

CHEMICAL COMPATIBILITY BETWEEN ALUMINIUM BASE MATRICES AND LIGHT REFRACTORY CARBIDE REINFORCEMENTS

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SUMMARY: The main features of the interface chemistry of Al/B₄C, Al/TiC and Al/SiC couples at temperatures up to 1000 °C are presented and discussed in terms of thermodynamics, kinetics and reaction mechanism. The Al/B₄C couple appears reactive whatever the temperature whereas a reactive-non reactive transition occurs at 812 °C on heating for the Al/TiC couple and at 650 °C on cooling for the Al/SiC couple. The reaction products are Al₃BC and AlB₂ or β-AlB₁₂ for the Al/B₄C couple, Al₄C₃ and Al₃Ti for Al/TiC and finally Al₄C₃ and dissolved silicon for Al/SiC. Whatever the couple, interaction always proceeds via a dissolution-precipitation mechanism which ends in certain instances with the passivation of the base carbide surface by a continuous Al₃BC or Al₄C₃ layer. Some examples are given illustrating how advantage can be taken of these features for interface tailoring.

KEYWORDS: metal matrix, aluminium, boron carbide, titanium carbide, silicon carbide, interface, chemical reactions.

INTRODUCTION

The physical and mechanical characteristics of the light refractory carbides SiC, TiC and B₄C make them suitable for being used as reinforcement in aluminium base metal matrix composites. Discontinuously reinforced composites or cermets have thus been produced by incorporating particles, small crystals or whiskers of these carbides in the metal matrix by various pyrometallurgic techniques [1-3]. Attempts have also been made to elaborate such products by in-situ reaction of carbon particles with appropriate alloy melts [4, 5]. For applications where higher strength and stiffness were required, melt infiltration has been used to produce aluminium base composites unidirectionally reinforced with SiC multifilaments [6]. More recently, a method for coating carbon fibres with B₄C, TiC or SiC has been developed and these fibres have been incorporated in aluminium base matrices by pressure infiltration [7].

In all the above-cited examples, processing of the metal matrix composites or cermets requires medium or high temperatures at which chemical reactions between the constituents either may develop or are deliberately activated. In this respect, successful elaboration of a composite material and further optimization of its mechanical properties imply a thorough understanding of the chemistry of the matrix/reinforcement interface. The aim of the present paper is to point out the general principles governing the interface chemistry of the Al/B₄C, Al/TiC and Al/SiC couples and to illustrate how advantage can be taken of these principles for elaborating metal matrix composites with tailored interfaces.

INTERFACE CHEMISTRY: THE GENERAL PRINCIPLES

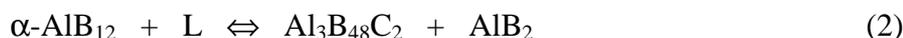
The Al/B₄C couple

Most of the data presently available on the phase equilibria in the Al-B-C ternary system under atmospheric pressure are summarized by the isothermal section at 1000 and 727 °C presented in Fig. 1. In these figures, bold lines represent phase equilibria that can be considered as non-ambiguously established and thin lines phase equilibria whose existence can only be assumed on the basis of some experimental indications or theoretical considerations. An important feature of the Al-B-C system is the existence of the ternary carbide Al₃BC, whose composition, crystal symmetry and cell parameters have been determined only recently [8]. Between 1000 and 727 °C, three invariant transformations involving an Al-rich liquid occur [9]:

- a peritectic reaction in the Al-B subsystem which has been found to occur at 892 ± 5 °C:



- a peritectic reaction in the ternary Al-B-C system which occurs between 892 and 868 °C:



- a quasi-peritectic reaction occurring at 868 ± 4 °C:

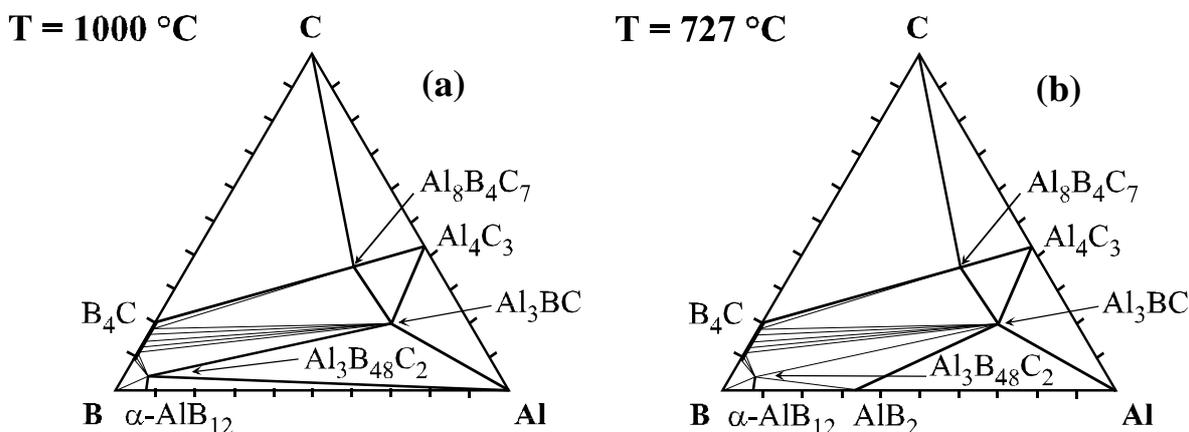


Fig. 1: Isothermal sections of the Al-B-C phase diagram; (a) at 1000 °C; (b) at 727 °C.

It flows from these thermodynamic data that B₄C can be decomposed by reaction with solid or liquid aluminium at any temperature lower than or equal to 1000 °C. It has been observed that this decomposition proceeds at a very slow rate as long as the temperature is lower than 660 °C, i.e. as long as aluminium is in the solid state. At 660 °C, aluminium melts and the decomposition rate suddenly rises. Then, further increase in temperature results in a faster decomposition rate. The reaction products are the ternary carbide Al₃BC and either the diboride AlB₂ or the complex borocarbide Al₃B₄₈C₄ (β-AlB₁₂), according as the temperature is lower or higher than 868 ± 4 °C. It is worth noting that no trace of aluminium carbide Al₄C₃ is formed in the chemical interaction between Al and B₄C, which differentiates the Al/B₄C couple from the two other couples examined.

Whatever the temperature, interaction at the Al/B₄C interface always proceeds via the same mechanism. After an incubation period which corresponds to the breakage of the interfacial oxide films, a true Al/B₄C interface is created in some points. In these points, the metal rapidly saturates in boron and carbon by simple dissolution of the carbide. The solubility of

carbon and boron in aluminium being very low (about 10 and 1000 at.ppm for C and B at 727 °C, respectively), this simple dissolution process is rapidly followed by the nucleation and growth first of Al_3BC and then of AlB_2 or $\text{Al}_3\text{B}_{48}\text{C}_2$ crystals. Nuclei of these products do not form, however, at the same rate and in the same place: Al_3BC easily nucleates at the surface of B_4C whereas AlB_2 or $\text{Al}_3\text{B}_{48}\text{C}_2$ nucleate with difficulty and only on impurity seeds in the metal matrix. Once this stage is arrived at, interaction progresses via a classical dissolution-precipitation mechanism: carbon and boron atoms migrate by liquid-phase diffusion from the surface of B_4C where aluminium supersaturates in carbon and boron (dissolution) to faces of Al_3BC and AlB_2 or $\text{Al}_3\text{B}_{48}\text{C}_2$ crystals that are growing from the metal (precipitation). In places where Al_3BC crystals are fixed, B_4C is protected against further attack while in places where aluminium remains in direct contact with the surface of B_4C , dissolution continues. This gives rise to the formation of dissolution pits at the B_4C surface (Fig. 2a). As long as an important part of this surface is directly exposed to aluminium, the amount of B_4C dissolved increases quasi-linearly with the reaction time. When the growing Al_3BC crystals have joined together, they form a passivating layer and the rate at which B_4C is decomposed becomes quasi-null (Fig. 2b).

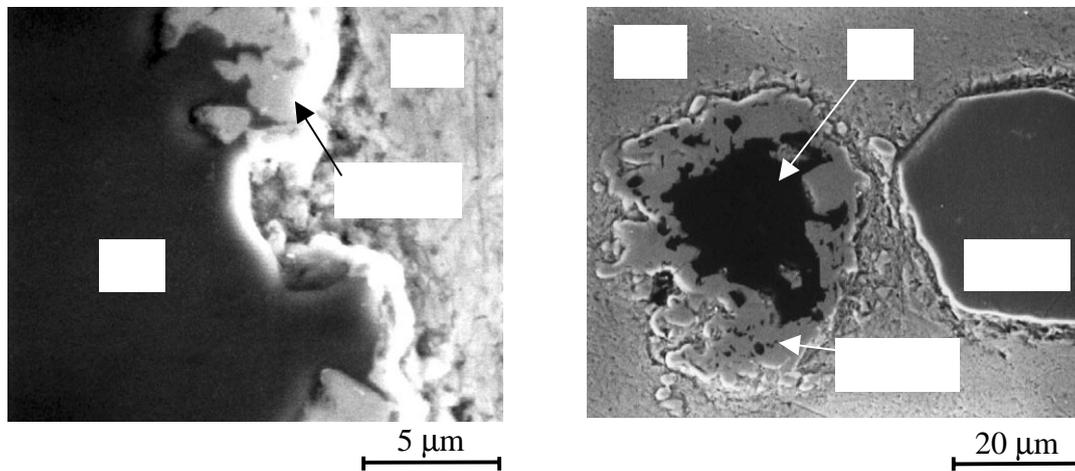


Fig. 2: Typical morphology of the $\text{Al}/\text{B}_4\text{C}$ interface after reaction at 727 °C: (a) after 15 h reaction (beginning of the interaction); (b) after 160 h (passivation stage attained).

The Al/TiC couple

An experimental investigation of the phase equilibria in the Al-C-Ti system has led to the construction of the two isothermal sections presented in Fig. 3. These sections differ in the drawing of the tie lines in the quadrilateral Al- Al_4C_3 - TiC_x - Al_3Ti . Differential thermal analyses and isothermal diffusion experiments carried out in the temperature range 827-727 °C under atmospheric pressure have shown that at 812 ± 15 °C, occurs in the Al-C-Ti system the following quasi-peritectic invariant transformation:



where L is an aluminium base liquid (with less than 5 at.ppm of carbon and about 0.4 at.% of titanium dissolved) and TiC_x a carbon-rich composition in the homogeneity range of the titanium carbide phase with $0.90 < x < 0.95$ [10]. As a consequence of this transformation, carbon-rich titanium carbide is in equilibrium with an aluminium base liquid at temperatures higher than 812 °C but can react with liquid or solid aluminium at any temperature lower than this value. As far as carbon-rich compositions of the homogeneity range of titanium carbide are concerned, the reaction products are aluminium carbide Al_4C_3 and a titanium aluminide with the chemical formula Al_3Ti .

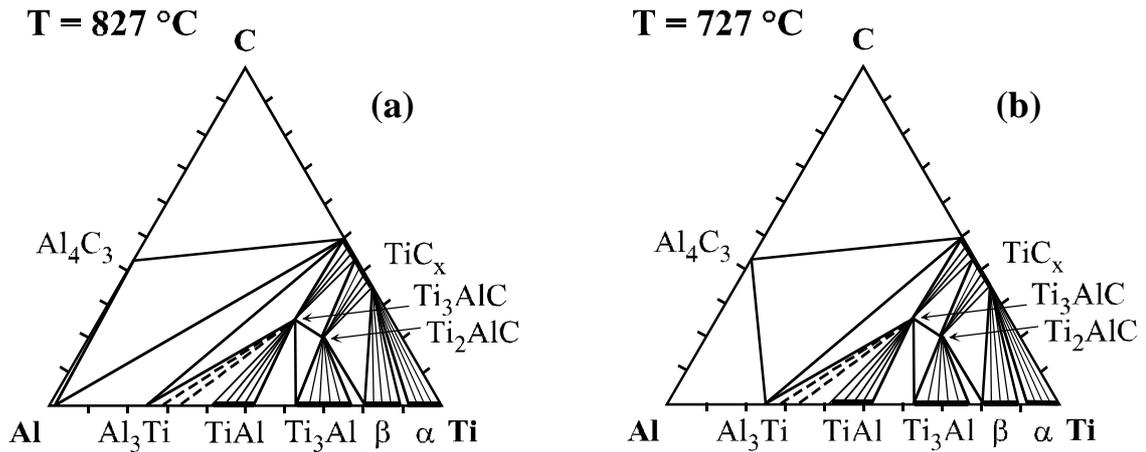


Fig. 3: Isothermal sections of the Al-C-Ti phase diagram; (a) at 827 °C; (b) at 727 °C.

As in the case of the Al/B₄C couple, TiC is decomposed at a much faster rate by liquid aluminium than by solid aluminium. However, due to the invariant transformation (4), this rate does not regularly increase with the temperature but goes through a maximum near 750 °C before falling down to zero when the temperature reaches 812 °C (Fig.4).

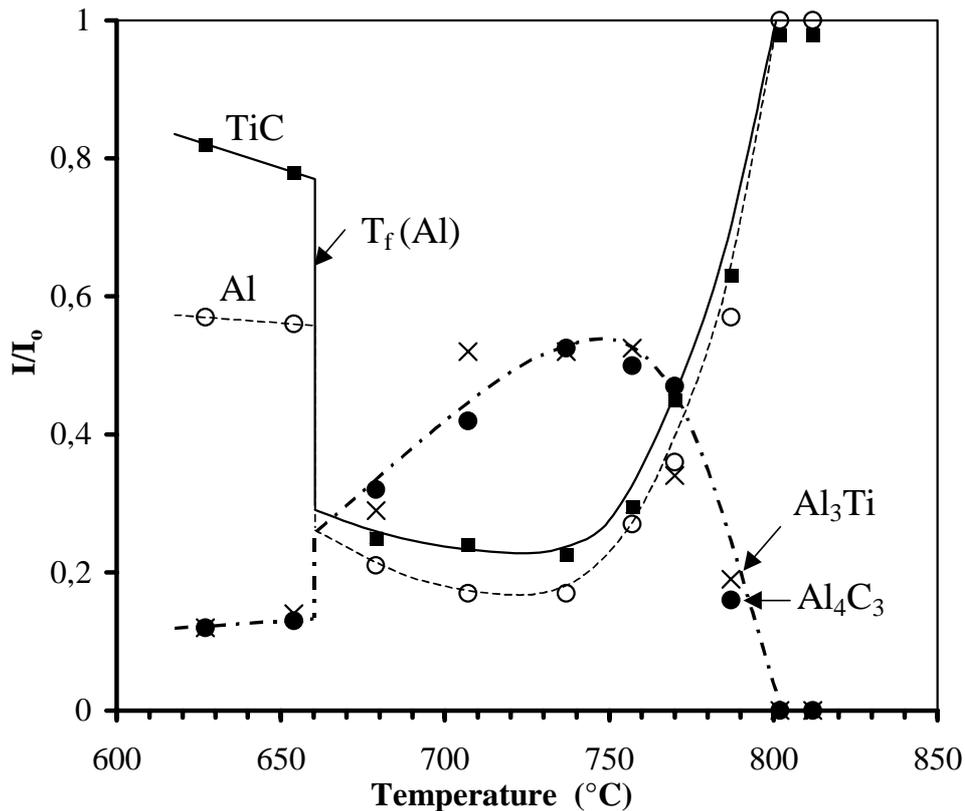


Fig. 4: Relative abundance of the phases characterized by X-ray diffraction in Al:TiC powder mixtures after reaction for 160 h at different temperatures.

Interaction between titanium carbide and aluminium below 812 °C proceeds via a dissolution-precipitation mechanism very analogous to that previously described for the Al/B₄C couple, with Al₄C₃ and Al₃Ti respectively replacing Al₃BC and AlB₂ or β-AlB₁₂. However, the Al/B₄C and Al/TiC couples can be distinguished by two points:

- firstly, whereas a thin and continuous passivation layer of Al₃BC develop rapidly at the B₄C surface (Fig. 2b), Al₄C₃ crystals produced at the Al/TiC interface form a broad and

discontinuous Al-infiltrated two-phased layer which cannot protect the TiC surface from further attack (Fig. 5a)

- secondly, the rate at which TiC is decomposed at a given temperature decreases considerably when the titanium content in the aluminium matrix increases. This clearly appears by comparing Figs. 5a and 5b: after heating at the same temperature and for the same time (727 °C, 160 h), TiC_{0.95} single crystals are readily attacked by a pure aluminium melt (Al₄C₃ + Al layer, rough TiC surface) while no indication of a possible reaction is obtained (smooth TiC surface without any trace of Al₄C₃) for TiC_{0.95} crystals immersed in an aluminium melt first oversaturated with 1 at.% of titanium.

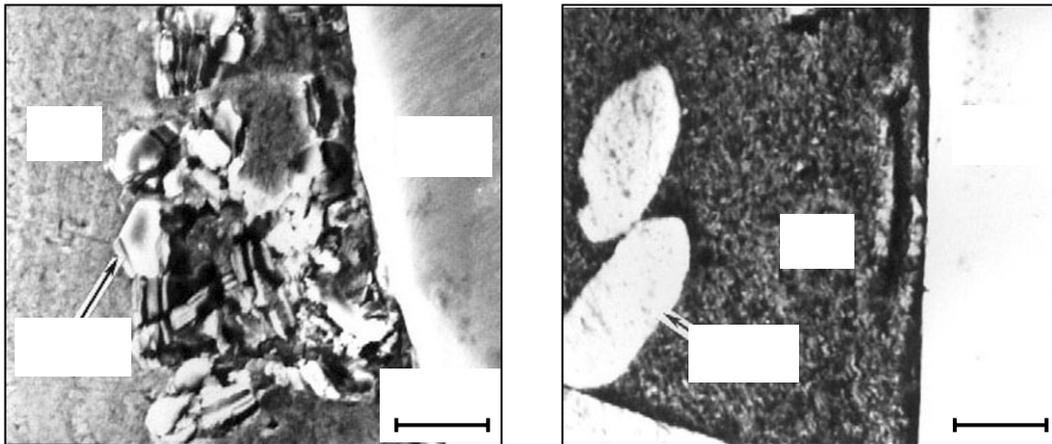
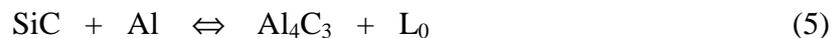


Fig. 5: TiC_{0.95} single crystals after 160 h heating at 727 °C in the presence of (a) pure aluminium and (b) aluminium oversaturated in Ti (1 at.%Ti)

The Al/SiC couple

The thermodynamic principles governing the chemical interaction between aluminium and silicon carbide can now be considered as well understood. High temperature isothermal sections ($T > 1900$ °C) of the Al-C-Si ternary phase diagram have been determined [11] and a model based on stable and metastable phase equilibria has been developed for describing the Al-SiC interaction at the medium and low temperatures of interest for composite manufacture. According to this model [12], SiC is in thermodynamic equilibrium with solid aluminium at every temperature lower than 650 °C (Fig. 6a). At 650 ± 3 °C, the following invariant transformation occurs in the Al-C-Si system (point T in Fig. 6c):



where L₀ is a ternary liquid phase containing aluminium (major constituent), silicon (1.5 ± 0.4 at.%) and carbon (less than 1 ppm).

At temperatures higher than 650 °C, solid ($650 < T < 660$ °C) or liquid aluminium ($T > 660$ °C) reacts with SiC, producing Al₄C₃ and silicon. If SiC is in excess, a three-phased monovariant equilibrium involving unreacted SiC, Al₄C₃ and a ternary liquid phase L₁ can be attained (Fig. 6b). The carbon content of this liquid phase L₁ simultaneously in equilibrium with SiC and Al₄C₃ remains very low (about 30 at.ppm at 1000 °C) whereas its silicon content increases with the temperature from 1.5 at.% at 650 °C to 4.5 at.% at 727 °C and 12.5 at.% at 1000 °C (Fig. 6c).

As in the two former cases, the chemical decomposition of SiC by aluminium proceeds via a dissolution-precipitation mechanism. Experiments realized at 727 °C on 6H α-SiC crystals with broad Si (0001) and C (000-1) faces have moreover revealed a marked influence of the polarity of the crystal surface on the chemical reactivity of silicon carbide with liquid aluminium [13].

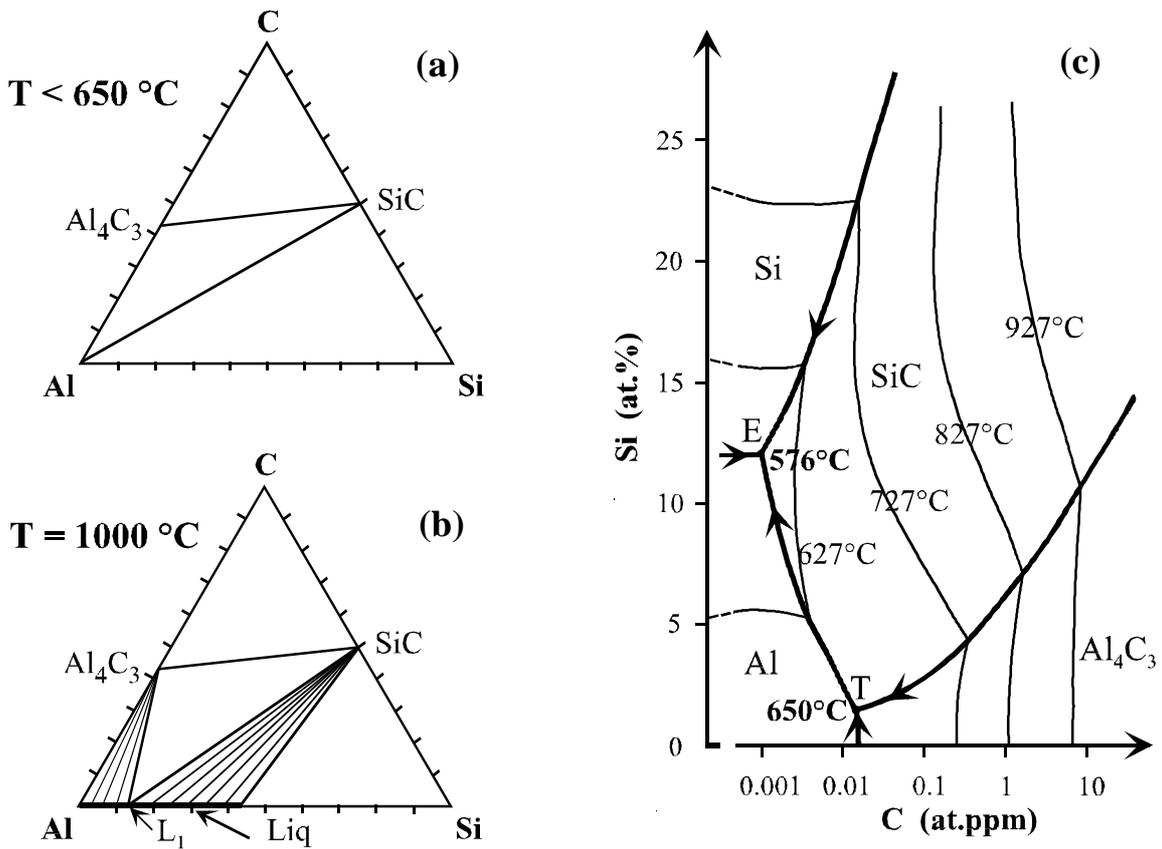


Fig. 6: Thermodynamic aspect of the chemical interaction between Al and SiC up to 1000 °C ($P = 1\text{ atm}$): (a, b) isothermal Al-C-Si sections; (c) liquidus projection.

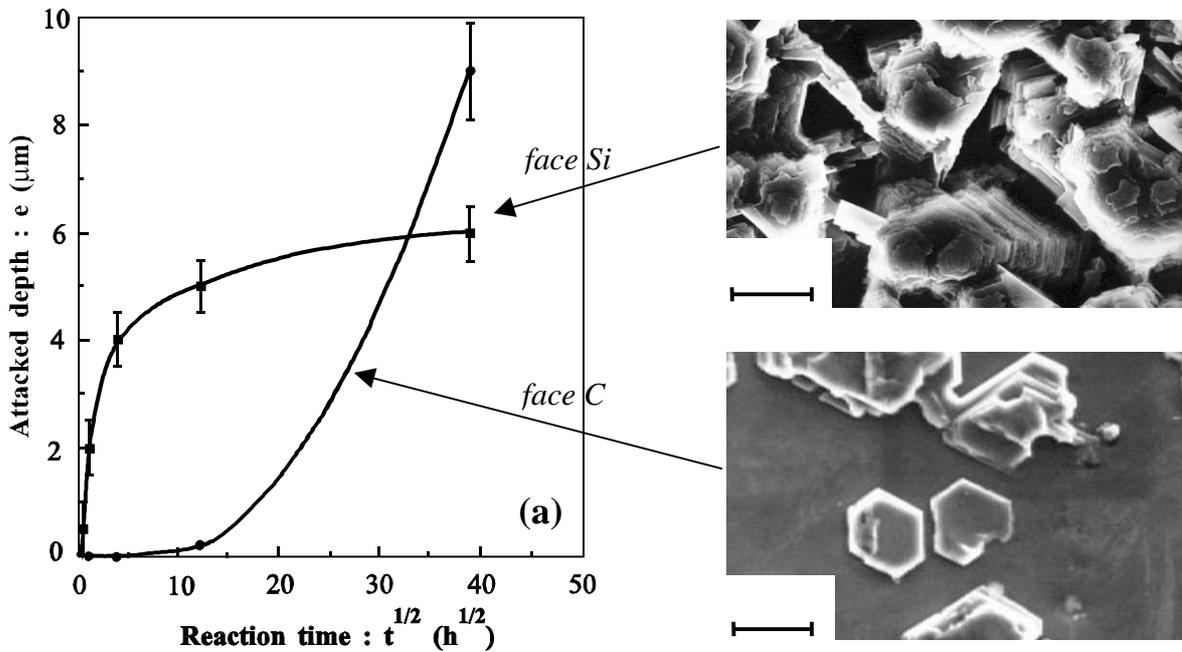


Fig 7: Chemical interaction at 727 °C between Al and α -SiC single crystals: (a) average depth on which SiC is decomposed at the Si and C faces as a function of the square root of the reaction time; (b, c) surface morphology of these faces after 150 h reaction (Al and Al_4C_3 have been chemically etched).

It has more especially appeared that dissolution progresses much more slowly at the C face than at the Si face or at any other randomly oriented crystal face. In this sense, the C face can be considered as less reactive than all the others. This is all the truer since deep dissolution pits are dug out at the Si face (Fig. 7b) while the C face remains smooth (Fig. 7c). However, it has also been observed that while a barrier layer of aluminium carbide Al_4C_3 is rapidly formed onto the Si face protecting it against further attack, the major part of the C face remains directly exposed to liquid aluminium. As a consequence, the C face continues to dissolve at a slow but constant rate and it is finally by dissolution of the "less reactive" C face that α -SiC crystals will be the most severely damaged after long time reaction (Fig.7).

APPLICATION TO INTERFACE TAILORING

The mechanical properties of composite materials depend to a large extent on the nature and strength of the bond at the matrix-reinforcement interface. In this regard, interfacial chemical reactions have to be carefully controlled during processing and use to attain and preserve the desired properties. For composites based on the three couples studied in the present work, interaction at the metal/carbide interface always proceeds via a dissolution-precipitation mechanism which implies both the formation of more or less deep dissolution pits at the base carbide surface and the growth of well-faceted Al_3BC or Al_4C_3 crystals near or onto it. By favouring stress concentration, crack initiation and crack propagation, these two features may have detrimental effects on the mechanical properties. Moreover, easy hydrolysis of Al_4C_3 in humid air may cause additional corrosion problems. Interface reactions should then be avoided during the elaboration of Al- B_4C , Al-TiC and Al-SiC composites. Only the creation of a smooth and true metal/carbide interface without any oxide skin or reaction product should be sought for.

In the case of the Al- B_4C couple which is reactive at any temperature up to at least 1000 °C, interface tailoring can only be based on kinetics considerations. The elaboration parameters have to be adjusted in such a way that interaction progresses at a very slow rate or has no time to develop. In this respect, solid-state processing or squeeze casting appear as the most appropriate elaboration techniques for avoiding interface reaction. At this point, it is worth recalling that the carbide produced by reaction at the Al/ B_4C interface is not Al_4C_3 but Al_3BC . As the latter is much more stable in humid air than the former, the corrosion problem is not so acute. In that particular case, starting up a limited interaction could contribute to the local development of a true Al/ B_4C interface and have thereby an overall beneficial effect.

The Al-TiC couple is reactive below 812 °C. Interface tailoring in Al-TiC composites elaborated at low temperature can then only be based on kinetics, as in the former case. On the one hand, formation as reaction product of Al_4C_3 which is easily hydrolyzed instead of Al_3BC requires an improved control of the chemical interaction. On the other hand, a wider degree of freedom for adjusting the elaboration parameters is provided by the fact that the rate of this interaction does not regularly increase with the temperature and is considerably lowered if titanium is first added to the matrix. At temperatures higher than 812 °C, an equilibrium is established between liquid aluminium and carbon-rich titanium carbide. Consequently, no interface reaction will develop in Al-TiC composites elaborated by melt infiltration at temperatures higher than 812 °C. Another way to exploit this thermodynamic equilibrium consists in reacting at high temperature carbon particles with an Al-Ti alloy: TiC is formed in-situ and after rapid cooling in the 800-650 °C range, particulate composites with a true and strongly bonded Al/TiC interface are obtained [4, 5].

Contrarily to Al-TiC, the Al-SiC couple is non-reactive at temperatures lower than 650 °C and reactive above. In the latter case, the couple can however be rendered non-reactive by the addition to aluminium of sufficient amounts of silicon. From these thermodynamic principles flow two different manners to avoid formation of Al_4C_3 at the matrix/reinforcement interface during the elaboration of Al-SiC composites: either these composites are processed in the solid state at temperatures lower than 650 °C or they are elaborated at temperatures higher than 650 °C by melt infiltration with a Al-Si alloy containing the appropriate amount of silicon. In the latter case, precautions have however to be taken to avoid bridging of SiC by Si crystals on cooling (addition to the alloy of a Si modifier, control of the solidification,

appropriate heat-treatment). Both processing routes have been developed on an industrial plant to produce particulate reinforced composites (Alcoa and Alcan products).

To end up with interface tailoring, it will be recalled that if the three carbides SiC, TiC and B₄C react with liquid aluminium at temperatures ranging from 660 to 750 °C, they are attacked at a slower rate than any carbon substrate in a low-graphitized or turbostratic form. Consequently, thin coatings of these carbides can protect low-graphitized carbon fibres against aluminium attack during the elaboration of Al-C composites by melt infiltration at these temperatures. This has been effectively verified for T300 and M40 carbon fibres at the surface of which a 50-500 nm thick carbide layer had been deposited by reactive chemical vapour deposition [7].

CONCLUSION

A careful control of the bonding at the matrix-reinforcement interface is one of the numerous problems that have to be solved in the elaboration of aluminium base matrix composites. It is hoped that the general principles and examples exposed in the present paper will bring some keys to solve this problem and contribute thereby to the successful elaboration of high performance materials.

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