INFLUENCE OF K₂ZrF₆ ON INFILTRATION OF CARBON FIBRE TOWS BY ALUMINIUM

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The influence of potassium hexafluorozirconate (K_2ZrF_6) on aluminium infiltration of TORAYCA T300 and T800 as well as T800 carbon fibres coated with SiC is described. This chemical substance deposited on carbon fibre increases quality of infiltration of unidirectionally oriented carbon fibres. The composites also exhibit higher tensile strength and Young's modulus comparing with pure aluminium matrix.

VPLYV K₂ZrF₆ NA PREPLAVENIE PRADENCOV UHLÍKOVÝCH VLÁKIEN HLINÍKOM

V článku sa zaoberáme vlyvom hexafluorozirkoničitanu draselného (K_2ZrF_6) na preplavenie uhlíkových vlákien TORAYCA T300, T800, ako aj vlákien T800 s vrstvou SiC hliníkom. Táto chemická zlúčenina zlepšuje proces preplavenia jednosmerne usporiadaných uhlíkových vlákien. Pripravené kompozitné materiály. mali v porovnaní s čistou hliníkovou matricou vyššiu medzu pevnosti aj modul pružnosti v ťahu.

1. Introduction

In recent years metal matrix composites have received increasing attention to their excellent combination of physical and mechanical properties such as low density, high specific strength, high elastic modulus, and a desirable coefficient of thermal expansion [1, 2].

Liquid metal infiltration is commonly used for the fabrication of metal-matrix composites. This method involves infiltration of a liquid metal into a porous preform. The preform is an agglomerate or a compact of the reinforcement, which may be in the form of particles, whiskers, or fibres. The attractiveness of this method is that the preform may be conveniently shaped or machined to the desired shape of the composite, resulting in a near net-shape component after liquid metal infiltration. At this technology of production of aluminium matrix composites the following two main difficulties are properly solved.

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1. Most of ceramic fibres (e.g. carbon and silicon carbide fibres) react with liquid aluminium forming aluminium carbide which causes lowering of the fibre strength and an embrittlement of the matrix [1]. Forming of Al_4C_3 ought to cause not only strength degradation of the fibres itself, but also stronger bonding at the interface. This stronger bonding is favourable for the crack propagation from the Al_4C_3 layer into the core fibre.

2. The ceramic fibres are usually poorly wetted by liquid aluminium at temperatures lower than 1223–1273 K. Thus, (i) high pressures are commonly used to infiltrate fibrous ceramic preforms (squeeze casting) or (ii) vigorous stirring is necessary to incorporate short ceramic fibres in liquid or semi-liquid aluminium.

One way of overcoming the problem of wettability is a modification of the matrix composition. Also, an improvement of the wettability without introducing the interfacial chemical reaction has been pursued through surface treatment of the fibres. The fabrication of composite therefore involves two stages: a pretreatment of the fibres to improve wetting characteristics and the second stage of incorporation of these fibres into the aluminium matrix. Various fibre treatments such as thermo-vacuum treatment, coating the fibres with metal (Cu, Ni, Ta, and Na) and refractory carbides (TiC, SiC, ZrC, etc.) have been used in the past with varying degrees of success [3, 4].

The poor wettability of most ceramics by liquid aluminium and its light alloys at low temperatures is thought to be related to the thin layer of alumina that always coats the liquid [5, 6]. Therefore, removal of this thin layer (e.g. by a chemical reaction taking place near the ceramic surface and resulting in the formation of new species which are able to dissolve or vaporize alumina) should improve the wetting of ceramic fibrous preforms by allowing their impregnation by liquid aluminium alloys. With the purpose of producing aluminium matrix composite by a casting technique, various light alloy foundry fluxes were tested to dissolve the alumina layer. Although K_2TiF_6 or K_3TaF_7 led to rather good impregnations, the best results were obtained with K_2ZrF_6, which has a much higher solubility in water (e.g. 25 g/100 cm^3 water at 373 K).

In order to point out the efficiency of the K_2ZrF_6 surface treatment, sessile drop experiments were performed on those substrates (coated with either pyrocarbon or SiC) which have been treated with an aqueous solution of K_2ZrF_6 subsequent to the sessile drop experiments. The wetting ability of a pyrocarbon or SiC surface by liquid aluminium is dramatically improved when it is treated by an aqueous solution of K_2ZrF_6 at temperatures slightly above the melting point of aluminium. The reduction of the contact angle is directly related to the amount of K_2ZrF_6 that has been spread on the substrate surface [7].

It has been also reported that addition of a metal fluoride such as K_2ZrF_6, helps pressureless infiltration [8]. Al-7Si-1.6Mg based composite reinforced by 10 vol. % of Nicalon fibres was prepared by casting without using pressure or vacuum. The

strength of these composites was higher by 60% comparing to that of the matrix. The strength of fibres after infiltration was about 70% of the original strength [9].

Patankar and his co-workers [10] reported successful infiltration of molten Al into the array of TORAYCA T300 carbon fibres by application of K_2ZrF_6 onto the fibre surface. The extent of damage caused by K_2ZrF_6 to the C fibre during infiltration was observed at over 923 K and time of contact more than 30 s.

The aim of this paper is to determine the influence of K_2ZrF_6 on the quality of impregnation of pure TORAYCA T300 and T800 as well as T800 coated with SiC carbon fibres by aluminium matrix and to improve their wetting by liquid aluminium in the process of unidirectional composite material preparation by pressure infiltration.

2. Experiment

Three kinds of carbon fibres (their mechanical properties are given in Table 1) were used in the experiments: high strength TORAYCA T300 (diameter 7 μm) with 3000 fibres in a tow and TORAYCA T800 (diameter 5 μm) with 6000 fibres in a tow. The third kind were TORAYCA T800 carbon fibres coated by SiC to prevent the decrease of their strength during the aluminium-silicon carbide-coated carbon fibres composite preparation. Silicon carbide was deposited by chemical vapour deposition process from the reaction mix of metyltrichlorosilane and hydrogen.

Table 1. Mechanical properties of carbon fibres

Fibres	Tensile strength [GPa]	Young's modulus [GPa]	Elongation [%]
T300	3.5	240	1.6
T800	5.1	330	1.9
T800 + SiC	1.2	277	–

After removing an epoxy from the fibres not containing SiC, fibres were dipped into water solution of K_2ZrF_6 warmed up to the temperature of 363 K (solubility of K_2ZrF_6 in water is conspicuously increasing with temperature). Quality of the deposit was checked by electron microscopy. Fig. 1 shows the surface of T800 filaments with deposited crystals of K_2ZrF_6. Mechanical properties of original fibres as well as fibres with SiC and K_2ZrF_6 deposits were measured after Japanese Industrial Standard [11]. The given values are average values from 8 measurements. Tensile properties of fibres (and composites) were measured on Instron type testing machine. Modulus of elasticity was measured with an extensometer with a gauge length of 10 mm.

Two kinds of composite specimens were prepared: round with a diameter of 3.0 mm and parallelepiped 10.0 × 1.1 mm, the length in both cases was 42.0 mm. Carbon fibres (50 vol. %) were given into graphite form parallel with their longitudinal axis and the form was put into an autoclave. Form was heated up to 673 K and liquid aluminium was allowed to infiltrate the fibres in argon atmosphere at the temperature 973 K, pressure 4 MPa, and time 30 s. Parallelepiped-like composite specimens were narrowed in the middle. The neck for extensometer was 3.7 mm broad and 15 mm long. Rate of load was 1 mm min^{-1}.
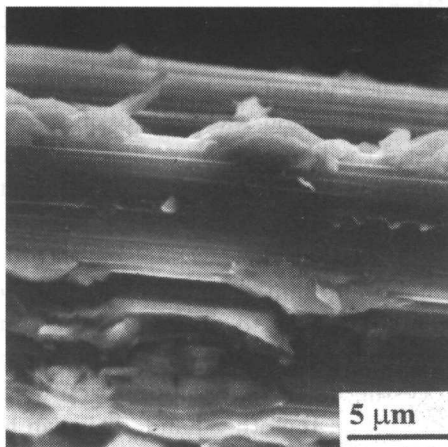

Fig. 1. K_2ZrF_6-coated   carbon   fibres (TORAYCA T300).

3. Results and discussion

Figs. 2 and 3 show cross sections of round composite samples with T800 + K_2ZrF_6 and T800 + SiC + K_2ZrF_6 fibres. These are fibres of smaller diameter and of twice the number of fibres in a tow comparing with T300 fibres that are mostly used for metallic composite preparation. Due to this fact their infiltration by
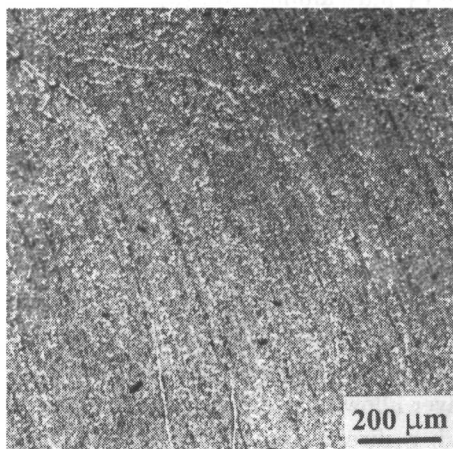

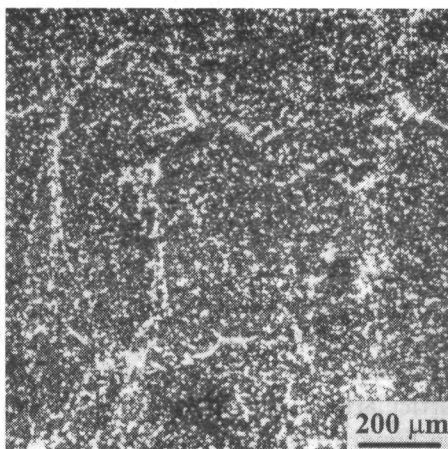Fig. 2. Structure of composite Al-carbon fibres (TORAYCA T800 + K_2ZrF_6).

Fig. 3. Structure of composite Al-SiC--coated carbon fibres (TORAYCA T800 + SiC + K_2ZrF_6).

liquid matrix is more difficult. These pictures reveal uniform distribution of carbon fibres in aluminium matrix without distinguishing the individual tows contrary to specimens prepared without using K_2ZrF_6. Very good distribution was observed also when preparing samples with lower volume amount of fibres whereas such good distribution was not possible to obtain without K_2ZrF_6 when liquid metal pressed the fibres to the wall of the form. This fact can be explained by separation of fibres in tow with crystals of salt that are stable until the liquid metal comes to the contact with them (melting point of K_2ZrF_6 is 1073 K).

After that the mechanism, according to which K_2ZrF_6 reacts with pure Al or light alloys investigated in [7], can be valid. The reaction of K_2ZrF_6 with pure aluminium leads to arising an intermetallic compound on the one hand, and to complex fluorides that have to be eliminated during aluminium matrix composite processing (either by vaporization or by the liquid metal flow through the fibre preform) on the other hand. This can be represented by the following equations:

$$3K_2ZrF_6 + 4Al \rightarrow K_3AlF_6 + 3KAlF_4 + 3Zr, \tag{1}$$

$$3Zr + 9Al \rightarrow 3Al_3Zr. \tag{2}$$

These were exothermic reactions, so that they activated the reaction between carbon fibre and aluminium

$$3C + 4Al \rightarrow Al_4C_3. \tag{3}$$

Several mechanisms can be suggested to be tried to explain why a pretreatment with an aqueous solution of K_2ZrF_6 improves the wettability of the carbon fibre or carbon fibre with SiC coating surface by pure aluminium: (a) the alumina thin layer is dissolved in liquid metal by the fluorides which are released by the reaction occurring between K_2ZrF_6 and liquid aluminium; (b) the carbon or SiC surface is cleaned and/or activated by these fluorides; (c) the gas phase involved in the wetting phenomenon is advantageously modified by gaseous fluoride species formed from K_2ZrF_6; and (d) the heat of the reactions that take place is high enough to increase the temperature locally giving rise to contact angle decrease. Although these four mechanisms can be expected to contribute to some extent to the wettability improvement, mechanism (a) is thought to be predominant [5, 6].

The alumina layer that exists on liquid aluminium appears to be a barrier impending the wetting phenomenon. The alumina layer is thin enough to permit a reaction between liquid aluminium and K_2ZrF_6, then the reaction products (e.g. particularly K_3AlF_6) dissolve the alumina layer allowing a direct contact between the liquid metal and the ceramics. Although a direct reaction between K_2ZrF_6 and alumina could also be expected, the presumable mechanism of the wetting improvement is related to reaction as already suggested by other investigators in a totally different field [5].

The mechanical properties of the used carbon fibres as well SiC coated carbon fibres both with K_2ZrF_6 coating are shown in Fig. 4 (tensile strength) and Fig. 5 (Young's modulus). The obtained results revealed that the mechanical properties of carbon fibres after coating by K_2ZrF_6 are not changed. However, strong decrease of the tensile strength of carbon fibres with SiC layer deposited on them was observed. The same results obtained also Shindo and Honjo [12] when silicon carbide coating of carbon fibre resulted in a marked strength loss. The SiC layer deposited on the carbon fibres is a brittle layer and fractures at small strains. Accordingly, when tensile stress is applied to such a fibre, the coating layer first fractures, and cracks are formed. When the thickness of the layer is above a certain value, the crack extends into the C fibre if the interfacial bonding between the coating and the C fibres is strong. However, if the interfacial bonding is week, debonding occurs owing to shear stress at the interface during the deformation of the fibre under tension, and the crack-edge is blunted, diminishing stress concentration. As a result, no loss in fibre strength takes place. Accordingly, the degradation in strength of the C fibre by the sole SiC coating suggests that the bonding between the coating and the fibre is as strong as to permit the extension of the crack into the fibre.

No reduction in strength occurs by the coating of carbon fibres by free carbon followed by SiC coating. Therefore Shindo and Honjo [12] prepared double layer-coated fibres with a carbon layer prior to the silicon carbide coating. When tensile stress was applied to the double layer-coated fibre the carbon film undercoat with the lamellar structure should effectively act as an arrester of cracks formed in
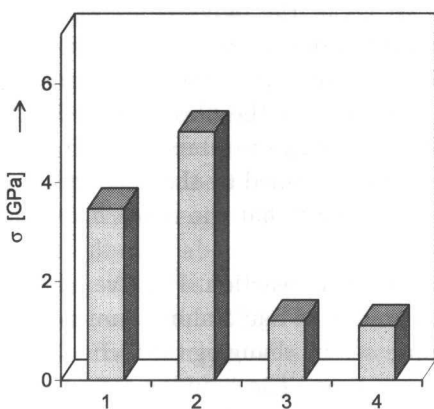

Fig. 4. Tensile strength of the carbon fibres TORAYCA: 1 – T300 + K_2ZrF_6, 2 – T800 + K_2ZrF_6, 3 – T800 + SiC, 4 – T800 + SiC + K_2ZrF_6.
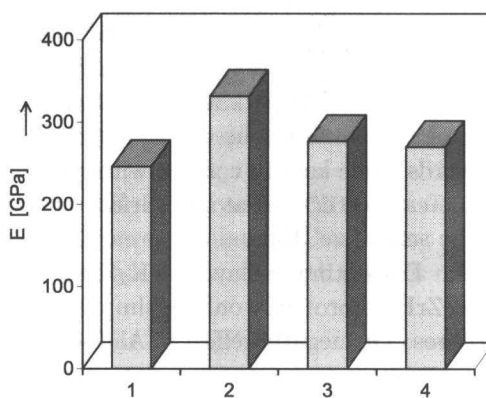
Fig. 5. Young's modulus of the carbon fibres TORAYCA: 1 – T300 + K_2ZrF_6, 2 – T800 + K_2ZrF_6, 3 – T800 + SiC, 4 – T800 + SiC + K_2ZrF_6.

the SiC upper layer. The strength recovery of the SiC coated fibre by the carbon undercoating seems to indicate that the bonding between the SiC layer and the core C fibre is relatively weak.

Mechanical properties (strength and Young's modulus) of composites with Al matrix reinforced with carbon fibres coated by SiC as well as without coating but with K_2ZrF_6 layer are given in Fig. 6. Young's modulus of composites is higher than that of Al matrix and reaches 75–80% of the value calculated according to the rule of mixture (ROM). Composites are brittle, and the strain at the fracture is less than 0.2%. The results further reveal that the strength of composite with T300 and T800 carbon fibres is higher than that of pure Al matrix (~ 60 MPa). The strength of these composites is however only about 10% of the ROM value. In the case of T800 carbon fibres with SiC layer the strength of composite reached around 30% of ROM value.
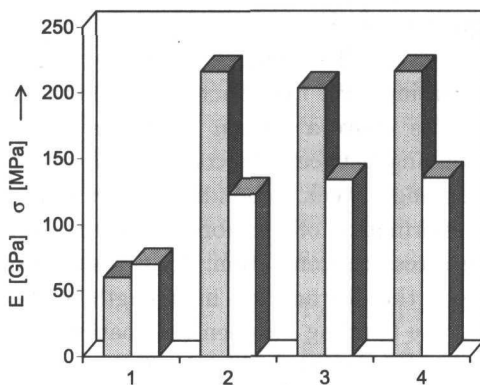

Fig. 6. Mechanical properties: strength and Young's modulus (white columns) of the 1 – pure Al matrix and composites: 2 – 4 (Reinforced TORAYCA fibres) 2 – Al-(T300 + K_2ZrF_6), 3 – Al-(T800 + K_2ZrF_6) and 4 – Al-(T800 + SiC + K_2ZrF_6).

One of the negative effects on the strength of Al-C composite is formation of Al_4C_3 at the interface between carbon fibre and Al matrix. Carbide grows into the inside of carbon fibre just like a root of carbide crystal. Because of the brittleness of Al_4C_3, the root portion of carbide crystals acts as a notch on a fibre surface when the fibre is pulled. The rapid decrease at the early stage and the gradual change in fibre strength afterwards while kept in contact with molten Al can be explained by the notch effect of the carbide crystal at the surface of the fibre, assuming that the notch has about the same size [13].

Discontinuous layer of K_2ZrF_6 does not stop this reaction. Positive effect of K_2ZrF_6 is probably only in simplifying the infiltration of liquid aluminium into the fibres. The negative effect of Al_4C_3 can be suppressed by changing the technological parameters to lower temperature and to shorter time. The liquidus temperature of the Al matrix can be lowered also by silicon alloying. If a lower fabrication temperature is adopted, the degradation of the carbon fibres will be reduced.

The influence of barrier layer of SiC on the composite strength was not positive, as well. During the SiC deposition on carbon fibres their strength was lowered. When the SiC coating was induced at the interface, a diffusion barrier was set up between carbon fibres and Al so that the reaction (3) was suppressed. As a result,

it prevented the carbon fibres from being damaged, while the reaction zone became much smaller. However, the SiC coating was still itself reacted.

The interface chemistry in the case of Al matrix composites reinforced with pure SiC is given in [14]. At temperatures below 923 ± 3 K, SiC is in equilibrium with solid Al, while it is readily attacked by Al at temperatures higher than 923 K, according to the reaction (4):

$$4Al + 3SiC \rightarrow Al_4C_3 + 3Si \ . \tag{4}$$
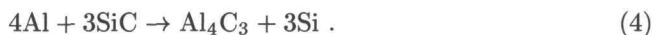
At completion, this reaction results in a three-phased monovariant equilibrium, which involves unreacted SiC, Al_4C_3, and a ternary Al-C-Si liquid phase with a very low carbon content. The amount of Si in this liquid phase increases regularly with the temperature from 1.5 at.% Si at 923 K to 4.8 ± 0.5 at.% Si at 1000 K. Hence, a proper addition of Si to the Al matrix can prevent the foregoing reaction during the elaboration of these composites by liquid metal infiltration.

The obtained results showed that the surface of carbon fibres is necessary to protect more effectively by barrier layers to diminish or to stop the reactions leading to the carbide formation (for example to deposit pyrocarbon prior to SiC coating) [15].

4. Conclusions

1. Potassium hexafluorozirconate in water solution was deposited on T300 and T800 carbon fibres as well as on silicon carbide coated T800 carbon fibres.

2. Strength and Young's modulus of all three kinds of carbon fibres are not influenced by K_2ZrF_6 coating.

3. Immersion of all three kinds K_2ZrF_6 coated carbon fibres into a molten aluminium results in wetting of the fibres and complete infiltration of the matrix into the fibre bundle.

4. The strength of Al matrix reinforced by K_2ZrF_6 coated T300 and T800 carbon fibre is about 100% higher than that of pure Al matrix. Comparing this values with those calculated after ROM, the increase of the strength reaches only 10% or less of the ROM values.

5. The strength of the composite Al-T800 (SiC + K_2ZrF_6 coating) reaches ∼ 30% of the ROM values.

6. Young's modulus of the composites reaches 1.8–1.9 times comparing to pure Al matrix and corresponds to the 75–80% of ROM values.

REFERENCES

[1] KELLY, A.: Concise Encyclopaedia of Composite Materials. London, Elsevier Science 1994.
[2] LAPIN, J.: Kovove Mater., *34*, 1996, p. 265.
[3] KASHIN, O. A.—ZABOLOTSKII, A. A.: Met. Sci. Heat Treat., *22*, 1982, p. 809.
[4] ŠTEFÁNIK, P.—KAVECKÝ, Š.—ŠEBO, P.: Kovove Mater., *34*, 1996, p. 318.
[5] EUSTATHOPOULOS, N.—JOUD, J. C.—DESRE, P.—HICTER, J. M.: J. Mater. Sci., *9*, 1974, p. 1233.
[6] COUDURIER, L.—ADORIER, J.—PIQUE, D.—EUSTATHOPOULOS, N.: Rev. Int. Hautes. Temp., *21*, 1984, p. 81.
[7] ROCHER, J.—QUENISSET, J. M.—NASLAIN, R.: J. Mater. Sci., *24*, 1989, p. 2697.
[8] Pat Jpn. JP 01279720 A2.
[9] ROCHER, J. P.—QUENISSET, J. M.—NASLAIN, R.: J. Mater. Sci. Letters, *4*, 1985, p. 1527.
[10] PATANKAR, S. N.—GOPINATHAN, V.—RAMAKRISHNAN, P.: J. Mater. Sci. Lett., *9*, 1990, p. 912.
[11] Japanese Industrial Standard R7601.
[12] SHINDO, A.—HONJO, K.: In: Proceedings of Japan-US Conference on Composite Materials. Eds.: Kawata, K. et al. Tokyo, Japan Society for Composite Materials 1986, p. 767.
[13] KOHARA, S.—MUTO, N.: In: Proceedings of 5th International Conference on Composite Materials. Eds.: Harrigan, W. C. Jr. et al. San Diego, The Metallurgical Society of AIME 1985, p. 631.
[14] VIALA, J. C.—FORTIER, P.—BOUIX, J.: J. Mater. Sci., *25*, 1990, p. 1842.
[15] KAVECKÝ, Š.—ŠTEFÁNIK, P.—ŠEBO, P.: In: Proceedings of the Conference on Construction Materials '97. Eds.: Šebo, P. et al. Vedecká spoločnosť pre náuku o kovoch Bratislava, IMMM SAS 1997, p. 134.