JOURNAL OF MATERIALS SCIENCE **24** (1989) 1496–1502

Growth kinetics of interface intermetallic compounds in stainless steel fibre reinforced aluminium matrix composites

R. B. BHAGAT*
Indian Institute of Technology, Bombay, India

Growth kinetics of binary intermetallic compounds in the fibre/matrix interface has been studied in stainless steel fibre reinforced aluminium matrix composites fabricated by the P/M hot pressing, squeeze casting, and infiltration techniques. As expected in most binary diffusion couples, more than one intermetallic compound of the type Fe_xAl_y forms at the interface. However, not all the iron–aluminide intermetallic compounds possible as dictated by the binary phase diagram are present. This is primarily the result of the non-equilibrium conditions at the interphase boundaries as the activation-controlled and diffusion-controlled interfacial reactions progress between the fibre and the matrix. Two equations have been established for the growth kinetics of the interface; one relates to hot pressing, the other to squeeze casting and infiltration. Parabolic rate constants have been determined. A rate constant of about $0.7 \times 10^{-16}\,m^2\,sec^{-1}$ for hot-pressed composites produces an optimum thickness of the interface of about $3\,\mu m$ and results in the maximum strength of the composites. In addition to the FeAl and Fe_2Al_5 that form at the interface, the presence of $NiAl_3$ intermetallic compound is also predicted. Further investigation is suggested for the determination of the rate constants in squeeze-cast and infiltrated composites.

1. Introduction

The unique properties of the fibre-reinforced composite materials are to a great extent dependent on the unique nature of the fibre/matrix interface which is defined as "the region of significantly changed chemical composition constituting the bond between the matrix and the reinforcement for transfer of loads between these members of the composite structure" [1]. In fabricating reliable composites, therefore, achieving a "suitable" interface is of primary importance [2, 3]. Growth kinetics studies of the interface intermetallic compound(s) may provide a means to predict optimum fabrication parameters such as temperature, pressure, and time to produce composites with good mechanical properties. Snide [4] determined apparent parabolic growth rate constants for the reactions of the various grades of titanium with boron, silicon carbide and titanium diboride filaments and found that the rate constants were significantly lower for Ti–6Al–4V compared to those for commercial and high-purity titanium matrix. No attempt was made to optimize the hot pressing temperature of boron/aluminium composites based on the premise that at a particular temperature the partial diffusion coefficient of boron will equal that of aluminium in the intermetallic layer of AlB_2 [5]. They met with only limited success. The reasons are two-fold. First, they ignored the effects of hot-pressing pressure on the rate constant. Second, they did not establish the hot-pressing time which will result in an optimum intermetallic layer thickness. Shatyanski *et al.* [6] presented a theory of multiphase binary diffusion based on the assumptions that the interface layer growth is parabolic and the equilibrium conditions prevail at the interphase boundaries. In fibre composites it is not known, a priori, that the interface reaction zone will follow a parabolic growth. Also the requirements of the equilibrium boundary conditions are, in general, not met because of the need to minimize the fibre/matrix contact time at the fabrication temperature. Van Loo and Rieck [7] found non-parabolic growth of an intermetallic layer in the Ti–Al couple and attributed this to a contribution from the grain-boundary diffusion. Dewing and Iyer [8] found parabolic growth of the reaction product in 304 stainless steel–aluminium couple, and linear growth in plain-carbon steel–aluminium, 1.3Co–0.4Mo steel–aluminium, and 2.2Co–0.9Mo steel–aluminium couples. According to them only Fe_2Al_5 formed as a result of the reaction between aluminium and steels. However, there is a strong likelihood that other intermetallic compounds may form in these couples, as other investigators have found in other systems. For example, Snide [4] demonstrated the presence of complex reaction products in SiC/Ti–8Al–1Mo–1V composites and Steed and Rhodes [9] found the presence of VB in addition to

---

**Present address*: Applied Research Laboratory, Pennsylvania State University, Post Office Box 30, State College, Pennsylvania 16804, USA.

0022–2461/89 $03.00 + .12

TiB and TiB_2 in boron-reinforced titanium alloy composites [10]. In general, the number of possible reaction products present at the interface in composites is dictated by a combination of events, such as activation-controlled reaction, solid-state diffusion-controlled process, and such competing processes as simultaneous growth and consumption or dissolution during the fabrication of the composites. It is unlikely that all the phases predicted by a binary phase diagram will form. This follows from a general lack of local equilibrium at the phase boundaries during the fabrication process. Further, nucleation and growth constraints may inhibit the formation of one or more of the possible phases.

The objectives of the present investigation were, therefore, to present a generalized interface growth kinetics formulation for fibre-reinforced metal matrix composites, to determine rate constants of the reaction products in these composites, and to predict an optimum thickness of the fibre/matrix interface which will result in the maximum tensile strength of the composites. The following section deals with the growth kinetics formulation.

2. Growth kinetics formulation

A generalized formulation for the interface growth rate in fibre composites with allowance for the rate of the chemical reaction, the diffusion of atoms in the intermetallic layer, and the dissolution of the solid in the liquid metal is presented below.

In fabrication methods such as squeeze casting and infiltration of composites, the fibres come into contact with excess atoms of liquid metal. It follows from the basic postulate of chemical kinetics that the initial step of the fibre matrix reaction process can be described by the following equation

$$dx/dt = k_0 \tag{1}$$

where x is the thickness of the interface (m), t is time (sec) and k_0 is the rate constant for the growth of the intermetallic layer or the interface ($m\,sec^{-1}$). As the growing interface reaches a particular thickness, the growth mechanism changes from activation to diffusion-control and follows the following relation [11, 12]:

$$dx/dt = k_p/x \tag{2}$$

where k_p is the parabolic rate constant ($m^2\,sec^{-1}$). Adding $1/k_0$ and x/k_p and taking the reciprocal of the resulting sum, the entire growth process can be represented by

$$(dx/dt)_{gr} = k_0/(1 + xk_0/k_p) \tag{3}$$

The linear velocity of dissolution of the intermetallic compound layer taking place in parallel with layer growth [13, 14] is expressed as

$$(dx/dt)_{diss} = b \exp(-at) \tag{4}$$

where $a = k_d\, s/v$, $b = c_H k_d/\varrho_\phi \phi$, k_d is the dissolution rate constant ($m\,sec^{-1}$), s is the surface area of the fibre (m^2), v is the volume of the liquid metal (m^3), c_H is the solubility of the fibre material in the matrix at the fabrication temperature ($kg\,m^{-3}$), ϱ_ϕ is the density of the intermetallic layer ($kg\,m^{-3}$) and ϕ is the concentration of the fibre material in the intermetallic layer (fraction by weight). The dissolution rate constant, k_d, is obtained from the Shchukarev–Nernst equation [13, 14],

$$c = c_H[1 - \exp(-at)] \tag{5}$$

which describes the change in concentration of the dissolving solid in the volume of the melt as a function of time. The generalized growth rate can be taken as the difference between the growth rate as expressed by Equation 3 and the dissolution rate, Equation 4

$$(dx/dt)_{gen} = (dx/dt)_{gr} - (dx/dt)_{diss} \tag{6}$$

or

$$(dx/dt)_{gen} = k_0/(1 + xk_0/k_p) - b \exp(-at) \tag{7}$$

Equation 7 represents the generalized growth-rate equation for the intermetallic layer formed as a result of the reaction between fibre and matrix during the fabrication of composites. Application of Equation 7 to the specific fabrication methods used in the present investigation will be discussed later. The next section includes a brief description of the experimental work.

3. Experimental work

The experimental work of the present investigation on growth kinetics included fabrication of stainless steel/aluminium composites, determination of the rate constants, and the characterization of the fibre/matrix interface. The properties of aluminium matrix materials and stainless steel wire, and the methods of fabrication are presented in Table I. Detailed descriptions of hot pressing, squeeze casting, and infiltration methods can be found in the author's earlier publications [15, 17]. A brief account of the fabrication methods follows.

In hot pressing, fabrication parameters were optimized to control diffusion bonding between matrix and fibre in order to obtain composites having maximum tensile strength at any fibre volume fraction. The optimum hot-pressing temperature, pressure, and time thus established are 800 K, 140 MPa, and 60 sec, respectively. In squeeze casting, the molten metal was force-infiltrated into, around, and through an array of stainless steel wires placed horizontally in a preheated tool steel die under a high pressure until its complete solidification. From preliminary experiments, a die preheating temperature of 820 K, metal pouring temperature of 1120 K and a pressure of 110 MPa were found to be suitable for fabricating the composites with good reproducibility. In the infiltration method, a bundle of preheated wires (570 to 970 K) held in a graphite tube was introduced into the molten metal (990 to 1120 K) in a graphite crucible and suction was applied.

The fibre/matrix interface was characterized by optical and scanning electron microscopy (SEM), and energy dispersive spectroscopy (EDS). Determination of the rate constants and the identification of intermetallic compounds in the interface are included in the following section.

4. Results and discussion

Application of the generalized growth equation,

TABLE I Details of matrix and fibre materials used in different fabrication techniques

Fabrication methods	Matrix materials	σ_m (MPa)	Fibre materials	σ_f (MPa)
1. Infiltration	Commercial grade aluminium	92	304 type stainless steel wire (annealed) diameter = 0.30 mm	760
2. Squeeze casting	(a) Commercial grade aluminium (b) Age-hardenable aluminium alloy (Al–0.7Mg–0.61Si–0.8Mn–0.4Fe)	94 139	as above	760
3. Hot pressing	Aluminium powder grade 'D' (INDAL)		(a) as above	760
	Characteristics: Apparent density = 0.982 g cm^{-3} tap density = 1.218 g cm^{-3} flow rate = 50 g/91.25 sec			
	Sieve analysis: −80 +150 78.5% −150 +200 19.0% −200 2.5%		(b) 304 type stainless steel wire (annealed) diameter = 0.167 mm	623
	Hot-pressed aluminium matrix (800 K, 140 MPa, 60 sec)	90		

Equation 7, to the interface in hot-pressed, squeeze-cast, and infiltrated stainless steel/aluminium composites is described below. Calculation of the rate constants and the prediction of an optimum interface thickness are also reported and discussed in this section.

4.1. Growth kinetics (hot pressing)

Hot-pressed composites were fabricated at a temperature and pressure of 800 K and 140 MPa, respectively, for extended periods ranging from 1 min to 1 h. In hot pressing, the dissolution component of Equation 7 can be completely ignored. Thus Equation 7 can be rewritten as

$$\mathrm{d}x/\mathrm{d}t = k_0/(1 + xk_0/k_p) \qquad (8)$$

The solution of Equation 8 for initial conditions of $x = 0$ at $t = 0$ can be easily obtained as

$$x/k_0 + x^2/2k_p = t \qquad (9)$$

Equation 9 is termed here the generalized growth equation for the interface in hot-pressed composites. Some of the special cases of Equation 9 are discussed below.

(a) For $k_0 \ll k_p/x$, Equation 9 reduces to

$$x = k_0 t \qquad (10)$$

Equation 10 describes the activation-controlled step of the growth of the interface. In the present investigation it was found that the experimental data on the interface thickness (x) and the hot-pressing time (t) were not well represented by the linear relationship as expressed in Equation 10. This indicated that the interface growth in hot pressing cannot be accurately described by activation-controlled reaction alone.

(b) For $k_0 \gg k_p/x$, Equation 9 reduces to

$$x^2 = 2k_p t \qquad (11)$$

Equation 11 describes the diffusion-controlled growth of the interface. Experimental data obtained in this investigation for the interface thickness (x) and the hot pressing time (t) were used to plot x^2 against $2t$; see Fig. 1.

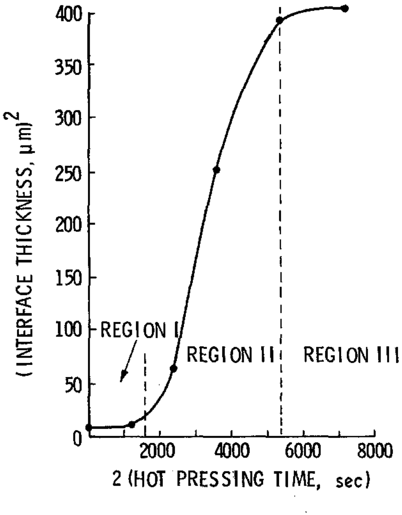

Figure 1 Parabolic rate constant curve for hot-pressed 304 stainless steel/aluminium composites.

The slope of the curve in Fig. 1 represents the parabolic rate constant, k_p. To develop a better understanding of the growth kinetics, the curve was divided into three regions for different periods of hot pressing. The values of k_p for Region I ($0 < 2t < 1500$ sec), Region II (1500 sec $< 2t <$ 5000 sec) and Region III ($2t >$ 5000 sec) were 0.71×10^{-16}, 0.18×10^{-12} and 0.44×10^{-14} m^2 sec^{-1}, respectively. The lowest value

TABLE II EDS results from elemental analysis on the cross-section of hot-pressed composites (800 K, 140 MPa, 60 sec)

Distance from fibre (μm)	Region	Elemental analysis by weight fraction				
		Al	Fe	Cr	Ni	Cu
0.00	Fibre	0.00	0.74	0.18	0.08	0.00
2.73	Interface	0.27	0.52	0.12	0.05	0.00
5.46		0.32	0.55	0.11	0.06	0.02
7.50		0.42	0.48	0.08	0.02	0.03
8.50	Matrix	0.59	0.08	0.01	0.01	0.04
9.50		0.56	0.05	0.01	–	0.05
10.50		0.76	0.05	0.01	–	0.01
22.50	Matrix	0.97	0.03	–	–	0.01

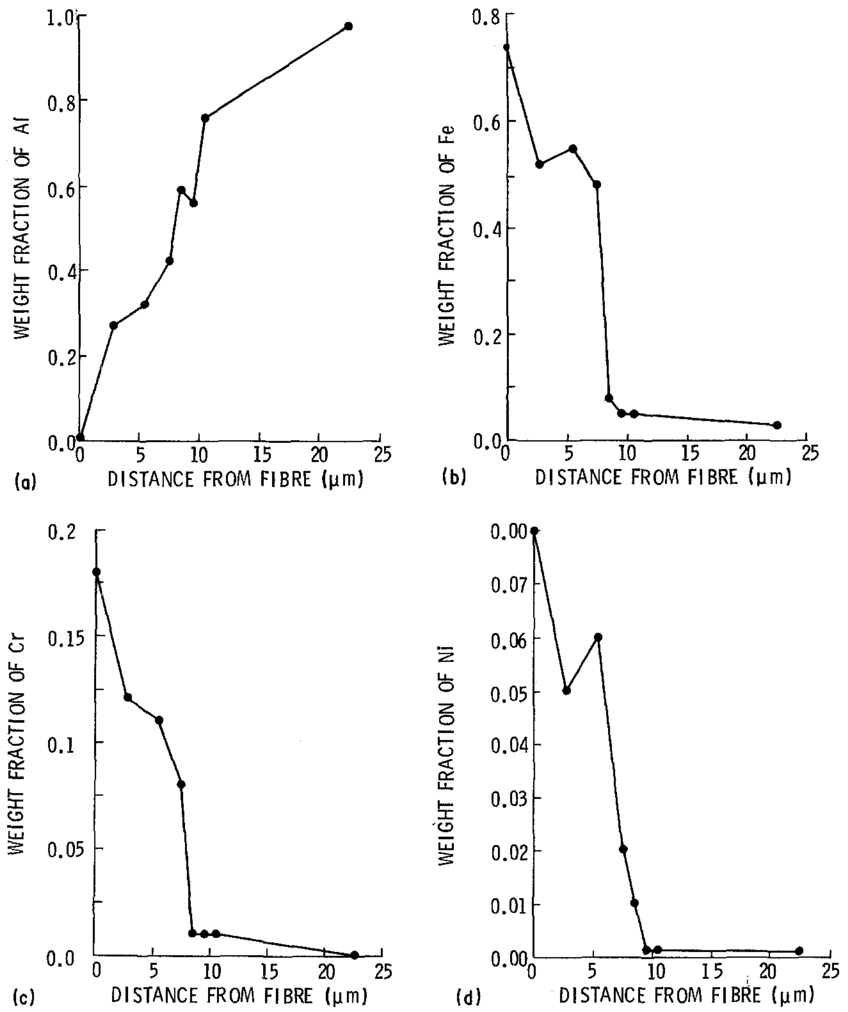

Figure 2 EDS elemental analysis results across the interface in hot-pressed 304 stainless steel/aluminium composites, (a) Al, (b) Fe, (c) Cr and (d) Ni.

of the parabolic rate constant (Region I) is interpreted as signifying that the inherent oxide layer on the 304 stainless steel wire remains almost intact up to a hot-pressing time of about 10 min at a temperature and pressure of 800 K and 140 MPa, respectively. As a result, this oxide layer acts as a barrier to the diffusion process. However, under the hot-pressing conditions, enough diffusion takes place to provide "just adequate" diffusion bonding of the fibre to the matrix in addition to their mechanical bonding. Thus the composites fabricated by hot pressing at a temperature, pressure, and time of 800 K, 140 MPa, and 1 to 10 min, respectively, will have an ideal interface resulting in their maximum tensile strength. This is confirmed by the author's earlier reported tensile strength data for the hot-pressed composites [15].

Transition from Region I to Region II for k_p is gradual as can be seen in Fig. 1. This signifies that towards the beginning of the Region II, the oxide layer on the wire starts disappearing under the continued diffusion-controlled reaction at the fibre/matrix interface. At the complete disappearance of this oxide layer the rate constant attains a maximum value and remains constant up to a hot-pressing time of about 40 min. Towards the end of the Region II the interface grows to a thickness of about 20 μm which is probably too large to allow rapid diffusion process. This marks the beginning of the Region III leading to a sluggish interface growth. Tensile strength data previously reported [15] revealed that the composites having an interface thickness of more than 4 μm have very poor strength. In view of the foregoing, it is clear that for the hot-pressed stainless steel/aluminium composites a parabolic rate constant of about 0.7×10^{-16} m^2 sec^{-1} provides just sufficient fibre/matrix reaction to provide an ideal interface having a thickness of about 2 to 4 μm. To identify the intermetallic compound(s) in the interface, elemental analysis on the cross-section of several hot-pressed composites was carried out. The results of this analysis are presented in Table II as the average fraction by weight at different locations across the interface. The weight fraction was converted into molar fraction for aluminium, iron, chromium and nickel. Based on these molar fractions and the microhardness data presented in Table III, it was predicted that FeAl, Fe_2Al_5, and $NiAl_3$ intermetallic compounds formed at the fibre/matrix interface during the hot pressing. Plots in Fig. 2 further reveal that the most dominant element among iron, chromium and nickel diffusing into aluminium is iron. Therefore, the growth of the interface is mainly dependent on the growth kinetics of the iron aluminides. Further investigation is required to determine the rate constants of the individual intermetallic compounds and to establish their relation to the overall rate constant determined in this investigation.

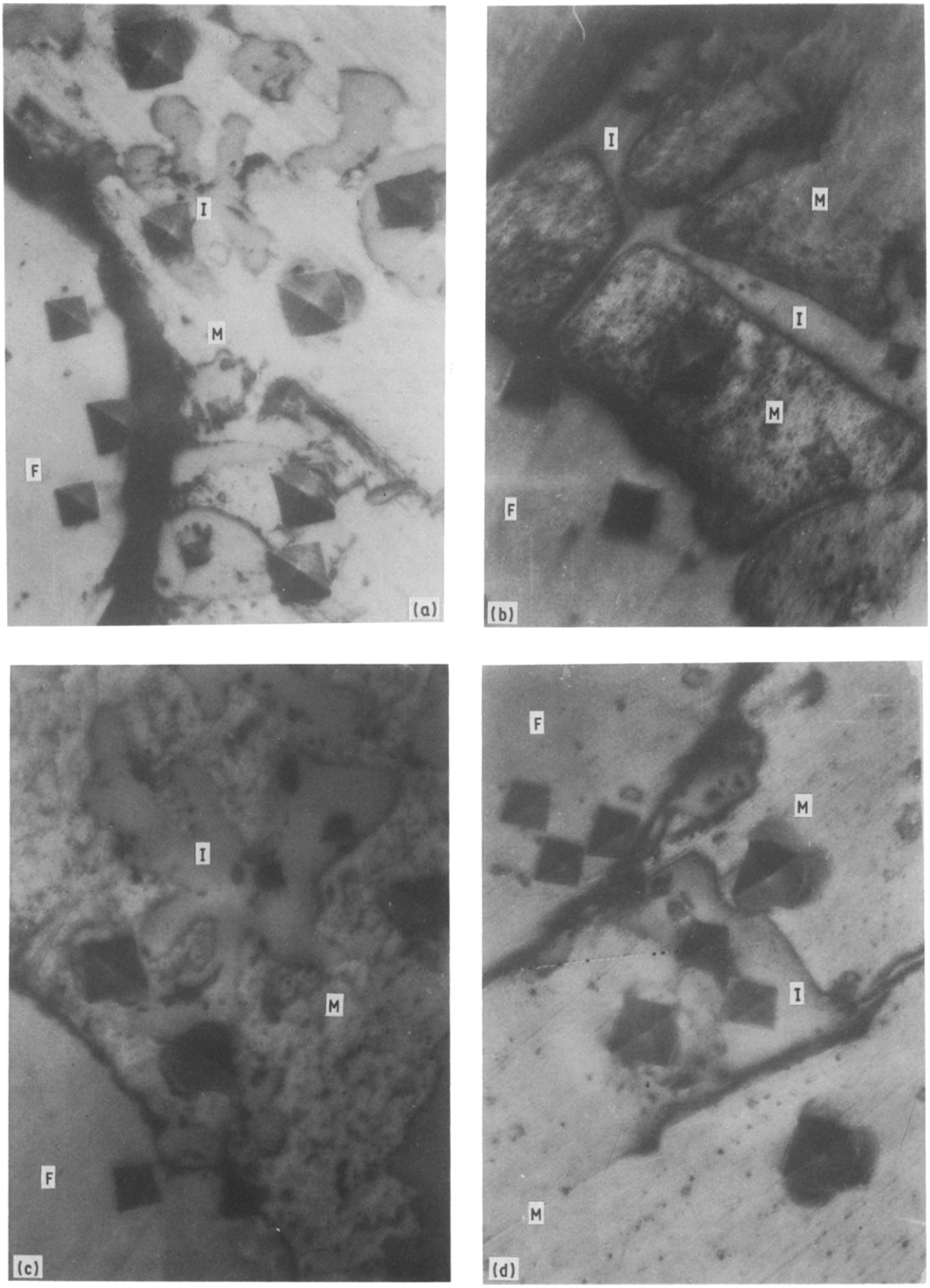

Figure 3 Fibre/matrix reaction products (I) and their relative hardness in squeeze-cast 304 stainless steel/aluminium composites. F and M represent fibre and matrix, respectively.

4.2. Growth kinetics (squeeze casting and infiltration)

In squeeze casting and infiltration methods of fabricating composites, fibres come into contact with the molten matrix. The interface growth and the dissolution of the solid will compete against each other. This process can be adequately described by Equation 7 which is an equation of the Abel type [18]. Its exact solution is not easy to find. A close approximation will require the use of a modern computer. Alternatively,

TABLE III Experimental micro-hardness values of fibre/matrix interface in composites fabricated by hot pressing

Fabrication conditions			Matrix side			Fibre side		
Temp. (K)	Pressure (MPa)	Time (sec)	Mean	S.D.	EOR*	Mean	S.D.	EOR*
575	140	60	123.5	42.8	211, 342	369.3	28.6	–
800	140	60	213.5	142.7	769, 1149	243.6	76.0	123, 400
885	140	60	117.1	55.0	930	–	–	–
800	140	3600	207.3	143.6	595, 703, 769	359.7	37.4	510, 930

*Extra ordinary readings.

however, Equation 7 can be easily solved for some limiting cases. Pertinent to the present investigation, the following special cases are considered.

(a) Assuming that the rate of dissolution is constant and has its maximum value, b, Equation 7 reduces to

$$\mathrm{d}x/\mathrm{d}t = k_0/(1 + k_0 x/k_p) - b \qquad (13)$$

The solution of Equation 13 can be easily obtained as

$$-(k_p/b^2) \ln [1 - k_0 bx/k_p(k_0 - b)] - x/b = t \qquad (14)$$

(b) Under the steady state condition ($\mathrm{d}x/\mathrm{d}t = 0$), which is likely to prevail in infiltration, if not in high-pressure casting, Equation 13 will reduce to

$$x = (k_0 - b)k_p/bk_0 \qquad (15)$$

which happens to be the maximum value of x. Thus Equation 15 can be rewritten as

$$x_{\max} = (k_0 - b)k_p/bk_0 \qquad (16)$$

This means that at this value of $x_{\max}$, a steady state has been reached, with the growth rate equal to the rate of dissolution. Therefore Equation 16 defines the maximum layer thickness achievable for a constant rate of dissolution, b. Further, it can be seen that Equation 14 describes the asymptotic approach of the layer thickness to the limiting value given by Equation 16.

(c) For $k_0 \gg b$, Equation 16 will reduce to

$$x_{\max} = k_p/b \qquad (17)$$

(d) According to Equation 16, the condition for the absence of a layer of intermetallic compound at the interface is given by the inequality

$$k_0 \leqslant b \qquad (18)$$

This condition shows that the presence (or absence) of a layer at the interface is determined by the relative rates of the chemical reaction and dissolution of the solid in the liquid phase. If $k_0 > b$, the thickness of the layer takes a positive value and this condition should be treated as the basic requirement of the processing of the composites.

However, satisfaction of the condition $k_0 > b$ alone will not be of any use if the rate constant, k_0, is not kept to a minimum during the fabrication of composites. What is required in a composite is just a bare minimum amount of fibre–matrix reaction to give an adequate interfacial bonding. To meet such a requirement, the processing has to be done fast enough to minimize the contact time between the fibres and the molten matrix. Obviously the steady state condition is not desirable and, as such, Equations 15 to 17 are of only limited use for studying the growth kinetics in composites. However, the author considers it reasonable to treat Equation 14 as the generalized growth equation for the interface in composites fabricated by squeeze casting or infiltration technique. Attempts to determine the rate constants in the squeeze-cast and infiltrated stainless steel fibre-reinforced aluminium matrix composites were not very successful, primarily because of somewhat more than desirable fibre/matrix reaction and a large scatter in the measured values of the interface thickness (see Fig. 3).

5. Conclusions

Two equations have been established for the growth kinetics of fibre/matrix interface in composites

$$x/k_0 + x^2/2k_p = t \qquad \text{(hot pressing)}$$

and

$$-(k_p/b^2) \ln [1 - k_0 bx/k_p(k_0 - b)] - x/b = t$$

(squeeze casting and infiltration)

where x is the interface thickness (m), k_0 is the activation-controlled rate constant (m sec^{-1}), k_p is the diffusion-controlled parabolic rate constant (m^2 sec^{-1}), t is the processing time (sec), and b is a dissolution parameter (m sec^{-1}). A parabolic rate constant of about 0.7×10^{-16} m^2 sec^{-1} has been determined for hot-pressed 304 stainless steel/aluminium composites to produce an optimum thickness of the interface of about 3 μm. The interface in the hot-pressed composites has been characterized to contain FeAl, Fe_2Al_5 and $NiAl_3$ intermetallic compounds. In squeeze-cast and infiltrated composites, the interfacial reaction between the stainless steel wire and the aluminium matrix has been found to be somewhat more than desirable. Determination of the rate constants for the growth of the interface in these composites will require further investigation.

Acknowledgement

This paper was presented at the Annual Meeting of The Metallurgical Society in New Orleans, Los Angeles, 2 to 6 March 1986.

References

1. A. G. METCALFE, Introduction and Review, in "Composite Materials", Vol. 1, "Interfaces in Metal Matrix Composites" (Academic, New York, 1974) pp. 1–30.
2. S. FISHMAN, "Interfaces in Composites – Research Needs", Paper presented at the 1985 ASM Metals Congress, Toronto, Canada, 14 to 17 October 1985.
3. I. J. EBERT and P. R. WRIGHT, Mechanical Aspects of

the Interface, in "Composite Materials", Vol. 1, "Interfaces in Metal Matrix Composites" (Academic, New York, 1974) pp. 31-64.

4. J. A. SNIDE, "Compatibility of Vapor Deposited B, SiC, and TiB_2 Filaments with Several Titanium Matrices", Report AFML-TR-67-345, Wright Patterson Air Force Base, Columbus, Ohio, 1968.
5. V. S. POSTNIKOV, V. I. LAVRENT'EV and M. KH. SHORSHOROV, *Fizika i Khimiya Obrabotki Materialov* **17**(5) (1983) 96.
6. S. R. SHATYANSKI, J. P. HIRTH and R. A. RAPP, *Acta Metall.* **24** (1976) 1071.
7. F. J. J. VAN LOO and G. D. RIECK, *ibid.* **21** (1973) 61.
8. E. W. DEWING and S. P. IYER, *Metall. Trans.* **2** (1971) 2931.
9. J. W. STEEDS and C. G. RHODES, *J. Amer. Ceram. Soc.* **68** (5) (1985) 136.
10. A. G. METCALFE and G. K. SCHMITZ, "Development of Filament Reinforced Titanium Alloys", paper presented at the SAE Aeronautic and Space Engineering and Manufacturing Meeting, Los Angeles, California, 26 October 1967.
11. C. WAGNER, "Atom Movements" (American Society for Metals, Cleveland, Ohio, 1951) p. 153.
12. *Idem*, *Acta Metall.* **17** (1969) 99.
13. V. I. DYBKOV, *Russ. J. Phys. Chem.* **55** (1981) 1489.
14. V. N. YEREMENKO, YA. V. NATANZON and V. I. DYBKOV, *J. Mater. Sci.* **16** (1981) 1748.
15. R. B. BHAGAT, *Met. Trans. A* **16A** (1985) 623.
16. *Idem*, "Squeeze Casting Fiber Reinforced Aluminum Matrix Composites", in Proceedings of the First European Conference on Composite Materials, ECCM1, Bordeaux, France, 25 to 27 September 1985.
17. *Idem*, PhD thesis, Indian Institute of Technology, Bombay, 1981.
18. M. D. GREENBERG, "Foundations of Applied Mathematics" (Prentice Hall, Englewood Cliffs, New Jersey, 1978) p. 116.

Received 27 January
and accepted 10 June 1988