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Compatibility between carbon fibre and binary aluminium alloys

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Compatibility between carbon fibre and various binary aluminium alloys is investigated. Series of aluminium alloys are coated onto the fibre surface and the wetting behaviour of these alloys are observed by scanning electron microscopy after heating the coated fibres at 1073 K, well above the melting point of the alloys. It is found that the aluminium alloys containing such elements as indium, lead and thallium showed excellent wetting behaviour. These alloying elements have significantly smaller surface energies as compared to aluminium and they are practically insoluble with aluminium, even in the liquid states. Tensile test shows that the strength of carbon fibres is not degraded after heating at 1073 K when fibres are coated with an Al–1 at% Tl alloy. The reasons for these elements in aluminium to substantially improve the compatibility against carbon fibres are discussed from the thermodynamical point of view.

1. Introduction

When fabricating carbon fibre reinforced aluminium composite, poor wettability between carbon fibre and aluminium is one of the major problems in obtaining a sound composite with strong fibre–matrix cohesion. The wettability of aluminium against carbon fibre has been shown to improve if the temperature is raised over approximately 1273 K [1, 2]; however, interfacial chemical reaction is known to take place between fibre and matrix at above 773 K [1–5] or even below [6]. Such an interfacial reaction product is Al_4C_3, the formation of which has been known to severely deteriorate composite mechanical properties [3–6] and is thus undesirable.

Improvement in the wettability between fibre and matrix without introducing the interfacial chemical reaction has been pursued through fibre surface treatments such as immersion of fibres into molten sodium [7] or coating of carbon fibre, for example with TiC [8, 9], SiC [10], nickel [11], and copper [12], prior to the fabrication of composites. Only a few cases, however, have been reported to be successful to achieve nearly the strength expected from the rule of mixture at limited volume fractions of the fibres [11, 12].

There would be an alternative way to improve the wettability between carbon fibre and aluminium by modifying the matrix composition. Pepper *et al.* [13] have shown that excellent compatibility was obtained when composite was fabricated by hot pressing carbon fibres coated with Al–Si alloys.

In the present investigation the effect of alloying aluminium matrix by a small amount of various solute elements on the compatibility between fibre and matrix is examined. Carbon fibres are coated on the surface by various binary aluminium alloys, then the wetting behaviour of alloys on the fibre is observed by scanning electron microscopy after heating the composite at 1073 K, sufficiently above the melting point of the alloys. Tensile tests are then carried out for those coated fibres which show excellent wetting in order to evaluate the compatibility between fibre and coating alloys.

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TABLE I Nominal properties of carbon fibre

Weight ($g\,m^{-1}$)	0.38
Single fibre diameter (μm)	6.6–6.7
Tensile strength (MPa)	2.45×10^3
Elasticity modulus (MPa)	3.43×10^6
Density ($g\,cm^{-1}$)	1.8
Thermal conductivity ($kcal\,mol^{-1}\,h^{-1}\,K^{-1}$)	100
Specific heat ($cal\,g^{-1}\,K^{-1}$)	0.17
Tensile elongation (%)	0.6
Linear thermal expansion coeff. ($10^{-6}\,K^{-1}$)	– 0.5
Specific resistivity (Ω cm)	9.0×10^{-4}

2. Experimental procedure

Carbon fibre, high modulus type, used in the present investigations was provided by Toho Beslon and the nominal properties of the fibre are listed in Table I.

Various binary aluminium alloys in three categories were coated on the surface of the fibres. The first series of alloys contains alloying elements by an amount within their maximum solubility limit in the solid state with aluminium. They were 0.5 at% Cr, 2.5 at% Cu, 1 and 2.3 at% Ge, 1 and 5 at% Mg, 0.5 at% Mn and 1 at% Si alloys. In the second series of alloys, concentration of alloying elements exceeds the above solubility limit, and they are 5 at% Si, 1 at% Ga, and 1 and 5 at% Sn alloys. The third series are the alloys in which alloying element and aluminium are practically insoluble in the solid state, and even so in the liquid state, where existence of miscibility gap is characteristic. They are 1 at% In, 1 at% Tl and 1 at% Pb alloys. All the alloys were prepared using 99.9 to 99.99% purity metallic elements by arc melting in an argon atmosphere. Weight loss after melting was minimal in all the alloys, thus the nominal compositions are accepted.

Deposition of aluminium alloys onto carbon fibre surfaces was carried out in a high vacuum electron beam evaporation apparatus, ULVAC DRP-40E. Tows of carbon fibres were unravelled and then attached to a drum frame which was rotated at a rate of $420\,rev\,min^{-1}$ during the evaporation in an argon atmosphere, and thereby uniform deposition was achieved on each fibre. Thickness of alloy layer was monitored using a Sloan Digital Thickness Monitor-200 and was controlled to be approximately $0.2\,\mu m$. Carbon fibres were then encapsulated in a silica tube under 6.6×10^{-3} Pa and heated to 1073 K for 1.8 ksec followed by water quench. Wetting behaviour between fibre and aluminium alloys at the fibre surfaces was examined using a JEOL JSM-15 scanning electron microscope operated at 20 kV.

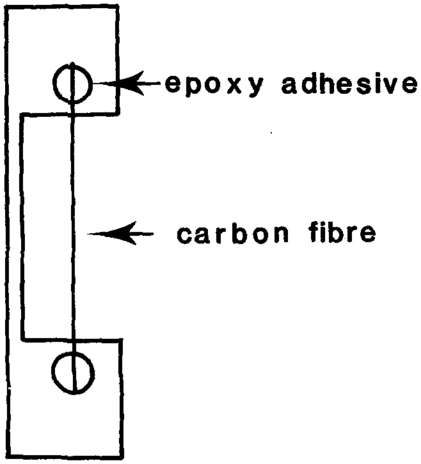

Figure 1 Schematic drawing of tensile test piece for single fibre.

Tensile strength of the carbon fibres was measured by a mini-Instron-type testing machine made by Toyo Measuring Instrument. A single fibre was attached by epoxy adhesive to a sheet of paper with a shape shown in Fig. 1. The paper support was cut at the middle after mounting to grips. Sixty tests were carried out for each specimen in order to obtain Weibull distribution of strength. Single fibre diameter was not measured and the nominal value given in Table I is used to obtain the strength. This is valid because the fibre diameter is quite uniform, as will be shown later in the micrographs.

3. Results

3.1. Scanning electron microscopic observation of fibre surfaces coated with aluminium and its alloys

The surface of the original carbon fibres and that of pure aluminium coated fibres is shown in Figs. 2a and b. Aluminium layer on the carbon fibres is quite uniform in thickness, as is shown in Fig. 2c.

Fig. 3 shows the surface state of carbon fibres coated with various binary aluminium alloys after heating at 1073 K for 1.8 ksec, clearly demonstrating wetting behaviour between fibres and alloys. Wettability of pure aluminium to a carbon fibre is found to be poor, as evidenced by the formation of metal droplets during heating on the surface of the fibre (Fig. 3a). The same situation can be observed in such coatings of the first series of binary alloys as 0.5 at% Mn (Fig. 3b), 1 at% Mg

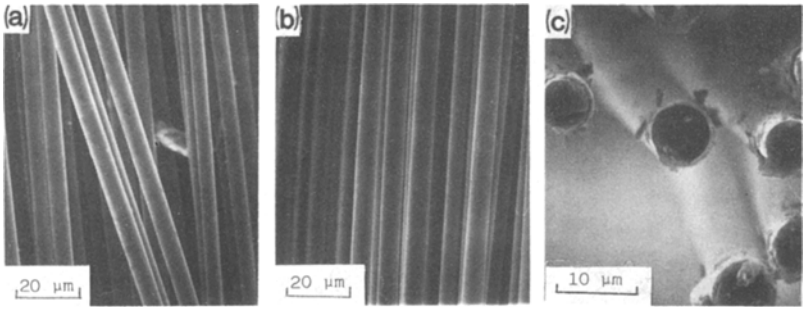

Figure 2 Scanning electron micrographs of carbon fibre surfaces; (a) as-received, (b) and (c) coated with pure aluminium.

(Fig. 3c), 1 and 2.3 at% Ge (Figs. 3e and f), 0.5 at% Cr (Fig. 3g), 2.5 at% Cu (Fig. 3h) and 1 at% Si (Fig. 3i) and 5 at% Ge (Fig. 3m). It is found that among alloys that could form homogeneous solution in the solid state, only a 5 at% Mg alloy (Fig. 3d) exhibits good wettability with carbon fibre. In the second series of the alloys, where alloy concentration exceeds the maximum solubility limit in the solid state, only 5 at% Si alloy shows good wettability, as shown in Fig. 3j. In 1 at% Ga (Fig. 3k) as well as in 1 and 5 at% Sn (Figs. 3l and 3m) alloys, the wettability is found to be poor. All the alloys, on the other hand, in which the alloying element and aluminium are practically insoluble, the third series, exhibit excellent wetting behaviour, as are shown in Figs. 3n to 3p for 1 at% In, 1 at% Tl and 1 at% Pb alloys.

3.2. Tensile strength of carbon fibres

Fig. 4 shows the Weibull distribution of the tensile strength of as-received carbon fibres (no coating) with or without heat treatment at 1073 K and that of pure aluminium coated fibres after the heating. Fig. 5 shows comparison of those for the fibres coated with 5 at% Mg, 5 at% Si, and 1 at% Tl alloys to that of aluminium coated fibres after heating at 1073 K. These alloy coatings exhibit excellent wetting behaviour against carbon fibre upon melting, as is observed in scanning electron microscopy (Figs. 3d, j and o). Average strength, intercept (B) and slope (A) in the Weibull distribution are tabulated in Table II, where $\ln F(\sigma) = \ln B + A \ln \sigma$. The value A indicates the degree of scattering in the distribution and the larger A is, the less the scattering. The value B gives probability of fracture at a stress level of 10 MPa, and therefore for a smaller B, the strength is considered higher. In Fig. 4, it can be seen that the strength of carbon fibre is not deteriorated by simply heating to 1073 K, but coating with aluminium clearly reduces the strength of fibre by the heating. As is shown in Fig. 5 and in Table II, the loss in strength is considerably reduced if aluminium is alloyed by 1 at% Tl but not by the other two alloy additions.

4. Discussion

4.1. Wettability of binary aluminium alloys against carbon fibre

The type of wetting of interest in the present investigation is the spreading wet where work of spread (W_s) between solid and liquid, which is work necessary to reduce the interface area, is expressed as

$$W_s = \gamma_s - \gamma_l - \gamma_{sl} \qquad (1)$$

where γ_s and γ_l are the surface tension of solid and liquid and γ_{sl} is interfacial tension between solid and liquid [14]. In the present case the surface tension of carbon fibre (γ_s) is unknown but

TABLE II Tensile strength, slope (A) and intercept (B) in the Weibull distribution obtained for the carbon fibres coated with various binary alloys after heating at 1073 K for 1.8 ksec

	Strength (MPa)	A	B
As-received (no coating)*	2.16×10^3	1.77	5.85×10^{-5}
No coating	2.02×10^3	1.80	5.63×10^{-5}
Pure aluminium	9.90×10^2	1.35	1.74×10^{-3}
Al–5 at% Si alloy	4.50×10^2	1.22	7.60×10^{-3}
Al–5 at% Mg	8.13×10^2	1.30	2.58×10^{-3}
Al–1 at% Tl	1.25×10^3	1.64	3.01×10^{-4}

*Not heated at 1073 K.

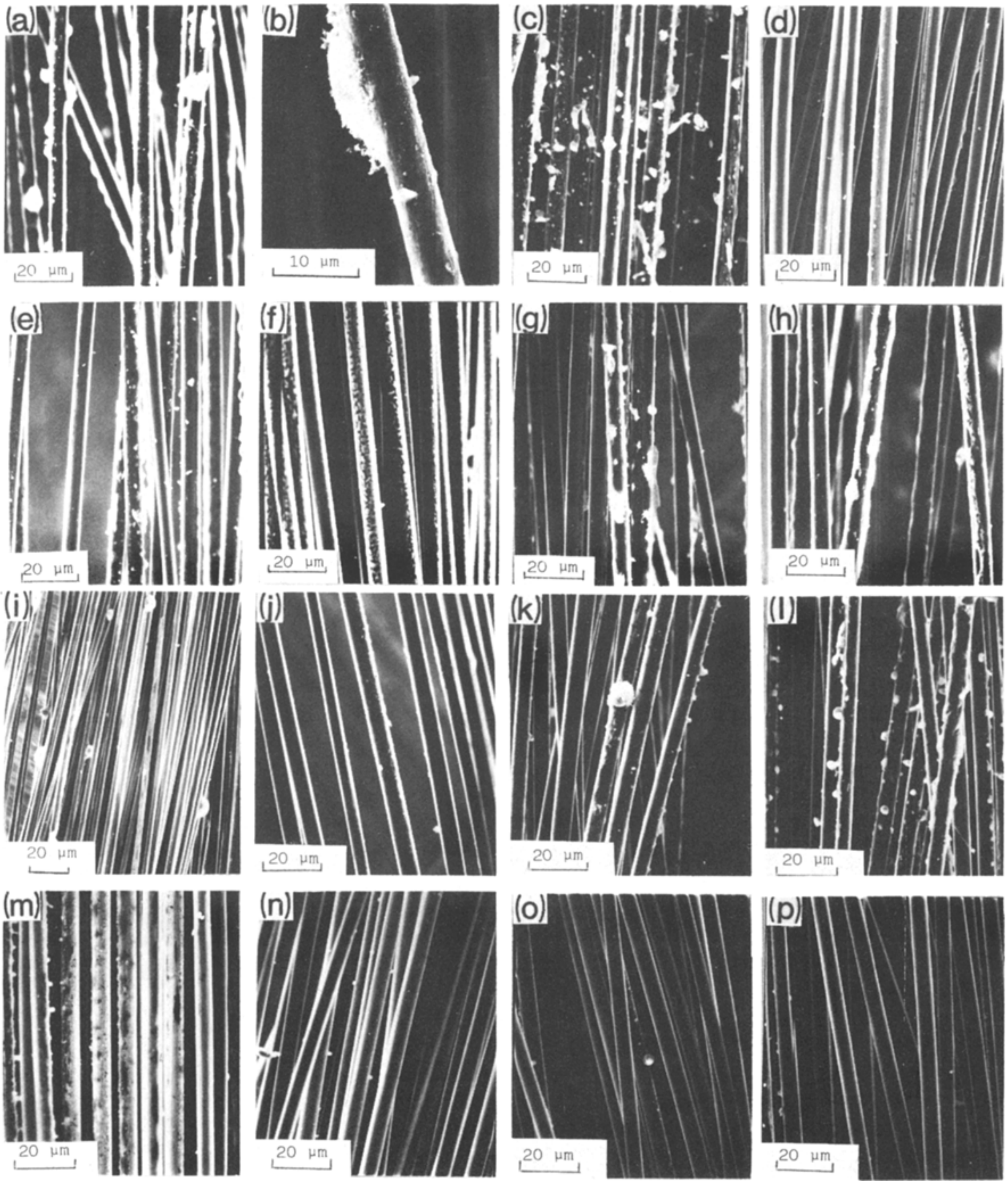

Figure 3 Scanning electron micrographs of carbon fibre surfaces after heating at 1073 K for 1.8 ksec coated with (a) pure aluminium, (b) Al–0.5 at % Mn alloy, (c) Al–1 at % Mg alloy, (d) Al–5 at % Mg alloy, (e) Al–1 at % Ge alloy, (f) Al–2.3 at % Ge alloy, (g) Al–0.5 at % Cr alloy, (h) Al–2.5 at % Cu alloy, (i) Al–1 at % Si alloy, (j) Al–5 at % Si alloy, (k) Al–1 at % Ga alloy, (l) Al–1 at % Sn alloy, (m) Al–5 at % Sn alloy, (n) Al–1 at % In alloy, (o) Al–1 at % Tl alloy and (p) Al–1 at % Pb alloy.

constant, therefore, the smaller the γ_l and/or γ_{sl}, the larger the work of spread, which leads to better wettability between fibre and liquid aluminium.

4.2. Surface tension of aluminium alloys (γ_l)

The surface tension of aluminium with various alloy additions was determined at 973 K by

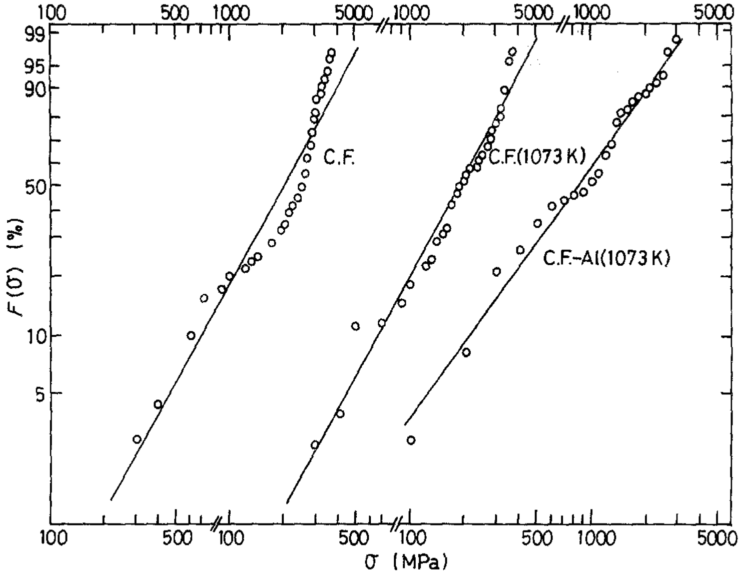

Figure 4 Weibull distributions of the tensile strength of as-received carbon fibres (no coating) with or without heating at 1073 K for 1.8 ksec and that of pure aluminium coated fibres after the heat treatment.

Ranshofen [15] and is shown in Fig. 6. It is clearly seen that the surface tension of liquid aluminium decreases with increasing amount of alloying element in most cases. Such effect is drastic with bismuth, lead and thallium additions and moderate with tin, indium and magnesium additions. In view of the results on the observation of wetting behaviour by scanning electron microscopy, the alloy additions to improve the wettability mostly fall into those categories where surface tension of aluminium, γ_l, is significantly reduced. It should be noted that they are always the element with low melting point.

Surface tension of binary aluminium alloys in the liquid state can be given by Gibbs' adsorption equation [16],

$$d\gamma_l = -\Gamma\, d\mu \qquad (2)$$

where Γ is the excess solute concentration adsorbed on the surface, γ_l is the liquid surface energy and μ is the chemical potential of solute in the liquid.

Chemical potential of the solute is then rewritten as

$$\mu = RT \ln a_B \qquad (3)$$

where a_B is the activity of solute element.

Then the surface tension can be expressed as

$$d\gamma_l = -RT\Gamma\, d\ln a_B \qquad (4)$$

It is thus clear that when either the excess solute concentration at the surface or the activity of the solute is increased, then the surface energy of aluminium is reduced.

First it is possible to qualitatively estimate whether a certain alloying element would be adsorbed to the surface of liquid aluminium. It is doubtlessly so for such elements as lead and

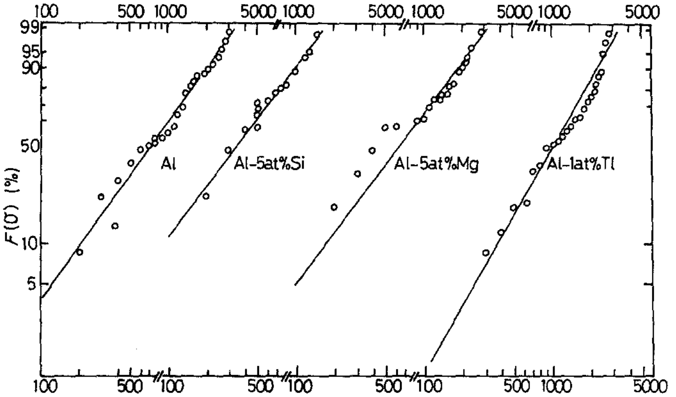

Figure 5 Weibull distribution of the tensile strength of carbon fibres coated with pure aluminium, Al–5 at% Si alloy, Al–5 at% Mg and Al–1 at% Tl alloy, all heated at 1073 K for 1.8 ksec.

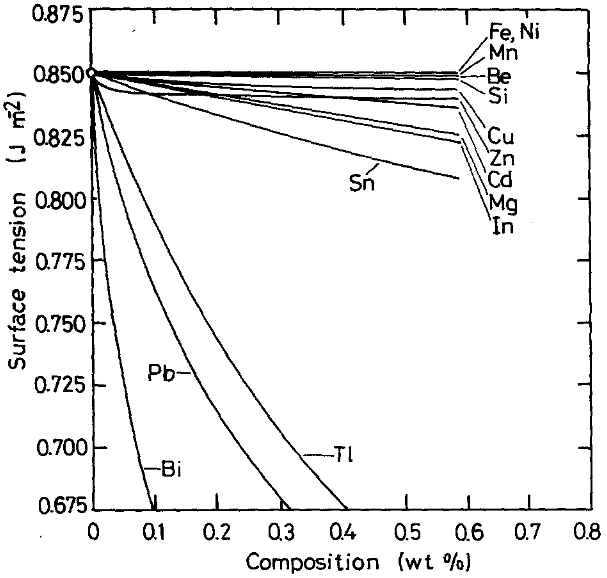

Figure 6 The surface tension of aluminium at 973 K with various alloy additions, after Ranshofen [15].

thallium, in the third group alloys. The binary system of aluminium and one of these elements is characterized by the presence of a miscibility gap in the liquid state and therefore these elements and aluminium are practically insoluble. It is then likely that either solute or solvent atoms should segregate to the surface of the liquid in order to minimize the surface tension. Table III shows selected measured surface energy of several elements as well as aluminium [17, 18], and it is clear that the surface energy of the two elements, Pb and Tl, is significantly lower than that of aluminium. Such solute atoms should segregate to the surface of aluminium and therefore the excess solute concentration, Γ, will become large. There will be some excess solute concentration in binary alloys containing other solute atoms whose surface energy is considerably lower than that for aluminium. However, as compared to the above two elements, they are soluble in the liquid state and hence the degree of adsorption of such elements would be lower.

Another variable which affects the surface tension of binary aluminium alloys in the liquid state is, in Equation 4, the activity of solute atoms. Unfortunately, activity data for various solute elements in binary aluminium alloys are not always available in the literature for both composition and temperature of interest. In order to deduce the effect of solute activity on the surface energy of liquid aluminium the following treatment is applied.

Consider the dissolution process of solute into aluminium,

TABLE III Selected measured surface energy of elements

Metal	Temperature (K)	Surface tension (J m^{-2})
Al	933	0.915
	973	0.900
	1073	0.865
Cr	2171	1.880
Cu	1356	1.350
	1473	1.300
Ga	302.8	0.735
	323	0.735
In	430	0.559
	473	0.555
	573	0.545
	673	0.535
	773	0.525
	873	0.515
Mg	923	0.556
	973	0.542
	1023	0.515
Mn	1516	1.293
Pb	600	0.444–0.480
	673	0.438–0.462
	773	0.431–0.438
	873	0.426–0.414
	1073	0.409
Sn	504.9	0.586
	573	0.580
	673	0.573
	773	0.566
	873	0.560
Tl	576	0.490
	623	0.401
Ge	1209	0.621

TABLE IV Enthalpy of mixing of selected alloying elements with aluminium

	Cr	Cu	Ga	Ge	In	Mg	Mn	Pb	Si	Sn	Ti	Tl
ΔH (kJ g atom^{-1})	− 36	− 32	+ 4	− 8	+ 31	− 8	− 70	+ 49	− 9	+ 19	− 135	+ 51

$$(1-x)\mathrm{Al} + x\mathrm{B} = \mathrm{Al}_{1-x}\mathrm{B}_x \qquad (5)$$

where free energy of mixing is given as

$$\Delta G = RT \ln a_{\mathrm{Al}}^{1-x} a_{\mathrm{B}}^{x} \qquad (6)$$

Here, a_{Al} is the activity of aluminium and a_{B} is the activity of solute B.

In a dilute solution of B in aluminium, a_{Al} can be assumed to be a constant regardless of the solute species, and therefore,

$$\mathrm{d}\Delta G = RT\mathrm{d} \ln a_{\mathrm{B}} \qquad (7)$$

Also taking the regular solution approximation

$$\mathrm{d}\Delta G = \mathrm{d}\Delta H \qquad (8)$$

then we have

$$\mathrm{d}\Delta H = RT\mathrm{d} \ln a_{\mathrm{B}} \qquad (9)$$

From Equation 9, activity of the solute in the binary solution can be known if the data on enthalpy of mixing are at hand. Although such data are again not always available, a semi-empirical equation to calculate the enthalpy of mixing for any binary alloys has been derived through a series of works by Miedema and co-workers [19–21]. Calculated values using this method are tabulated in Table IV for those elements alloyed to aluminium in the present investigation. According to Equation 9, a large enthalpy of mixing value gives a large solute activity and thereby reduces the surface tension of the binary liquid. It is clearly shown that the elements in the third group, indium, lead and thallium, have the large positive values per gram atom addition in aluminium.

Through the present discussion, it now becomes possible to predict the effect of alloying on the surface tension of liquid aluminium for any binary systems with B-subgroup elements.

4.3. Interfacial tension between carbon fibre and aluminium alloys (γ_{sl})

Surface tension between carbon fibre and liquid aluminium has not been measured and the effect of alloying is unknown. It seems there would be no theoretical estimation possible for this particular quantity. However, it will be definitely small if there is some chemical reaction to form some compound that is coherent with carbon fibre. In the present investigation, 5 at% Si alloy showed fairly good wetting with carbon fibre, as is shown in Fig. 3j. However, in Fig. 6, it was shown that the surface tension of aluminium was hardly affected by the addition of silicon, thus, in Equation 1, improvement in wettability cannot be expected solely by reduction in γ_{l} in this case. Therefore the interfacial tension between carbon fibre and 5 at% Si alloy, γ_{sl}, should be low because of formation of a compound, most likely SiC. Since aluminium itself is known to form carbide at the interface and to exhibit poor wettability with carbon fibre, the reason for 5 at% Si alloy to give better wettability with carbon fibre seems complex. It would be due to less extent of carbide formation or to better cohesion between carbon fibre and the carbide formed. According to the available data on standard free energy of carbide formation, carbide forming tendency at 1073 K among the elements presently investigated can be found as aluminium, silicon, chromium and magnesium in a decreasing order.

The results on the tensile tests of carbon fibres coated with those aluminium alloys that showed good wetting after heating at 1073 K clearly indicate that only 1 at% Tl alloy exhibited nearly equal properties to the original carbon fibres. Considerable deterioration in tensile strength resulted in fibres coated with 5 at% Si or 5 at% Mg alloy. This would further support the speculation in which good wettability between carbon fibres and 5 at% Si alloys is attributed, at least partly, to the formation of carbide. The same situation might be occurring at the interface between 5 at% Mg alloy and carbon fibres, which resulted in poor compatibility.

5. Conclusion

Wettability between carbon fibres and various binary aluminium alloys after heating at 1073 K for 1.8 ksec was investigated and its effect on the room temperature tensile strength of fibres was examined. The following are the conclusions drawn.

1. Wettability between fibres and aluminium is found significantly improved by a small amount of alloying of indium, lead or thallium.

2. The improvement in wettability can be attributed to the significant reduction in surface tension of liquid aluminium. These elements and aluminium are insoluble in the liquid state, leading to the adsorption of solute with low surface tension to the surface of the liquid.

3. Among the rest of the binary aluminium alloys, Al–5 at% Mg and Al–5 at% Si alloys exhibit fairly good wettability with carbon fibres. In silicon-containing alloy and in magnesium containing alloy to a lesser degree, it is attributed to the reduction in interfacial tension between fibre and the alloy where carbide formation would play an important role.

4. Degradation in tensile strength of carbon fibres does not result with Al–1 at% Tl alloy coatings but is considerable with Al–5 at% Si and Al–5 at% Mg alloy coatings. Excellent compatibility between fibre and aluminium can be achieved by alloying 1 at% Tl, probably by alloying 1 at% Pb or 1 at% In also, because of good wettability to the fibres with no interfacial reaction occurring.

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