JOURNAL OF MATERIALS SCIENCE 30 (1995) 4770–4774

Interfacial reactivity of aluminium/fibre systems during heat treatments

S. MERCIER, P. EHRBURGER, J. LAHAYE
Centre de Recherches sur la Physico-Chimie des Surfaces Solides, 24, Avenue du Président Kennedy, 68200 Mulhouse, France

The interfacial reactivity of specimens composed of aluminium coated on SiC-based fibres, carbon fibres and protected carbon fibres, was investigated. The woven fibres were coated with aluminium by physical vapour deposition and the obtained materials were heat treated in a furnace which was connected to a mass spectrometer. It was shown that reactions occur between CO and CO_2 gases, which are released by the fibres, and aluminium, when the temperature is above 650 °C. These gases react during their passage through the aluminium layer and form aluminium carbide. Aluminium carbide is also produced by reactions between the solid-species constituents of the fibres and the metal. The amount of aluminium carbide formed at the fibre/metal interface during heat treatment was determined by hydrolysis. It was thus possible to ascertain that the aluminium carbide is mainly formed by the latter reactions. The efficiency of various protective coatings against the formation of aluminium carbide was also investigated.

1. Introduction

Although they have been studied for many years, the development of aluminium composites reinforced with fibres is still limited by two major problems: the low wettability of the fibres by liquid metals which hinders the infiltration of molten aluminium through fibre bundles [1], and the possibility of chemical reactions between the fibre and the matrix, that can lead to composite brittleness [2]. This second phenomenon accounts for the formation of aluminium carbide that can be beneficial in small amounts, due to the formation of an interface that allows the charge transfer from the matrix to the fibres. However, if the interface is too important, no pull-out of the fibres can occur and the mechanical properties of the composites are lower than estimated, because of the brittleness of the interfacial aluminium carbide.

Many authors have studied the reaction between carbon and aluminium [3–7], and between silicon carbide and aluminium [8–13], both leading to the formation of aluminium carbide. It is also well known that during heat-treatment, fibres release gases such as hydrogen, water vapour, carbon monoxide and carbon dioxide [14].

The purpose of the present work was to study the behaviour of the gases evolved by the fibres during heat treatment of aluminium/fibre composites, and to determine the amount of aluminium carbide formed at the interface.

2. Experimental procedure

2.1. Samples and sample preparation

Several fibres have been studied: SiC-based fibres (Nicalon NML 202), carbon fibres (M40 and T300), and carbon fibres protected with various coatings (SiC and B_4C coatings). The coatings were fabricated by reactive chemical vapour deposition (RCVD). In this method, no carbon species are present in the initial gaseous phase, and the protective deposit is formed exclusively by a reaction with the carbon present at the fibre surface [15]. Unlike the classical chemical vapour deposition (CVD), the coating formed is uniform on the fibres, even inside the bundles.

2.2. Metallization

Woven fibres were coated with a thin layer (200 nm) of aluminium (purity 99.99%) by physical vapour deposition (PVD) under vacuum. The thickness of the deposit was controlled by a quartz crystal. In order to maintain constant the characteristics of the deposit, the metallization was performed in the following conditions: residual pressure in the metallization chamber equal to 2×10^{-4} mbar and deposition rate close to 2.5 nm s^{-1}. After metallization, the samples were left 2.5 h in air.

2.3. XPS analysis

In order to determine the amount of aluminium oxides in the deposit, aluminium is coated on a flat carbon surface, in the conditions mentioned in Section 2.2 and the sample is analysed by X-ray photoelectron spectroscopy (XPS). The decomposition of the shape of the Al 2p signal of the aluminium surface before sputtering allows a characterization of the component corresponding to metallic aluminium, and the characterization of the component corresponding to the aluminium oxide. The sample is then sputtered by argon

0022–2461

ions with an energy of 1.5 kV. Assuming that the characteristics of the metallic aluminium are not affected by sputtering, the amount of metallic aluminium in the total deposit is then proportional to the area of the peak corresponding of the signal of metallic aluminium divided by the area of the total signal Al 2p.

2.4. Vacuum desorption

About 1 g aluminium-coated fibres are introduced into a furnace connected to a mass spectrometer. The samples are then heat treated under vacuum at a linear heating rate of 300 K h^{-1} and the gases evolved are analysed both qualitatively and quantitatively. This approach enables a study of the possible reactions occurring between the gases and aluminium during heat treatment.

2.5. Quantitative determination of aluminium carbide

In order to determine the amount of aluminium carbide formed during heat treatments, aluminium-coated samples are held at a fixed temperature for 30 min, then cooled down, and the amount of aluminium carbide formed during this heat treatment is determined by the amount of CH_4 released after the decomposition of Al_4C_3 by water. A knowledge of the volume of the reactor, the total gas pressure in the reactor and the gas composition given by the mass spectrometer, permits the calculation of the amount of methane released. The decomposition of Al_4C_3 by water is slow, but this method was chosen because the very thin thickness of the aluminium deposit (200 nm) allows the decomposition to be complete and to take place in a reasonable length of time. It is thus possible to compare the reactivity of various aluminium/fibre systems towards the formation of aluminium carbide.

3. Results and discussion

3.1. Characterization of the aluminium deposit

The profiles of aluminium, carbon and oxygen during sputtering are shown in Fig. 1. Owing to a roughness in the carbon substrate, the interface metal/carbon is not totally abrupt, and thus a determination of the exact sputtering time required to reach the carbon substrate is not possible. This time is estimated to be 160 min according to Fig. 1.

From the decomposition of the Al 2p signal in two components corresponding to metallic aluminium and aluminium oxide, and the integration of the obtained curve between time 0 (corresponding to no sputtering) and time 160 (corresponding to the aluminium/carbon interface), the total amount of metallic aluminium in the coated layer can be calculated. This amount, as shown in Fig. 2, is equal to 60%–65% of the total deposit. The high quantity of aluminium oxides in the deposit is attributed not only to the oxidation of the deposit when in air, but mainly to the incorporation of oxygen in the metallic layer during PVD. This incorporation is due to the residual gases H_2O and O_2 present in the metallization tank.

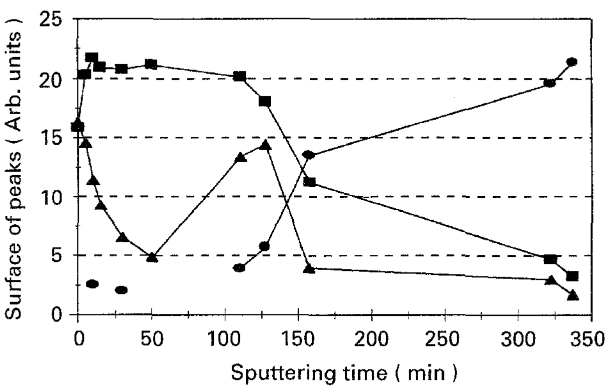

Figure 1 XPS profile of a carbon substrate coated with aluminium. (■) Al 2p, (●) C′ 1s, (▲) O′ 1s.

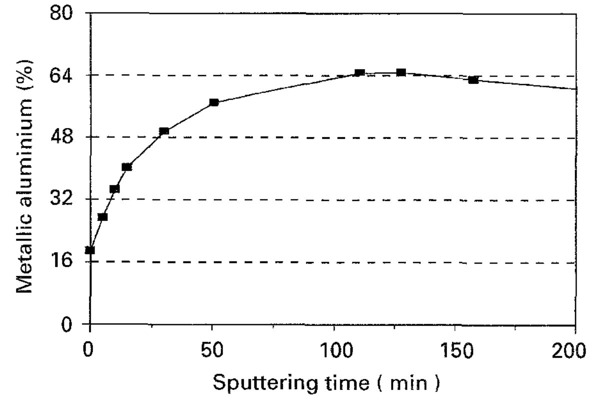

Figure 2 Cumulative amount of metallic aluminium in the deposit.

3.2. Thermal treatment

As already mentioned in Section 1 the fibres release some gases when heat treated. Fig. 3 represents the amounts of gases present during heat treatment in a closed reactor containing the fibres or the aluminium-coated fibres. The curves representing the thermodesorption of hydrogen have the same profile for the fibres and the aluminium-coated fibres (Fig. 3a). This effect is not observed for some other gases. Fig. 3b and c show the amount (μmol g^{-1}) of CO and CO_2 present in the closed reactor during heat treatment between 400 and 1000 °C for M40 carbon fibres. For a temperature higher than 650 °C, the amount of these two gases decreases clearly in the presence of aluminium. This effect is also observed for other PAN-based carbon fibres and for SiC-based fibres. It is thus assumed that CO and CO_2 react with aluminium according to the following reactions

$$6Al + 3CO \rightleftharpoons Al_2O_3 + Al_4C_3 \qquad (1)$$

$$8Al + 3CO_2 \rightleftharpoons 2Al_2O_3 + Al_4C_3 \qquad (2)$$

Taking into consideration the CO and CO_2 pressure in the reactor, the variation of the free enthalpy of these two reactions is lower than −400 kJ mol^{-1} between 400 and 1000 °C. The two reactions are hence thermodynamically possible.

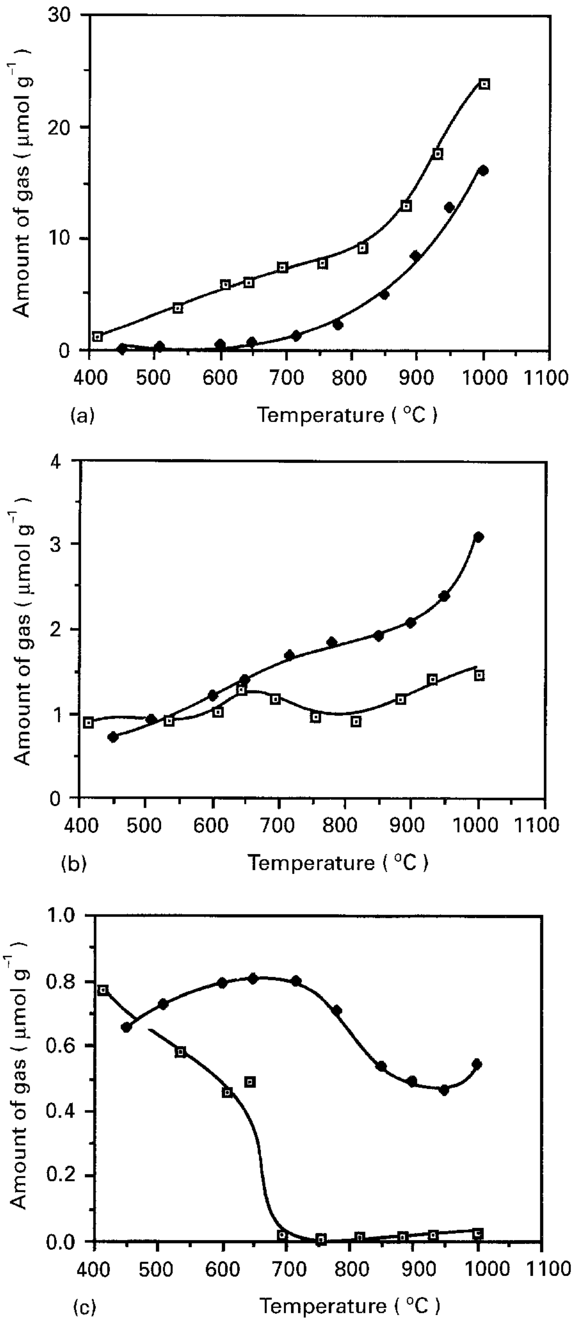

Figure 3 Amounts of gases present in the reactor during heat treatment of (◆) M40 fibres, (▣) aluminium-coated M40 fibres, for (a) H_2, (b) CO and (c) CO_2.

In order to verify that the reaction between aluminium and carbon monoxide actually occurs and that the decrease in the amount of CO is not due to a trapping of this gas in the aluminium layer, an amount of CO, much greater than that produced during the thermodesorption of the fibres, is introduced at room temperature into the reactor containing aluminium-coated fibres. The system is then heat treated up to 1000 °C. Fig. 4 shows that the amount of CO initially introduced decreases sharply for temperatures above 650 °C. The phenomena already observed in Fig. 3b and c are thus confirmed.

After this first set of experiments, it is possible to assert that aluminium reacts with the CO and CO_2 produced during thermal treatment of the fibres when the temperature is above 650 °C. However, it is not possible to gain any information about where and when these reactions occur, for the gases accumulate in the closed reactor. If the evolved gases are continuously evacuated out of the reactor by pumping, they do not linger in the reactor and a reaction between them and aluminium can take place only at the fibre/metal interface, that is during the migration of the gases through the aluminium layer. Fig. 5 shows the results of such a thermal treatment for Nicalon

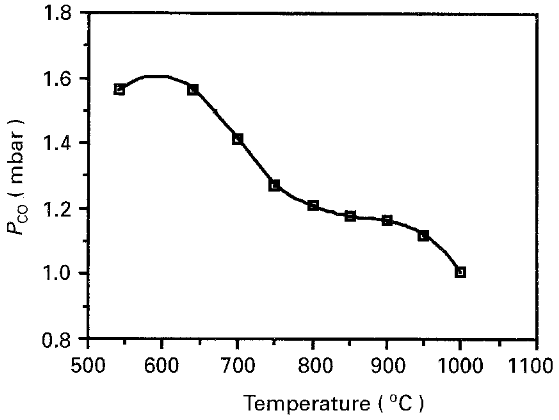

Figure 4 Evolution of the pressure of CO introduced.

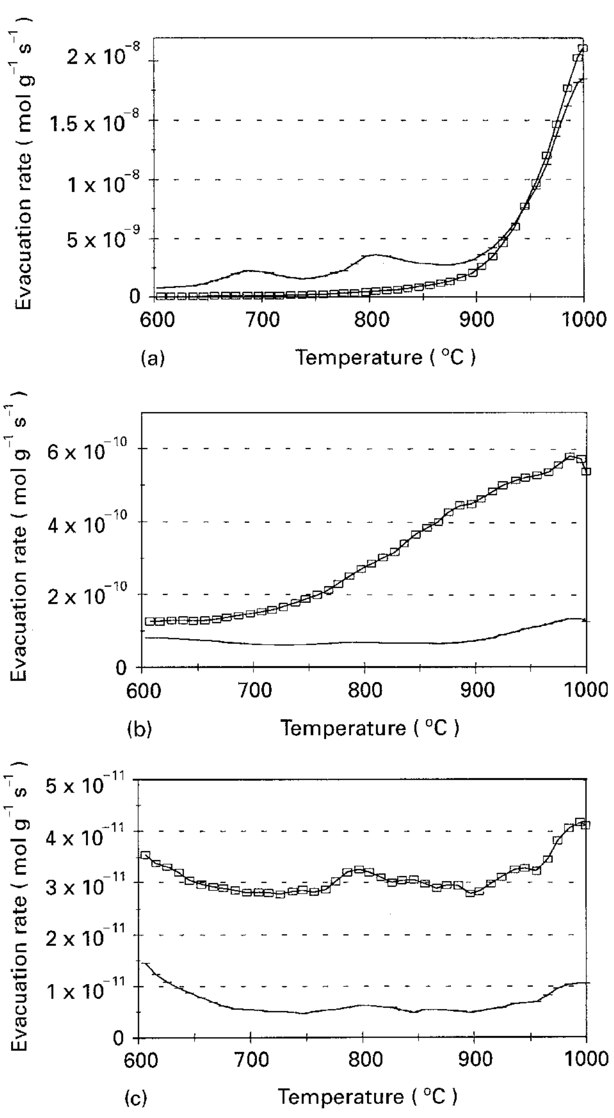

Figure 5 Heat treatment of Nicalon fibres. (∗) Nicalon fibres, (+) aluminium-coated Nicalon fibres, for (a) H_2, (b) CO, (c) CO_2.

fibres and aluminium-coated Nicalon fibres. Similar curves are obtained for PAN-based carbon fibres. The amounts of CO and CO_2 detected above 650 °C are lower when the fibres are coated with aluminium (Fig. 5b and c), whereas the amounts of H_2 remain the same (Fig. 5a).

These results prove that the reactions between CO, CO_2 and aluminium occur during the passage of the gases produced by the fibres in the aluminium layer.

3.3. Quantitative determination of the aluminium carbide

Owing to the results presented in Section 3.2, it is possible to assert that aluminium reacts with some of the gases released by the fibres during heat treatment to produce Al_4C_3. However, it is well known that Al_4C_3 is also formed by the reactions between aluminium and the carbon of the fibres [16], or the carbon and the silicon carbide for SiC-based fibres [17]. The total amount of Al_4C_3 formed during heat treatment of the aluminium-coated fibres was quantitatively detected as explained in Section 2.2. after the decomposition of Al_4C_3 to CH_4. It was thus found that the maximum amount of Al_4C_3 that could be formed during heat treatment corresponds to 60% of the initial amount of aluminium, this latter being calculated assuming that all the deposit is composed of metallic aluminium, which is of course, not the case. The previous study of the aluminium deposit by XPS (cf. Section 3.1) showed that only 60%–65% of the deposit is made of metallic aluminium. So, only aluminium in the metallic state is able to react to form aluminium carbide.

It is possible to calculate the amount of Al_4C_3 formed by reactions with CO and CO_2 during a given heat treatment by the decrease of the amount of these two gases detected by mass spectrometry. The amount of the total Al_4C_3 formed during the same heat treatment is known after the hydrolysis of the carbide. It is hence possible to calculate the amount of Al_4C_3 due to the reactions between the gases released by the fibres and aluminium. This amount is equal to less than 0.4% of the total aluminium carbide. Reactions between gases and aluminium thus produce only a very small amount of Al_4C_3, this amount depending on the amount of gases released by the fibres, and so on the thermal treatment.

Using the methane decomposition method, the protective effect of various coatings on fibres, against the formation of aluminium carbide can be compared. The thermal treatment chosen to compare these samples consists of holding them for 30 min at 640 °C before cooling. On the one hand, these conditions are sufficient to produce enough aluminium carbide for carbon fibres and SiC-based fibres coated with aluminium, to be determined with enough accuracy. On the other hand, they are not sufficient to transform all the metallic aluminium into Al_4C_3 and thus provide a good means of comparing the reactivity of several samples. Besides, SiC and B_4C are not decomposed by water [18].

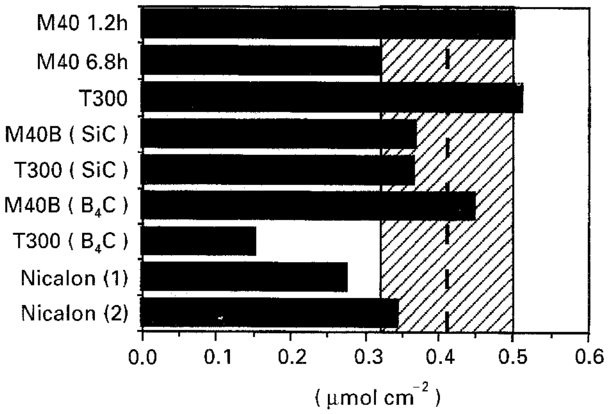

Figure 6 Reactivity of different aluminium-coated fibres towards the formation of aluminium carbide.

Fig. 6 shows the amount of aluminium that reacted to produce carbide for different fibres and different coatings on the fibres. Before atmospheric ageing (usually 2.5 h) the coated fibres were heated at 640 °C for 30 min. The results are given in micromoles of aluminium converted into carbide per cm^2 for an hydrolysis time of 70 h (with the exception of Nicalon(2) for which the hydrolysis time was 160 h).

The M40 fibre coated with aluminium is taken as a reference. For 2.5 h ageing before hydrolysis, a value of 0.41 $\mu mol\,cm^{-2}$ is found (dotted vertical line). The values obtained for 1.2 and 6.8 h ageing are somewhat different. When the amount of aluminium converted into carbide is located in (or close to) the hatched rectangle, the reactivity with aluminium of the fibre is considered as identical to those of the M40 fibre.

The reactivity of all the samples is approximately the same, except for T300 carbon fibre coated with B_4C.

These results can be explained knowing that the nitrogen in T300 carbon fibres is 7.3% by weight and in M40 carbon fibres 0.2%. The RCVD coating on T300 that was supposed to form B_4C produced, in fact, a mixture of B_4C and BN, BN being present in a relatively large amount [19], whereas the RCVD coating on M40 is formed only of B_4C.

4. Conclusions

1. For temperatures higher than 650 °C, aluminium reacts with carbon monoxide and dioxide evolved by the fibres to form aluminium carbide. These reactions occur during the migration of the gases through the aluminium layer.

2. The amount of aluminium carbide formed by these reactions is much lower than the amount of aluminium carbide formed by the reactions between the solid-species constituents of the fibres and aluminium.

3. Amongst the coatings tested on the fibres, the only real protective coating against the formation of aluminium carbide is that containing B_4C and BN.

Acknowledgements

We thank Professors J. Bouix and C. Vincent, Université Claude Bernard, Lyon, for providing fibres coated by RCVD. The research was supported by the D.R.E.T. (Paris).

References

1. J. C. VIALA and J. BOUIX, *Mater. Chem. Phys.* **11** (1984) 101.
2. A. MORTENSEN, J. A. CORNIE and M. C. FLEMINGS, *J. Metals* **40** (1988) 12.
3. I. H. KHAN, *Metall. Trans.* **7A** (1976) 1281.
4. H. S. YOON, A. OKURA and H. ICHINOSE, in "Proceedings of the International Conference on Interfacial Phenomena in Composite Materials", edited by I. Verpoest and F. Jones (Butterworth Heinemann, London, 1989) p. 258.
5. M. YANG and V. D. SCOTT, *Carbon* **29** (1991) 887.
6. A. P. DIWANJI and I. W. HALL, *J. Mater. Sci* **27** (1992) 2093.
7. T. A. CHERNYSHOVA and L. I. KOBELEVA, *ibid.* **20** (1985) 3524.
8. J. C. VIALA, P. FORTIER and J. BOUIX, *ibid.* **25** (1990) 1842.
9. K. YOSHII, S. INOUE, S. INAMI and H. KAWABE, *ibid.* **24** (1989) 3096.
10. R. WARREN and C. H. ANDERSSON, *Composites* **15** (1984) 101.
11. S. KOHARA and N. MUTO, *J. Jpn Inst. Metals* **45** (1981) 411.
12. T. R. BREIVIK and K. PETTERSEN in "Proceedings of the Interfacial Phenomena in Composite Materials", edited by I. Verpoest and F. Jones (Butterworth Heinemann, London, 1991) p. 219.
13. A. H. CARIM, *Mater. Lett.* **12** (1991) 153.
14. P. SCHRECK, VIX-GUTERL, P. EHRBURGER and J. LAHAYE, *J. Mater. Sci.* **27** (1992) 4237.
15. H. VINCENT, C. VINCENT, J. P. SCHARFF, H. MOURICHOUX and J. BOUIX, *Carbon* **30** (1992) 495.
16. S. G. WARRIER, C. A. BLUE and R. Y. LIN, *J. Mater. Sci.* **28** (1993) 760.
17. B. KINDL, Y. LIU, E. NYBERG and N. HANSEN, *Compos. Sci. Technol.* **43** (1992) 85.
18. T. YA. KOSOLAPOVA, in "Carbides (properties, production, and applications) " (Plenum Press, New York, London, 1971).
19. C. VINCENT, H. VINCENT, H. MOURICHOUX and J. BOUIX, *J. Mater. Sci* **27** (1992) 1892.

Received 22 December 1994
and accepted 2 May 1995