
| **Longitudinal Arrangement of Fibers** |                |          |
| Formula                | $\alpha$-Al$_2$O$_3$ | Al       |
| PDF number             | 010-71-1241      | 010-71-4625 |
| Concentration, % wt.   | 58              | 42       |
| Total Peaks            | 25              | 5        |
| **Transversal Arrangement of Fibers** |                |          |
| Formula                | $\alpha$-Al$_2$O$_3$ | Al       |
| PDF number             | 010-82-1468      | 010-71-4624 |
| Concentration, % wt.   | 59%             | 41%      |
| Total Peaks            | 25              | 5        |

Table 2. Results of the X-ray fluorescent analysis in terms of oxides and in terms of metallic phase.

|                        | In terms of Metallic Phase | In Terms of Oxides |
|------------------------|----------------------------|--------------------|
| Element                | Content                | Oxide             | Content |
| Al                     | 94.14                  | Al$_2$O$_3$       | 96.30   |
| Cu                     | 2.03                   | CuO               | 1.01    |
| Si                     | 1.15                   | MgO               | 0.941   |
| Mg                     | 0.908                  | SiO$_2$           | 0.752   |
| Fe                     | 0.667                  | Fe$_2$O$_3$       | 0.395   |

We could assume that all founded magnesium and copper oxides may be the parts of spinel phases. In this case, based on the known values of density of compounds and weight content of elements that are part thereof, we could establish that the maximum volume fractions of spinel in a composite shall not exceed 7 %. The probable areas of location of spinel particles are interfacial zones near fibers [2-7]. The average probable thickness of spinel layers on fibers were calculated considering the known average diameter of one fiber (11 µm) and the value of the volumetric content of the spinel phase was found. This value equals, approximately, 0.74 µm. For these areas, we further perform an X-ray microanalysis.

Micrographs of composite cross-sections and individual fibers are given in Figure 2 and 3. Light areas in Figure 2b are the areas of high concentration of copper and iron and the black areas among fibers are the areas of high concentration of carbon admixtures. Sets of points at different distances
from the fiber surface were chosen for the X-ray microanalysis (Figure 3a). The elemental composition was defined at each point. Totally, 12 such sets have been studied for several fibers around which a sufficiently thick layer of matrix alloy is located without the visible content of admixtures. Each set contained 3 points: located near the fiber surface; located at a distance of 0.5 µm and those 1 µm distant. Figure 3b shows the established change of the volumetric content of elements in the matrix distant from the fiber surface. The given results are averaged for 12 sets of point. The variation of the concentration values has been found at points located at the same distance from the fiber surface amounted to a maximum of 50%. The aluminum concentration is not shown on this graph as it amounts to the remaining value of 100% of the volumetric content.

Figure 2. The overall view of the microstructure of the composites cross-sections (a) and the presence of admixtures in the matrix (b).

Figure 3. Points of the X-ray microanalysis in the interphase area between the fiber and the matrix (b) and their results (b).

4. Conclusions
We presented the results of studies of the composites based on Russian alloy D16 (similar to AA in 2024) reinforced with alumina continuous fibers. According to the data of the X-ray analysis, only Al and Al₂O₃ phases have been found in MMC samples. MgAl₂O₄ and CuAl₂O₄ spinel phases have not been found, which may be a consequence of the method error that equals 5% wt. Based on the acquired results of the analysis of the sample chemical composition, an estimation of the possible maximum volumetric content of interphase areas in the MMC structure has been performed. The estimation has shown that the phase of spinel in a composite could equal up to 7 vol. %. Therefore, the
average thickness of interphase areas could equal up to 740 nm. As a result of the X-ray microanalysis, it has been established that near the fibers almost no change of the weight content of magnesium and copper elements occurs. The mass fractions are 0.65 % and 1.25 %, respectively. This may mean that in the studied composite samples there were no spinel phases formed near the surface of the fibers. Otherwise, the spinel crystals could be formed locally not causing formation of a solid interphase layer with constant thickness. The X-ray microanalysis has also revealed the fact that near the fibers the mass fraction of silicon is 0.75% and the farther it is from the fiber, the higher it gets. The composition analysis has revealed the fact that the alloy structure contains a large amount of carbon admixtures.

Acknowledgments
The authors acknowledge the funding support from FP ‘Research and development in priority areas of scientific-technological complex of Russia, 2014 – 2020’ event 1.3, agreement № 14.577.21.0171.

References
[1] Chawla N and Chawla K 2006 Metal Matrix Composites (NY: Springer)
[2] Munitz A et al 1979 Metall. Mat. Trans. A 10 1491
[3] Zhong W et al 1995 Metall. Mat. Trans. A 26 2625
[4] Moser B et al 2004 Acta Materialia 52 573
[5] Sreekumar V et al 2008. Metall. Mat. Trans. A 39 919
[6] Shen P et al 2004 J. Am. Ceram. Soc.. 87 2151
[7] Levi C et al 1978 Metall. Trans. A. 9 697
[8] Jonas T et al 1995 Metall. Trans. A. 26 1491.
[9] Hallstedt B et al 1993 Mater. Sci. Eng. A. 169 149