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Development of aluminum hydroxides in Al–Mg–Si/SiC$_p$ in infiltrated composites exposed to moist air

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Abstract

In this work the degradation of metal/composite interfaces (M/C) in Al–Mg–Si/SiC$_p$ composites exposed to moist environments was investigated. The formation of Al(OH)$_3$ at the M/C interface indicated the development of Al$_4$C$_3$ during processing. It was found that at room temperature Al$_4$C$_3$ slowly reacts with moisture in the atmosphere. As a result, the degradation rate increases logarithmically with time. In particular, it was found that the kinetics of degradation is influenced by the atmospheric conditions and the air quality.

Keywords: Al/SiC$_p$ composites; Pressureless infiltration; Degradation of Al$_4$C$_3$

1. Introduction

Metal matrix composites (MMCs) reinforced with ceramic particles such as the Al–Mg–Si/SiC$_P$ system, have a high potential to be considered as structural components such as brakes, electronic packaging, aerospace, etc. Yet, during MMCs processing by alloy melting, undesirable reactions occur which can lead to Al$_4$C$_3$ formation [1–6]. Apparently, Al$_4$C$_3$ is unstable in environments such as water, methanol, HCl, etc. [1–4] as it can easily react to form aluminum hydroxides. Consequently, Al$_4$C$_3$ can have severe detrimental effects on the mechanical integrity of the resultant MMC.

In general, the development of Al$_4$C$_3$ phases is strongly influenced by temperature, holding times and silicon content in the matrix [1–8]. Park and Lucas [9] investigated the formation of Al$_4$C$_3$ and the propensity for its dissolution when exposed to de-ionized water environments. In their work, they found that Al$_4$C$_3$ dissolves relatively fast when in direct contact with water causing pitting on SiC/6061 Al interfaces. There is considerable work on the degradation of Al$_4$C$_3$ when in contact with moist environments [9]. Yet, there is only limited information on the evolution and kinetics of the reaction products in MMCs containing Al$_4$C$_3$ exposed to moist atmospheres. Hence, the present work is aimed at investigating the long term degradation effects exhibited in an Al–Mg–Si/SiC$_p$ composite containing Al$_4$C$_3$ in the presence of moisture.

2. Experimental

High purity SiC with a 20 μm average particle size was used in preparing preforms of 20 mm in diameter by 20 mm in height. The preforms (50 vol.% porosity) were obtained by mixing the SiC powders with 10 wt.% dextrin and 0.5 ml distilled water. An Al–10Mg–12Si (wt.%) alloy was employed for infiltration purposes. Infiltration was performed in a horizontal furnace by heating the preform at a rate of 150 °C/min up to 600 °C in contact with the Al-alloy in ultra high purity argon. The atmosphere was then switched to ultra high purity nitrogen all the way to the test temperatures (950–1100 °C), with the chamber held isothermically for test times of 0–60 min. Afterwards, the system was

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cooled down to 550 °C and then air cooled to room temperature. The infiltrated composites were then removed from the furnace and sectioned for chemical and microstructural characterizations. In addition, various infiltrated samples where exposed to air moisture for times of up to 510 days. A scanning electron microscope (SEM) Philips XL30 ESEM equipped with a Falcon energy dispersive X-ray spectroscopy (EDX) was employed for microstructural determinations. Moreover, a Philips-3040 X-ray diffractometer was used for phase identification purposes.

3. Results and discussion

Fig. 1a–b are SEM micrographs of the metal/composite (M/C) reinforcement interface of an infiltrated perform exposed to air for 20 days. In these figure, the metal matrix component was removed by electrochemical etching. From this figure, it is found that a discontinuous reaction zone develops along the metal/reinforcement interface. The phases present at this interface were mainly AlN, Si and partially dissolved SiC particles.

In particular, notice the partial dissolution of SiC particles by molten aluminum (Fig. 1b) in agreement with reports of preferential pitting on SiC [10]. In Al–SiC MMCs, partial dissolution of SiC by the aluminum melt often leads to the formation of unwanted Al_3C_4 phases [10].

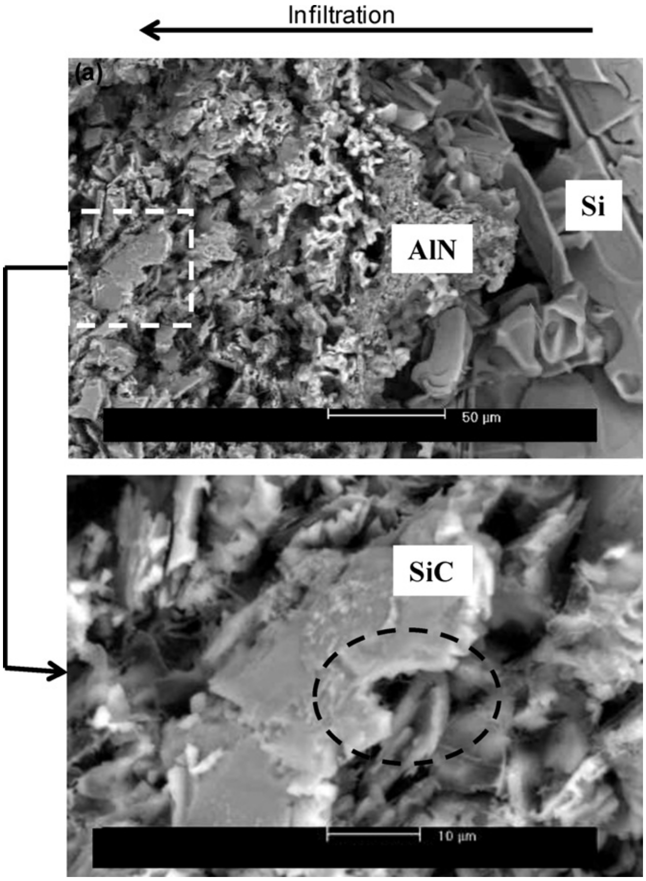

Fig. 1. SEM micrographs of the metal/composite interface showing (a) the various phases formed (SiC, AlN and Si) after infiltration for 20 days and (b) SiC pitting at encircled region. The sample was electrochemically etched using HNO_3.

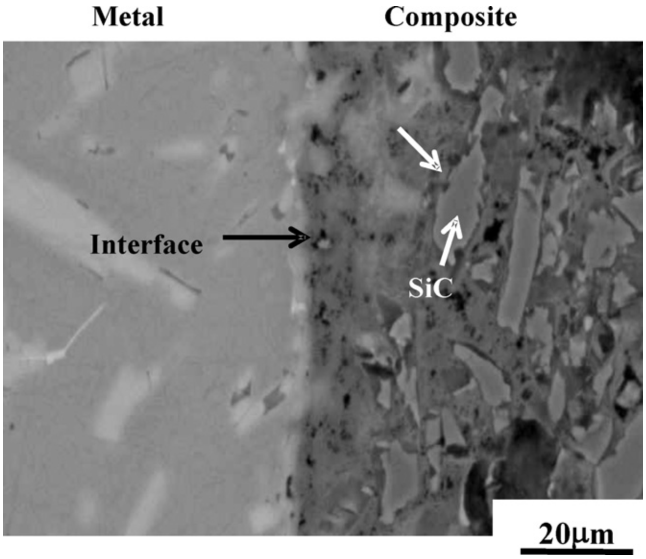

Fig. 2. SEM micrograph of the infiltrated metal/composite interface after 20 days air exposure.

In this work, the formation of Al_4C_3 was intentionally promoted by infiltration at relatively high temperatures (1100 °C) and long processing times (up to 60 min.). The formation of Al_4C_3 can be described by the reaction

$$4Al + 3SiC \leftrightarrow Al_4C_3 + 3Si \tag{1}$$

The effect of moisture on the infiltrated MMCs was disclosed by exposing the infiltrated preforms to the ambient air for various times of up to 510 days. The exposed MMC interfaces were examined under the SEM, indicating that the SiC reinforcement particles underwent severe dissolution. Fig. 2 is a micrograph of the resultant M/C reinforcement interface 20 days after infiltration. The degradation of the SiC particles is indicated by the arrow in the figure. EDX determinations of the M/C interface did not reveal the presence of the Al_4C_3 phase. Additional evidence for the lack of Al_4C_3 was obtained from the corresponding X ray diffraction pattern (see Fig. 3a). Notice from this figure that SiC, Si, Al, Mg_2Si and AlN are present in the MMC, but not Al_4C_3.

In samples exposed for 120 days to the moist environment, the MMC developed an apparent reaction zone characterized by a porous region in the metal/composite interface (see Fig. 4a). X-ray diffraction (Fig. 3b) of the porous region indicated the presence of SiC, Si, Al, AlN and γ-AlOOH. The γ-AlOOH phase is known as Boehmite and it possesses an orthorhombic crystal structure ($a = 0.369$ nm, $b = 1.224$ nm and $c = 0.286$ nm, JCPDS: 17-0940) corresponding to the group of aluminum hydroxide ($Al(OH)_3$).

The $Al(OH)_3$ phase can be formed in the presence of Al_4C_3, which due to its hydrophilic nature tends to degrade in environments such as water, methanol, HCl, other. Among the possible reactions that take place in the presence of the Al_4C_3 phase and moisture are [4,9,11].

$$Al_4C_3 + 12H_2O \rightarrow 4Al(OH)_3 + 3CH_4 \tag{2}$$

$$Al_4C_3 + 18H_2O \rightarrow 4Al(OH)_3 + 3CO_2 + 12H_2 \tag{3}$$

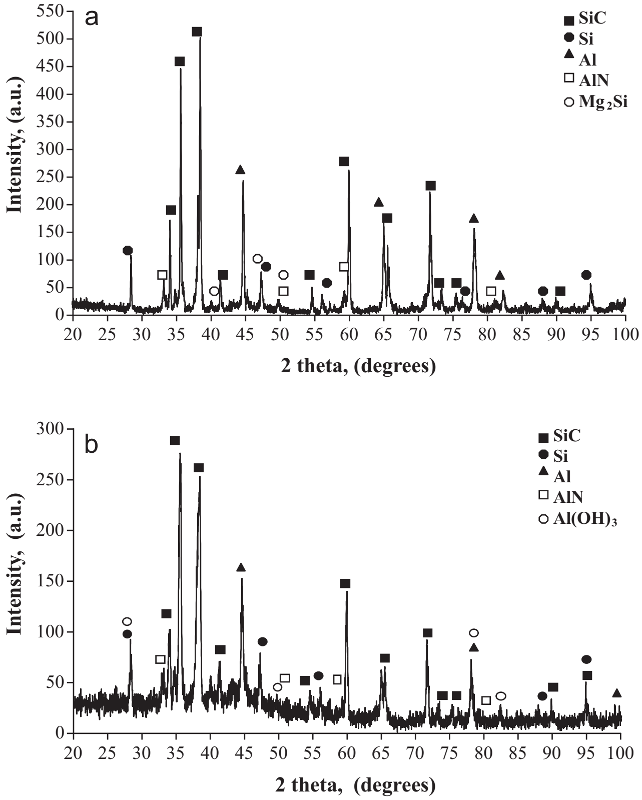

Fig. 3. XRD patterns of the infiltrated metal/composite interface after exposure to air for (a) 20 days and (b) 120 days.

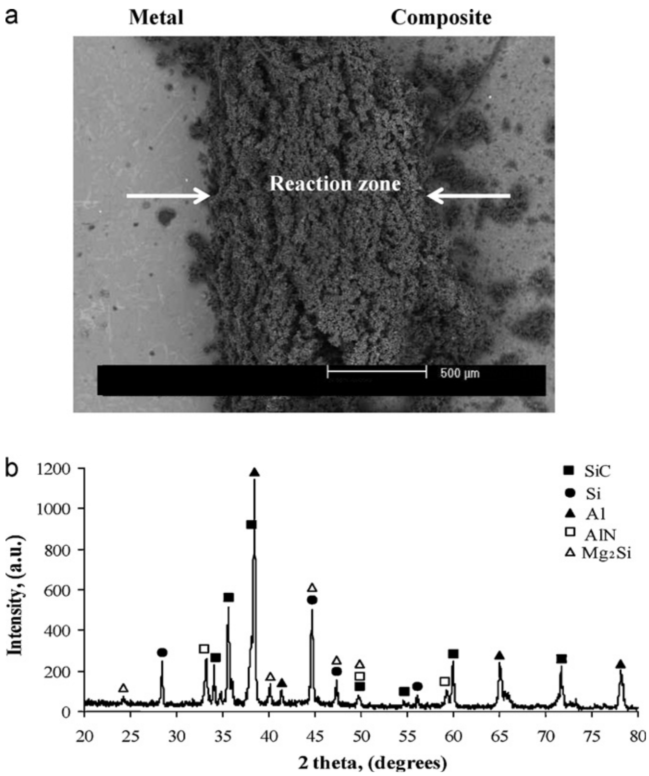

Fig. 4. (a) SEM micrograph of the infiltrated metal/composite interface after exposure to air for 510 days and (b) corresponding XRD pattern.

Since the composite specimens were not immersed in water, but exposed to ambient air, it is expected that formation of $Al(OH)_3$ is closely related to the interaction of Al_4C_3 with the surrounding moisture. According to Kosolapova [11], reaction (2) takes place slowly at room temperature with the liberation of methane gas. Alternatively, Park and Lucas [9] suggest that CO_2 gas is evolved during the interaction of aluminum carbide with water according to reaction (3). This in agreement with observations of bubbles emerging from polished surfaces in a SiC/6061-MMC [9].

Fig. 4a is a SEM micrograph of the M/C interface after 510 days infiltration. In this case the reaction zone seems to exhibit significant volume expansion due to reaction between the Al_4C_3 and moisture from the atmosphere to generate AlOOH. Since the density of AlOOH is relatively low, its formation is accompanied by a relatively large volume expansion. In turn, the net volume expansion induces hydrostatic stresses on the metal/reinforcement interface, leading to degradation of the interfacial strength [12].

The X ray diffraction pattern of powders collected from the M/C interface after 510 days exposure is shown in Fig. 4b. Accordingly, the XRD patterns reveal the presence of SiC, Si, Al, and AlN in samples exposed to air with no evidence of Al_4C_3 nor $Al(OH)_3$ phases. Apparently, continuous changes in the reaction products at the M/C interface occurred with time. After 120 days, there was clear evidence for the formation of boehmite (γ-AlOOH). This phase is metastable and transforms into other phases of amorphous nature by hydrolysis in moist air (80–90% humidity) [13]. Within the group of aluminum oxides and hydroxides, it is known that aluminum hydroxide can be formed as an amorphous phase known as pseudo-boehmite ($AlO(OH)\cdot\alpha H_2O$) which has a porosity of 90% and a rather low density of 0.23–0.25 g/cm^3, with $\alpha = 0.25$.

Fig. 5 shows the reaction zone thickness as a function of the exposure time. Notice that the reaction zone increases from 647 μm (after 120 days) to 1038 μm (after 510 days). In particular, it is apparent that the reaction zone thickness increases logarithmically with air exposure times.

Thus, the outcome of this work indicates that $4Al(OH)_3$ achieves its most stable condition which is as an amorphous phase, highly porous and with very low density [13]. The amorphous

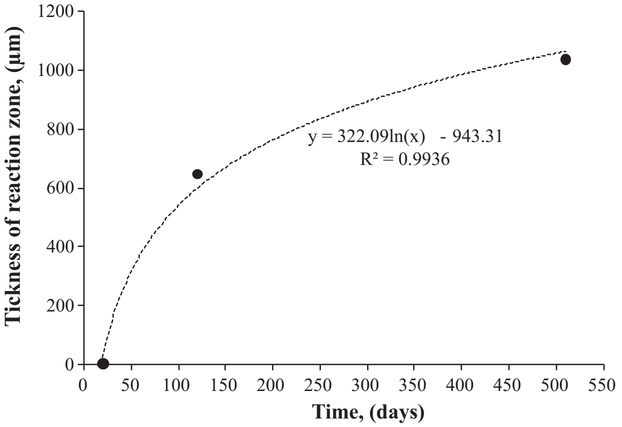

Fig. 5. Reaction zone thickness as a function of exposure time in atmospheric moisture.

phase is characterized by having its structure saturated with water, which in turn is accompanied by a volume expansion and thus fracture of the M/C interface. Hence, Al_4C_3 is not desirable in the development of MMCs as its degradation in air moisture can lead to catastrophic failure. In general, the degradation is slow and it depends on the air chemistry and moisture content.

4. Conclusions

In this work, the unwanted Al_4C_3 phase was not identified shortly after processing MMCs via infiltration. However, the presence of $Al(OH)_3$ after infiltration indicated that the Al_4C_3 phase actually forms under the processing conditions employed in this work. Amorphous $Al(OH)_3$ phase apparently results from exposure to the moist environment. In addition, a reaction zone is found to develop at the M/C interfaces with thickening versus time following a logarithmic trend. Apparently, degradation of the Al_4C_3 phase at the metal/reinforcement interfaces is ongoing for relatively long times and it is affected by atmospheric conditions, such as temperature and air moisture.

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