

Interfaces in discontinuously reinforced metal matrix composites: An overview

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Abstract. The fundamental and engineering aspects pertaining to the matrix-reinforcement interfaces in discontinuously reinforced metal matrix composites are presented in this overview. The interfaces play a key role in determining mechanical properties, namely Young's modulus, yield strength, elongation, creep and fracture behaviour, as well as physical properties like coefficient of thermal expansion, thermal conductivity and damping characteristics of metal matrix composites; these are discussed in detail. The ratio of the experimental value of the Young's modulus to that predicted from the rule of mixtures has been used as a measure of interfacial bond strength. Various issues such as the nature of the interfacial bond, chemical reaction at the interfaces, and effect of alloying and processing on the structure of the interfaces and the properties of the composite are examined. In order to exploit the full potential of reinforcing the metallic matrix, the suggested strategies include creation of metallic bonding at the interface, use of *in situ* processing, choice of right type of alloying elements, and heat treatments and engineering of interfaces.

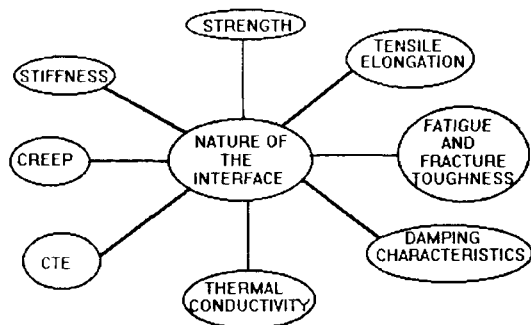
Keywords. Interfaces; bonding; wetting; coherency; Young's modulus; physical and mechanical properties; *in situ* composites; orientation relationship; interfacial energy.

1. Introduction

In recent years, the development of metal matrix composites (MMCs) has been receiving worldwide attention on account of their superior strength and stiffness, wear resistance, corrosion fatigue behaviour and creep resistance in comparison to the corresponding wrought alloys. The idea involved in the design of a composite material is to combine the good attributes of metals with ceramics. Metals have low stiffness values, and are ductile. Ceramics are stiff and strong, but are brittle and fail catastrophically. In MMCs, we exploit the strength of the ceramic while avoiding brittle failure. The performance of the composite depends, besides the matrix microstructure and the nature of the ceramic reinforcement, very critically on the matrix-reinforcement interface. This is schematically illustrated in figure 1. The interface plays a crucial role in the load transfer between the matrix and the reinforcement as well as in dislocation-particle interactions, which is significant in strengthening and stiffening of the composite. Moreover, physical properties such as thermal conductivity, coefficient of thermal expansion (CTE), dimensional stability, etc are also closely related to the nature of the interface. Thus it is desirable to have a clear understanding of the interfacial characteristics of specific metal matrix composites and to tailor them to achieve optimum performance in applications. In particular, the present paper addresses the issues pertaining to the interfaces in discontinuously reinforced MMCs.

2. Matrix-reinforcement bonding

In metal matrix composites, strengthening by the reinforcing phase is critically dependent on the strength of the bond between matrix and reinforcement. Interfacial



IMPORTANCE OF THE INTERFACE

Figure 1. Schematic diagram showing relationship of interface characteristics to different physical and mechanical properties.

bonding can be categorized as mechanical and chemical (Chawla 1987). Mechanical bonding is significant only in the case of fibre-reinforced composites, when fibres have rough or faceted surfaces. Chemical bonding is important for all kinds of reinforcements: fibres, whiskers and particulates. A chemical bond is possible only if the atoms of the matrix and reinforcement are in direct contact and is accomplished by an exchange of electrons, and the type of exchange determines the character of the bond. It can be metallic, which is non-directional, or ionic or covalent, which are directional. An interface with a metallic bond is thus more ductile than that with ionic or covalent bonds. For example, Fe-Fe₃C interfaces in steel do not show fatigue crack initiation (Sunwoo *et al* 1982) as found in Fe-Al₂O₃ interfaces (Eid and Thomason 1979). Interface segregants and chemical reaction can also affect the strength of the individual atomic bonds at the interface, which ultimately reflects on the macroscopic strength.

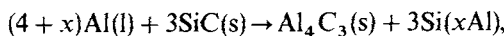
3. Reactive interfaces

A chemical reaction at the interface may lead to a strong bond between the matrix and the reinforcement, but a brittle reaction product can be highly detrimental to the performance of the composite. Table 1 gives matrices and reinforcements with reaction products seen at the interfaces. A ceramic-ceramic bond (reaction product-ceramic reinforcement) is weaker and more brittle than metal-ceramic or metal-intermetallic bond. Hence cracks initiate by cracking of the reaction product or the reaction product-matrix interface. For example, Al₄C₃ which forms as a reaction product at Al matrix-SiC fibre interface during processing by melting and casting acts as site for crack initiation (Clough *et al* 1990). Figure 2 shows an Al/TiC interface with reaction products comprising Al₃Ti and Al₄C₃; sharp cracks can be observed. These occurred during cold rolling (Mitra *et al* 1993a). Thus, it is essential that the matrix and reinforcement coexist in thermodynamic equilibrium under processing or service conditions. This is the first criterion in choice of ceramic reinforcements for any metal matrix. Alloying can be used to prevent progress of chemical reactions. Addition of

Table 1. Reaction products at some of the matrix/reinforcement interfaces.

Matrix	Reinforcement	Reaction products and precipitates	References
<i>Aluminium</i>			
Al	SiC	Al ₄ C ₃ , Al(Si)	Iseki <i>et al</i> (1984); Lee <i>et al</i> (1988)
Al–Mg	SiC	Mg ₂ Si, Al ₄ C ₃ , MgO	Rack (1988)
Al–Cu–Mg 1985	SiC	CuMgAl ₂ , MgO	Nutt (1986); Nutt and Carpenter (1985)
Al	B ₄ C	AlB ₂ , Al ₄ C ₃	Lucas <i>et al</i> (1992)
Al–Mg	B ₄ C	AlB ₂ , MgB ₂ , Al _x Mg _(1-x) B ₂ , Al ₄ C ₃ , Al _x (B–C–O) _{1-x} , MgB ₆	Lucas <i>et al</i> (1992)
Al	TiC	Al ₄ C ₃ , Al ₃ Ti	Yokokawa <i>et al</i> (1991); Satyaprasad <i>et al</i> (1992); Mitra <i>et al</i> (1993a)
Al	TiB ₂	No reaction	Mitra <i>et al</i> (1993); Mitra (1993)
Al–Mg	Al ₂ O ₃	MgAl ₂ O ₄	Levi <i>et al</i> (1978)
Al–Cu	Al ₂ O ₃	CuAl ₂ O ₄	Sritharan <i>et al</i> (1990)
Al–Li	Al ₂ O ₃	α–LiAlO ₂ , LiAl ₅ O ₈ , Li ₂ O	Chawla (1987); Sritharan <i>et al</i> (1990)
<i>Titanium</i>			
Ti	SiC	TiC, Ti ₅ Si ₃ , Ti _x Si _y	Jones <i>et al</i> (1989); Reeves <i>et al</i> (1991)
Ti	TiC	Ti ₂ C	Konitzer and Loretto (1989a)
Ti–Al–V–Nb	TiC	Ti ₂ (Al, Nb)C	Konitzer and Loretto (1989b)
Ti	TiB ₂	TiB	Reeves <i>et al</i> (1991)
<i>Magnesium</i>			
Mg	SiC	Mg ₂ Si, C	Brown (1993)
Mg–Li	SiC	Mg ₂ Si, Li ₂ C ₂	Warwick and Clyne (1989)
Mg–Li	SiC with SiO ₂ coating	Mg ₂ Si, Li ₂ O	Warwick and Clyne (1989)
Mg	Al ₂ O ₃	MgAl ₂ O ₄	Chawla (1987)
<i>Intermetallics</i>			
NiAl	SiC	Ni _x Si _y , Al ₄ C ₃	Chawla (1987)
NiAl	TiB ₂	No reaction	Wang and Arsenault (1991)
NiAl	TiC	No reaction	Fuchs (1990)
Ni–Al–Cr–Zr–B	TiB ₂	(Ti, Zr)B ₂	Fuchs (1990)
Al ₃ Ti	TiC	No reaction	Norman (1990)
TiAl/Ti ₃ Al	TiB ₂	No reaction	Feng <i>et al</i> (1991)
MoSi ₂	SiC	No reaction	Meschter and Schwartz (1989)
MoSi ₂	TiC	No reaction	Meschter and Schwartz (1989)
MoSi ₂	Al ₂ O ₃	SiO(g), Al(g)	Meschter and Schwartz (1989)
Ti ₅ Si ₃	SiC	TiSi, TiC	Meschter and Schwartz (1989)

3% Si, which raises significantly the activity of Si in Al, completely stops the reaction (Sritharan *et al* 1990)



from progressing in the forward direction according to the law of mass action.

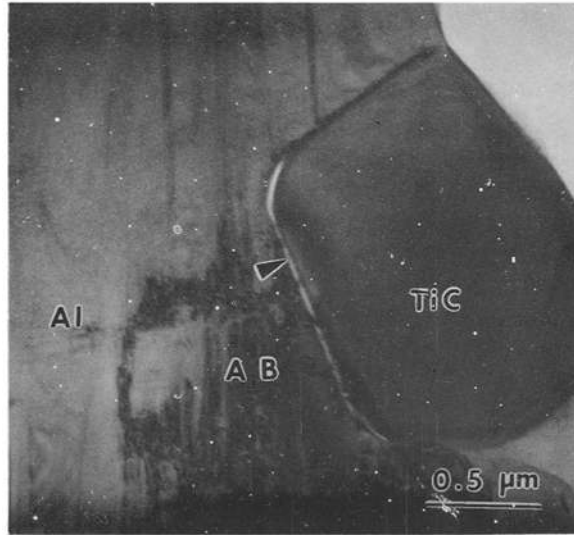


Figure 2. TEM micrograph showing interfacial cracking due to cold rolling of XD Al/TiC composite heat-treated for 24 h at 640°C. Heat treatment leads to formation of reaction product Al_3Ti (A) and Al_4C_3 (B) at interfaces (Mitra *et al* 1993a).

4. Type of reinforcement and electronic bonding

Even if the reinforcement is chemically compatible with the matrix, the strength and nature of the electronic interaction between matrix and reinforcement and structure and chemistry of interface are important for efficient load transfer. Thus it has been observed that for similar process variables, and in the absence of any chemical reaction product at the interface, the increase in Young's modulus by incorporation of the reinforcement in a metallic matrix provides a measure of the interfacial bond integrity between the matrix and the reinforcement. Two ways of averaging have been proposed: (i) Voight (1928) assumes uniform strain in both the constituent phases and (ii) Reuss (1929) assumes uniform stress in both the phases. The Voight averaging, also known as "rule of mixtures" (ROM) leads to

$$E_v = V_m E_m + V_p E_p, \quad (1)$$

where E_c , E_m and E_p are Young's modulus values of the composite, matrix and reinforcement particles respectively and V_m and V_p are volume fractions of matrix and reinforcement phases.

The Reuss averaging gives

$$E_r = 1 / \{ (V_m / E_m) + (V_p / E_p) \}. \quad (2)$$

Figure 3 consists of bar diagrams for pure Al matrix P/M composites with 20 vol% SiC, TiC, TiB_2 and B_4C particulate reinforcements showing the ratios of experimental Young's modulus (Kuruvilla *et al* 1989; Mahajan and Rama Rao 1992) values to those predicted by the rule of mixtures. TEM study did not reveal the presence of any reaction products at the matrix/reinforcement interface in these composites in the hot

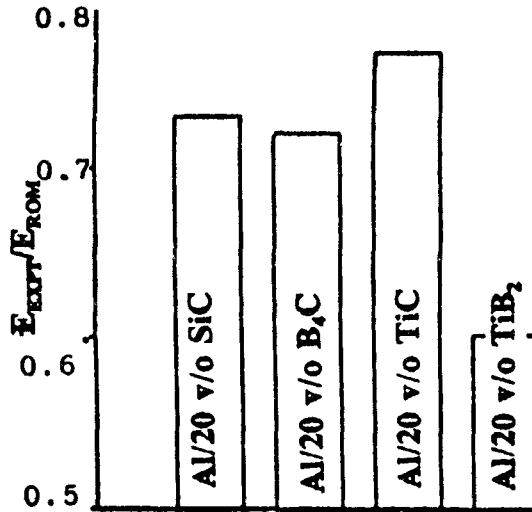


Figure 3. $E(\text{expt})/E(\text{ROM})$ for Al matrix composites with different reinforcements (Kuruville *et al* 1989). Al/TiC shows the highest ratio.

rolled condition (Kuruville *et al* 1989). The process details have been published elsewhere (Kuruville *et al* 1989; Jain *et al* 1993). It is clear from figure 3 that Al/TiC shows the best correlation between theoretical and experimental values and Al/TiB₂ composite shows the worst, suggesting that the former has the strongest interfacial bond and the latter has the weakest among the four systems studied. In another investigation with P/M Al–Ti alloy containing Al₃Ti, Al₄C₃ and Al₂O₃ as dispersoids (Hawk *et al* 1988), only changes in the volume fraction of the intermetallic compound Al₃Ti could be correlated with change in Young's modulus, whereas those of Al₄C₃ and Al₂O₃ had a negligible effect. It is also interesting to note that rule of mixtures (Voigt law of averaging) was closely followed. Observations of Zedalias *et al* (1985) with Al₃Zr dispersoids and Skinner (1988) with Al₁₃(FeV)₃Si dispersoids in pure Al also show excellent correlation between experimental values of Young's modulus and those predicted by rule of mixtures in the case of intermetallic dispersoids. Fine (1981) has shown that changes in Young's modulus values with volume fraction of MnAl₆ and Al₂O₃ dispersoids in pure Al follow the Voigt and Ruess laws of averaging, respectively. A well-bonded interface would allow the maximum transfer of load from the matrix to the reinforcement and is expected to exhibit a high value of $E(\text{expt})/E(\text{ROM})$ ratio, whereas a weakly bonded interface will result in lower $E(\text{expt})/E(\text{ROM})$ ratio. In the case of the latter, values predicted by Ruess law of averaging will be closer to experimental values. Figure 4 shows bar diagrams of $E(\text{expt})/E(\text{ROM})$ for four systems, namely Al/Al₃Zr (Zedalias *et al* 1985), Cu/Fe (Krock 1966), Al/SiC (Bonollo *et al* 1991) and Al/Al₂O₃ (Lyle 1967). It is seen that metal–intermetallic and metal–metal systems show $E(\text{expt})/E(\text{ROM})$ values close to 1. Also, $E(\text{expt})/E(\text{ROM})$ for Al/TiC was higher than those of Al/SiC, Al/TiB₂ and Al/B₄C (figure 3). In case of TiC and intermetallic compounds as dispersoids, it is obvious that the matrix–reinforcement bond is stronger. Of course, the bonds between Al and the intermetallic compounds are metallic. At a metal–ceramic interface, there is a sharp discontinuity in the electronic structure due to delocalized nature of

CHEMICAL NATURE OF DISPERSOID

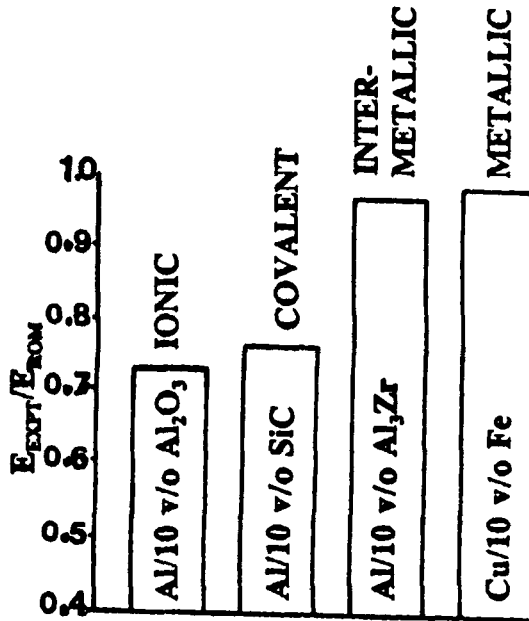


Figure 4. E_{EXPT}/E_{ROM} for Cu/Fe (Krock 1966), Al/ Al_3Zr (Zedalia *et al* 1985), Al/SiC (Bonollo *et al* 1991) and Al/ Al_2O_3 (Lyle 1967) systems.

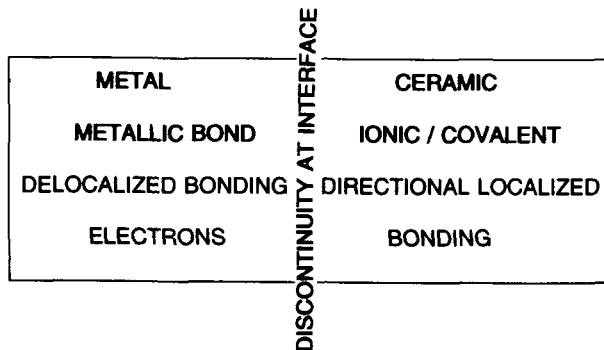


Figure 5. Schematic representation of discontinuity in the electronic structure at a metal-ceramic interface.

electrons in the metal and highly localized electrons in the covalently or ionically bonded ceramic reinforcement. Figure 5 shows a schematic diagram. This affects the wetting behaviour, and degree of interaction at the interface increases with lowering of this discontinuity. This agrees well with observations of Nicholas (1987), in which the degree of wetting of carbides and oxides by Cu decreased with increase in ionicity. Thus a weakly ionic or covalent ceramic will have a stronger bond with a metal compared to those which are strongly ionic or covalent. In metal-ceramic bonding, transition metal carbides like TiC which have partial metallic nature (Rhee 1970) thus

show stronger bond with Al, a reactive metal, than more covalent bonded ceramics (Delannay *et al* 1987) like TiB_2 (table 2). Rhee (1970) observed that wetting increased in the order $AlN < TiB_2 < TiN < TiC$, and suggested the metallic character of TiC to be the reason for excellent wetting characteristics. Goretzki *et al* (1971) suggested a higher degree of overlapping of the electronic state wave functions in cases where both the components are metallic. For metal-like transition carbides, the density of states and work of adhesion vary with valence electron concentration in the same manner.

Comparing TiC and TiB_2 , it is also clear that the latter has a higher heat of formation and is more stable. It has also been reported by Ramqvist (1965) that carbides with lower heat of formation are wetted better by metals than those with higher heat of formation. Also, from table 1, it is clear that TiC reacts with Al under certain conditions, whereas TiB_2 does not. Thus higher stability of TiB_2 in Al compared to that of TiC is another reason why the latter is wetted better.

Ni-16Al-8Cr-1Zr-0.1B matrix with TiC, Al_2O_3 and TiB_2 reinforcement prepared by P/M route has also been investigated (Fuchs 1990). While TiB_2 was not chemically compatible with the matrix, both TiC and Al_2O_3 were stable in the matrix. Interestingly, reinforcing with TiC has shown excellent bond integrity leading to much higher modulus and yield strength compared to those with Al_2O_3 . This again can be explained by the metallic nature of TiC and strong interaction of Ti with both Ni and Al.

The above observations can be better appreciated with an understanding of wetting mechanisms. Wetting defines the extent of interaction between a liquid and a solid during fabrication of a composite and determines the bond strength. The mechanisms include, other than chemical reaction, Van der Waals and image forces, adsorption and electronic bonding (Oh *et al* 1989). It makes sense to believe that the adhesive force between a reactive metal and a reinforcement is dependent on the electronic properties of the latter, as the former will always have free electrons in the conduction band. Thus a ceramic reinforcement with more metallic nature is wetted better than those which are more covalent or ionic. Thus TiC and Al_3Ti act as effective nucleants during solidification of Al as has been reported by Cisse *et al* (1972). The fact that Al solidified with an epitaxial orientation relationship with respect to Al, that is, $(001)Al // (001)TiC$ and $[001]Al // [001]TiC$, of course suggests that under equilibrium conditions interfaces of low energy form between Al and TiC. A similar phenomenon was observed for Al_3Ti too, and it has been seen from the data reported earlier that bond integrity between Al and these reinforcements are excellent. Thus good wetting

Table 2. A comparison of bonding, reactivity with Al and wetting characteristics of TiC and TiB_2 .

Compound	H_f (kJ/mol)	% Covalent bond	Reactivity with reaction G_f product (kJ)	Contact angle with Al(l) at 1080 K ($\cos \theta$)
TiC	10.5	80	Al_3Ti , -5 Al_4C_3	0.7
TiB_2	19.6	92	Al_3Ti , 44.6 AlB_2	0.4

of TiC by Al occurs as has been reported in the literature (Samsonov *et al* 1968; Manning and Gurganus 1969; Rhee 1970).

Chemistry and crystallography of surfaces, which play a significant role in determining electronic density of states of surface atoms, also affect the wetting behaviour. For example, photoemission spectra from TiC $\{111\}$ surfaces have shown high density of states near the Fermi level similar to Ti $\{0001\}$ surfaces (Bradshaw *et al* 1980) and hence their behaviour with respect to wetting by Al is similar. An interesting observation in XD Al/TiC composite was that the interface plane of TiC was mostly $\{111\}$ (figure 6) (Mitra *et al* 1993b). Besides its metallic nature which improves bonding, these planes are densely packed and result in maximization of number of bonds with matrix and lowering the interfacial energy. Similar observations were also made by Gao and Merkle (1992) for equilibrium and nonequilibrium metal-metal oxide interfaces.

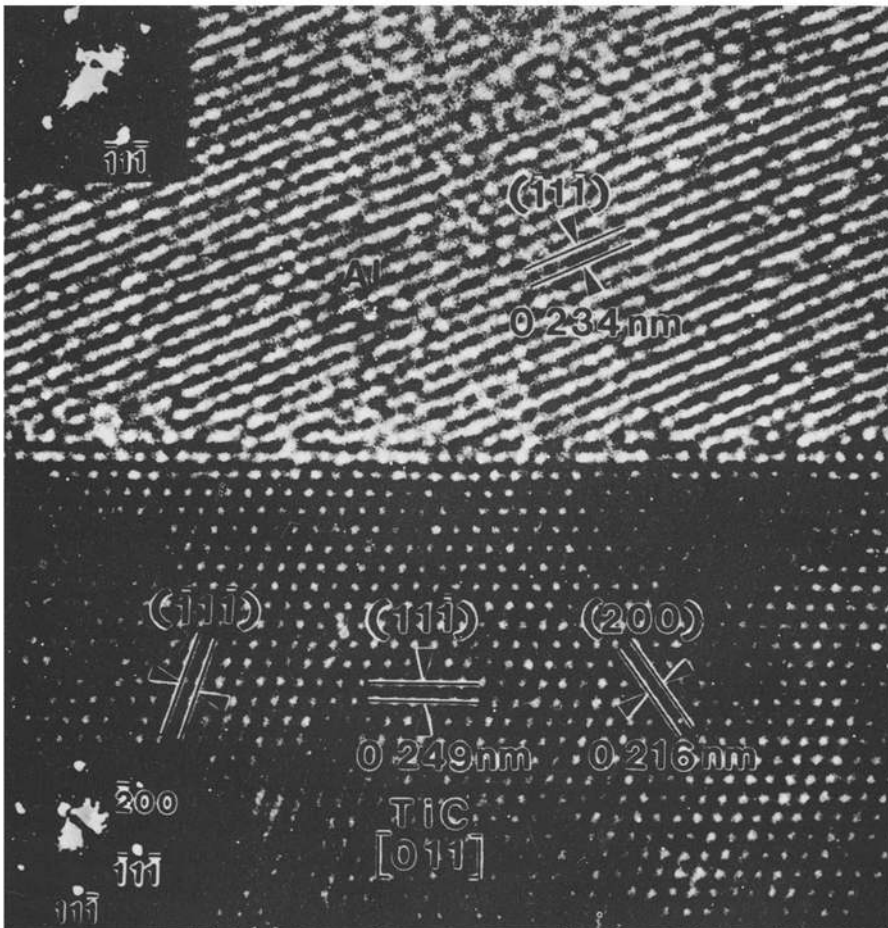


Figure 6. High-resolution TEM micrograph showing the particle/matrix interface in Al/TiC composite prepared by XD process. The interface is abrupt on an atomic scale and is parallel to TiC(11 $\bar{1}$) plane, which is densely packed (Mitra *et al* 1993b).

In another experiment, Ohuchi (1987) observed that Cu adhered more strongly to AlN {0001} surfaces compared to AlN {1012} or AlN {1011} surfaces. The reason for this was the fact that Cu bonds to Al atoms during interaction and hence AlN {0001} surfaces containing only Al atoms were more favourable.

The differences in dielectric constants of the metal and the ceramic reinforcements (mainly oxide and carbide) also play a leading role in chemical bonding as this gives rise to image forces at the interface (Stoneham and Tasker 1985; Finnis *et al* 1990). The effect is strengthened if there are charged defects on the surfaces of the ceramic as these will have lower energy of formation at the interface than at a free surface. Thus an oxide or carbide which tends to lose stoichiometry more easily or have lower binding energy will be wetted better compared to one that is more stable. In a study of wetting characteristics of MgO single crystal by Pb, Sn and Bi liquid metals by Nogi *et al* (1992), it was observed that degree of polarization, type of charge distribution and atomic arrangements on the surface controlled the degree of wetting by the liquid metal.

TiC also is an excellent example. Atom fraction of carbon in TiC varies from 33% to 48% without any change in its crystal structure (Goretzki 1967). Nicholas (1987) has reported the wetting behaviour of TiC by Cu for different atom fractions of C in TiC, and the contact angle decreased with decrease in atom fraction of C, proving the better wettability of nonstoichiometric carbides. Stacking faults and dislocations have been seen close to Al–TiC interface using high-resolution transmission electron microscopy (HRTEM), and figure 7 shows an example. The fact that charged defects at the surface of ceramic reinforcement improves wetting suggests that irradiation of ceramic substrates or fibres will lead to better bonding with metal and this has been observed by Tombrello (1984). Fuchs *et al* (1989) observed significant improvement in Cu–Al₂O₃ bonding due to ion-beam mixing of interface. After irradiation with 1.5 MeV Xe⁺ ions of an Al₂O₃ substrate, the surface roughness increased and the 6-nm-thick interface region was modified.

5. Work of adhesion and bonding: Effect of alloying elements and coherency

Work of adhesion W_{ad} of a particle–matrix interface is strongly affected by alloying element additions. Work of adhesion is defined as the energy of creation of free surfaces of particle and matrix by rupturing of the interfacial bond. Work of adhesion for solid/solid interface is given by

$$W_{ad} = \tau_{mv} + \tau_{pv} - \tau_{mp}, \quad (3)$$

where τ_{mv} and τ_{pv} are the surface energies of matrix and particle and τ_{mp} is the particle–matrix interfacial energy. Figure 8 is a schematic diagram of a void formed at a particle–matrix interface. The void is created during deformation, and annealing treatment is conducted to reach equilibrium. If θ is the contact angle between a particle facet and a spherical cap-shaped void, the force equilibrium in the horizontal direction gives

$$\tau_{mp} = \tau_{mv} \cos \theta + \tau_{pv}. \quad (4)$$

This is Young's equation (1805). Substituting (4) in (3), we get

$$W_{ad} = \tau_{mv}(1 - \cos \theta). \quad (5)$$

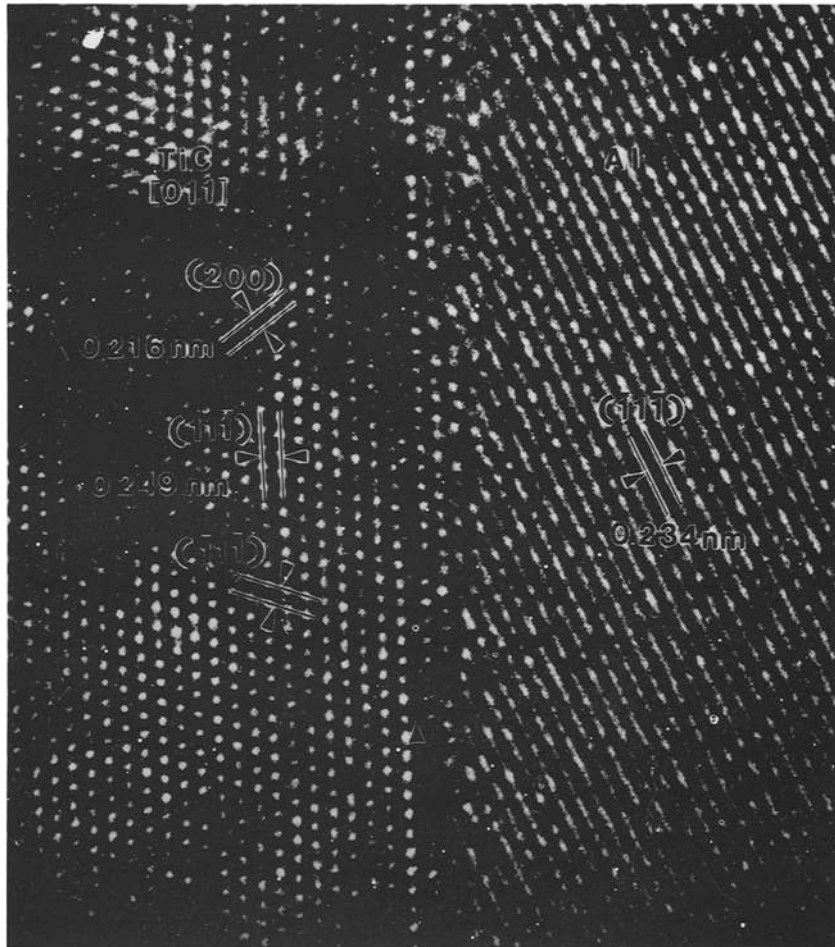


Figure 7. High-resolution TEM micrograph showing the particle/matrix interface in Al/TiC composite prepared by XD process. The first three atomic layers inside TiC near the interface appear distorted due to a stacking fault (arrowed) on the $(\bar{1}\bar{1}\bar{1})$ TiC planes (shown with an arrow-head). Position of an extra half plane of an edge dislocation is shown with an arrow (Mitra *et al* 1993b).

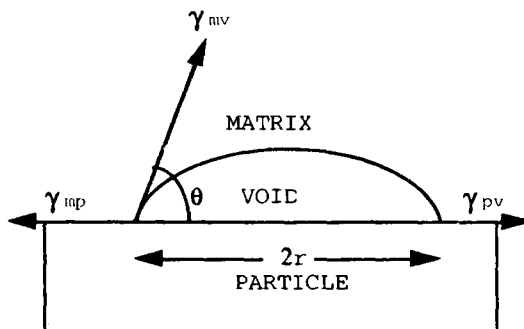


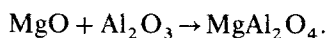
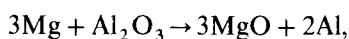
Figure 8. A spherical cap-shaped void formed at the interface a TiC particle facet and matrix (Mitra 1993).

Contact angle and interfacial energies were measured for XD Al/TiC composite from voids created by deformation followed by annealing at 500°C for 2 h. There was a variation in the interfacial energy from 200 to 850 mJ m⁻². It is believed that for partially coherent interfaces, interfacial energy varies based on the orientation relationships and degree of coherency. Particles occurring at grain boundaries are expected to have much higher interfacial energies.

Easterling *et al* (1973) used (5) for determining the W_{ad} between the particle and the matrix in the Fe–Ni/Al₂O₃ composite. Contact angle was seen to change very sharply with changes in atomic fraction of alloying elements in the matrix and so did the work of adhesion as shown in table 3. It was also observed that the flow stress was directly related to the work of adhesion.

Segregation of alloying elements to the interface reduces interfacial energy due to the Gibbs adsorption phenomenon. However, this may be detrimental to interface toughness if the alloying elements lead to an increase in the ionic or covalent character of the interface bonding (Fine *et al* 1988). Alloying elements play a significant role in coarsening behaviour of precipitates in metal–intermetallic composites (Calderon *et al* 1988). For example, in Fe–Ni–Al alloys containing a few per cent of Mo, the NiAl particles remain spherical upon ageing even though the particle–matrix lattice misfit is considerable. This is in contrast to that in absence of Mo, when the precipitates turn cuboidal. It has been suggested that Mo segregation at the interface relaxes the elastic misfit strains or changes the interfacial energy such that even large precipitates remain spherical.

Nature of the chemical bond also depends on alloying elements. For example, addition of Mg to Al–Al₂O₃ composites leads to the formation of MgO and MgAl₂O₄ at the interface (Levi *et al* 1978; Chawla 1987; Sritharan *et al* 1990) and this enhances the wettability which is otherwise poor. The reactions are:



Mg also improves the wetting between Al and SiC particles by reducing the SiO₂ layer on the surface of SiC and aiding in removal of Al₂O₃ film on Al melt. The reaction is (Quigley *et al* 1982):

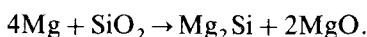


Table 3. Table showing variation in critical strain to interface cavity formation, contact angle and work of adhesion with alloying elements in a Fe–alloy/Al₂O₃ composite (Easterling *et al* 1973).

Matrix	ε_c	θ (degrees)	W(mJm ⁻²)
Fe–40 Ni	0.05	< 10	44
Fe–40 Ni–5 Cr	0.05	16	112
Fe–40 Ni–5 Mn	0.10	15	99
Fe–40 Ni–5 Mo	0.15	65	1674
Fe–1 Ti		35	524
Fe–10 Co	0.08	60	1450
Fe–5 Cr	0.10	80	2397

It has been reported by Sritharan *et al* (1990) that ideal matrices for SiC reinforcement, which show the maximum strengthening effect, are high Mg-containing 5XXX and 6XXX alloys as more of Mg_2Si can be precipitated. On the other hand, reduction in strength has been reported in case of Al–Cu–Mg alloys (with respect to monolithic alloy) as Mg segregation at interfaces results in the depletion of Mg content in the matrix. Similar lowering of strength is reported for 7XXX alloys as Mg content is depleted by formation of $MgZn_2$ and Mg_2Si at the interfaces. In certain other studies, addition of Mg to Al–SiC composites has proved to be detrimental due to formation of Mg-rich amorphous region (Nutt and Carpenter 1985; Nutt 1986), or intermetallic precipitates like $CuMgAl_2$ (Nutt and Carpenter 1985; Bhanuprasad 1991) at the interface. In cast alloy–matrix MMCs, coarse intermetallic particles are quite often seen at the interfaces because the residual melt enriched in solute solidifies near poorly heat-conducting ceramic reinforcement.

Other than Mg, Li has been successfully used as an alloying element to enhance the wetting between Al and Al_2O_3 (Dhingra 1980) and SiC (Webster 1982) reinforcements. The mechanism is similar to that of Mg, that is reduction of oxide layers at the interface, which otherwise prevents direct contact between Al and the ceramic reinforcement. Webster (1982) has systematically investigated the effect of Li additions (3–5%) to Al on mechanical properties of Al/SiC_w composites. Strengthening effect was significantly enhanced by additions of Li as shown in table 4 and this has been attributed to increase in the matrix–reinforcement bond strength. Li increases the reactivity of Al and as a consequence promotes its interaction with SiC at the interface. Thus Young's modulus values were close to those predicted by the rule of mixtures. No chemical reaction product could be observed at the interface using TEM. Alloying with indium, lead and thallium has improved wetting between Al and carbon fibres by reducing the surface tension of liquid metal (Kimura *et al* 1984). However, to our knowledge these have not been studied for Al/SiC composites. McDonald and Ransley (1954) observed that addition of Ni or Co to Al improved the wettability of Al/TiC system.

Effect of matrix on bond integrity can also be appreciated by analysing the modulus values of Mg/SiC and Al/SiC metal matrix composites. Figure 9 is a comparison between $E(\text{expt})/E(\text{ROM})$ of P/M Mg/SiC (Skinner *et al* 1990) and that of P/M Al/SiC, where the matrices are commercially pure metals. It is evident that the Mg/SiC composite has smaller value of the ratio compared to the Al/SiC composite, indicating that the interfacial bond is stronger in the latter. The possible reason is matrix–reinforcement chemical interaction is stronger in the latter as Al forms a stable carbide as well as alloys with Si.

Table 4. Variation in Young's modulus with addition of Li to Al/SiC_w composites based on Webster's data (Webster 1982).

Matrix	Modulus (GPa)	% Increase with respect to matrix
Al	70	
6061 – Al + 20% SiC _w	100	43.0
Al + 3.5% Li	86	
Al + 3.5% Li + 20.9 SiC _w	139	62.0

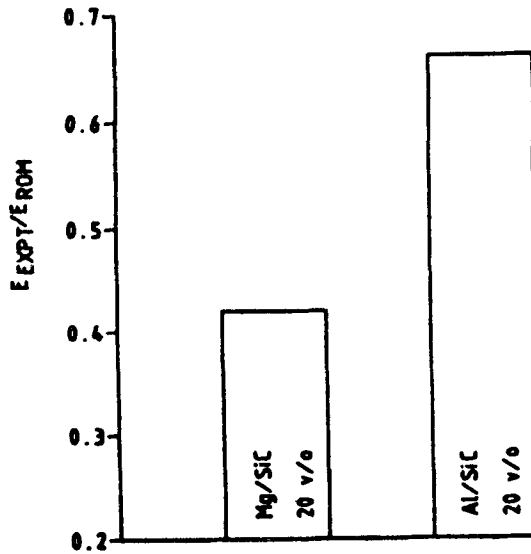


Figure 9. Comparison between $E(\text{expt})/E(\text{ROM})$ ratios of Mg/20 v/o SiC and Al/20 v/o SiC (Schroder *et al* 1991) metal matrix composites.

6. Effect of processing: Conventional and *in situ* processing

Processing variables play a very significant role in control of interfacial characteristics. Based on processing, composites can be classified as 'conventional' or '*in situ*'. 'Conventional' composites are those which are prepared by powder metallurgy routes, which involves blending of matrix and reinforcement powders followed by cold compaction and hot pressing or casting routes. The flowchart in figure 10 shows the process developed and followed at DMRL. Hot pressing is carried out in two steps, the first being above solidus and for a short duration and the next for longer time below the solidus. Without a liquid phase formed during hot pressing or sintering, high modulus values are not achievable (McDonald and Ransley 1954). The mechanisms of bonding in absence of a liquid phase are mechanical interlocking of particles and solid-state diffusion leading to a chemical bond.

In casting route, conventional composites are fabricated by adding reinforcements to molten metal and distributing using a stirrer, or rheocasting or melt infiltration to ceramic preform or green compact by liquid metal. Higher processing temperature may promote wetting in many cases, but often leads to degradation of reinforcements by chemical reactions as is observed in Al-SiC system. Chiou and Chung (1990) prepared Al/SiC composite by infiltration of liquid Al into a porous preform of SiC whiskers in vacuum under inert gas pressure at 665°C, 690°C and 720°C and observed that tensile strength, Young's modulus, as well as the extent of elongation decreased with increase in processing temperature. Also, significant whisker pullout could be observed during tensile failure of the composites prepared at higher temperature. All this is attributed to formation of brittle reaction product Al_4C_3 formed at the interface.

Sometimes processing in certain temperature ranges can only lead to chemical reactions between matrix and reinforcement. For example, Al and TiC react as

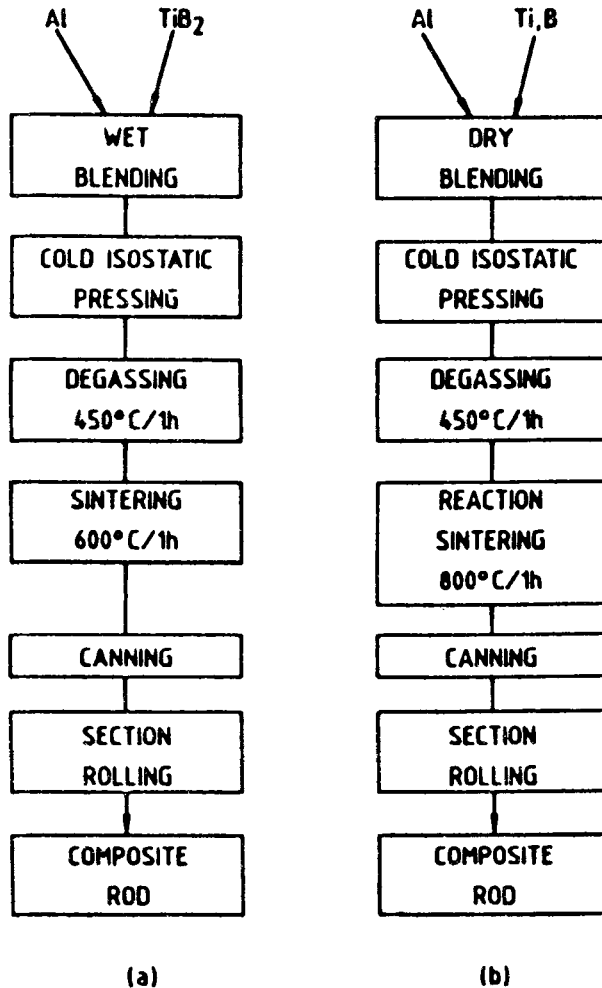
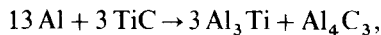


Figure 10. Flowchart showing conventional P/M and XD process developed at DMRL for preparing metal matrix composites.

(Satyaprasad *et al* 1992; Mitra *et al* 1992a, 1993a)



at temperatures below 752°C, above which the free energy of formation is positive and the chemical reaction is not feasible. Extent of chemical reaction also varies with time and a systematic study has been performed for Al–TiC (Mitra *et al* 1992b, 1993a) and Al–SiC (Lloyd and Jin 1988).

It has been discussed in the earlier section that coarse intermetallic particles precipitate at the matrix–reinforcement interface in MMCs prepared by casting as the solute-rich residual melt solidifies at the interface towards the end. However, in MMCs prepared by spray deposition (White *et al* 1983) TEM investigations have shown clean interfaces with negligible precipitation. This can obviously be explained

on the basis of the fact that contact time between liquid matrix phase and reinforcement is of the order of a few seconds in spray deposition processing and a few minutes in case of squeeze casting. Thus in Al–alloy composites prepared by spray deposition attractive combination of strength and modulus could be achieved because of excellent bond integrity.

In the above processing techniques, reinforcement particles or whiskers are prepared in a separate process before processing of the composites. During this or subsequent handling, the surfaces of the particles pick up impurities or get oxidized, and continue as a third continuous or discontinuous phase at the interface. XPS studies on isolated Si_3N_4 whiskers have shown $\text{Si}_2\text{N}_2\text{O}$ and oxygen impurities (Homeny *et al* 1990). SiO_2 has also been observed on the SiC whisker surfaces using XPS (Date 1994). These oxide layers participate in interfacial reactions during processing of MMCs and interface chemistry becomes complex. The interface in these cases fails to reach the state of thermodynamic equilibrium. Amorphous oxide layers often found at interfaces (Nutt and Carpenter 1985; Nutt 1986; Ning *et al* 1992) are responsible for interfacial void formation or cracking during external loading at room and elevated temperatures (Marcus and Rabenberg 1987; Ribes *et al* 1990; Xia *et al* 1990).

Amorphous phase (7–30 nm) has also been noticed at diffusion-bonded pure Al/SiC interface by Ratnaparkhi and Howe (1992). Auger studies have revealed that this region is enriched in Al, Si, C and O and there is diffusion of Al and O into the highly strained region of SiC, immediately adjacent to the interface. However, there is no evidence of C or Si diffusion into Al. This amorphous phase could have originated from solidification of Al–Si–C–O eutectic liquid at the interface. But *in situ* hot-stage microscopy, where specimen was reheated to 650°C, did not show any mechanical instability in the region, proving that a solid-state reaction was responsible for formation of amorphous region during processing.

Figure 11 shows a typical interface in MoSi_2/SiC composite containing an amorphous phase 5–8 nm thick. This composite was fabricated at DMRL, Hyderabad, by hot-pressing an intimate mixture of elemental Mo + Si (stoichiometric ratio) and SiC powders in vacuum, where Mo and Si react to form MoSi_2 *in situ*. SiC was HF-treated to remove SiO_2 . The composition of amorphous region is under investigation. Such amorphous regions at the matrix–reinforcement interfaces have also been noticed in XD MoSi_2/SiC composite (Suzuki *et al* 1993) as well as RBSC– MoSi_2 composites (Lim *et al* 1989).

In a recent review, Arsenault (1994) has reported the absence of orientation relationships in nonequilibrium interfaces or those with amorphous areas. This is common in composites fabricated by conventional P/M processes. For example, Radmilovic *et al* (1991) did not observe any preferred orientation relationship in 2014 Al/SiC composites fabricated by conventional P/M process. This is similar to the observations of Van Den Burg and De Hosson (1992). However in case of P/M 6061 Al/SiC composites, Van Den Burg and De Hosson noticed a preferred orientation relationship of $(0001)_{\text{SiC}}//\{111\}_{\text{Al}}$ and $\langle 2\bar{1}\bar{1}0 \rangle_{\text{SiC}}//\langle 110 \rangle_{\text{Al}}$. In cast composites, a consistent orientation relationship could be seen (Arsenault 1994; Weimin *et al* 1991):

$$[11\bar{2}0]_{\text{SiC}}//[110]_{\text{Al}} \text{ and } (0001)_{\text{SiC}}//(112)_{\text{Al}}.$$

A variant relationship $[11\bar{2}0]_{\text{SiC}}//[110]_{\text{Al}}$, $(01\bar{1}0)_{\text{SiC}}//(111)_{\text{Al}}$ has also been observed. In all cases (Arsenault 1994), (111) Al planes are aligned either perpendicular or at 70° to

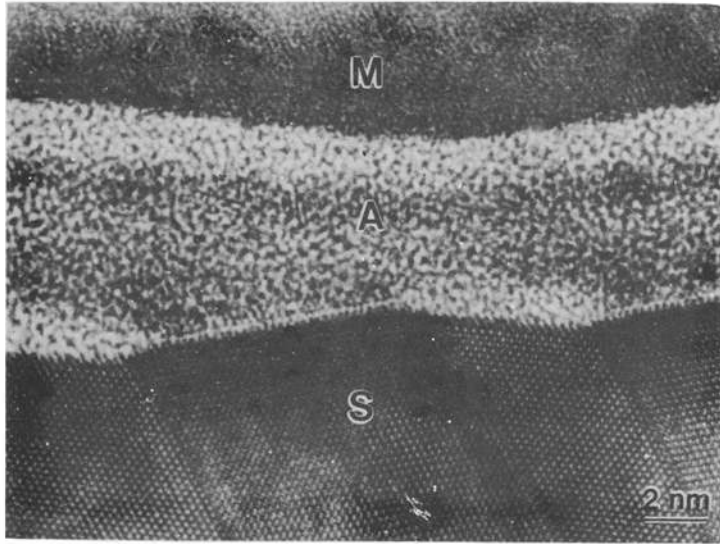


Figure 11. An amorphous phase (A) observed at the interface between MoSi₂ (M) and SiC (S) in the MoSi₂-20 vol SiC composite (Mitra *et al.* 1995).

the interfacial axis when the SiC basal planes are perpendicular to the interfacial axis. If SiC basal planes are parallel to the interfacial axis, the (111) Al planes are oriented at 20° to the interface. Again in contrast to observations in P/M 2014 Al-SiC composite, Carim could observe an orientation relationship of $(1\bar{1}01)_{\text{SiC}} \parallel (557)_{\text{Al}}$ in cast 2014 Al-SiC composites. In P/M processes, without a liquid phase, the particles bonded together are randomly oriented leading to nonequilibrium and high-energy interfaces. In cast composites, there is a tendency for the liquid metal to solidify forming low-energy interfaces. This explains further the need for liquid phase in P/M processing, such as hot pressing.

Back in 1954, Medonald and Ransley (1954) through a series of investigations found that incorporation of high-modulus dispersoids in Al matrices resulted in moduli less than that of the matrix by itself. It was obvious that increase of dispersoid content fails to affect the modulus. On the other hand, wetting took place automatically if the high-modulus phase was an 'intermetallic compound precipitated *in situ* by reaction between elements' and the same was difficult to induce by mechanical mixing of powders and purely solid-state processing. This is because the composites prepared by *in situ* processing have clean interfaces as the chemical reaction between elements to produce the dispersoid takes place inside the solid or liquid metal. Some of the *in situ* processing techniques involving molten metal and developed in recent years are XD (exothermic, dispersoid) developed at Martin Marietta Laboratory, Baltimore, USA (Westwood 1988) and gas injection process developed by Koczak at Drexel University, Philadelphia, USA (Koczak and Kumar 1989). Similarly, solid-state processing techniques like internal oxidation or reduction (Mader 1992) and displacement reactions (Henager *et al.* 1992) have also been developed. Solid-state *in situ* processes normally lead to second-phase precipitates with an equilibrium low-energy orientation relationship with respect to the matrix and interfaces can show varying degrees of

coherency based on lattice misfit and strength of interaction between the matrix and the reinforcement (Mader 1992).

Atomic-resolution TEM studies of the interface between Al matrix and TiC particle in XD Al/TiC composite have proved that interface is abrupt on an atomic scale (figures 6 and 7) (Mitra *et al* 1993b). No impurities or sign of oxidation of particle surfaces could be seen by EDS and EELS at the interface. This is possible only because the particles were precipitated *in situ*, which prevents them from contamination.

EDS using a probe size of 3 nm (including effect of beam broadening) was used to investigate the interface in XD 2024 Al/TiB₂ composite in a field emission analytical TEM (Mitra *et al* 1993b). No segregation of Mg or Cu alloying elements could be found near the interface. This suggests that the interfaces formed are of sufficiently lower energy, and there is little driving force for interfacial segregation.

Apart from the fact that the interfaces are clean, some other interesting features are associated with the XD composites. Many of the Al/TiC interfaces in 0.7 μm particle XD composite (cast and extruded at a ratio of 27:1 at 375°C) were semicoherent and showed localized strain contrast in the TEM (Mitra *et al* 1993b). Figure 12a is a bright-field TEM micrograph of a semicoherent Al/TiC interface, where interface dislocations and facets can be seen. Figure 12b is a weak-beam dark-field TEM image of an Al/TiC interface showing misfit strain localization. Normally, particles which were finer and located inside Al grains and surrounded by some Al subgrains had semicoherent interfaces. On cold rolling to 75% of its original thickness followed by annealing, the material recrystallized leading to a microstructure in which faces of the

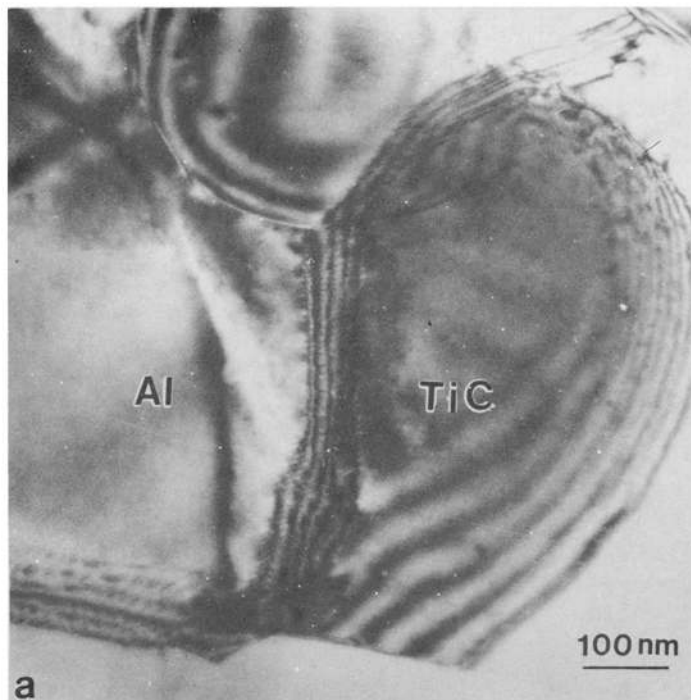


Figure 12a.

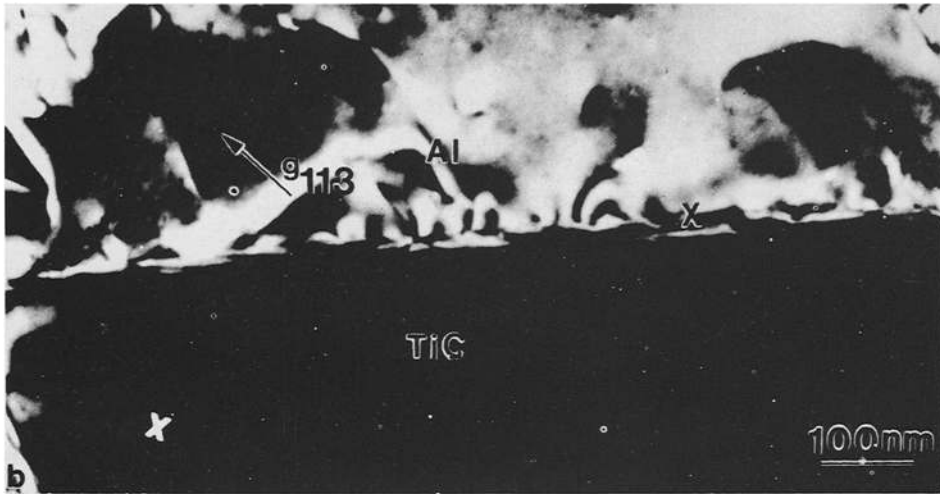


Figure 12. TEM micrographs of a semicoherent interface in cast and extruded XD Al/TiC composite (Mitra *et al* 1993b). (a) Bright-field image and (b) weak-beam dark-field image of a different particle-matrix interface 'X'. Misfit strain contrast can be distinguished.

TiC particles were surrounded by one or more subgrains (Mitra *et al* 1992a; Fine *et al* 1993). The interfaces between these and TiC particles were in most cases semicoherent with misfit strain localization (figure 13). As shown in figure 5, interfaces were always parallel to $\{111\}$ TiC planes. In another investigation, Wang and Arsenault (1991) observed that the NiAl/ Al_2O_3 interfaces in XD NiAl/ Al_2O_3 /TiB₂ composites were semicoherent and showed misfit localization. Presence of semicoherency of course supports the idea that particle-matrix is strong in XD composites, where there is direct contact between the atoms of the two phases.

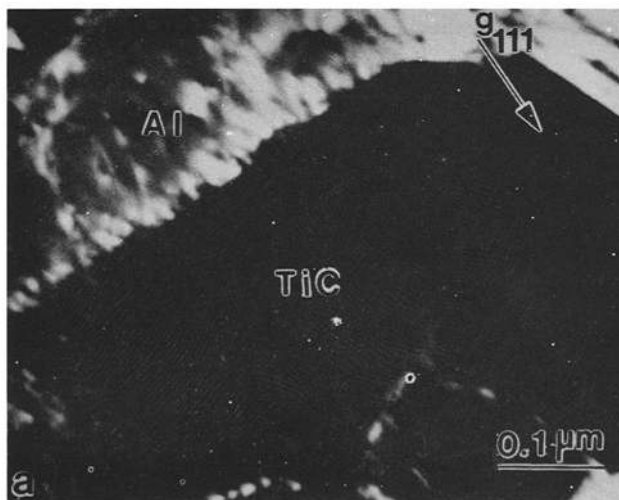


Figure 13a.

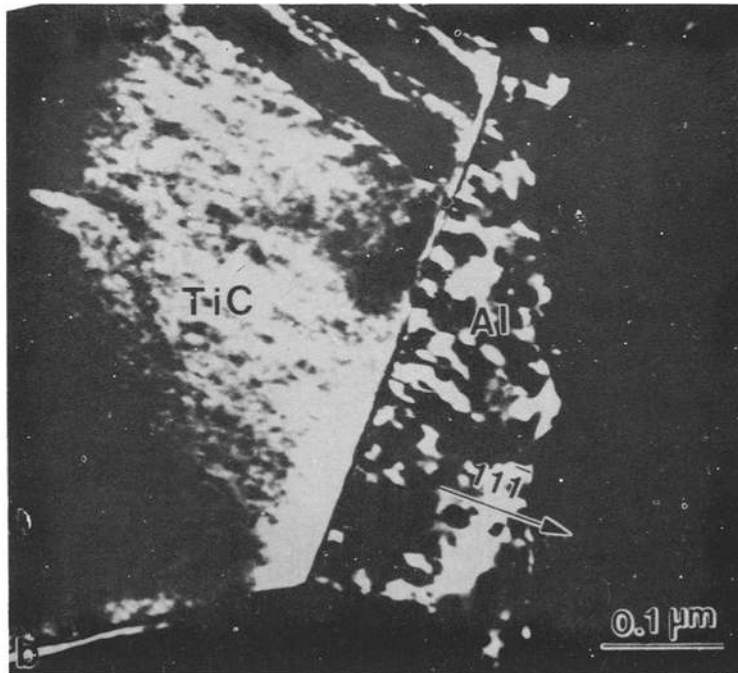


Figure 13. a-b. Dark-field TEM micrograph of a semicoherent interface between an Al subgrain and TiC particle in the XD Al/TiC composite. The composite was cold-rolled and annealed for recrystallization (Mitra 1993). Interface dislocations can be seen.

In situ composites have consistently shown higher modulus compared to those prepared by conventional techniques like casting and powder metallurgy (Westwood and Winzer 1987; Kuruvilla *et al* 1990). Young's modulus of Al/TiB₂ prepared by XD process at DMRL, Hyderabad (Kuruvilla *et al* 1990) is much higher as is clear from the bar chart for $E(\text{expt})/E(\text{ROM})$ shown in figure 14. Young's modulus value of 15 vol% XD Al/TiC was found to be 94 GPa (Mitra *et al* 1993b), which is well within the lower and upper limits provided by Hashin–Shtrikman model (Hashin and Shtrikman 1963). Similar observations were made by Aikin for 15 vol% XD Al/TiB₂ (Aikin 1989). A significant improvement in Young's modulus over the monolithic metal or alloy is achievable mainly because of excellent chemical bond between atoms of metal and the reinforcement which are again in direct contact as has been seen in XD Al/TiC.

7. Effect of ageing and heat treatment

Ageing heat treatments in 7XXX and 2XXX Al–SiC composites, particularly the former, significantly alter the structure and chemistry of the interface (Manoharan and Lewandowski 1989). Interfacial segregation of Cu, Mg or Zn could be seen in both underaged as well as overaged conditions. In underaged 2XXX matrix composite, the region of segregation was in the form of a diffuse layer 20 nm into the matrix from the interface. The profiles of Mg and Cu were fairly broad and peaked away from the

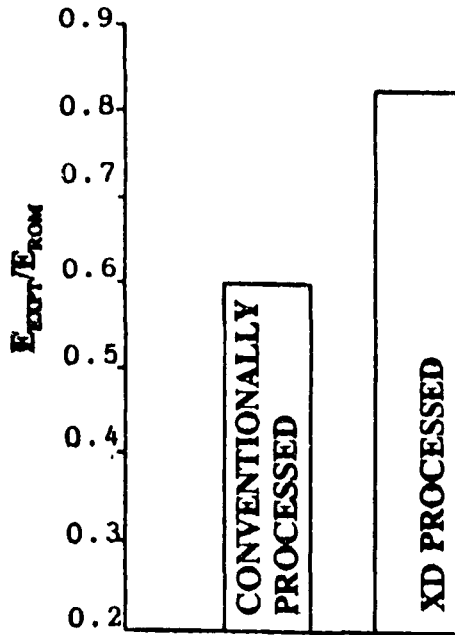


Figure 14. Comparison of $E(\text{expt})/E(\text{ROM})$ ratios of Al/TiB₂ composites prepared by conventional P/M and XD process (Kuruville *et al* 1990). It is clear that the latter has higher modulus.

Table 5. Effect of isothermal annealing treatment (600°C) on tensile ductility of Al matrix composites.

Material	Time exposure (hours)	% Elongation	
		Initial	After exposure
Al/20 v/o B ₄ C*	48	9.0	2.5
Al/20 v/o TiC*	96	6.8	0.8
Al/20 v/o SiC**	96	10.0	4.0
Al/20 v/o TiB ₂ **	100	12.2	12.2

*Vigorous reaction

**No reaction

interface because of nonequilibrium segregation of vacancies. However, after overaging, vacancies were segregated at the interface to meet the equilibrium conditions and the peak shifted to the interface. Similarly, a diffuse interface precipitate layer 10–20 nm wide was seen near the interface. On overaging, fairly regularly spaced particles Mg₃₂(Al,Zn)₄₉ appeared with a distinct PFZ next to them extending 35–40 nm in the matrix, which is depleted in solute. In response to equilibrium vacancy segregation at the interface, there is a decrease in their concentration in the region where PFZ forms as solute atoms migrate by diffusion and segregate at the interface.

Recently, isothermal heat treatment of Al MMCs containing 20 vol% SiC, TiB₂, B₄C or TiC was performed at 600°C for different periods of time, and the results are shown in table 5 (Satyaprasad and Mahajan 1994). TiB₂ is thermodynamically stable

Table 6. Effect of heat treatment at 600°C for 96 h on properties of Al/SiC and Al/TiB₂ composites (Satyaprasad and Mahajan 1994).

Material	Young's modulus (GPa)		Yield strength (MPa)	
	Initial	Heat-treated	Initial	Heat-treated
Al/20 v/o SiC	97.5	100	115	190
Al/20 v/o TiB ₂			105	121

in Al at 600°C and obviously the elongation properties are not affected. TiC and B₄C react extensively with Al resulting in reaction products at the interface (Al₃Ti and Al₄C₃ in case of TiC and Al₄C₃ and AlB in case of B₄C), which adversely affects tensile ductility. Al/SiC composite also shows lower elongation after heat treating and this is surprising as no reaction product could be seen at the interface using conventional TEM. However, some discontinuous precipitates of MgO and MgAl₂O₄ could be seen, which possibly originated from Mg impurities in the matrix. Al/SiC also showed some changes in Young's modulus and a significant change in yield strength after heat treating as shown in table 6. This suggests strengthening of the interfacial bond during heat treatment. It appears that at a temperature of 600°C (0.94 T_m) where diffusivity of Al is large, rearrangement on an atomic scale is possible near the interface leading to a structure closer to equilibrium. Slight but quite noticeable increase could be seen in the yield strengths of the Al/TiB₂ composite also (table 6). A detailed investigation of the interface is necessary to explain this. Recently, Warner and Stobbs (1989) noticed an increase in elastic modulus in Al-1.9% Mg/14 v/o SiC_p composite on isothermal heat treatment, with the 0.2% yield stress remaining unchanged. Wu and Lavernia (1991) on the other hand, saw noticeable increase in yield and ultimate tensile strength of the MMCs prepared by spray deposition process on annealing at 560°C for 22 h prior to extrusion. It was observed that the failure mechanism involved fracture of SiC particles, rather than pull-out. This was explained based on the fact that annealing helped in improving the bond strength between matrix and reinforcement. Interdiffusion between Al and SiC was suggested as the reason for increase in bond strength. This was noticed earlier by Arsenault (1984).

8. Influence of the interface on physical properties

Interfaces play a significant role in determination of the physical and mechanical properties of the composite. The physical properties include coefficient of thermal expansion, thermal conductivity and damping.

Coefficient of thermal expansion is an important criterion for the design of dimensionally stable composites. Recently, the coefficients of thermal expansion were measured for 15 vol% XD Al/TiC composite with 0.7 or 4.0 μm particle size and it was observed that the former had smaller coefficient of thermal expansion (Xu *et al* 1994). The matrix being pure Al in either situation, it is surely due to more interface area in smaller-particle-size composite. The lattice distortion observed close to the matrix-reinforcement interfaces in XD Al/TiC (Mitra *et al* 1993b) has been suggested to alter the behaviour of the interface with respect to thermal expansion. The coefficient of

thermal expansion of the composite α_c can be expressed as

$$\alpha_c = \alpha_p V_p + \alpha_m V_m + \alpha_i V_i, \quad (6)$$

where α_p , α_m and α_i are coefficients of thermal expansion of particle, matrix and interfaces respectively, and V_p , V_m and V_i are volume fractions of particle, matrix and interfaces. α_i can be determined indirectly by using (6) for curve-fitting with the experimental data.

Hasselmann and Donaldson (1992) reported thermal conductivity in Al/SiC metal matrix composites for particle sizes varying between 0.7 and 28 μm . It was observed that thermal conductivity decreased with smaller particle size. This phenomenon can again be explained based on the fact that finer-particle-size composite has larger interface area. The interface acts as a thermal barrier. Thus for maximizing thermal conductivity, particle size needed is the largest possible as this will reduce the total interface area. Geiger *et al* (1993) observed that 6090 Al/SiC composites with 10.2 and 28 μm particles had higher thermal conductivity than that of the unreinforced matrix. This was possible probably due to excellent bonding. However, with decrease in SiC particle size, thermal conductivity of the composite fell. Geiger and Jackson (1989) have also reported that 6061 Al/SiC shows higher thermal conductivity than 2124 Al/SiC. Besides the interface, the temper of the matrix alloy also affects the thermal conductivity and thus the above is difficult to explain.

Interfaces with reaction products or precipitates are likely to act as stronger barriers to heat conductivity than cleaner ones. This was investigated in detail by Reeves *et al* (1987) for the case of Ti/SiC composites, where the reaction products were a mixture of TiC and Ti_5Si_3 . For a reaction layer of 0.5 μm or thinner, the thermal conductivity of the composite was similar to that of the unreinforced matrix. This could be due to the fact that SiC particles possessed lower thermal conductivity than typical dense bulk SiC or because of the barrier created by the reaction layer. If the reaction layer was relatively thick (greater than 1 μm), thermal conductivity values of the composite were markedly reduced. The values were below those expected for composites reinforced with similar volume fractions of insulating particles.

To estimate the role of the interface, Hasselmann and Johnson (1987) proposed a model for composite conductivity, K_c . This includes the interfacial heat transfer coefficient or thermal conductance, h ($\text{W m}^{-2} \text{K}^{-1}$).

$$K_c = K_M \frac{2f(K_I/K_M - K_I/rh - 1) + K_I/K_M + 2(K_I/rh) + 2}{f(1 - K_I/K_M + K_I/rh) + K_I/K_M + 2(K_I/rh) + 2}, \quad (7)$$

where f is the volume fraction of inclusions; C , M and I refer to composite, matrix and inclusion respectively; and r is the radius of the inclusions assumed to be spherical. This equation is valid only for 'dilute' composites, in which disturbance to the thermal field around an inclusion does not overlap with the disturbance from surrounding inclusions.

The effect of reinforcement/matrix interface on the damping behaviour of the composites has been investigated by Zhang *et al* (1993). Schoek theory which was proposed to explain the phenomenon of internal friction in alloys has been used to explain the same for MMCs. According to the theory, internal friction is increased by the relaxation at semicoherent or incoherent precipitate/matrix interfaces and the anelastic strain contributed by dislocations close to the interface. Resultant composite

internal friction was found to be proportional to the volume fraction of reinforcement in the composite. In the MMCs, not only is the interface area large, but also CTE mismatch between particulates and matrix result in stress concentration at the incoherent interfaces, which increases the internal friction. At higher temperatures, when the matrix softens relative to the hard reinforcement, a reversible movement of vibrations is expected to occur at the interface and this can be used to explain increase in interface damping with temperature. In 2519 Al MMCs, the largest role of interface could be seen at temperatures between 250°C and 350°C.

9. Effect on yield strength and elongation

We have earlier discussed the effect of brittle reaction products at the interface on the load transfer efficiency of the interface which is adversely affected. Similarly, coarse intermetallic precipitates at the Al–Cu–Mg alloy/SiC interfaces are detrimental to all mechanical properties. The feedback from the above reports is that a clean interface is always desirable.

Even if there are no reaction products at the interface and the matrix, particle sizes and shapes are the same, the yield strength, modulus and tensile ductility vary based on the nature of chemical bond. This is evident from the data shown in table 7 for mechanical properties of pure Al and Al/SiC, Al/B₄C, Al/TiC and Al/TiB₂ composites prepared by P/M process at DMRL.

It is obvious that the highest increase in yield and ultimate tensile strength is observed for Al/TiC. Improvement in strength is through load transfer at the interface as well as dislocation–particle and dislocation–dislocation interactions. Of course, the excellent bond integrity of Al/TiC interface explains why Al/TiC composite has the highest increase in yield and ultimate tensile strength.

The resistance of the interface to cracking even at high strains in the surrounding matrix is also essential for a significant role in load transfer. A brittle interface will crack at lower strains leading to little load transfer. In table 7, Al/TiC composite also shows maximum strain to fracture. Remarkable elongation of 20% or more has been seen in 15 vol% XD Al/TiC at room temperature, partly as the particles were equiaxed and also because interfacial bonding was excellent (Mitra 1993). Even after cold rolling to 75% reduction, cracks could be seen at only a few interfaces, where particles formed clusters. This is unlike the situation seen in many other interfaces like Al/Al₂O₃ (Ruedl 1969) and Cu/SiO₂ and Cu/Al₂O₃ (Humphreys and Stewart 1972). The regions around the interface are highly misoriented with respect to surrounding

Table 7. Tensile properties of some P/M as-extruded aluminium matrix composites (Kuruvilla *et al* 1989).

Composite	YS(MPa)	UTS(MPa)	Elongation (%)
Pure Al (P/M)	64	90	21
Al/20 v/o SiC	117	200	11.4
Al/20 v/o TiC	148	233	15.6
Al/20 v/o B ₄ C	143	208	9.0
Al/20 v/o TiB ₂	121	166	14.8



Figure 15. TEM micrograph of microstructure of XD Al/TiC composite after room-temperature tension test (area close to fracture surface). Regions around the particles are misoriented with respect to each other and hence the contrasts are different (Fine *et al* 1993).

regions resulting in local lattice rotation as shown in figure 15 (Fine *et al* 1993; Mitra 1993). The mechanism of local lattice rotation in dispersion-hardened alloys has been discussed by Ashby (1966) and Humphreys (1979). The high ductility of the Al/TiC interface can only be explained based on the metallic nature of bonding. In another investigation (Earvolino *et al* 1992), Al containing 15 vol% tetragonal $D0_{23}$ structured $Al_3Zr_{0.25}Ti_{0.75}$, prepared by casting, was cold-rolled to 0.017% of the original thickness with a few intermediate anneals. While the intermetallic was fractured, the Al flow kept the interface intact and no cracks could be seen at Al-intermetallic interfaces. The Al Al_2O_3 , Cu SiO_2 and Cu Al_2O_3 interfaces, which are less ductile, will crack at smaller strains and not much local lattice rotation can take place as has been explained by Humphreys.

10. Effect on creep resistance

The creep threshold stress σ_0 is the index of resistance to creep and for particle-reinforced composites this is given by

$$\sigma_0 = K \cdot (E_c/E_m)^m. \quad (i)$$

σ_0 is independent of particle size and temperature, and increases with increase in the volume fraction of the reinforcement. The origin of σ_0 is related to the load transfer at

the matrix–reinforcement interface, which of course depends on the interface bond integrity. This can be seen from table 8. The XD Al/TiB₂ composite has shown higher threshold stress compared to that prepared by conventional P/M process, which is due to stronger interface as well as finer particle size in the former. Al/SiC shows the highest creep threshold stress, as the matrix–reinforcement bonding is stronger than that in Al/TiB₂, which is indicated by comparison of $E(\text{expt})/E(\text{ROM})$ ratio (figure 3).

11. Interface engineering

It is well understood how important interfaces are in determining the performance of MMCs. We have seen how processing methods, ageing and heat treatments can affect the interfacial bond and properties. Hence there is a drive for developing the technology to tailor interfaces to achieve desired properties. Of course, processing methods and heat treatments can be devised and alloying elements can be added in order to modify interfaces. The other option is to treat the surfaces of the reinforcements, which play a crucial role in wetting. Some of the strategies to improve interfacial properties are outlined in table 9.

Table 8. Table reporting $E(\text{expt})/E(\text{ROM})$ and σ_0 values (Pandey 1993) for composites with different reinforcement and processing methods.

Material	$E(\text{expt})/E(\text{ROM})$	σ_0 (MPa)
PM Al/20 v/o SiC _p	0.73	25.2
PM Al/20 v/o TiB ₂	0.60	14.3
XD Al/20 v/o TiB ₂	0.82	19.2

Table 9. Strategies to exploit full potential of metal matrix composites by tailoring interfaces.

Strategy	Example
1. Use of <i>in situ</i> processes	XD, reactive casting
2. Use of nonstoichiometric compounds as reinforcements	TiC _{1-x} instead of TiC
3. Development and use of novel reinforcements with metallic bonding	Ti ₅ Si ₃ , TiSi ₂ , Cr ₃ C ₂ , etc.
4. Novel techniques to modify reinforcement surfaces for improved bonding	Decarburization of TiC, Ion implantation, Irradiation
5. Matrix alloying for enhanced bonding	Addition of Ti, Cr, La, Ce, Li in Al/SiC system; Mg and Li to Al/Al ₂ O ₃ system
6. Development of innovative coating techniques for reinforcements	Sputtered coatings, duplex coatings, graded coatings, sol-gel coatings, <i>in situ</i> modification of coatings
7. Thermomechanical treatment	Deformation and recrystallization in XD Al/TiC composites led to higher degree of semicoherency at interfaces

McDonald and Ransley (1954) pretreated TiC particles by heating in moist hydrogen at 1000°C leading to removal of the oxide layer on the surface and partial decarburization of surfaces. This leaves a metallic Ti layer on the surface. It has already been discussed in an earlier section that TiC {111} surfaces ending with Ti have the same surface electronic structure as Ti {0001} and Ti sites on {100} surfaces are more active when these are carbon-deficient. Removal of oxide layer also probably resulted in establishment of direct contact and an equilibrium between the atoms of matrix and reinforcing phase and hence a strong chemical bond. Thus pretreatment with hydrogen resulted in significant increase in Young's modulus. This also proves once again our earlier proposition that metallic bonds result in a more efficient load transfer.

Another and quite popular surface modification method is coating with a third phase to improve wetting or prevent adverse chemical reaction. Coating material is normally wetted well by the Al matrix, such as Ni on TiC. TiB₂ coating applied by CVD, which is also an excellent wetting agent works on a different principle (Maruyama *et al* 1991). Bulk TiB₂ is not wetted as well by Al as CVD TiB₂ coating on SiC and C fibres is. It has been reported by Wu (1988) that CVD-deposited TiB₂ contains significant amounts of chlorine and wetting in C/Al system is related to the concentration of chlorine. Thus it was hypothesized that enhanced wetting action was due to the fluxing action of chlorine, which destabilized the surface aluminium oxide and allowed direct contact between liquid Al and the reinforcement.

Recently, Johnson and Sonuprlak (1993) investigated the effect of coating diamond particles (modulus = 1050 GPa) with SiC using chemical vapour infiltration. SiC not only helps in improving wettability, but retards formation of Al₄C₃, which is detrimental because of its tendency to corrode in moist environments. Also, Al₄C₃ has poor thermal conductivity and it defeats the purpose of reinforcing with diamond for preparing composites having high thermal conductivity. The increase in SiC coating thickness of diamond reinforcements monotonously increases the thermal conductivity of the composites. It is visible that Young's modulus increases with increase in coating thickness; there is also an overall decrease in the coefficient of thermal expansion. These are due to changes in the interface bond due to coating as well as increase in volume fraction of SiC.

12. Conclusions

In this paper, we have analysed some of the existing information about interfaces in the composites of interest to understand their nature and relationship with mechanical properties. The variables controlling the characteristics of interfaces are quite large in number, such as processing (technique, temperature, etc.) as well as composition and chemical nature of matrix and reinforcement. Processing variables can be manipulated to enhance the wetting between matrix and reinforcement, like addition of alloying elements, pretreatment or coating of reinforcements, increase of temperature of molten metal, hot pressing the blended metal and ceramic powders above solidus temperature, etc. Ageing of the matrix with high solid solubility also affects the interface structure and chemistry.

The chemical bond at the interface can be through a chemical reaction or electronic. The former is detrimental as it leads to a brittle reaction product at the interface, whereas

the latter is desirable. For electronic bonding, intimate contact between the atoms of the matrix and of the ceramic phase is necessary and this is found more easily in the *in situ* composites. That is the reason some matrix–particle interfaces in XD composites are semicoherent and improvement in Young's modulus values are higher than those seen in composites prepared by conventional processes. Factors responsible for enhancement of interfacial bonding in metal/ceramic systems are: (i) presence of densely packed planes parallel to interface in either or both the reinforcement and the matrix phases, (ii) presence of charged defects close to interface, (c) substoichiometric composition of the reinforcement, and (d) lower heat of formation of the reinforcements.

Of a variety of reinforcements, the ones having metallic character form metallic bonds with the metal matrix. In such cases, the matrix–reinforcement interfacial bonding is stronger than in other metal–ceramic composites and this leads to a greater improvement in Young's modulus, yield and ultimate tensile strength values over those of the matrix material. Tensile ductility is also impressive in case of metallic bonding at interfaces as they can withstand higher strains. Although the incorporation of the reinforcements which give rise to metallic bonding at the interfaces results in superior properties compared to others, most of the potential ceramic reinforcements possess ionic or covalent bonding. Hence modification of interfaces is necessary to enhance the metallic character of the bond. Because of the critical role played by interfaces in the composites, it is necessary to plan the choice of matrix and reinforcement and processing conditions while keeping an eye on the nature of the interfaces expected.

Acknowledgements

The authors gratefully acknowledge several useful discussions and research results from M/s V V Bhanuprasad, B V R Bhat, M K Jain, A B Pandey, V K Varma, Dr S V Kamat, K S Prasad and Dr A K Kuruvilla. One of the authors (RM) is thankful to Professor Morris E Fine and Professor Julia R Weertman for their guidance in successful completion of his PhD research at the Northwestern University, USA. Thanks are also due to Sri S L N Acharyulu, Director, Defence Metallurgical Research Laboratory, for his encouragement.

References

- Aikin Jr R M 1989 NASA Contractor Report 4365, Contract NAS 1-18531
- Arsenault R J 1984 *Scr. Metall.* **18** 1131
- Arsenault R J 1994 *Composites* **27** 540
- Ashby M F 1966 *Philos. Mag.* **14** 1157
- Bhanuprasad V V, Prasad K S, Kuruvilla A K, Pandey A B, Bhat B V R and Mahajan Y R 1991 *J. Mater. Sci.* **26** 460
- Bonollo F, Guerriero R, Sentimenti E, Tangerini I and Jang L M 1991 *Advanced structural inorganic composites* (ed.) P Vincenzini (Amsterdam: Elsevier Science Publishers) p. 259
- Bradshaw A M, Van der Veen J F, Himpel F J and Eastman D E 1980 *Solid State Commun.* **37** 37
- Brown N R 1993 *Effect of heat treatment on interfaces in magnesium metal matrix composites*, Ph D Dissertation, Northwestern University, Illinois, USA
- Calderon H A, Fine M E and Weertman J R 1988 *Metall. Trans.* **A19** 1135
- Carim A H 1991 *Mater. Lett.* **12** 153
- Chawla K K 1987 *Composite materials: Science and engineering* (New York: Springer Verlag) p. 83

- Chiou J -M and Chung D D L 1990 *Metal and ceramic matrix composites: Processing, modelling and mechanical behaviour* (eds) R B Bhagat, A H Clauer, P Kumar and A M Ritter (Warrendale, PA: TMS) p. 107
- Cisse J, Bolling G F and Keer H W 1972 *J. Cryst. Growth* **13/14** 771
- Clough R B, Biancaniello F S, Wadley H N G and Kattner U R 1990 *Metall. Trans.* **A21** 2747
- Date S K 1994 Private communication, NCL, Pune
- Delannay F, Froyen L and Deruyttere A 1987 *J. Mater. Sci.* **22** 1
- Dhingra A K 1980 *Philos. Trans. R. Soc.* **A294** 151
- Earvolino P A, Fine M E, Weertman J R and Parameswaran V R 1992 *Scr. Metall. Mater.* **26** 945
- Easterling K E, Fischmeister H F and Navara E 1973 *Powder Metall.* **16** 128
- Eid N M A and Thomason R F 1979 *Acta Metall.* **27** 1239
- Feng C R, Michael D J and Crowe C R 1991 *Mater. Sci. Eng.* **A145** 257
- Fine M E 1981 *Scr. Metall.* **15** 523
- Fine M E, Bourell D L, Eliezer Z, Persad C and Marcus H L 1988 *Scr. Metall.* **22** 907
- Fine M E, Mitra R and Weertman J R 1993 *Z. Metallkd.* **4** 282
- Finnis M W, Stoneham A M and Tasker P W 1990 *Metal-ceramic interfaces: Acta Scripta Metallurgica Proceedings Series* (eds) M Ruhle, A G Evans, M F Ashby and J P Hirth (New York: Pergamon Press) Vol. 4, p. 35
- Fuchs G E 1990 *Metal and ceramic matrix composites: Processing, modelling and mechanical behaviour* (eds) R B Bhagat, A H Clauer, P Kumar and A M Ritter (Warrendale, PA: TMS) p. 391
- Fuchs G E, Abonneau E, Treilleux M and Perez A 1989 *Mater. Sci. Eng.* **A109** 83
- Gao Y and Merkle K L 1992 *Structure and properties of interfaces in materials: MRS Symp. Proc.* (eds) W A T Clark, U Dahmen and C L Briant (Pittsburgh, PA: MRS) Vol. 238, p. 775
- Geiger A L, Hasselman D P H and Donaldson K Y 1993 *J. Mater. Sci. Lett.* **12** 420
- Geiger A L and Jackson M 1989 *Adv. Mater. Proc.* **7** 23
- Goretzki H 1967 *Phys. Status Solidi* **20** K141
- Goretzki H, Exner H E and Scheuermann W 1971 *Modern developments in powder metallurgy* (ed) H H Hausner **4** 327
- Hashin Z and Shtrikman S 1963 *J. Mech. Phys. Solids* **11** 127
- Hasselmann D P H and Johnson L F 1987 *J. Compos. Mater.* **21** 508
- Hasselmann D P H and Donaldson K Y 1992 *J. Am. Ceram. Soc.* **75** 3137
- Hawk J A, Mirchandani P K, Benn R C and Wilsdorf H G F 1988 *Dispersion strengthened aluminium alloys* (eds) Y -W Kim and W M Griffith (Warrendale, PA: TMS) p. 551
- Henager Jr C H, Brimhall J L and Hirth J P 1992 *Ceram. Sci. Eng. Proc.* **13** 596
- Henriksen B R and Gionnes J 1991 *Advanced structural inorganic composites* (ed.) P Vincenzini (Amsterdam: Elsevier Sci. Pub.) p. 251
- Homeny J, Neergard L J, Harasek K R, Donner J T and Bradley S A 1990 *J. Am. Ceram. Soc.* **73** 102
- Howe J M 1993 *Inter. Mater. Rev.* **38** 233
- Humphreys F J 1979 *Acta Metall.* **27** 1801
- Humphreys F J and Stewart A T 1972 *Surf. Sci.* **31** 389
- Iseki T, Kameda T and Maruyama T 1984 *J. Mater. Sci.* **19** 1692
- Jain M K, Bhanuprasad V V, Kamat S V, Pandey A B, Varma V K, Bhat B V R and Mahajan Y R 1993 *Int. J. Powder Metall.* **29** 267
- Johnson W B and Sonuparlak B 1993 *J. Mater. Res.* **8** 1169
- Jones C, Kiely C J and Wang S S 1989 *J. Mater. Res.* **4** 327
- Kimura Y, Mishima Y, Umekawa S and Suzuki I 1984 *J. Mater. Sci.* **19** 3107
- Koczak M J and Kumar K S 1989 US Patent 4, 808, 372
- Konitzer D G and Loretto M H 1989a *Acta Metall.* **37** 397
- Konitzer D G and Loretto M H 1989b *Mater. Sci. Technol.* **5** 627
- Kuruvilla A K, Bhanuprasad V V, Prasad K S and Mahajan Y R 1989 *Bull. Mater. Sci.* **12** 495
- Kuruvilla A K, Prasad K S, Bhanuprasad V V and Mahajan Y R 1990 *Scr. Metall.* **24** 873
- Krock R H 1966 *Modern developments in powder metallurgy* (ed.) H H Hausner (New York: Plenum Press) p. 105
- Lagace H and Lloyds D J 1989 *Canadian Met. Quart.* **28** 145
- Lee D J, Vaudin M D, Handwerker C A and Kattner U A 1988 *Mater. Res. Soc. Symp. Proc.* **120** 357
- Levi C G, Abbaschian G J and Mehrabian R 1978 *Metall. Trans.* **A9** 697
- Lim C B, Yano T and Iseki T 1989 *J. Mater. Sci.* **24** 4144

- Lloyd D J and Jin I 1988 *Metall. Trans.* **A19** 3107
- Lucas J P, Yang N Y C and Stephens J J 1992 *Structure and properties of interfaces in materials; Mater. Res. Soc. Symp.* (eds) W A T Clark, U Dahmen and C L Briant (Pittsburgh, PA: MRS) Vol. 238, p. 877
- Lyle J P Jr 1967 *Aluminum* (ed.) K R Van Horn (Metals Park, OH: ASM) Vol. 1, Ch. 10, p. 337
- Mader W 1992 *Structure and properties of interfaces in solids; MRS Symp. Proc.* (eds) W A T Clark, U Dahmen and C L Briant (Pittsburgh, PA: MRS) p. 763
- Mahajan Y R and Rama Rao P 1992 *New materials* (eds) S K Joshi, C N R Rao, T Tsuruta and S Nagakura (New Delhi: Narosa Pub. House) p. 322
- Manning C R and Gurganus T B 1969 *J. Am. Ceram. Soc.* **52** 115
- Manoharan M and Lewandowski J J 1989 *Scr. Metall.* **23** 301
- Marcus H L and Rabenberg L K 1987 ONR Contract N00014-84-K-0687, Technical Report UTCMSE-87-3, p. 160
- Maruyama B, Barrera E V and Rabenberg L 1991 *Metal matrix composites: Processing and interfaces* (eds) R K Everett and R J Arsenault (San Diego, CA: Academic Press) p. 181
- McDonald N F and Ransley C E 1954 *Metal powder review: Symp. on powder metallurgy*, p. 242
- Meschter P J and Schwartz D S 1989 *JOM* **41** 52
- Mitra R 1993 *Microstructure and interfaces in XD Al/TiC metal matrix composites*, Ph D Dissertation, Northwestern University, Illinois, USA
- Mitra R, Chiou W-A, Weertman J R, Fine M E and Aikin Jr R M 1992a *Structure and properties of interfaces in materials; MRS Symp. Proc.* (eds) W A T Clark, U Dahmen and C L Briant (Pittsburgh, PA: MRS) Vol. 238, p. 871
- Mitra R, Weertman J R, Fine M E and Aikin Jr R M 1992b *Developments in ceramic and metal matrix composites* (ed.) K Upadhy (Warrendale, PA: TMS) p. 125
- Mitra R, Fine M E and Weertman J R 1993a *J. Mater. Res.* **8** 2370
- Mitra R, Chiou W A, Fine M E and Weertman J R 1993b *J. Mater. Res.* **8** 2380
- Mitra R, Mahajan Y R, Prasad N E, Chiou W A and Ganguly C 1995 *Key engineering materials: Metal and ceramic matrix composites* (ed.) F H Wohlbiel (Switzerland: Trans Tech Publications)
- Nicholas M G 1987 *Fundamentals of diffusion bonding* (ed.) Y Ishida (New York: Elsevier) p. 25
- Ning X G, Pan J, Hu K Y and Ye H Q 1992 *Structure and properties of interfaces in solids* (eds) W A T Clark, U Dahmen and C L Briant (Pittsburgh, PA: MRS) Vol. 238, p. 865
- Nogi K, Tsujimoto M K, Ogino K and Iwamoto N 1992 *Acta Metall. Mater.* **40** 1045
- Norman J H, Reynolds G H and Brewer L 1990 *Mater. Res. Soc. Symp. Proc.* (Pittsburgh, PA: MRS) p. 369
- Nutt S R 1986 *Interfaces in metal matrix composites* (eds) A K Dhingra and S G Fishman (Warrendale, PA: TMS) p. 157
- Nutt S R and Carpenter R W 1985 *Mater. Sci. Eng.* **75** 169
- Oh S Y, Cornie J A and Russel K C 1989 *Metall. Trans.* **A20** 533
- Ohuchi F S 1987 *Interface science and engineering: J. Phys.* (eds) R Raj and S L Sass (New York) Vol. C5, p. 783
- Pandey A B 1993 *Creep behaviour of particulate reinforced aluminium matrix composites*, Ph D Dissertation, Banaras Hindu University, Varanasi
- Quigley B F, Abbaschian G J, Wunderlin R and Mehrabian R 1982 *Metall. Trans.* **A13** 93
- Rack H J 1988 *Dispersion strengthened aluminium alloys* (eds) Y -W Kim and W M Griffith (Warrendale, PA: TMS) p. 649
- Radmilovic V, Thomas G and Das S K 1991 *Mater. Sci. Eng.* **A132** 171
- Ramqvist J V 1965 *Int. J. Powder Metall.* **1** 2
- Ratnaparkhi P L and Howe J M 1992 *Scr. Metall. Mater.* **27** 133
- Reeves A J, Stobbs W M and Clyne T W 1987 *Metal matrix composites—Processing, microstructure and properties* (eds) N Hansen, D Juul Jensen, T Leffers, H Liholt, T Lorentzen, A S Pederson, O B Pederson and B Ralph (Roskilde, Denmark: Riso National Laboratory Press) p. 631
- Reeves A J, Taylor R and Clyne T W 1991 *Mater. Sci. Eng.* **A141** 129
- Reuss A 1929 *Z. Angew. Math. Mech.* **9** 55
- Rhee S K 1970 *J. Am. Ceram. Soc.* **53** 386
- Ribes H, Da Silva R, Suery M and Bretheau T 1990 *Mater. Sci. Tech.* **6** 621
- Ruedl E 1969 *J. Mater. Sci.* **4** 814
- Satyaprasad K, Mahajan Y R and Bhanuprasad V V 1992 *Scr. Metall. Mater.* **26** 711
- Satyaprasad K and Mahajan Y R 1994 *Scr. Metall. Mater.* **30** 1049

- Skinner D J 1988 *Dispersion strengthened aluminum alloys* (eds) Y -W Kim and W M Griffith (Warrendale, PA: TMS) p. 181
- Sritharan T, Xia K, Heathcock J and Mihelich J 1990 *Metal and ceramic matrix composites: Processing, modelling and mechanical behaviour* (eds) R B Bhagat, A H Clauer, P Kumar and A M Ritter (Warrendale, PA: TMS) p. 13
- Samsonov G V, Panasyuk A D and Kozina G K 1968 *Sov. Powder Metall. Met. Ceram.* **71** 874
- Schroder V, Kainer K U and Mordike B L 1989 *Developments in the science and technology of composite materials: Proc. of the third European conf. on composite materials, Bordeaux, France* (eds) A R Bunsell, P Lamicq and A Massiah (Amsterdam: Elsevier Applied Science) p. 221
- Schroder J, Kainer K U and Mordike B L 1991 *Proc. P/M 91: Int. conf. on P/M aerospace materials, Lausanne, Switzerland*
- Skinner D J, Zedalias M S, Frazier W E, Kockzak M J and Sahoo P 1990 *Metal and ceramic matrix composites: Processing, modelling and mechanical behaviour* (eds) R B Bhagat, A H Clauer, P Kumar and A M Ritter (Warrendale, PA: TMS) p. 535
- Stoneham A M and Tasker P W 1985 *J. Phys.* **C18** L543
- Sunwoo H, Fine M E, Meshi M and Stone D H 1982 *Metall. Trans.* **A13** 2035
- Suzuki M, Nutt S R and Aikin R M Jr 1993 *Mater. Sci. Eng.* **A162** 73
- Tombrello T A 1984 *Mater. Res. Soc. Symp. Proc.* **25**
- Van Den Burg M and De Hosson J Th M 1992 *Acta Metall. Mater.* **40** S281
- Voigt W 1928 *Lehrbuch der Kristallphysik* (Leipzig: Teubner) p. 716
- Wang L and Arsenault R J 1991 *Metall. Trans.* **A22** 3013
- Warner T J and Stobbs W M 1989 *ICCM: Proc. 7th Int. conf. on comp. mater.* (eds) Wu Yunshu, Gu Zhenlong and Wu Renjie (New York: International Academic Press and Pergamon Press) Vol. 1, p. 503
- Warwick M and Clyne R T W 1989 *Developments in the science and technology of composite materials: Third European conf. on composite materials* (eds) A R Bunsell, P Lamicq and A Massiah (France: Elsevier Applied Science) p. 205
- Webster D 1982 *Metall. Trans.* **A13** 1511
- Weimin S, Pengxing L and Geyang L 1991 *Composites: Design, manufacturing and application, Proc. ICCM/VIII* (eds) S Tsai and G S Springer (Covina, CA: SAMPE) 19k3
- Westwood A R C 1988 *Metall. Trans.* **A19** 749
- Westwood A R C and Winzer S R 1987 *Advancing materials research* (eds) P A Paras and H D Langford (Washington, D.C.: Nat. Acad. Press) p. 225
- White J, Willis T C, Hughes I R and Jordan R M 1983 *Dispersion strengthened aluminium alloys* (eds) Y -W Kim and W M Griffith (Warrendale, PA: TMS) p. 693
- Wu R 1988 *Interfaces in polymer, ceramic and metal matrix composites* (ed.) H Ishida (New York: Elsevier) p. 43
- Wu Y and Lavernia E J 1991 *JOM* **43** 16
- Xia K, Nieh T G, Wadsworth J and Langdon T G 1990 *Fundamental relationships between microstructure and mechanical properties of metal-matrix composites* (eds) P K Liaw and M N Gungor (Warrendale, PA: TMS) p. 543
- Xu Z R, Chawla K K, Mitra R and Fine M E 1994 *Scr. Metall. Mater.* **31** 1525
- Yokokawa H, Sakai N, Kawada T and Dokiya M 1991 *Metall. Trans.* **A22** 3075
- Young T 1805 *Trans. R. Soc.* **94** 65
- Zedalias M S, Ghate M V and Fine M E 1985 *Scr. Metall.* **19** 647
- Zhang J, Perez R J, Gupta M and Lavernia E J 1993 *Scr. Metall.* **28** 91